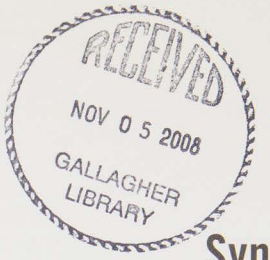
Synopsis of Research

Conducted under the 2001–2003 Northern Contaminants Program

Indian and Northern Affairs Canada
Affaires indiennes et du Nord Canada

Canada



Synopsis of Research Conducted under the 2001–2003 Northern Contaminants Program

Published under the authority of the
Minister of Indian Affairs and Northern Development
Ottawa, 2003
www.ainc-inac.gc.ca
1-800-567-9604
TTY only 1-866-553-0554

QS-8602-020-EE-A1
Catalogue No. R71-19/76-2004E
ISBN 0-662-36210-1

This report was prepared under the Northern Contaminants Program, coordinated by the Northern Science and Contaminants Research Directorate, Department of Indian Affairs and Northern Development.

The views, conclusions and recommendations expressed herein are those of the authors and not necessarily those of the Department.

Table of Contents

Foreword

This report provides a summary of the progress to date of research and monitoring studies on contaminants in northern Canada, and related education, communications and policy activities that were conducted in 2001–2003 under the auspices of the Northern Contaminants Program (NCP). The projects cover all aspects of northern contaminants issues, as outlined in the NCP blueprints, including human health, monitoring the health of Arctic peoples and ecosystems and the effectiveness of international controls (abiotic monitoring and modelling, biotic monitoring, local contaminants concerns), education and communications, international policy and program management.

These projects were evaluated, as proposals, by external peer reviewers, technical review teams, a social/cultural review team, territorial/regional contaminants committees and the NCP Management Committee to ensure that they support the overall Northern Contaminants Program objectives.

Further information about the Northern Contaminants Program is available on the NCP website at www.ainc-inac.gc.ca/ncp.

Préface

Ce rapport résume l'avancement de recherches et d'études de surveillance portant sur les contaminants dans le Nord canadien, ainsi que d'activités connexes au sujet de l'éducation, de la communication et de la politique qui ont eu lieu en l'année 2001–2003. Ces études et activités ont été menées dans le cadre du Programme de lutte contre les contaminants dans le Nord (PLCN). Ces projets, tels que décrit dans les plans directeurs liés au programme, représentent tous les aspects portant sur les contaminants, incluant la santé humaine, la surveillance de la santé des habitants et des écosystèmes de l'Arctique et de l'efficacité des mesures de contrôle internationales (surveillance et modélisation milieux abiotiques, surveillance — milieux biotiques, préoccupations locales concernant les contaminants), l'éducation et la communication, la politique internationale et la gestion des programmes.

Ces projets ont été examinés par des pairs, des comités d'examen technique, un comité d'examen social et culturel, les comités territoriaux/régionaux sur les contaminants environnementaux, et le comité de gestion de la PLCN afin de s'assurer qu'ils répondent à l'ensemble des objectifs du programme de lutte contre les contaminants dans le Nord.

Pour de plus amples renseignements au sujet du programme de lutte contre les contaminants dans le Nord, visitez le site Web du PLCN au www.ainc-inac.gc.ca/ncp.

Introduction

The Northern Contaminants Program (NCP) was established in 1991 in response to concerns about human exposure to elevated levels of contaminants in fish and wildlife species that are important to the traditional diets of northern Aboriginal peoples. Early studies indicated that there was a wide spectrum of substances — persistent organic pollutants, heavy metals, and radionuclides — many of which had no Arctic or Canadian sources, but which were, nevertheless, reaching unexpectedly high levels in the Arctic ecosystem. The Program's key objective is *to reduce and, where possible, eliminate contaminants in northern traditionally harvested (country) foods while providing information that assists informed decision making by individuals and communities in their food use.*

Under the first phase of the NCP (NCP-I), research was focussed on gathering the data required to determine the levels, geographic extent, and source of contaminants in the northern atmosphere, environment and its people, and the probable duration of the problem. The data enabled us to understand the spatial patterns and temporal trends of contaminants in the North, and confirmed our suspicions that the major sources of contaminants were other countries. The data, which included information on the benefits from continued consumption of traditional/country foods, was also used to carry out assessments of human health risks resulting from contaminants in those foods. Results generated through NCP-I are synthesized in the *Canadian Arctic Contaminants Assessment Report.*

Extensive consultations were conducted in 1997–1998 to find the common elements between the concerns and priorities of northern communities and the scientific needs identified as critical for addressing the issue of contamination in Canada's North. As a result, priorities for current and future research are based on an understanding of the species that are most relevant for human exposure to contaminants in the North, and geographic locations and populations that are most at risk.

In 1998–1999, the NCP began its second phase (NCP-II), which continued until 2002–2003. Results of this phase are synthesized in the *Canadian Arctic Contaminants Assessment Report II (CACAR II).* NCP-II supports research designed to answer questions about the impacts and risks to human health that may result from current levels of contamination in key Arctic food species. To ensure a balanced assessment of the risks, an emphasis is placed on characterizing and quantifying the benefits associated with traditional diets. Communications activities are also emphasized and supported under NCP-II. Under the leadership of the northern Aboriginal organizations, the dialogue between northerners and the scientific community, which was initiated in NCP-I, continues to build awareness and an understanding of contaminants issues, and helps to support the ability to deal with specific contaminant issues at the local level.

In addition, the NCP effort to achieve international controls of contaminants remains strong in NCP-II. The legally binding POPs protocol, under the United Nations Economic Commission for Europe (UN ECE) Convention on Long-range Transboundary Air Pollution, has been successfully negotiated and was signed by 34 countries (including Canada) at the UN ECE Ministerial Conference in Aårhus, Denmark in June 1998. Canada ratified this agreement in December 1998. Negotiations for a legally binding global instrument on POPs under the United Nations Environment Programme have now also been completed with the signing of the POPs Convention in Stockholm, Sweden, May 23, 2001. The Convention has been signed by more than 100 countries; Canada has signed and ratified the Convention. Cooperative actions under the Arctic Council, including the circumpolar Arctic Monitoring and Assessment Programme (AMAP) and the Arctic Council Action Plan (formally launched in October 2000), are continuing. NCP-II continues to generate the data that allows Canada to play a leading role in these initiatives.

The NCP is directed by a management committee that is chaired by the Department of Indian Affairs and Northern

Development, and which includes representatives from four northern Aboriginal organizations (Council of Yukon First Nations, Dene Nation, Inuit Tapirisat of Canada and Inuit Circumpolar Conference), the Yukon, Northwest Territories and Nunavut Territorial Governments, Nunavik, and four federal departments (Environment, Fisheries and Oceans, Health, and Indian Affairs and Northern Development). The management committee is responsible for establishing NCP policy and research priorities and for final decisions on the allocation of funds. Three territorial contaminants committees in the Yukon, Northwest Territories and Nunavut (established in May 2000), and a regional contaminants committee in Nunavik support this national committee. Funding for the NCP-II's $5.4 million annual research budget comes from the Treasury Board and the four participating federal departments.

The NCP Operational Management Guide, developed in 2000–2001, and available on the NCP website (www.ainc-inac.gc.ca/ncp), provides a summary of the management structures and review processes used to effectively implement the NCP. The Guide explains the overall management structures currently used, the proposal review process and outlines a protocol to be used to publicly disseminate health and harvest information generated by the NCP. Background information on all NCP committees and review teams is also provided.

In 1998, the NCP Management Committee redesigned the NCP-Phase II for application under the 1999–2000 funding year. The two main initiatives undertaken were: 1) the development of blueprints that represent the long-term vision and strategic direction for NCP-II; and 2) the implementation of a more open and transparent proposal review process. This new management structure is designed to ensure that the NCP remains scientifically defensible and socio-culturally aware, while at the same time, achieving real progress in terms of the Program's broad policy objectives.

Blueprints were developed for each of the four main NCP subprograms: i) Human Health, ii) Monitoring the Health of Arctic People and Ecosystems and the Effectiveness of International Controls, iii) International Policy, and iv) Education and Communications. The blueprints are used to provide the necessary guidance to project proponents for the development of proposals as well as to peer reviewers, review teams and the NCP Management Committee for evaluating proposals. They are evolving documents that are reviewed at least annually.

Under a revamped proposal review process, the NCP Technical Committee was replaced with an external peer review process facilitated by review teams. The review of proposals is a two-pronged approach involving a scientific review by external peer reviewers, facilitated by technical review teams, and a socio-cultural review facilitated by a review team and the regional and Territorial Contaminants Committees (TCCs). Both sets of recommendations are considered by the Management Committee in making final funding decisions. Proposals submitted under the Education and Communications subprogram are evaluated by a review team and the TCCs. All peer reviewers, review teams and TCCs use evaluation criteria and the blueprints to review and rate proposals. Written consent from the appropriate northern community authority or national-level Aboriginal organization is required for all projects involving field work in the North and/or analyses of samples as a condition of approval for funding. The Social/Cultural Review Team ensures that each applicable proposal has a written consent form attached and signed by the applicable authority.

This report provides a summary of the progress to date of research and activities funded by the Northern Contaminants Program in 2001–2003, the third year of NCP-II. It is a compilation of reports submitted by project teams, emphasizing the results of research and related activities that took place during the 2001–2003 fiscal years. The report is divided into chapters that reflect the broad scope of the NCP: Human Health; Monitoring the Health of Arctic People and Ecosystems and the Effectiveness of International Controls (including abiotic monitoring and biotic monitoring), Education and Communications, International Policy, and Program Coordination.

Human Health

PCBs and Neurodevelopment: The Role of Hydroxy-PCBs and Other Phenolic Compounds as Thyroid Hormone Disrupters

Project leader

Pierre Ayotte, Public Health Research Unit, CHUL-CHUQ, 945 avenue Wolfe, Quebec (Quebec) G1V 5B3; phone: (418) 650-5115 (ext. 4654); fax: (418) 654-2148; e-mail: pierre.ayotte@inspq.qc.ca

Project team

Courtney Sandau, Centers for Disease Control and Prevention, Atlanta, Georgia; Gina Muckle, Éric Dewailly, Public Health Research Unit, CHUQ, Beauport, Quebec; Joseph L. Jacobson, Sandra W. Jacobson, Wayne State University, Detroit, Michigan.

Abstract

Previous studies have linked prenatal exposure to polychlorinated biphenyls (PCBs) at environmental levels to delayed gross motor development, and deficits in physical growth and cognitive development. Recent data indicate that hydroxylated metabolites of PCBs (OH-PCBs) that accumulate in the blood could be responsible for these adverse effects by affecting thyroid hormone status in the newborn. This project is linked to the ongoing cohort study on environmental contaminants and infant development that involves the participation of 300 Inuit infants from Nunavik and Greenland. In the cohort study, the impact of PCBs and mercury exposure on newborn's thyroid hormones, physical growth, physical and neurological maturity, overall health, mental, psychomotor and neurobehavioral development, and in visual and spatial information processing is being studied. This additional study will enhance our capacity to find relevant associations between these effects and exposure to PCBs by focusing on the reactive metabolites of PCBs and conducting a more complete investigation of the newborn's thyroid hormone status. During the first year of this project, methodological development for automated extraction and analysis of OH-PCBs was finalized.

Key Project Messages

1. A new automated method of solid phase extraction has been developed for the efficient extraction of PCBs, persistent pesticides and PCB metabolites.
2. Analysis of OH-PCBs will be performed early during Fall 2003 in 260 plasma samples.
3. Relations between HO-PCBs concentrations and thyroid hormones as well transport proteins will be examined.

Objectives

To examine the role of OH-PCBs in producing adverse effects on the development of the nervous system in Inuit, by virtue of their interaction with the thyroid hormone pathway.

Introduction

PCBs have been well studied in possibly affecting newborn and infant when it was determined that PCBs could effectively pass through the placental barrier and that they were associated with lower birth weights (Fein et al. 1984). Jacobson et al. (1985) found that prenatally exposed children showed a delayed gross motor development, and deficits in physical growth and cognitive development. In the same cohort, *in utero* PCB exposure was associated with reductions in cognitive function at 4 years of age (Jacobson et al. 1990) and with lower IQs at 11 years of age (Jacobson and Jacobson 1996). This evidence indicates a link between PCBs and neurodevelopment. Although many theories exist on how PCBs affect neurodevelopment, the main hypothesis involves disruption of thyroid hormone homeostasis (Porterfield and Hendry 1998). Thyroid hormones regulate neuronal proliferation, cell migration and differentiation including control on when differentiation begins and when cell proliferation ends (Hamburgh 1969). Studies in the rat showed that the main transport mechanism of thyroid hormones to the brain requires passing through the blood brain barrier via a thyroid hormone transport protein called transthyretin (TTR) (Chanoine and Braverman 1992). Although PCBs show some binding affinity for TTR (Chauhan et al. 2000), OH-PCBs have much higher *in vitro* binding affinities that can be as high as 12x the binding affinity of the natural ligand, thyroxine (T4) (Brouwer 1991; Cheek et al. 1999; Lans et al. 1994). Binding to TTR is not limited to OH-PCBs. Other chlorinated phenolic compounds such as pentachlorophenol (PCP), halogenated phenols and brominated flame retardants (Meerts et al. 2000; van den Berg 1990; van den Berg et al. 1991) also have strong affinities for TTR. Recently, we showed that PCP was the dominant phenolic compound in Inuit whole blood (Sandau et al. 2000). Thus, other halogenated phenolic compounds may also be important contaminants in plasma (Klasson-Wehler et al. 1997) as they have been found to exhibit similar toxicological properties to OH-PCBs (Kester et al. 2000; Schuur et al. 2000; van den Berg 1990).

OH-PCBs have been shown to decrease circulating levels of thyroid hormones through this mode of thyroid hormone disruption (Bastomsky 1974; Brouwer and van den Berg 1986; Kohn et al. 1996). TTR is also responsible for retinol transport by forming a dimer with retinol binding protein. Thus, circulating retinol concentrations can also be affected by PCB and OH-PCB exposure (Brouwer et al. 1988a, 1988b, 1989).

The foetus may be especially vulnerable to PCB and OH-PCB exposure. When foetal mice were exposed *in utero* to 4′-OH-CB-79, a metabolite of CB77, both maternal and foetal plasma T4 levels decreased significantly compared to controls (Sinjari and Darnerud 1998). In this same study, foetal plasma had two times the 4′-OH-CB79 concentration of the maternal plasma (Sinjari et al. 1998). These experiments were recently repeated on pregnant rats who were orally exposed to 4-OH-CB107 (Meerts et al. unpublished data), one of the main OH-PCBs found in human plasma (Sandau et al. 2000; Sjodin et al. 2000). In this study, both maternal and foetal thyroid hormones were reduced by exposure to 4-OH-CB107, with foetal total T4 concentrations decreasing to 89% of that of the controls (Meerts et al. unpublished data). The decreased plasma T4 levels also resulted in decreased forebrain and cerebellum T4 concentrations as compared to controls (Meerts et al. unpublished data), which could lead to neurodevelopmental deficits. PCP has also been shown to decrease brain T4 availability in dosed rats (van Raaij et al. 1994). Another interesting finding in the 4-OH-CB107 rat dosing study was an accumulation of 4-OH-CB107 in foetal plasma, liver and brain.

Thus, prenatal exposure to PCBs, OH-PCBs, and PCP may all lead to thyroid hormone disruption and possibly neurodevelopmental effects. Umbilical cord plasma is unique in that it is a direct indication of *in utero* circulating concentrations of xenobiotics, now including phenolic compounds in the newborn. PCBs have been previously measured in umbilical cord plasma (Huisman et al. 1995; Koopman-Essebom et al. 1994a, 1994b; Skaare et al. 1988). However, few studies have examined levels of hydroxylated metabolites in human blood and to our knowledge levels in cord blood have not been reported.

We conducted a pilot study to measure the concentrations of PCBs, OH-PCBs and other chlorinated phenolic compounds such as PCP in umbilical cord plasma samples from three different regions of Quebec (Sandau et al. 2002). Ten samples were obtained from Inuit neonates and another 10 samples from newborns from the Lower North Shore of the Gulf of St. Lawrence (subsistence fishermen). Ten samples were also obtained from a southern Quebec urban centre where PCB exposure is at background levels (Quebec City). The main chlorinated phenolic compound in all regions was PCP. The ratio of PCP to PCB congener no. 153 for all samples ranged from 0.72 to 42.3, which indicates the relative importance of PCP in blood. Total OH-PCB concentrations were different among the regions, with geometric mean concentrations of 553 (range 238–1,750), 286 (103–788) and 234 (147–464) $pg \cdot g^{-1}$ wet weight plasma for the Lower North Shore, Nunavik and the southern Quebec groups, respectively. Total PCB (sum of 49 congeners) concentrations for the regions also ranked similar to total OH-PCBs with the Lower North Shore

samples having the highest geometric mean concentration of 2,710 (525–7,720) $pg \cdot g^{-1}$ wet weight plasma. Total PCBs for the Nunavik samples and southern samples were 1,510 (309–6,230) and 843 (290–1,650) $pg \cdot g^{-1}$ wet weight plasma. Total OH-PCBs were significantly correlated to total PCBs ($r = 0.62$, $p < 0.001$) and all identified OH-PCB congeners were highly inter-correlated to the main PCBs, even metabolically unrelated congeners. Interestingly, log normalized free T4 concentrations were negatively associated with log normalized total quantitated phenolic compounds (sum PCP and OH-PCBs) ($r = -0.62$, $p = 0.003$, $N = 20$) and were not associated with PCBs. This indicates that PCP and OH-PCBs have similar modes of action and are possibly altering thyroid hormone status in newborns, which could lead to neurodevelopmental effects in infants. The present research project was set up to examine the effects of chlorinated phenolic compounds on thyroid hormone status in newborns, and in turn on neurodevelopmental endpoints that are being measured in Inuit infants in the course of the cohort study on infant development.

Activities

In 2001–2002

A new automated method of solid phase extraction has been developed for the efficient extraction of PCBs, persistent pesticides and PCB metabolites. Using the Zymark Rapidtrace®, up to 50 samples per day can be processed for GC-MS analysis. The extraction conditions for human plasma samples were optimized by testing different solid phase extraction sorbents such as C18 (Varian), ENV (Varian), NEXUS (Varian), OASIS (Watters), and Chromabond (Nagel-Magerey) and different denaturant reagents (methanol, ethanol, formic acid). The final method efficiently extracts 1–4 ml of human plasma or serum. The method has been tested on human plasma samples and a spiked human QA/QC serum pool.

In 2002–2003

All standards for the accurate quantitation of HO-PCBs were synthesized and have been incorporated into one standard mixture. Several new ^{13}C-labeled internal quantitation standards and new native standards are now available to accurately quantify HO-PCBs and other halogenated phenolic compounds. A research assistant also set up ELISA methods for TTR and retinol binding protein analyses in plasma samples. Cord blood samples from the last participants in Nunavik were collected in September 2001 and plasma samples were shipped to the CDC laboratory for analysis in early 2002. However, we are still missing most of the samples from Greenland, due to delays in subject recruitment and problems with shipping. The remaining samples that are still in Nuuk were sent to Quebec City in September 2003. A post-doctoral fellow is currently in Atlanta at the CDC to finalize the analytical procedures. All samples from the Nunavik and Greenland cohorts will be analysed during Fall 2003.

Results

In 2001–2002

Results for the analysis of 8 human plasma samples are given in Table 1. The drop off in recoveries is a common observance in SPE extraction of PCBs from human plasma/blood (Janak et al. 1999). This result was noted throughout method developing and consistent for all the sorbents tested. The effect is minimized by spiking the recovery standards in ethanol and increasing the sorbent bed. The maximum sorbent for a 3 cc cartridge using OASIS HLB and the Zymark Rapidtrace® is 540mg.

A control pool of spiked human serum was then characterized using the described methodology. The results in Table 2 show the calculated concentrations of selected HO-PCBs, PCBs and persistent pesticides in the human control pool.

In 2002–2003

There are no results from this project yet. As mentioned earlier, all samples will be analysed this Fall.

Table 1. Percentage recoveries of 13C-labeled internal quantitation standards from random human serum samples (n = 8)

13C-labelled Standard	Recovery	Std. Dev.
4-HO-CB120	61.1	9.8
4-HO-CB159	75.7	10.5
4-HO-CB187	82.9	12.7
beta-HCH	133.5	21.9
trans-chlordane	111.1	19.3
trans-nonachlor	103	19.8
4,4'-DDE	114.4	21.4
CB153	73.6	14.2
CB105	81.8	15.1
CB138	79.7	15.6
CB180	65.8	14.2
CB194	59.6	14.5
CB209	40	12.8

Table 2. Characterization of human serum pool using new SPE method of extraction. Compounds in bold include natural and additional spiked levels. Other compounds were background levels found in the human serum

Analyte	Average Conc (pg/mL)	% RSD (n = 12)
4-MeO-CB107	1.06	19.2
4-MeO-CB187	1.79	29.3
4-MeO-CB202	0.10	19.1
4-diMeO-CB202	0.28	5.5
4-MeO-CB208	0.29	16.4
hexachlorobenzene	0.638	2.1
trans-chlordane	0.155	16.5
cis-chlordane	0.187	19.0
trans-nonachlor	0.902	2.2
cis-nonachlor	0.095	26.5
pentaCB-118	0.284	2.9
pentaCB-105	0.198	29.9
hexaCB-156	0.279	2.5
heptaCB-183	0.204	12.5
heptaCB-177	0.337	7.2
octaCB-199	0.447	3.3
octaCB-195	0.042	13.9
nonaCB-208	0.312	5.9
nonaCB-206	0.373	7.8
decaCB-209	0.264	6.0

Discussion and Conclusions

In 2001–2002

Results indicate that the current method is capable of efficient extraction of both non-polar (PCBs, persistent pesticides) and polar (HO-PCBs) compounds as well as successfully separating them into two fractions for mass spectral analysis. All extractions, fractionations and purification steps are done using the automated SPE system allowing rapid sample processing.

Standards for the accurate quantitation of HO-PCBs were synthesized by Wellington Laboratories. These standards include more 13C-labeled internal quantitation standards and more native standards for the accurate quantitation of HO-PCBs and other halogenated phenolic compounds. These new standards will be incorporated into the analysis of the umbilical cord plasma samples upon their receipt. Cord blood samples from the last participants were collected in September 2001 and plasma samples were shipped to the CDC laboratory for analysis in early 2002. A chemist researcher from the Québec Toxicology Centre will perform the analyses of the first batch of samples in Dr. Sandau's laboratory at the CDC in Atlanta. The method will then be set up in Quebec where the second batch of samples will be analysed in 2002–2003. Inter-laboratory control will be established to insure that data will be comparable between both batches of analyses.

In 2002–2003

We have encountered several delays in completing this research project. All methods are ready and samples were analysed starting in September 2003. Data analysis will follow. We expect that these new data will be helpful in establishing links between exposure to POPs and developmental endpoints in both Nunavik and Greenland cohorts.

Expected Completion Date

December 31, 2003

References

Bastomsky, C.H. 1974. Effects of a polychlorinated biphenyl mixture (Aroclor 1254) and DDT on biliary thyroxine excretion in rats. *Endocrinology.* 95:1150–1155.

Brouwer, A. 1991. Role of biotransformation in PCB-induced alterations in vitamin A and thyroid hormone metabolism in laboratory and wildlife species. *Biochem Soc Trans.* 19:731–737.

Brouwer, A. and K.J. van den Berg. 1986. Binding of a metabolite of 3,4,3',4'-tetrachlorobiphenyl to transthyretin reduces serum vitamin A transport by inhibiting the formation of the protein complex carrying both retinol and thyroxin. *Toxicol Appl Pharmacol.* 85:301–312.

Brouwer, A., W.S. Blaner, A. Kukler, and K.J. van den Berg. 1988a. Study on the mechanism of interference of 3,4,3',4'-tetrachlorobiphenyl with the plasma retinol-binding proteins in rodents. *Chem Biol Interact.* 68:203–217.

Brouwer, A., A. Kukler, and K.J. van den Berg. 1988b. Alterations in retinoid concentrations in several extrahepatic organs of rats by 3,4,3',4'-tetrachlorobiphenyl. *Toxicology.* 50:317–330.

Brouwer, A., P.J.H. Reijnders, and J.H. Koeman. 1989. Polychlorinated biphenyl (PCB)-contaminated fish induces vitamin A and thyroid hormone deficiency in

the common seal *(Phoca vitulina). Aquat Toxicol.* 15: 99–106.

Chanoine, J.P. and L.E. Braverman. 1992. The role of transthyretin in the transport of thyroid hormone to cerebrospinal fluid and brain. *Acta Med Austriaca.* 19 (Suppl 1):25–28.

Chauhan, K.R., P.R.S. Kodavanti, and J.D. McKinney. 2000. Assessing the role of ortho-substitution on polychlorinated biphenyl binding to transthyretin, a thyroxine transport protein. *Toxicol Appl Pharmacol.* 162:10–21.

Cheek, A.O., K. Kow, J. Chen, and J.A. McLachlan. 1999. Potential mechanisms of thyroid disruption in humans: interaction of organochlorine compounds with thyroid receptor, transthyretin, and thyroid-binding globulin. *Environ Health Perspect.* 107:273–278.

Fein, G.G., J.L. Jacobson, S.W. Jacobson, P.M. Schwartz, and J.K. Dowler. 1984. Prenatal exposure to polychlorinated biphenyls: effects on birth size and gestational age. *J Pediatr.* 105:315–320.

Hamburgh, M. 1969. The role of thyroid and growth hormones in neurogenesis. In: A. Moscona and A. Monroy (eds.), *Current Topics in Developmental Biology.* New York, NY: Academic Press. pp. 109–148.

Huisman, M., C. Koopman-Esseboom, V. Fidler, M. Hadders-Algra, C.G. van der Paauw, L.G.M. Tuinstra, N. Weisglas-Kuperus, P.J.J. Sauer, B.C.L. Touwen, and E.R. Boersma. 1995. Perinatal exposure to polychlorinated biphenyls and dioxins and its effect on neonatal neurological development. *Early Hum Dev.* 41:111–127.

Jacobson, J.L. and S.W. Jacobson. 1997. Evidence for PCBs as neurodevelopmental toxicants in humans. *Neurotoxicology.* 18:415–424.

Jacobson, S.W., G.G. Fein, J.L. Jacobson, P.M. Schwartz, and J.K. Dowler. 1985. The effect of intrauterine PCB exposure on visual recognition memory. *Child Dev.* 56: 853–860.

Jacobson, J.L., S.W. Jacobson, and H.E. Humphrey. 1990. Effects of in utero exposure to polychlorinated biphenyls and related contaminants on cognitive functioning in young children. *J Pediatr.* 116:38–45.

Janak, K., E. Jensen, and G. Becher. 1999. Determination of polychlorinated biphenyls in human blood by solid-phase extraction including on-column lipid decomposition. *J Chromatogr B Biomed Sci Appl.* 734: 219–227.

Kester, M.H.A., S. Bulduk, D. Tibboel, W. Meinl, H. Glatt, C.N. Falany, M.W.H. Coughtrie, Å. Bergman, S.H. Safe, G.G.J.M. Kuiper, A.G. Schuur, A. Brouwer, and T.J. Visser. 2000. Potent inhibition of estrogen sulfotransferase by hydroxylated PCB metabolites: a novel pathway explaining the estrogenic activity of PCBs. *Endocrinology.* 141:1897–1900.

Klasson-Wehler, E., L. Hovander, and Å. Bergman. 1997. New organohalogens in human plasma — Identification and quantification. *Organohalogen Compounds.* 33:420–425.

Kohn, M.C., C.H. Sewall, G.W. Lucier, and C.J. Portier. 1996. A mechanistic model on effects of dioxin on thyroid hormones in the rat. *Toxicol Appl Pharmacol.* 165:29–48.

Koopman-Esseboom, C., M. Huisman, N. Weisglas-Kuperus, C.G. van der Paauw, L.G.M.T. Tuinstra, E.R. Boersma, and P.J.J. Sauer. 1994a. PCB and dioxin levels in plasma and human milk of 418 dutch women and their infants. Predictive value of PCB congener levels in maternal plasma for fetal and infant's exposure to PCBs and dioxins. *Chemosphere.* 28:1721–1732.

Koopman-Esseboom, C., D.C. Morse, N. Weisglas-Kuperus, I.J. Lutkesschipholt, C.G. van der Paauw, L.G.M.T. Tuinstra, A. Brouwer, and P.J.J. Sauer. 1994b. Effects of dioxins and polychlorinated biphenyls on thyroid hormone status of pregnant women and their infants. *Pediatr Res.* 36:468–473.

Lans, M.C., C. Spiertz, A. Brouwer, and J.H. Koeman. 1994. Different competition of thyroxine binding to transthyretin and thyroxine-binding globulin by hydroxy-PCBs, PCDDs and PCDFs. *Eur J Pharmacol.* 270:129–136.

Meerts, I.A.T.M., Y. Assink, P.H. Cenijn, K.J. van den Berg, B.M. Weijers, Å. Bergman, J.H. Koeman, and A. Brouwer. Placental transfer of a hydroxylated polychlorinated biphenyl and effects on fetal and maternal thyroid homeostasis in the rat. Unpublished data.

Meerts, I.A.T.M., J.J. van Zanden, E.A.C. Luijks, I. van Leeuwen-Bol, G. Marsh, E. Jakobsson, Å. Bergman, and A. Brouwer. 2000. Potent competitive interactions of some brominated flame retardants and related compounds with human transthyretin *in vitro. Toxicol Sci.* 56:95–104.

Porterfield, S.P. and L.B. Hendry. 1998. Impact of PCBs on thyroid hormone directed brain development. *Toxicol Ind Health.* 14:103–120.

Sandau, C.D., P. Ayotte, É. Dewailly, J. Duffe, and R.J. Norstrom. 2000. Analysis of hydroxylated metabolites of PCBs (OH-PCBs) and other chlorinated phenolic compounds in whole blood from Canadian Inuit. *Environ Health Perspect.* 108:611–616.

Sandau, C.D., P. Ayotte, É. Dewailly, J. Duffe, and R.J. Norstrom. 2002. Pentachlorophenol and hydroxylated polychlorinated biphenyl metabolites in umbilical cord plasma of neonates from coastal populations in Quebec. *Environ Health Perspect.* 110:411–417.

Schuur, A.G., F.F. Legger, M.E. van Meeteren, M.J. Moonen, I. van Leeuwen-Bol, Å. Bergman, T.J. Visser, and A. Brouwer. 1998. In vitro inhibition of thyroid hormone sulfation by hydroxylated metabolites of halogenated aromatic hydrocarbons. *Chem Res Toxicol.* 11:1075–1081.

Sinjari, T. and P.O. Darnerud. 1998. Hydroxylated polychlorinated biphenyls: placental transfer and effects on thyroxine in the foetal mouse. *Xenobiotica.* 28:21–30.

Sinjari, T., E. Klasson-Wehler, L. Hovander, and P.O. Darnerud. 1998. Hydroxylated polychlorinated biphenyls: distribution in the pregnant mouse. *Xenobiotica.* 28:31–40.

Sjodin, A., L. Hagmar, E. Klasson-Wehler, J. Bjork, and Å. Bergman. 2000. Influence of the consumption of fatty Baltic Sea fish on plasma levels of halogenated environmental contaminants in Latvian and Swedish men. *Environ Health Perspect.* 108:1035–1041.

Skaare, J.U., J.M. Tuveng, and H.A. Sande. 1988. Organochlorine pesticides and polychlorinated biphenyls in maternal adipose tissue, blood, milk, and cord blood from mothers and their infants living in Norway. *Arch Environ Contam Toxicol.* 17:55–63.

van den Berg, K.J. 1990. Interaction of chlorinated phenols with thyroxine binding sites of human transthyretin, albumin and thyroid binding globulin. *Chem Biol Interact.* 76:63–75.

van den Berg, K.J., J.A. van Raaij, P.C. Bragt, and W.R. Notten. 1991. Interactions of halogenated industrial chemicals with transthyretin and effects on thyroid hormone levels in vivo. *Arch Toxicol.* 65:15–19.

van Raaij, J.A., C.M. Frijters, L.W. Kong, K.J. van den Berg, and W.R. Notten. 1994. Reduction of thyroxine uptake into cerebrospinal fluid and rat brain by hexachlorobenzene and pentachlorophenol. *Toxicology.* 94: 197–208.

Perinatal Organochlorine Exposure in Rats: Effects on Humoral and Cellular Immune Parameters

Program leader

Pierre Ayotte, Ph.D., Professor, Université Laval, Unité de recherche en santé publique CHUQ-CHUL, Direction de la Toxicologie Humaine-INSPQ, 945 avenue Wolfe, Sainte Foy, QC G1V 5B3; phone: (418) 650-5115 (ext 4654); fax: 654-2148; e-mail: pierre.ayotte@inspq.qc.ca

Project team

Raynald Roy and Marthe Belles-Isles, Unité de Recherche en Rhumatologie et Immunologie, Centre de Recherche du CHUL-CHUQ; Éric Wagner, Division d'Hématologie-Oncologie, Hôpital Sainte-Justine, Montréal, QC; Janice L. Bailey and Anas Idris Centre de Recherche en Biologie de la Reproduction Département des sciences animales, Université Laval, QC.

Abstract

Traditional foods consumed by Northern populations are contaminated with endocrine-disrupting chemicals such as PCBs and chlorinated pesticides. Our general hypothesis is that *in utero* and lactational exposure to a mixture of organochlorines, known to bioaccumulate in the Arctic food chain, interferes with the development of the immune system and in turn increases susceptibility to infections. We assessed the effects of *in utero* and lactational exposure to this mixture on specific elements of the immune system in 90-days-old F1 male rats. Exposure to the mixture induced activation-like changes in splenic dendritic cells (DC) such as increased expression of MHCII and CD86, in the absence of antigen stimulation. Treatment with the mixture also increased mitogen-induced secretion of IL-12 by DC and basal TNF-α secretion by peripheral blood mononuclear cells (PBMC). Organochlorine treatment had no effect on IFN-γ secretion by PBMC or the complement activity. Taken together, these results suggest that the organochlorine mixture provides an activation stimulus to DC that may lead to their premature deletion, altered survival of T cells and dysregulation of the immune system.

Key Project Messages

1. *In utero* and lactational exposure of rats to the environmentally-relevant organochlorine mixture induces inappropriate activation of dendritic cells. These cells are involved in initiating normal immune response following exposure to an antigen.
2. Altered dendritic cell activation may represent a novel mechanism by which developmental exposure to organochlorines induces immunosupresssion.

Objectives

To assess the effect on the immune system of rats following developmental exposure to a complex organochlorine mixture, similar to that found in the Arctic aquatic food-chain, by measuring the following specific immune parameters:

1. splenic dendritic cell maturation and cytokine secretion;
2. cytotoxic T-cell and natural killer (NK) cytokine secretion;
3. complement system activity.

Introduction

Due to their high consumption of sea mammal fat, the Inuit people living in Nunavik display a body burden of organochlorines (OC) that exceeds that of inhabitants of Southern Québec. In both laboratory animal models and human studies, members of the organochlorine compound family have been shown to affect the reproductive system, the neuroendocrine system, the immune system, and to induce teratogenic and hepatotoxic effects (Van den Berg et al. 1998).

High incidences of infectious diseases have been reported in Inuit infants of Nunavik. These include meningitis, broncho-pulmonary infections and middle-ear infections (Dufour 1988; Duval and Thérien 1982; Proulx 1988). Otitis media is a serious problem in this population since hearing loss in one or both ears is observed in as many as 25% of school age children (Julien et al. 1987; Proulx 1988). While genetic and lifestyle factors may be implicated in this unusually high susceptibility displayed by Inuit infants to infectious diseases, we formulated the hypothesis that developmental exposure to OC could suppress immune system function and therefore might play a role. Indeed, a first epidemiological study conducted by our group in Nunavik showed that the risk of otitis media increased with prenatal exposure to some organochlorines (Dewailly et al. 2000).

In view of increasing the biological plausibility of this association and obtaining insights in possible mechanisms of action, we initiated experimental studies in animal models featuring developmental exposure to an organochlorine mixture designed to approximate that found in marine mammal fat consumed by Inuit people. The composition of the OC mixture is presented in Table 1. Using a vaccination protocol against *Mycoplasma hyopneumoniae* in pigs exposed to this OC mixture *in utero* and through lactation, we observed a low antibody production in piglets from the highest exposure group compared to animals in the other treatment groups, indicating that the humoral immune response was affected by developmental exposure to the mixture (Bilrha et al. *unpublished data*). These findings are in agreement with those of a recent study in rats showing that perinatal dioxin exposure was associated with suppression of specific antibody response (Ross et al. 2001).

Table 1. Composition of the organochlorine mixture

Compound	CAS number	% weight
PCB mixture[a]		32.59
Technical chlordane	57-74-9	21.3
p,p'-DDE	72-55-9	19.24
p,p'-DDT	50-29-3	6.79
Technical toxaphene	8001-35-2	6.54
α-HCH	319-84-6	6.17
Aldrin	309-00-2	2.52
Dieldrin	60-57-1	2.09
1,2,4,5-tetrachlorobenzene	95-94-3	0.86
p,p'-DDD	72-54-8	0.49
β-HCH	319-85-7	0.46
Hexachlorobenzene	118-74-1	0.35
Mirex	2385-85-5	0.23
γ-HCH	58-89-9	0.20
Pentachlorobenzene	608-93-5	0.18

[a] Mixture containing 2,4,4'-trichlorobiphenyl (320mg), 2,2',4,4'-tetrachlorobiphenyl (256mg), 3,3',4,4'-tetrachlorobiphenyl (1.4 mg), 3,3',4,4', 5-pentachlorobiphenyl (6.7mg), Aroclor 1254 (12.8g) and Aroclor 1260 (19.2g)

Dendritic cells (DC) have the capacity to induce the primary immune response to foreign antigen and therefore are important in generating the immune response to infection (Bancherau et al. 2000). DC are the most effective antigen-presenting cells to promote activation of cytotoxic T cells and natural killer (NK) cells. Because the cytotoxic cells are implicated in defence system against microbes, DC function constitutes a critical endpoint to be measured in the immunotoxicological evaluation of xenobiotics.

When exposed to an antigenic stimulus, DC are induced to migrate to the spleen or draining lymph nodes and to undergo a maturation process (Banchereau et al. 2000). Mature DC are able to up-regulate a variety of cytokines and ultimately promote the differentiation of Th1 vs Th2 cells. Following xenobiotics exposure, disruption in DC maturation could play a predominant effect on regulation of humoral and cell-mediated immunity.

Several immunotoxicity studies have focused on the effects of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), which

induces specific responses mediated through binding to the aryl-hydrocarbon receptor (Whitlock 1991). It was shown that TCDD induced a lower resistance to infectious diseases, suppression of cell mediated and thymus-dependent humoral response in mice (Kerkvliet and Burleson 1994). More recently, it was also shown that although treatment of mice with TCDD lead to a lower level of DC *in vivo*, increased expression of ICAM-1, B7.2, CD40 and IL-12 was observed (Vorderstrasse and Kerkvliet 2001). Since activation of naive T cells is initiated primarily by DC, as mentioned earlier, these cells represent a potential target for dioxin-like compound immunotoxicity. Dioxin-like compounds are important constituents of the OC mixture found in the Arctic aquatic food web.

In the present study, we examined the effect of prenatal and lactational exposure to the OC mixture on the maturation of splenic DC and its consequences on the regulation of circulating Th1/Th2 lymphocytes, on cell cytotoxicity and on complement activities involved in humoral response. The potential for OC to influence DC in terms of suppression of immune function was the major endpoint of this study.

Activities

In 2002–2003

Five-week-old Sprague-Dawley female rats were housed, two per cage, in a university facility with 12 h light cycle (6:45–18:45), 22±1°C temperature and 46±10% humidity. After 10 days of acclimatization, the rats were randomly assigned to four groups (10 per group) and were administered the organochlorine mixture thrice weekly by gavage (corn oil as vehicle) to yield the following daily doses of polychlorinated biphenyls (PCBs): 0 (control group), 0.05, 0.5, 5 mg kg^{-1} body weight (BW) day^{-1}. Doses of other OC that are part of the mixture can be calculated from composition data presented in Table 1. After five weeks of treatment, each pair was housed with an unexposed male for 10 days. Mating was confirmed by the presence of a vaginal plug. OC administration continued throughout gestation until parturition. Fertility data and pups characteristics at birth are reported in another synopsis (Project H-05, Janice Bailey et al.). Because only two dams of the 5 mg PCBs group delivered live litters, this treatment group was excluded from analysis.

Male pups were sacrificed at PND90. Blood was collected by cardiac puncture in a tube containing heparin and PBMC were isolated using Ficoll-hypaque gradient centrifugation. The serum was stored at –70°C for complement analysis.

Activity of the classical pathway was assayed according to established methods (Rapp and Borsos 1970; Wagner et al. 2001). Briefly, serial dilutions of serum samples were incubated with optimally-sensitized sheep erythrocytes at 37°C. The extent of haemolysis in the supernatant was assessed spectrophotometrically and the total haemolytic complement titer (CH50) calculated as described previously (Wagner et al. 2001).

DC was enriched from spleens using the method described by Vorderstrasse and Kerkvliet (2001). Briefly, splenic tissues were digested with collagenase D (Boehringer Mannheim) at 37°C for 45–60 min to release DC from the capsule and to increase recovery. Cell suspensions were then diluted in Ca-/Mg-free HBSS and pelleted. Recovered cells were spun over a bovine serum albumin gradient and cells in the low-density fraction were collected. These freshly isolated DC-enriched populations were then stained for flow cytometry analysis of cell surface markers. To this end, we used mAbs to HLA-DR (OX6-FITC-conjugated; Serotec) and CD86 (PE-conjugated; Serotec). IL-12 secretion by DC was measured using an enzyme-linked immunosorbent spot assay (ELISPOT).

Results

Effect of developmental OC exposure on DC maturation

Several cell surface proteins play important roles in the function of DC. We initially examined the expression of some accessory molecules on splenic DC from rats exposed *in utero* and through lactation to different doses of the OC mixture. The expression of MHC class II was significantly increased in male rats from the 0.5 mg·kg^{-1} BW day^{-1} dose group compared to the control group ($P<0.05$). We also noted a dose-dependent increase in the expression of the CD86 accessory molecule (control group vs 0.05 mg·kg^{-1} BW day^{-1} group, $P<0.05$; 0.05 mg·kg^{-1} BW day^{-1} group vs 0.5 mg·kg^{-1} BW day^{-1} group, $P<0.05$). There was a tendency towards higher secretion of IL-12 by LPS-stimulated DC with increasing doses of the OC mixture, although the analysis of variance did not reveal statistically significant differences between groups ($P = 0.111$). Levels of IL-12 secretion by unstimulated DC were similar.

Effect of developmental OC exposure on T and NK cell immunity

In order to evaluate the role of DC maturation and IL-12 production on induction of IFN-γ secretion from Th1 cells and NK cells, we measured capacity of PBMC to secrete IFN-γ secretion using the ELISPOT. Memory

T cells and NK cells are the major IFN-γ producing cells and therefore IFN-γ production reflects the cellular immune response. No effect of the OC treatment was observed on the number of PBMC secreting IFN-γ, both with and without mitogenic stimulation (ConA).

In order to assess the impact of the OC treatment on T cells, we measured TNF-α secretion in PBMC supernatant following mitogenic stimulation, using an ELISA method. In ConA-stimulated PBMC from rats in OC-treated groups (0.05 or the 0.5mg·kg^{-1} BW day^{-1}) secreted more TNF-α than PBMC from animals in the control group, although the difference was not statistically significant. However, in the absence of mitogenic stimulation, TNF-α secretion by PBMC was significantly increased for animals belonging to the 0.5mg·kg^{-1} BW day^{-1} dose group compared to animals belonging to the other experimental groups ($P<0.05$).

Effect of developmental OC exposure on complement activity

Serum samples from F1 male rats were tested for haemolytic complement activity. Neither the classical pathway nor the alternative pathway of complement activation was affected by developmental exposure to OC.

Discussion and Conclusions

Considering the possible immunosuppressive properties of OCs, we hypothesized that developmental exposure to these compounds would suppress the expression of these accessory molecules on DC and consequently disrupt their ability to activate T cells. Contrary to our expectation, enhanced expression of MHC II and CD86 molecules was observed in animals exposed during development to the OC mixture. These results suggest that the OC mixture induced an inappropriate maturation of DC, similarly to that reported previously in adult mice treated with an immunosupresive dose of TCDD (Vorderstrasse and Kerkvliet 2001). In the latter study, a premature deletion of DC was observed, which might lead to a dysregulation of the immune system. A similar mechanism might be involved here.

In order to further substantiate that DC activation is induced by OC exposure, we measured the production of IL-12 by cultured DC. This cytokine is produced by DC and other antigen presenting cells involved in the differentiation of Th1 vs Th2 cells. A marginally-significant increase in IL-12 production by LPS-stimulated DC was noted in animals developmentally-exposed to the OC mixture. However, we did not observe an increase in IL-12 production by DC from OC treated animals in the absence of LPS stimulation. This suggests that the OC mixture did not induce activation of DC directly but rather influenced the capacity of DC to prime naive T cells during normal adaptive immune response. Furthermore, some evidence of T-cell priming defect was noted in PBMC from OC-treated animals, as shown by the decrease in basal secretion of TNF-α noted in these animals.

Finally, our results indicate that developmental exposure to OC does not lead to major alterations in complement activity, either via the classical or the alternative pathway. Only major changes in complement activity can be measured using these assays. Nevertheless, a normal CH50 or AH50 titer does not rule out modifications of individual components in both pathways. Functional titrations of complement components C2 (classical pathway) and C3 (classical and alternative pathways) will be performed, which represent far more sensitive assays. Results of these assays will be communicated at a later time.

Expected Completion Date

September 30, 2003

References

Banchereau, J., F. Briere., C. Caux, J. Davoust, S. Lebecque, Y.J. Liu, B. Pulendran and K. Palucka. 2000. Immunobiology of dendritic cells. *Annu Rev Immunol.* 18: 767–811.

Bilrha, H., R. Roy, É.Wagner, M. Belles-Isles, J.L. Bailey, B. Bérubé and P. Ayotte. 2003. Effects of gestational and lactational exposure to organochlorine compounds on cellular, humoral and innate immunity in swine. *Submitted for publication.*

Dewailly, É., P. Ayotte, S. Bruneau, S. Gingras, M. Belles-Isles and R. Roy. 2000. Susceptibility to infections and immune status in Inuit infants exposed to organochlorines. *Environ Health Perspect.* 108:205–11.

Dufour, R. 1988. The otitis media among Inuit children. Proposal for a new approach. *Arctic Med Res.* 47(suppl 1):659–665.

Duval B and F. Thérien. 1982. Natalité, mortalité et morbidité chez les Inuit du Québec arctique. *Recherches amérindiennes au Québec.* 12:41–50.

Julien, G, J.D. Baxter, M. Crago, H.J. Ilecki and F. Thérien. 1987. Chronic otitis media and hearing deficit among native children of Kuujjuaraapik (Northern Quebec): a pilot project. *Can J Pub Health.* 78:57–62.

Kerkvliet, N.I. and G.R. Burleson. 1994. Immunotoxicity of TCDD and related halogenated aromatic

hydrocarbons. In: J.H. Dean, M.I. Luster, A.E. Munson and I. Kimber (eds.), *Immunotoxicology and Immunopharmacology.* New York, NY: Raven Press. pp. 97–121.

Proulx, J.F. 1988. *Toward healthy communities on Hudson coast.* Povungnituk, QC: Inulitsivik Health Centre.

Rapp, H.J and T. Borsos (eds.). 1970. *Molecular Basis of Complement Action.* Appleton-Century-Crofts, New York.

Ross, P.S., R.L. de Swart, H. van der Vliet, L. Willemsen, A. de Klerk, G. van Amerongen, J. Groen, A. Brouwer, I. Schipholt, D.C. Morse, H. van Loveren, A.D. Osterhaus and J.G. Vos. 1997. Impaired cellular immune response in rats exposed perinatally to Baltic Sea herring oil or 2,3,7,8-TCDD. *Arch Toxicol.* 71:563–574.

Van den Berg, M., L. Birnbaum, A.T. Bosveld, B. Brunstrom, P. Cook, M. Feeley, J.P. Giesy, A. Hanberg, R. Hasegawa, S.W. Kennedy, T. Kubiak, J.C. Larsen, F.X. van Leeuwen, A.K. Liem, C. Nolt, R.E. Peterson, L. Poellinger, S. Safe, D. Schrenk, D. Tillitt, M. Tysklind, M. Younes, F. Waern and T. Zacharewski. 1998. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ Health Perspect.* 106: 775–792.

Vorderstrasse, B.A. and N.I. Kerkvliet. 2001. 2,3,7,8-Tetrachlorodibenzo-p-dioxin affects the number and function of murine splenic dendritic cells and their expression of accessory molecules. *Toxicol Appl Pharmacol.* 171:117–125.

Wagner, É., H. Jiang and M.M. Frank. 2001. Complement and kinins: mediators of inflammation. In: J.B. Henry (ed.), 20th ed., *Clinical Diagnosis and Management by Laboratory Methods.* Philadelphia, PA: W.B. Saunders Company. pp. 892–913.

Whitlock, J.P. Jr. 1991. Mechanism of dioxin action: relevance to risk assessment. In: M.A. Gallo, R.J. Scheuplein and K.A. Van Der Heijden (eds.), *Biological Basis for Risk Assessment of Dioxins and Related Compounds.* Cold Spring Harbor, NY: Cold Spring Harbor Laboratory Press. pp. 351–366.

Effects of an Environmentally-Pertinent Mixture of Organochlorines on Reproductive Development and Health in the Porcine and Rat Models

Project leader

Janice L. Bailey, Centre de Recherche en Biologie de la Reproduction, Département des sciences animales, Université Laval; Pavillon Paul-Comtois, local 4147, Ste-Foy, QC G1K 7P4; phone: 418-656-2131 (ext 3354); fax: 418-656-3766; e-mail: janice.bailey@crbr.ulaval.ca

Project team members

Pierre Ayotte, Project Co-Investigator, Public Health Research Unit, Université Laval Beauport, QC; Marc-André Sirard, Professor & Centre Director; Jean-Paul Laforest, Professor & Department Chair; Christine Guillemette, Research Associate; Céline Campagna; Anas Idris, Centre de Recherche en Biologie de la Reproduction, Département des sciences animales, Université Laval, Ste-Foy, QC; Tiaan de Jager, Medical Sciences Laboratory, Department of Urology, University of Pretoria, Pretoria, South Africa.

Abstract

Traditional foods of Northern aboriginal populations are persistently contaminated with endocrine-disrupting PCBs and chlorinated pesticides. The toxicity of these organochlorines on human health, reproduction and development remains unclear. The foetus is particularly sensitive, since much reproductive development occurs during gestation. The porcine model is used for the first experimental series. *In vitro* assays are being conducted using serum extracts from organochlorine-treated pigs to test the hypothesis that gametes and embryos are susceptible to a mixture containing organochlorines and their metabolites. A second series is determining the effects of *in utero* and lactational exposure to organochlorines on neonatal size and male offspring reproductive health using the rat model to validate and continue our previous findings in the pig that maternal exposure to an environmentally-relevant organochlorine mixture alters sex ratio and reduces neonatal length, testicular size and sperm motility of pubertal male offspring. These experiments are providing critical information as to whether exposure to a mixture of contaminants that persists in the Arctic food chain threatens reproductive and developmental health.

Key Project Messages

Direct exposure to an environmentally-pertinent organochlorine mixture adversely affects oocyte maturation, sperm function, fertilisation and embryo competence.

Objectives

Short term-objectives for the 2001–2003 duration of the project:

1. To understand the effects *in vitro* of organochlorines and their metabolites, extracted from the serum from treated animals, on the maturation and function of oocytes and sperm using the porcine model. These experiments represent an assessment of female reproductive potential.
2. To establish the impact of these organochlorines and their metabolites on the functional parameters of pig spermatozoa using *in vitro* assays. These experiments will be conducted in order to estimate the impact these toxicants found within the female genital tract on *in vivo* fertility and embryonic development.
3. To evaluate *in vitro* the effects of these same serum extracts on the formation and developmental competence of embryos, also using the pig as the animal model. These assays will be indicative of any early developmental toxicity of the organochlorine metabolites.
4. To determine the effects of *in utero* and lactational exposure to the environmentally relevant organochlorine mixture on the reproductive ontogeny of male rat pups.

Introduction

Steroid hormones regulate the development and maintenance of reproductive tissues. Persistent organic pollutants found in highly exposed human populations contain a large variety of compounds, including substances with estrogenic (e.g. *o,p'*-DDT, β-HCH), anti-estrogenic (e.g. dioxin-like polychlorinated biphenyls, PCBs) or anti-androgenic capacities (e.g. *p,p'*-DDE). These environmental contaminants alter the function of endocrine and reproductive systems by mimicking or antagonizing endogenous hormone action, modulating the synthesis and metabolism of endogenous hormones, or altering hormone receptor production (Sonnenschein and Soto, 1998). Therefore, complex real-life mixtures can interact with the hormone messengers involved in cell differentiation and growth, and could affect all phases of reproduction.

Traditional diets of Northern populations are contaminated with a complex mixture of organochlorines (Dewailly et al., 1993; Kuhnlein et al., 1995; Chan et al., 1997). Consequently, this unusually high exposure has elevated their levels in the blood (Ayotte et al., 1997), breast milk (Dewailly et al., 1996), placenta (Lagueux et al., 1999) and other organ tissues (Dewailly et al., 1999).

Reproductive health risks associated with these contaminants include breast cancers (Demers et al., 2000) and male reproductive dysfunctions. In men, declining sperm counts, testicular cancer, hypospadias, cryptorchodism and small penile size have been associated with endocrine disruption by organochlorines (reviewed by Cheek and McLachlan, 1998), although a clear causal role is lacking, resulting in unprecedented controversy. Trapp et al. (1984) reported the presence of various organochlorine compounds in human follicular fluid such as PCBs, DDT, dieldrin and hexachlorocyclohexane. Consequently, exposure of the gametes (oocytes, sperm) and embryo-foetus to these endocrine disruptors is assured by the presence of environmental contaminants in the female reproductive tract. Furthermore, granulosa cells, which surround the oocytes, are highly susceptible to endocrine disruptors such that they have been used for *in vitro* screening of reproductive toxicants (Hughes et al., 1990). In various species, *in vitro* oocyte maturation, fertilisation and embryo development are compromised in the presence of certain agents when tested individually (Kholkute et al., 1994; Lindow and Fischer, 1996; Kholkute and Dukelow, 1997; Alm et al, 1998). However, this is controversial since other investigations have showed no adverse effects (Greenfeld et al., 1998).

Since these investigations were conducted using only one chemical *in vitro*, the relevance to reproduction *in vivo* is questionable. Therefore, the impact of persistent organic pollutants on male and female reproduction, as well as on fertilisation and embryo development, remains to be elucidated in an environmentally-pertinent manner. Most studies evaluate the effects of only one or two organochlorines. In the environment, however, populations are exposed to spectrum of compounds (including substances with estrogenic, anti-estrogenic or anti-androgenic capacities). A real-life mixture containing components that interact with each other in an additive and/or non-additive fashion (synergistic or antagonistic) and bind different receptors is needed to provide a better representation of what occurs in nature. Therefore, our project investigates physiological responses to a complex, environmentally-relevant mixture of organochlorine chemicals designed to match the levels found in ringed seal blubber (Muir, 1995).

Activities

In 2001–2002

1. Inclusion of an organochlorine mixture during *in vitro* maturation or *in vitro* fertilisation of porcine oocytes affects maturation, fertilization and embryonic development.

Using the pig as a toxicological model for humans, we tested the hypothesis that exposure to a mixture of more

Table 1. Composition of the organochlorine mixture (based on the composition found in ringed seal blubber; Muir 1995)

Compound	CAS number	% weight
PCB mixture		32.59
Technical chlordane	57-74-9	21.30
p,p'-DDE	72-55-9	19.24
p,p'-DDT	50-29-3	6.79
Technical toxaphene	8001-35-2	6.54
α-HCH	319-84-6	6.17
Aldrin	309-00-2	2.52
Dieldrin	60-57-1	2.09
1,2,4,5-tetrachlorobenzene	95-94-3	0.86
p,p'-DDD	72-54-8	0.49
β-HCH	319-85-7	0.46
Hexachlorobenzene	118-74-1	0.35
Mirex	2385-85-5	0.23
γ-HCH	58-89-9	0.20
Pentachlorobenzene	608-93-5	0.18

than 15 environmental contaminants negatively affects *in vitro* maturation, fertilization and development of pig oocytes. The organochlorine mixture was prepared by dissolving the pure powders and oils of organochlorine compounds in dimethyl sulfoxide (DMSO) to obtain the proportions listed in Table 1.

Dilutions of the stock solution (1:10, 1:100, 1:1000, 1:10000 and 1:10000) were made in DMSO so that the *in vitro* culture media contain a total concentration of 0.1% DMSO for all treatments. Treatments are expressed in terms of total PCB concentration (or final dilution of stock solution). The tested doses were: Control without DMSO, Control with 0.1% DMSO ('solvent control'), 4.2 ng/·mL^{-1} (1:107), 42 ng/·mL^{-1} (1:10^6), 0.42 μg/mL^{-1} (1:10^5), 4.2 μg·mL^{-1} (1:10^4), 42 μg·mL^{-1} μg/mL (1:10^3).

1. *Effects on oocyte maturation* — It was hypothesized that exposing immature cumulus-oocyte complexes to an organochlorine mixture during *in vitro* maturation would adversely affect oocyte maturation, fertilization and subsequent embryo development. Porcine cumulus-oocyte complexes were cultured in *in vitro* maturation medium containing increasing concentrations of the organochlorine mixture, similar to that found in women of highly-exposed populations. Organochlorines reduced the quality of cumulus expansion and the viability of cumulus cells in a dose-response manner. The proportion of apoptotic cumulus cells also increased due to organochlorine exposure. Half of the oocytes were fixed after insemination and the remainders were cultured for 8 days.
2. *Electron microscopy* — Dr. Poul Hyttel from Denmark (via our collaborator, Dr. Marc-André Sirard) invited the team to conduct electron microscopy on the oocytes that had been matured *in vitro* with the organochlorine mixture. It was hypothesized that the organochlorine treatment would alter the ultrastructure of the oocytes, reflecting their reduced developmental competence.
3. *Effects on fertilisation* — The effects of the organochlorines on *in vitro* fertilization and development of pig oocytes and sperm exposed during *in vitro* fertilization period were evaluated. Oocytes were co-cultured with sperm in *in vitro* fertilization medium containing increasing concentrations of an organochlorine mixture, similar to that found in women of highly-exposed populations.
4. *Effects on sperm* — Given the poor *in vitro* penetration rates of treated sperm (Campagna et al., 2002), the hypothesis that organochlorines reduce porcine sperm quality after incubation *in vitro* in conditions that mimic the female reproductive tract was tested. Fresh sperm were co-incubated with the organochlorine mixture and sperm quality was assessed.

II. Effects of organochlorine serum metabolites on fertilisation and development in the pig model.

Currently the lab is purifying the metabolites from the pig serum of organochlorine treated pigs (and controls; Table 1). This serum is being tested for toxic effects on the gametes as we have had to ultrapurify the metabolites to remove traces of hexane (used in the extraction process). Furthermore, the lab is now completely competent to conduct the *in vitro* assays as proposed. We are ready to start once we obtain ourthe necessary funds are obtained.

III. Susceptibility of the foetus and neonate transplacental and lactational exposure to a mixture of organochlorines in the rat model.

This *in vivo* rat study is still in preliminary stages, because of a lack of personnel funds. The lab is presently completing the preliminary trials on female rats to confirm the organochlorine levels (Table 1) that will be administered during the major study.

Results

Inclusion of an organochlorine mixture during *in vitro* maturation or *in vitro* fertilization of porcine oocytes affects maturation, fertilization and embryonic development.

1. *Effects on oocyte maturation* — None of the levels of the organochlorine mixtures affected the rates of oocyte degeneration, sperm penetration and development to morula. However, incidence of incompletely matured oocytes increased and polyspermy rate decreased, both in a dose-response manner with increasing organochlorine concentrations. Blastocyst formation and number of cells per blastocyst declined with organochlorine concentration.

2. *Electron microscopy* — We hypothesized that the organochlorine treatment would alter the ultrastructure of the oocytes. Very interestingly and in stark contrast to our hypothesis, the organochlorines did not modify oocyte ultrastructure.

3. *Effects on fertilization* — Exposure to the organochlorine mixture diminished the rates of oocyte penetration and polyspermy in a linear manner. The mixture did not affect the rates of cleavage and development to multicell embryos. However, development to blastocyst stage was lower at the highest concentration at which oocyte penetration was observed. The same experiment was performed using oocytes pre-exposed during *in vitro* maturation. This increased exposure to the mixture also reduced penetration in a dose-response manner and affected polyspermy. Frozen-thawed pig sperm were also cultured in an *in vitro* fertilization medium containing the same organochlorine concentrations. Sperm motility parameters were immediately reduced in a dose-dependant manner by the organochlorines, followed by diminished viability 2 h later.

4. *Effects on sperm* — With increasing organochlorine concentrations, sperm motility reduced markedly at exposure and over time. The sperm motility of the control group was always higher than the treated groups ($P<0.05$). Surprisingly, the sperm viability of treated groups decreased over time in a manner corresponding to the motility levels, however, not to such a drastic extent. The organochlorines appear, therefore, to affect sperm motility to a greater degree than viability. Normally, when semen is incubated in physiological conditions, progressive motility increases with time. This was indeed observed in the control group, however, in the treated groups, progressive motility decreased over time in a manner inversely proportional to organochlorine concentration. The assessment of sperm maturation and membrane status was conducted using the chlorotetracycline fluorescence assay. Sperm were stained and classed according to three different fluorescent patterns (uncapacitated, capacitated or acrosome-reacted). As the concentrations of organochlorines increased, the rates of capacitated and acrosome-reacted sperm also increased. In particular, the pattern B (corresponding to capacitated sperm) increased considerably with dose ($P<0.05$).

Discussion and Conclusions

Inclusion of an organochlorine mixture during *in vitro* maturation or *in vitro* fertilization of porcine oocytes affects maturation, fertilization and embryonic development.

1. *Effects on oocyte maturation* — Exposing porcine cumulus-oocyte complexes to an environmentally-pertinent organochlorine mixture during *in vitro* maturation disturbs oocyte development, supporting recent concerns that such pollutants harm reproductive health in humans and other mammalian species (Campagna et al., 2001).

2. *Electron microscopy* — We must consider that the reduced functionality of these treated oocytes is therefore mechanistic, rather than structural.

3. *Effects on fertilization* — From these results, it appears that the reduced sperm quality would account for the decrease in fertilization, polyspermy and blastocyst formation. These results suggest that exposing porcine oocytes and sperm to an environmentally-pertinent organochlorine mixture *in vitro* disrupts the oocyte block to polyspermy, sperm fertility and further embryonic development, supporting recent concerns that such pollutants harm reproductive health in humans and other species (Campagna et al., 2002).

4. *Effects on sperm* — Our findings are interesting in light of observations that both capacitation and the acrosome reaction have been shown to be induced by progesterone (Melendrez et al., 1994; Barboni et al., 1995), suggesting that the hormonal properties of organochlorines may even affect non-traditional steroidal roles. Conversely, organochlorine insecticides also inhibit the ability of human sperm to undergo a physiological acrosome reaction (Turner et al., 1997). Clearly, these persistent environmental contaminants negatively affect male gametes in a way that could be manifest as reduced fertility *in vivo*. Contact with organochlorines is detrimental to sperm function and particularly to sperm motion and membrane parameters. The mechanism of damage, however, remains to be determined.

Expected Completion Date

The objectives pertaining to this project will be met by March 31, 2003.

Acknowledgements

We are grateful to the Centre d'insémination Porcine du Québec for generously donating the pig semen used in this project. Dr. Poul Hyttel (Royal Vet erinary and Agricultural University, Denmark) kindly collaborated with the electron microscopy work.

References

Alm H., H. Torner, U. Tiemann, and W. Kanitz. 1998. Influence of organochlorine pesticides on maturation and postfertilization development of bovine oocytes *in vitro*. *Reprod Toxicol.* 12:559–63.

Ayotte, P., É. Dewailly, J.J. Ryan, S. Bruneau, and G. Lebel. 1997. PCBs and dioxin-like compounds in plasma of adult Inuit living in Nunavik (Arctic Quebec). *Chemosphere.* 34:1459–68.

Campagna C., C. Guillemette, R. Paradis, M.A. Sirard, P. Ayotte and J.L. Bailey. 2002. An environmentally-relevant organochlorine mixture damages sperm function and fertility in the porcine model. *Biol Reprod.* 67:In press.

Campagna C., C. Guillemette, M.-A. Sirard, P. Ayotte and J.L. Bailey. 2001. Damaged porcine sperm function and oocyte fertilization following exposure to an environmentally relevant organochlorine mixture in vitro. 2nd International Conference on Male-Mediated Developmental Toxicity, July. Montréal, Quebec, p. 21.

Campagna C., C. Guillemette, M.-A. Sirard, P. Ayotte and J.L. Bailey. 2001. Damaged porcine sperm function and oocyte fertilization following exposure to an environmentally relevant organochlorine mixture in vitro. Annual Meeting of the Canadian Toxicology Society, December. Montreal, QC.

Campagna C., M.A. Sirard, P. Ayotte and J.L. Bailey. 2001. Impaired maturation, fertilization and embryonic development of porcine oocytes following exposure to an environmentally-relevant organochlorine mixture. *Biol Reprod.* 65:554–560.

Campagna C., M.-A. Sirard, P. Ayotte and J.L. Bailey. 2001. Exposure to an environmentally-relevant organochlorine mixture during in vitro maturation of porcine oocytes damages the steps of maturation, fertilization and embryonic development. (*Biol. Reprod.* 64S1:121) 34th Annual Meeting of the Society for the Study of Reproduction, July. Ottawa, Ontario.

Chan, H.M., P.R. Berti, O. Receveur, and H.V. Kuhnlein. 1997. Evaluation of the population distribution of dietary contaminant exposure in an Arctic population using Monte Carlo statistics. *Environ Health Perspect.* 105:316–21.

Cheek, A.O., and J.A. McLachlan. 1998. Environmental hormones and the male reproductive system. *J Andrology.* 19:5–10.

de Jager C., M.S. Bornman, N. Aneck-Hahn, M.H. Fourie and J.L. Bailey. 2001. The effects of p-nonylphenol, phytoestrogens and mycotocins on reproductive parameters in male rats. 2nd International Conference on Male-Mediated Developmental Toxicity, June. Montréal, Quebec, p. 23.

Dewailly, É., G. Mulvad, H.S. Pedersen, P. Ayotte, A. Demers, J.P. Weber, and J.C. Hansen. 1999. Concentration of organochlorines in human brain, liver, and adipose tissue autopsy samples from Greenland. *Environ Health Perspect.* 107:823–8.

Dewailly, É., P. Ayotte, C. Laliberte, J.P. Weber, S. Gingras, and A.J. Nantel. 1996. Polychlorinated biphenyl (PCB) and dichlorodiphenyl dichloroethylene (DDE) concentrations in the breast milk of women in Quebec. *Am J Public Health.* 86:1241–6.

Dewailly, É., P. Ayotte, S. Bruneau, C. Laliberte, D.C. Muir, and R.J. Norstrom. 1993. Inuit exposure to organochlorines through the aquatic food chain in Arctic Quebec. *Environ Health Perspect.* 101:618–20.

Greenfeld, C.R., W. Xiongquing, and W.R. Dukelow. 1998. Aroclor 1254 does not affect the IVF of cumulus-free mouse oocytes. *Bull Envrion Contam Toxicol.* 60: 766–772.

Guillemette, C., P. Ayotte, B. Bérubé and J.L. Bailey. 2001. In utero and lactational exposure to an environmentally-relevant organochlorine mixture advserely affects male reproductive parameters in the porcine model. 2nd International Conference on Male-Mediated Developmental Toxicity, June. Montréal, Quebec, p. 13.

Hughes, S.F., A.F. Haney, and C.L. Jr. Hughes. 1990. Use of human cumulus granulosa cells for in vitro screening of reproductive toxicants. *Reprod Toxicol.* 4:11–15.

Lindenau, A., and B. Fischer. 1996. Embryotoxicity of polychlorinated biphenyls (PCBs) forpreimplantation embryos. *Reprod Toxicol.* 10:227–230.

Kholkute, S.D., and W.R. Dukelow. 1997. Effects of polychlorinated biphenyls (PCB) mixtures on in vitro fertilisation in the mouse. *Bull Environ Contam Toxicol.* 59:531–536.

Kholkute, S.D., J. Rodriguez, and W.R. Dukelow. 1994. Reproductive toxicity of Aroclor-1254: effets on oocytes, spermatozoa, in vitro fertilization, and embryo development in the mouse. *Reprod Toxicol.* 8:487–493.

Kuhnlein, H.V., O. Receveur, D.C. Muir, and H.M. Chan. 1995. Soueida Arctic indigenous women consume greater than acceptable levels of organochlorines. *J Nutr.* 1125:2501–10.

Muir, D. 1995. Spatial and temporal trends of organochlorines in Arctic marine mammals. In Environmental Studies No. 73, *Synopsis of Research Conducted Under the 1994/1995 Northern Contaminants Program.*, J. Murray, R. Shearer and S. Han, Editors. 143–147.

Sonnenschein, C., and A.M. Soto. 1998. An updated review of environmental estrogen and androgen mimics and antagonists. *J Steroid Biochem Mol Biol.* 65:143–50.

Trapp, M., V. Baukloh, H-G. Bohnet, and W. Heeschen. 1984. Pollutants in human follicular fluid. *Fertil Steril.* 42:146–8.

Turner, T.T., C.E. Jones, S.S. Howards, L.L. Ewing, B. Zegeye, and G.L. Gunsalus. 1984. On the androgen microenvironment of maturing spermatozoa. *Endocrinology.* 115:1925–32.

Population Distribution of Dietary Exposure to Contaminants in Inuit Communities

Program leader

Peter R. Berti, Programme for Appropriate Technology in Health,
1105-One Nicholas Ave, Ottawa, Ontario K1V 7J4; phone: (613) 241-3927
(ext. 324); fax: (613) 241-7988; e-mail: pberti@pathcanada.org

Project members

Laurie Chan, CINE, McGill University, Ste-Anne-de-Bellevue, QC; Eric Loring,
Inuit Tapiriit Kanatami (ITK), Ottawa, ON.

Abstract

This project is a continuation of the previous NCP funded CINE project entitled "Assessment of Dietary Benefit: Risk in Inuit Communities" in which dietary information was collected from 1,930 individuals in 18 Inuit communities (CINE, 2000). We have estimated the usual or chronic average daily exposures over one year to the contaminants identified in earlier work as being of greatest concern, namely, mercury, lead, PCBs, toxaphene and chlordane. Food Frequency Questionnaire (FFQ) data for summer and winter and the 24-hour dietary recall data for the fall and spring are integrated. Median exposures to these five contaminants are at or below the tolerable daily intakes (TDIs), but the high end consumers have exposures 2 to 16 times greater than the TDIs. The exposures are generally higher in males, in older individuals, in summer, and in Baffin region. Exposures are generally lower in females, in younger individuals, in winter, and in Labrador. The greatest source of uncertainty in the results likely arises from gaps in the contaminant data set, including possible regional and local variations in contaminant levels. Continued monitoring is needed. Our results reaffirm the concerns of earlier exposure analyses executed using only the 24-hour dietary recall data representing two seasons.

Key Project Messages

1. The population distribution of daily exposure to mercury, lead, PCBs, toxaphene, and chlordane in the Inuit over a full year has been estimated for the first time, by integrating food frequency questionnaire data and 24-hour dietary recall data representing four seasons.
2. Median exposures to these five contaminants are at or below the TDIs, but the high end consumers have exposures 2 to 16 times greater than the TDIs.
3. The exposures are generally higher in males, in older individuals, in summer, and in Baffin region. Exposures are generally lower in females, in younger individuals, in winter, and in Labrador.
4. The greatest source of uncertainty in the results likely arises from gaps in the contaminant data set, including possible regional and local variations in contaminant levels.
5. These results reaffirm the concerns of earlier exposure analyses executed using only the 24-hour dietary recall data representing two seasons.

Objectives

The overall objective of this project was to estimate population distribution in chronic exposure levels to contaminants in the diet of Inuit, using the data collected in the CINE dietary survey.

Introduction

Under the NCP funded CINE project entitled "Assessment of Dietary Benefit: Risk in Inuit Communities", dietary information was collected from 1,930 individuals in 18 Inuit communities (CINE, 2000). One of the outcomes of the project was the estimation of exposure in the Inuit through the diet to four metals and eight organochlorines on single days in the fall and the spring. These estimates are useful for identifying the communities with the highest exposures, the contaminants of greatest concern, and the main dietary sources of the contaminants. However, because these estimates were single day exposures, not "usual" or chronic exposures, and did not account for the summer or winter diet, they do not represent the health risk from exposure to these chemicals (which is a function of long-term, rather than single-day, exposure). In this report we estimate the usual or chronic average daily exposures over one year to the contaminants identified in earlier work as being of greatest concern, namely, mercury, lead, PCBs, toxaphene and chlordane. We did this by analysing the previously unused Food Frequency Questionnaire (FFQ) data (which provide information on usual traditional food intake in the summer and winter), and by applying appropriate statistical methods to the 24-hour dietary recalls, representing the fall and spring.

Activities

In 2001–2002

Preparation of the FFQ data set: The FFQ questionnaire collected data only on frequency, not on portion size; for this work portion size was imputed using the data from the 24 hour recall. For each food we estimated intake in "grams·day^{-1}" by: frequency of consumption over previous three months · d^{-1} · imputed portion size (g·d^{-1}) · 91d^{-1}.

Update of contaminant data set: A set of rules were applied to previously compiled contaminant data to impute contaminant values data to fill gaps in the data set (e.g. ring seal contaminant values used for missing values for harp seal, hooded seal, ranger seal and bearded seal).

Conduct exposure analysis: The FFQ, 24 hour recall and contaminant data sets were integrated to estimate usual exposures to five contaminants (reported below).

Communicate results to ITK: The results were presented to ITK, and further breakdown of the results by community will be provided to support the ITK communication efforts.

Results and Discussion

Data preparation

The dietary data, collected and cleaned in previous years, is a large, rich data set, representing the diet of the Inuit in five regions of the Arctic. Portion sizes were imputed for the FFQ data, so that the frequency data could be converted to grams·day^{-1}, for exposure assessment. The food consumption data were merged with food contaminant data to estimate exposures.

Traditional food consumption

The consumption of traditional food is summarized in Table 1, with each season shown separately. Note that here and elsewhere in this report that FFQ data (summer and winter) represent the individuals average intake (grams·day^{-1}) over the course of the season, whereas the unadjusted 24 hour recall data (fall and spring) represent only a single day. The distribution of the 24 hour recall data is more skewed than the FFQ data. In the 24 hour recall data the 50th centile is 0 grams for every food group, and for some very uncommon foods, even the 99th centile is 0 grams. In each season, caribou meat is consumed by the most people, and is consumed in the greatest average amounts.

Contaminant exposure

1. In Figure 1 the exposures to mercury (Hg), lead (Pb), PCBs, toxaphene (Tox) and Chlordane (Chl) are shown, by season. The internal consistency of the data, and the close match between these data and anecdotal observations (e.g., traditional food consumption highest in the summer, lowest in the winter) are good evidence of the accuracy of the dietary data.

2. The average exposures by sex and age group are shown in Table 2 and by community in Table 3. FFQs and 24 hour recalls measure different phenomena. Their one commonality is that the group average in both represents the same thing: average daily intake of the group. Therefore, averages can be merged across seasons/methods, as in Table 2 and 3, but only averages, not centiles, or any other parameters.

3. Traditional food consumption and contaminant intake are correlated (see Figures 2a and 2b, in which each point represents a community). The points that fall far above the line of best fit are those communities that eat a disproportionately greater amount of more contaminated foods, such as Muktuk.

Table 1. Distribution of intake of traditional food, by food group and season, in *grams per day* (all sites, sexes, age groups combined)

Fall, (24 hr recall, n=900)			Percentile						
Food Group	**% > 0[1]**	**Mean**	**5th**	**25th**	**50th**	**75th**	**95th**	**99th**	**Max**
Caribou (meat)	37.0	132.9	0	0	0	225	664	915	1351
Fish flesh	14.2	47.6	0	0	0	0	338	675	1350
Seal and Walrus (meat)	8.3	32.9	0	0	0	0	338	619	1125
Whale (blubber, muktuk)	6.1	17.5	0	0	0	0	60	475	800
Bird (all parts)	5.0	12.8	0	0	0	0	30	394	675
Small Land Mammal (all parts)	1.7	6.4	0	0	0	0	0	235	900
Caribou (blood, marrow, cartilage, fat, organs)	3.7	4.8	0	0	0	0	0	169	1013
Large Land Mammals (all parts)	1.1	4.6	0	0	0	0	0	68	1128
Seal and Walrus (blood, flipper, joint, kauk, skin)	1.2	4.1	0	0	0	0	0	245	980
Seal and Walrus (organs)	1.2	3.8	0	0	0	0	0	71	900
Berries	6.0	3.4	0	0	0	0	20	110	200
Seal and Walrus (blubber, fat, oil)	2.7	2.4	0	0	0	0	0	100	300
"Sea food" (Clams, shrimp, plants, etc.)	0.4	1.9	0	0	0	0	0	0	720
Fish (bones, broth, eggs, fat, head, organs)	0.8	1.1	0	0	0	0	0	0	450
Polar bear (all parts)	0.3	0.6	0	0	0	0	0	0	220
Whale (broth, meat, organ)	0.2	0.3	0	0	0	0	0	0	225
Total (all food groups combined)	60	277	0	0	218	450	963	1463	1950

FFQ (Winter, n=1000)			Percentile						
Food Group	**% > 0**	**Mean**	**5th**	**25th**	**50th**	**75th**	**95th**	**99th**	**Max**
Caribou (meat)	94	82	0	15	47	106	301	503	524
Fish flesh	83	35	0	5	17	43	126	244	714
Caribou (blood, marrow, cartilage, fat, organs)	92	21	0	1	7	24	84	202	480
Bird (all parts)	48	16	0	0	0	14	77	198	554
Seal and Walrus (meat)	44	14	0	0	0	12	73	184	426
Seal and Walrus (blood, flipper, joint, kauk, skin)	36	9	0	0	0	6	46	145	237
Seal and Walrus (organs)	30	8	0	0	0	3	50	128	526
Fish (bones, broth, eggs, fat, head, organs)	64	8	0	0	1	6	34	93	350
Whale (blubber, muktuk)	46	7	0	0	0	5	33	115	338
Berries	39	4	0	0	0	3	22	61	240
Seal and Walrus (blubber, fat, oil)	27	3	0	0	0	1	17	49	124
Whale (broth, meat, organ)	9	1	0	0	0	0	4	29	139
"Sea food" (Clams, shrimp, plants, etc.)	15	1	0	0	0	0	5	17	136
Large Land Mammals (all parts)	13	0	0	0	0	0	1	8	99
Small Land Mammal (all parts)	17	0	0	0	0	0	1	6	14
Polar bear (all parts)	7	0	0	0	0	0	0	0	10
Total (all food groups combined)	99.0	209	13	63	138	281	622	1000	1481

[1] % > 0 indicates percentage of individuals who reported consuming food on previous day (in fall and spring), or in previous 3 months (i.e. winter and summer)

Table 1. Continued

Spring (24 hr recall, n=975)			Percentile						
Food Group	**% > 0**	**Mean**	**5th**	**25th**	**50th**	**75th**	**95th**	**99th**	**Max**
Caribou (meat)	40.4	163.5	0	0	0	225	676	1350	1820
Fish flesh	12.8	44.1	0	0	0	0	450	675	905
Seal and Walrus (meat)	6.3	20.4	0	0	0	0	225	450	900
Whale (blubber, muktuk)	2.5	8.9	0	0	0	0	0	400	800
Bird (all parts)	2.5	8.2	0	0	0	0	0	450	675
Polar bear (all parts)	1.4	5.5	0	0	0	0	0	225	900
Large Land Mammals (all parts)	1.6	5.4	0	0	0	0	0	225	750
Caribou (blood, marrow, cartilage, fat, organs)	2.4	4.7	0	0	0	0	0	225	900
Seal and Walrus (blood, flipper, joint, kauk, skin)	0.9	2.1	0	0	0	0	0	0	500
Seal and Walrus (organs)	0.7	1.6	0	0	0	0	0	0	563
Seal and Walrus (blubber, fat, oil)	1.6	1.4	0	0	0	0	0	60	300
Small Land Mammal (all parts)	0.5	1.2	0	0	0	0	0	0	450
"Sea food" (clams, shrimp, plants, etc.)	0.4	0.5	0	0	0	0	0	0	338
Whale (broth, meat, organ)	0.2	0.4	0	0	0	0	0	0	338
Berries	1.0	0.2	0	0	0	0	0	3	60
Fish (bones, broth, eggs, fat, head, organs)	0.1	0.0	0	0	0	0	0	0	28
Total (all food groups combined)	56	268	0	0	169	450	1012	1576	3635

FFQ (Summer, n=929)			Percentile						
Food Group	**% > 0**	**Mean**	**5th**	**25th**	**50th**	**75th**	**95th**	**99th**	**Max**
Caribou (meat)	94	77	0	15	44	100	287	411	869
Fish flesh	93	76	0	17	44	97	242	466	1036
Seal and Walrus (meat)	63	33	0	0	9	38	149	328	542
Caribou (blood, marrow, cartilage, fat, organs)	93	28	0	3	10	28	107	287	939
Fish (bones, broth, eggs, fat, head, organs)	80	24	0	0	7	25	103	247	475
Seal and Walrus (blood, flipper, joint, kauk, skin)	53	24	0	0	3	24	110	255	507
Seal and Walrus (organs)	48	22	0	0	0	19	117	260	463
Bird (all parts)	74	22	0	0	4	20	94	237	1595
Whale (blubber, muktuk)	68	18	0	0	6	22	74	189	333
Berries	88	13	0	3	7	16	51	86	143
Whale (broth, meat, organ)	36	6	0	0	0	4	33	73	281
Seal and Walrus (blubber, fat, oil)	36	6	0	0	0	3	35	89	128
"Sea food" (Clams, shrimp, plants, etc.)	37	4	0	0	0	3	18	67	92
Small Land Mammal (all parts)	13	1	0	0	0	0	1	28	81
Large Land Mammals (all parts)	10	0	0	0	0	0	1	11	93
Polar bear (all parts)	3	0	0	0	0	0	0	0	30
Total (all food groups combined)	99.8	355	37	124	253	463	962	1856	2903

Figure 1a. Mean of traditional food intake and contaminant exposure, by season

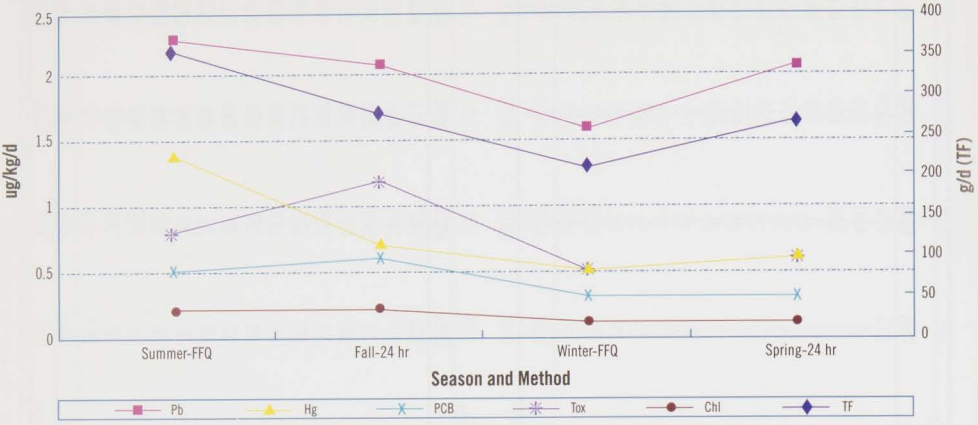


Figure 1b. 95th centile of traditional food intake and contaminant exposure, by season

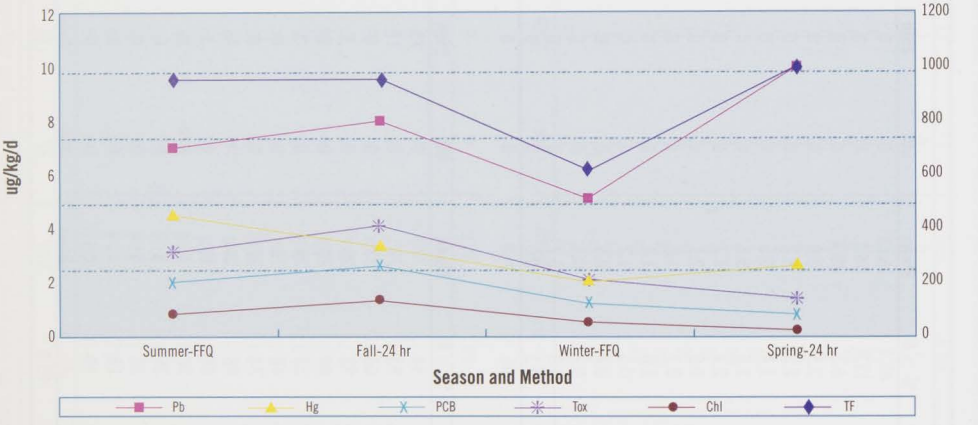


Table 2. *Average* exposures, by sex and age group

			ug·kg^{-1}·(d^2)$^{-1}$				
Sex	**Age**	**TF[1] (g·d^{-1})**	**Hg**	**Pb**	**PCB**	**Tox**	**Chl**
Female	16–40	181	0.51	1.50	0.28	0.49	0.11
	40+	345	1.03	2.59	0.58	1.15	0.25
Male	16–40	251	0.63	1.79	0.26	0.48	0.11
	40+	440	1.24	2.79	0.70	1.29	0.28
		PTDI:	**0.71**	**3.57**	**1**	**0.2**	**0.05**

[1] Traditional Food intake, grams·day^{-1}

[2] ug of contaminant exposure·kg of body weight^{-1}·day^{-1}

Figure 2a. TF intake and Hg exposure, by community

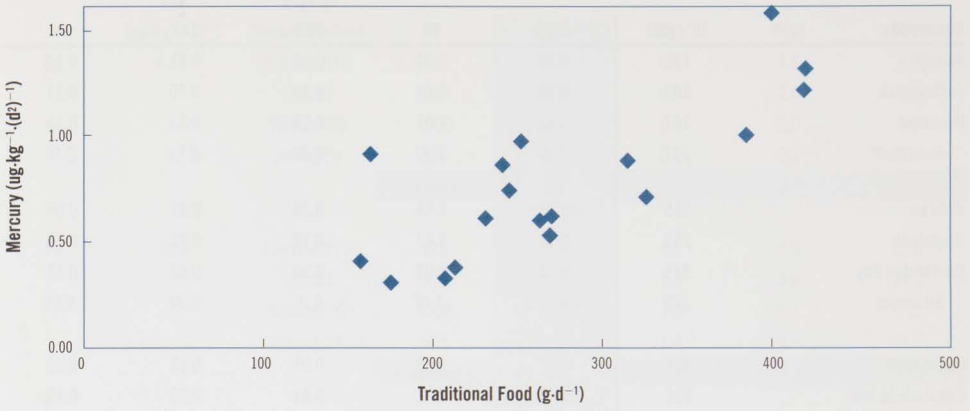
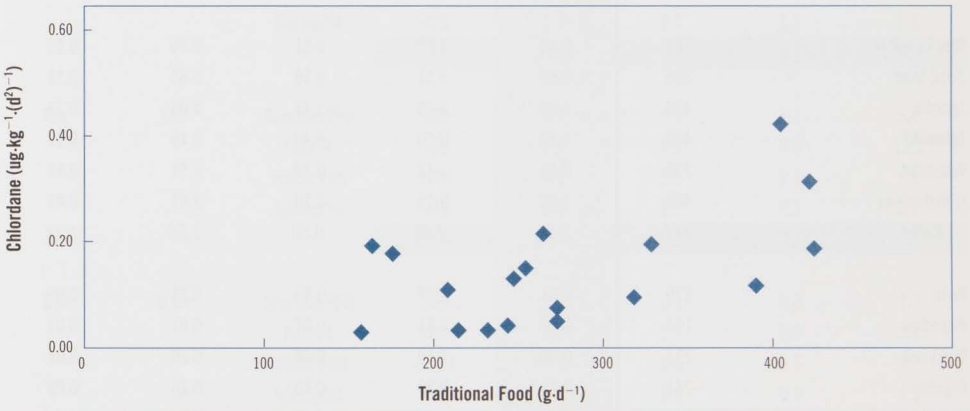


Figure 2b. TF intake and chlordane exposure, by community



4. The source of the contaminants (results not shown) are similar to that reported in Kuhnlein et al. (2000). Caribou meat, for example, contributes 41.2% of the total traditional food (by weight), but only 14.9% of the Hg, indicating that caribou meat has a relatively low level of Hg, and, in terms of Hg, is a relatively "safe" food. Conversely, Seal and Walrus blubber, fat and oil, which are only 1.1% of the total traditional food, contribute 32.2% of the Tox, indicating the large exposure of OCs that can come from small amounts of marine mammal fats.

Variability in exposure estimates due to uncertainty in contaminant levels

There is uncertainty in contaminant levels from the unmeasured variability between specific animals·parts^{-1}, and regional variability. In Table 3, the uncertainty introduced by local variation is demonstrated. In Igloolik and Chesterfield Inlet contaminant data are available for locally harvested animals (Chan 2001). The average exposure when using "Igloolik-specific" or "Chesterfield Inlet-specific" contaminant data is shown in the red lines.

Table 3. *Average* traditional food intake and contaminant exposures, by community and region

		ug/kg/d[2]				
Community	**TF[1] (g/d)**	**Hg**	**Pb**	**PCB**	**Tox**	**Chl**
Aklavik	175	0.30	1.04	0.34	0.55	0.17
Tuktoyaktuk	263	0.59	1.63	0.42	0.75	0.21
Paulatuk	207	0.32	2.05	0.26	0.35	0.10
Inuvialuit[3]	*215*	*0.40*	*1.57*	*0.34*	*0.55*	*0.16*
Holman	315	0.87	1.98	0.28	0.35	0.09
Kugluktuk	269	0.52	2.47	0.12	0.20	0.05
Cambridge Bay	245	0.73	2.09	0.30	0.48	0.13
Kitikmeot	*276*	*0.70*	*2.18*	*0.23*	*0.34*	*0.09*
Baker Lake	213	0.37	1.68	0.05	0.10	0.02
Chesterfield Inlet	326	0.70	2.72	0.44	0.70	0.19
Chesterfield Inlet[4]	326	0.56	1.30	0.34	0.27	0.11
Rankin Inlet	419	1.20	3.24	0.63	1.21	0.31
Kivalliq	*321*	*0.71*	*2.24*	*0.37*	*0.57*	*0.16*
Resolute Bay	163	0.90	1.02	0.51	0.70	0.19
Pond Inlet	385	0.99	3.51	0.39	0.63	0.11
Igloolik	420	1.30	3.28	1.41	4.06	0.73
Igloolik[4]	420	1.30	0.60	0.40	0.45	0.18
Kimmirut	252	0.96	1.42	0.38	0.54	0.14
Qikiqtarjuaq	400	1.56	2.75	1.30	2.01	0.42
Baffin	*324*	*1.14*	*2.40*	*0.80*	*1.59*	*0.32*
Nain	270	0.61	2.07	0.15	0.21	0.06
Hopedale	157	0.40	1.11	0.07	0.07	0.01
Makkovik	231	0.60	1.18	0.08	0.20	0.02
Rigolet	241	0.85	0.90	0.10	0.26	0.03
Labrador	*210*	*0.61*	*1.06*	*0.08*	*0.18*	*0.02*
	TDI:	**0.71**	**3.57**	**1**	**0.2**	**0.05**

[1] Traditional Food intake, grams per day

[2] ug of contaminant intake per kg of body weight per day

[3] Regional values are weighed in each community equally

[4] Values for Igloolik and Chesterfield were also calculated using contaminant data from samples harvested locally (Chan 2001). Compared to the exposures calculated using the general Arctic data (the previous line) these exposures are much lower. This is in large because the Walruses near Igloolik have lower contaminant concentrations, as they are non-predatory. The graph uses the lower exposure estimates

The differences are marked, in large part due to the Igloolik walruses having much lower contaminant levels, as they are non-predatory, unlike those used in the generation of the general Arctic data.

Calculation of usual exposures

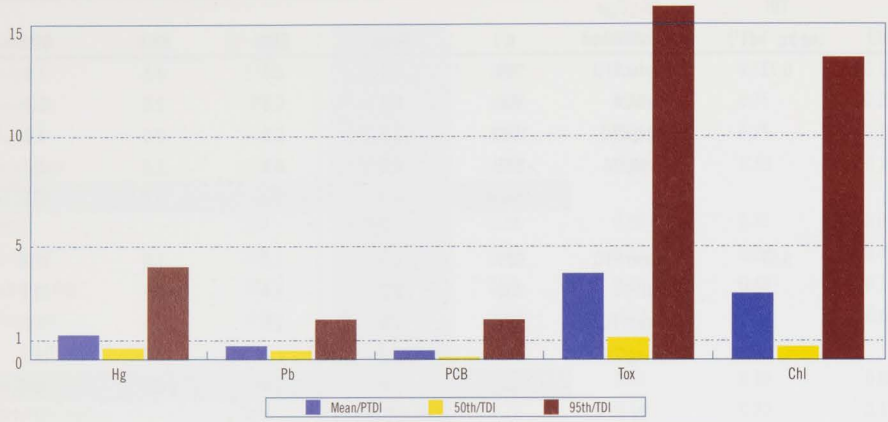
In general, the population distribution of contaminant exposures on a single day will be much wider than the population distribution of usual exposures. This is a function

Table 4. Population distribution of usual contaminant exposure (µg·kg body weight^{-1}·day^{-1})

	TDI (µg·kg^{-1}·d^{-1})	Season/Method	n	Mean	50th	95th	99th
Hg	0.71	Summer/FFQ	929	1.4	0.8	4.5	7.9
		Fall/24	900	0.7	0.3	2.6	5.4
		Winter/FFQ	1000	0.5	0.3	2.0	4.0
		Spring/24	975	0.6	0.3	2.2	4.7
			Annual	*0.8*	*0.4*	*3.0*	*6.2*
Pb	3.57	Summer/FFQ	929	2.3	1.5	7.0	12.6
		Fall/24	900	2.1	1.4	6.6	11.2
		Winter/FFQ	1000	1.6	1.0	5.1	7.6
		Spring/24	975	2.1	1.4	6.6	11.2
			Annual	*2.0*	*1.4*	*6.3*	*10.8*
PCB	1	Summer/FFQ	929	0.5	0.2	2.0	4.1
		Fall/24	900	0.6	0.2	2.5	5.9
		Winter/FFQ	1000	0.3	0.1	1.2	3.3
		Spring/24	975	0.3	0.1	1.2	2.9
			Annual	*0.425*	*0.1*	*1.8*	*4.2*
Tox	0.2	Summer/FFQ	929	0.8	0.4	3.1	5.8
		Fall/24	900	1.2	0.3	4.9	11.2
		Winter/FFQ	1000	0.5	0.1	2.1	5.6
		Spring/24	975	0.6	0.2	2.5	5.6
			Annual	*0.775*	*0.2*	*3.2*	*7.3*
Chl	0.05	Summer/FFQ	929	0.2	0.1	0.8	1.7
		Fall/24	900	0.2	0.0	0.9	2.3
		Winter/FFQ	1000	0.1	0.0	0.5	1.7
		Spring/24	975	0.1	0.0	0.5	1.1
			Annual	*0.15*	*0.0*	*0.7*	*1.7*

of the day-to-day variability in the human diet — one day an Inuk may eat 500 g of caribou liver, and then not eat it again for twelve months. The average of the diet on many days is needed to arrive at an individual's "usual" average daily intake. FFQs provides this "usual" average diet, single 24 hour recalls do not. In the absence of numerous repeated 24 hour recalls on each individual, alternative approaches are required to estimate usual daily intake. While there are various statistical approaches to this, we developed an empirical method, suitable to the Inuit data set, based on two observations: 1) Group averages from FFQs and the 24 hour recall both estimate the same thing — the average daily exposure of the group; 2) The population distribution of exposures derived from FFQs represents the population distribution of usual daily exposures; and 3) The assumption that the shape of the population distribution of exposures will be similar in different seasons. This assumption is supported by our evaluation of the distributions in the summer and winter, as derived using the FFQs (results not shown). There is a marked consistency between seasons in the ratio 95th centile/mean, for each of the contaminants (and to a slightly lesser extent for

Figure 4. Usual exposures relative to TDIs



the ratios of the 50th/mean and 99th/mean). For the metals the 95th centile is about 3.5 times the mean, and for the OCs, the 95th centile is about 4.25 times the mean.

Given the accuracy of the means in the 24 hour recalls, and the consistency of the shape of the distribution, we were able to multiply the means by the "95th/mean" ratio (and 50th and 99th/mean) to estimate the usual daily exposures in the fall and spring, and over the entire year (see Table 4).

Finally, in Figure 4 are presented estimates of the population distributions of usual exposures relative to the TDIs over an entire year. The median intake are all below the TDI but the high end exposed group (top 5%) had intake of mercury, toxaphene, and chlordane levels that are 4, 16 and 13 times higher than the TDIs. As shown in Table 2, this high risk group are older adults, i.e. older than 40 years old. Effects of chronic exposure of these three contaminants in this age group needs further study.

All the results presented herein are for the 18 communities combined. The results have also been prepared on a community basis, and are being shared with ITK for their community communication efforts. These results are available upon request.

Expected Completion Date

With the submission of this report, the work is completed.

References

Kuhnlein, H.V., O. Receveur, H.M. Chan, and E. Loring. 2000. Assessment of dietary benefit: risk in Inuit communities. CINE publication. ISBN# 0-7717-0558-1.

Chan, H.M., P. Berti, and E. Loring. Dietary Exposure to Contaminants in Two Inuit Communities (Year 2). Synopsis of Research Conducted Under the 2000/2001 Northern Contaminants Program.

A Comparison of Time-Related Changes in *Trans*-Nonachlor, Oxychlordane and *Trans*-Chlordane Residue Levels in Rat Tissues and the Relationship Between Tissue Residue Levels, Functional Changes and Gender

Project leader

Genevieve Bondy, Toxicology Research Division, Postal Locator 2204D2, Bureau of Chemical Safety, Food Directorate, Health Canada, Ottawa, ON K1A 0L2; phone: (613) 957-2051; fax: (613) 941-6959; e-mail: Genevieve_Bondy@hc-sc.gc.ca

Project team

Michael Barker, Gerard Cooke, Ivan Curran, Josée Doucet, Santokh Gill, Eric Lok, Rekha Mehta, Olga Pulido, Patrick Robertson, Paul Rowsell, Bureau of Chemical Safety, Health Canada, Ottawa, ON; Ross Norstrom and John Moisey, Environment Canada, Gatineau, QC.

Abstract

To address questions about the relative accumulation and toxicity of *trans*-chlordane and oxychlordane enantiomers, adipose tissues from rats treated with oxychlordane, *trans*-nonachlor and *trans*-chlordane were analysed for oxychordane enantiomers. In addition, adipose from rats treated with *trans*-chlordane were analysed for *trans*-chlordane enantiomer residues. These analyses provided much needed information on the following: 1. potential changes in enantiomer ratios in rat adipose tissues compared to ratios in test chemicals prior to dosing; 2. potential changes in enantiomer residue levels in rat adipose tissues over time; 3. potential sex-related differences in enantiomer accumulation in adipose tissues. Preliminary statistical analyses indicate that there were no significant differences in final body weights of male or female rats treated with oxychlordane, *trans*-nonachlor or *trans*-chlordane. In all rats oxychlordane levels in fat declined substantially over the 56 day depletion period. Oxychlordane and *trans*-nonachlor residues levels declined more rapidly in male rats than in females.

Key Project Messages

1. Why is *trans*-nonachlor more toxic to female rats than to male rats?
2. Is there a relationship between levels of *trans*-nonachlor and oxychlordane in tissues and toxicity, especially after time has elapsed since the initial exposure?

Objectives

1. To compare changes in *trans*-nonachlor, oxychlordane and *trans*-chlordane residue levels over time in male and female rat adipose, kidney and liver tissues;
2. To relate changes in tissue residue levels to sex, total body fat, and to biomarkers for toxicological changes;
3. To examine changes in tissue oxychlordane and *trans*-chlordane enantiomer ratios over time in male and female rats;
4. To provide current information on the toxicity of chlordane metabolites and constituents which can be used to reduce uncertainty factors used in the calculation of TDIs for chlordane-related food contaminants.

Introduction

Chlordane-related contaminants are present in traditional foods in the Arctic and in human adipose tissue and breast milk in North America. The original pesticide, chlordane, was a mixture of many structurally-related organochlorines. The existing literature provides extensive toxicological data on the parent chlordane mixture. Recent studies have expanded these data to include toxicological assessments of the chlordane constituents *trans*-nonachlor and *cis*-nonachlor (Bondy et al., 2000), and the metabolite oxychlordane (Bondy et al.). These studies indicate that *trans*-nonachlor and its major metabolite oxychlordane are the most toxic chlordane-related contaminants, and that they are more toxic to female rats than male rats. Liver microsomal enzymes are induced by *trans*-nonachlor, *cis*-nonachlor and oxychlordane. Biomarkers indicative of changes in kidney function were altered in male rats but not female rats treated with *trans*-nonachlor and *cis*-nonachlor. The present study was designed to address the following data gaps based on completed research:

Do *trans*-nonachlor levels in tissues gradually decline after exposure? In conjunction with potential changes in *trans*-nonachlor levels, do oxychlordane levels in tissues gradually increase if *trans*-nonachlor declines (indicating that *trans*-nonachlor is transformed to oxychlordane over time)? Do differences in total body fat in female versus male rats account for higher levels of *trans*-nonachlor and oxychlordane in female rat adipose tissues? What are the levels of *trans*-nonachlor and oxychlordane in kidneys, and are functional changes in male rat kidneys related to tissue residue levels?

The proposed study will also offer the opportunity to investigate the relationship between oxychlordane and *trans*-chlordane chirality and their toxicological properties. When a chiral chemical is synthesized a racemic mixture, or 1:1 ratio, of enantiomers is formed. However, there is some evidence that relative accumulation in animal tissues may differ for the (+) and (−) enantiomers of *trans*-chlordane and oxychlordane. Studies have shown that there are apparent species-dependent differences in the abundance of *trans*-chlordane enantiomers accumulating in tissues of fish from the Baltic, and that tissues from pigs given *cis*- or *trans*-chlordane have higher levels of (+)-oxychlordane (Müller and Buser, 1994). Furthermore, there is every reason to believe that the toxicity of the enantiomers of chiral POPs and metabolites will be different. Studies using cockroaches have found that (+)-*cis*-heptachlor epoxide was more toxic than the racemic mixture (Miyazaki et al. 1980). In rats the (−) *o,p*-DDT enantiomer is more estrogenic than the (+) enantiomer (McBlain and Lewin, 1976).

Activities

In 2001–2002

The animal phase of this study was completed in 2000. The dose groups and time line are summarized in Table 1 and Figure 1, respectively. Analyses of adipose, liver and kidney tissues for chlordane contaminants continued throughout 2001 and were completed in March 2002. Enantiomer analyses (by collaborators at Environment Canada) were dependent on the completion of residue analyses at Health Canada. Extracts were delivered in

Table 1. Summary of test groups for each necropsy (1 day, 28 days and 56 days after dosing)

	Number of rats/group		
Dose group*	Necropsy 1 (Oct 2000)	Necropsy 2 (Nov 2000)	Necropsy 3 (Dec 2000)
Control (corn oil)	18[a,b]	16	16
Trans-nonachlor (2.5 mg/kg)	16	16	16
Oxychlordane (2.5 mg/kg)	18[b]	16	16
Trans-chlordane (2.5 mg/kg)	16	16	16
Total	68	64	64

*Total rats required, including 8 quality controls: 204

[a] Groups will be composed of 8 males and 8 females, except where designated [b].

[b] Ten control and oxychlordane-treated female rats will be required for the first necropsy because data from these animals will also be used to supplement previous oxychlordane studies. We have previously exposed female rats to 1 and 10 mg/kg oxychlordane. These rats will be given a full toxicological evaluation, which requires a minimum of 10 rats per sex.

February 2002, enantiomer analyses are completed and the data is being analysed. All other clinical and toxicological data were completed and summarized in 2001.

Results

Preliminary statistical analyses indicate that there were no significant differences in final body weights of male or female rats treated with oxychlordane, *trans*-nonachlor or *trans*-chlordane (Table 2). During the depletion phase of the study all rats gained weight consistently.

Total body fat levels were determined in male and female rats at each of the necropsy time points (Table 3). For each rat, all subcutaneous and abdominal body fat deposits were dissected mechanically and weighed. Body fat levels increased with age in both male and female rats, and were higher in male rats. These data were used to calculate total chlordane body burdens in treated rats.

Preliminary analyses indicate that there were few significant or consistent changes in clinical and renal function indicators (data not shown).

Analyses of adipose tissue residue levels in male and female rats are summarized in Tables 4 and 5. Oxychlordane is a major metabolite of *trans*-nonachlor and *trans*-chlordane and was found, along with the parent compound, in fat from animals treated with *trans*-nonachlor or *trans*-chlordane. In all rats oxychlordane levels in fat declined substantially over the 56 day depletion period. Oxychlordane and *trans*-nonachlor residues levels declined more rapidly in male rats than in females. Nonetheless, because body fat levels are higher in male rats, total contaminant body burdens were higher at the end of the 28-day dosing period in male rats treated with oxychlordane and *trans*-nonachlor. Similar summaries will be prepared for residue data from liver and kidney tissues.

Relative oxychlordane enantiomer levels, expressed as enantiomer fractions or EFs, in adipose tissues from male and female rats are summarized in Tables 6 and 7. At the end of the 28 day dosing period (−)oxy levels dominated in adipose tissues from all treatment groups. Over the depletion period (+)oxy levels decreased even further relative to (−)oxy levels, resulting in declining oxy EF values as the depletion period progressed. This trend was particularly pronounced in male rats. Similar data summaries will be prepared for (+)oxychlordane and (−) oxychlordane in liver and kidney tissues and for *trans*-chlordane enantiomers in fat, liver and kidneys from male and female rats.

Table 2. Final body weights of male and female rats exposed to chlordane contaminants for 28 consecutive days by oral gavage

Test chemical and dose	Final body weight in g (mean ± SD) after: 28 d dosing	28 d dosing + 28 d depletion	28 d dosing + 56 d depletion
		Female rats	
Control (corn oil vehicle)	218.1 ± 12.9	266.1 ± 26.8	253.0 ± 15.3
Oxychlordane (2.5 mg/kg bwt)	202.4 ± 18.8	243.4 ± 17.8	266.4 ± 15.8
trans-Nonachlor (2.5 mg/kg bwt)	228.6 ± 11.7	258.6 ± 17.6	263.8 ± 22.7
trans-Chlordane (2.5 mg/kg bwt)	221.0 ± 10.5	255.9 ± 28.0	266.9 ± 21.8
		Male rats	
Control (vehicle only)	367.6 ± 35.3	460.4 ± 36.0	488.6 ± 35.1
Oxychlordane (2.5 mg/kg bwt)	352.8 ± 22.7	459.3 ± 44.4	496.6 ± 36.6
trans-Nonachlor (2.5 mg/kg bwt)	390.9 ± 17.6	473.1 ± 18.8	525.6 ± 53.9
trans-Chlordane (2.5 mg/kg bwt)	368.9 ± 24.6	464.4 ± 28.7	513.9 ± 43.0

Figure 1. Time line for dosing and necropsies of *trans*-nonachlor, oxychlordane and *trans*-chlordane-treated rats

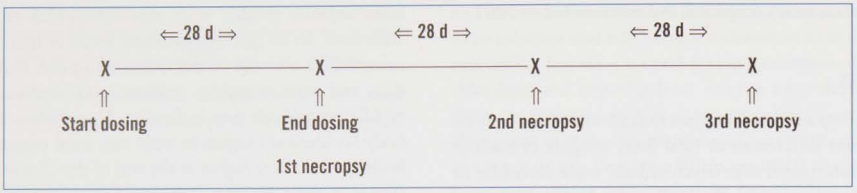


Table 3. Body fat composition of male and female Sprague-Dawley rats

	Total body fat in g (mean ± SD) after:		
	28 d dosing	28 d dosing + 28 d depletion	28 d dosing + 56 d depletion
Females	14.0 ± 5.4	20.0 ± 7.9	26.0 ± 6.0
Males	24.8 ± 7.6	48.9 ± 13.4	57.2 ± 17.0
	Total body fat as a % of body weight (mean ± SD) after:		
	28 d dosing	28 d dosing + 28 d depletion	28 d dosing + 56 d depletion
Females	6.1 ± 2.1	7.6 ± 2.2	9.9 ± 2.0
Males	7.0 ± 1.4	10.3 ± 2.2	10.7 ± 2.5

Table 4. Tissue residue levels and mean total body burdens of chlordane contaminants in abdominal fat from female rats exposed to oxychlordane, *trans*-nonachlor or *trans*-chlordane for 28 consecutive days by gavage

	Oxychlordane 2.5 mg/kg bwt/day		
	28 d dosing	28 d dosing + 28 d depletion	28 d dosing + 56 d depletion
Oxychlordane residue levels in fat (μg/g lipid)	269.4 ± 46.8	182.8 ± 47.7	112.0 ± 16.4
Mean oxychlordane body burden (μg per whole animal)	3326.1	3381.5	2953.8
	***trans*-Nonachlor 2.5 mg/kg bwt/day**		
	28 d dosing	28 d dosing + 28 d depletion	28 d dosing + 56 d depletion
Oxychlordane residue levels in fat (μg/g lipid)	41.4 ± 3.6	27.3 ± 5.5	20.0 ± 3.2
Mean oxychlordane body burden (μg per whole animal)	577.3	536.5	522.3
trans-Nonachlor residue levels in fat (μg/g lipid)	107.0 ± 16.0	43.9 ± 25.9	18.8 ± 7.9
Mean *trans*-nonachlor body burden (μg per whole animal)	1492.1	862.8	491.0
	***trans*-Chlordane 2.5 mg/kg bwt/day**		
	28 d dosing	28 d dosing + 28 d depletion	28 d dosing + 56 d depletion
Oxychlordane residue levels in fat (μg/g lipid)	88.2 ± 14.4	53.4 ± 22.5	33.9 ± 10.6
Mean oxychlordane body burden (μg per whole animal)	1189.0	1038.5	895.7
trans-Chlordane residue levels in fat (μg/g lipid)	12.7 ± 7.0	0.3 ± 0.4	0.0 ± 0.0
Mean trans-chlordane body burden (μg per whole animal)	171.2	5.8	0.0

All residue levels are expressed as mean ± SD for 6 rats. Mean body burden data were calculated using the following formula: (mean μg/g residue in tissue)(mean final body weight)(mean % body fat) = mean μg residue per whole animal

Table 5. Tissue residue levels and mean total body burdens of chlordane contaminants in abdominal fat from male rats exposed to oxychlordane, *trans*-nonachlor or *trans*-chlordane for 28 consecutive days by gavage

	Oxychlordane 2.5 mg/kg bwt/day		
	28 d dosing	28 d dosing + 28 d depletion	28 d dosing + 56 d depletion
Oxychlordane residue levels in fat (μg/g lipid)	201.4 ± 21.3	90.8 ± 18.4	44.1 ± 4.6
Mean oxychlordane body burden (μg per whole animal)	4973.8	4295.6	2343.3
	***trans*-Nonachlor 2.5 mg/kg bwt/day**		
	28 d dosing	28 d dosing + 28 d depletion	28 d dosing + 56 d depletion
Oxychlordane residue levels in fat (μg/g lipid)	28.4 ± 4.7	11.4 ± 3.6	5.1 ± 1.3
Mean oxychlordane body burden (μg per whole animal)	777.1	555.5	286.8
trans-Nonachlor residue levels in fat (μg/g lipid)	63.1 ± 14.7	11.3 ± 4.0	2.7 ± 0.5
Mean *trans*-nonachlor body burden (μg per whole animal)	1726.6	550.6	151.9
	***trans*-Chlordane 2.5 mg/kg bwt/day**		
	28 d dosing	28 d dosing + 28 d depletion	28 d dosing + 56 d depletion
Oxychlordane residue levels in fat (μg/g lipid)	41.2 ± 10.1	22.9 ± 4.1	9.0 ± 2.4
Mean oxychlordane body burden (μg per whole animal)	1063.9	1095.4	53.0
trans-Chlordane residue levels in fat (μg/g lipid)	7.2 ± 0.9	0.2 ± 0.1	0.0 ± 0.0
Mean *trans*-chlordane body burden (μg per whole animal)	185.9	9.6	0.0

All residue levels are expressed as mean ± SD for 6 rats. Mean body burden data were calculated using the following formula: (mean μg/g residue in tissue)(mean final body weight)(mean % body fat) = mean μg residue per whole animal

Table 6. Oxychlordane enantiomer fractions (EFs) in abdominal fat from female rats exposed to oxychlordane, *trans*-nonachlor or *trans*-chlordane for 28 consecutive days by gavage

		Oxychlordane EF *	
Treatment	**28 d dosing**	**28 d dosing + 28 d depletion**	**28 d dosing + 56 d depletion**
Oxychlordane (2.5 mg/kg bwt/day)	0.242 ± 0.069	0.230 ± 0.045	0.098 ± 0.197
trans-Nonachlor (2.5 mg/kg bwt/day)	0.587 ± 0.121	0.406 ± 0.181	0.349 ± 0.148
trans-Chlordane ($2.5\ mg \cdot kg^{-1}\ bwt \cdot day^{-1}$)	0.545 ± 0.101	0.253 ± 0.189	0.302 ± 0.159

* Formula for EF calculations: (+)oxy/ [(+)oxy + (−)oxy], where (+)oxy and (−)oxy refer to peak area values for each oxychlordane enantiomer using GC analyses. All data are expressed as mean ± SD for 6 rats

Table 7. Oxychlordane enantiomer fractions (EFs) in abdominal fat from male rats exposed to oxychlordane, *trans*-nonachlor or *trans*-chlordane for 28 consecutive days by gavage

Treatment	Oxychlordane EF *		
	28 d dosing	28 d dosing + 28 d depletion	28 d dosing + 56 d depletion
Oxychlordane (2.5 mg/kg bwt/day)	0.141 ± 0.029	0.019 ± 0.015	all (−)oxy
trans-Nonachlor (2.5 mg/kg bwt/day)	0.335 ± 0.068	0.146 ± 0.118	0.118 ± 0.045
trans-Chlordane (2.5 mg/kg bwt/day)	0.357 ± 0.079	0.065 ± 0.029	0.035 ± 0.045

* Formula for EF calculations: (+)oxy/ [(+)oxy + (−)oxy], where (+)oxy and (−)oxy refer to peak area values for each oxychlordane enantiomer using GC analyses. All data are expressed as mean ± SD for 6 rats

Discussion and Conclusions

The results confirm that oxychlordane is a major metabolite of both *trans*-nonachlor and *trans*-chlordane, and that the (−)enantiomer of oxychlordane predominates in adipose tissues from both male and female rats. Although all residues declined in adipose tissues over time, oxychlordane in particular was more persistent in female rats. The oxychlordane body burden in female rats dropped only 10–25% over the depletion period, compared to 53–95% in male rats. Similarly, EF values for oxychlordane enantiomers dropped more precipitously in male rats compared to females, indicating that (+)oxy is more amenable to metabolism than (−)oxy. Based on these data it was not possible to determine whether this was due solely to sex-related differences in the rate of oxychlordane metabolism, or whether metabolic pathways are different in male and female rats. Regardless, the relative persistence of oxychlordane in adipose tissues from female rats may explain why oxychlordane is more toxic than *trans*-nonachlor and *trans*-chlordane.

References

Bondy, G.S., W.H. Newsome, C.L. Armstrong, C.A. Suzuki, J. Doucet, S. Fernie, S.L. Hierlihy, M.M. Feeley, and M.G. Barker. 2000. Abstract *trans*-Nonachlor and *cis*-nonachlor toxicity in Sprague-Dawley rats: comparison with technical chlordane. *Toxicol Sci.* Dec;58(2):386–98.

McBlain, W.A., and V. Lewin. 1979. Differing estrogenic activities for the enantiomers of *o, p'*-DDT in immature female rats. *Can J Physiol Pharmacol.* 54:629–636.

Miyazaki, A., M. Sakai, and S. Marumo. 1980. Synthesis and biological activity of optically active heptachlor, 2-chloroheptachlor, and 3-chloroheptachlor. *J Agric Food Chem.* 28:1310–1311.

Müller, M.D., and H.-R. Buser. 1994. Identification of the (+)- and (−)-enantiomers of chiral chlordane compounds using chiral high-performance liquid chromatography/chiroptical detection and chiral high-resolution gas chromatography/mass spectrometry. *Anal Chem.* 66:2155–2162.

Developmental and Neurological Effects of Chemical Mixtures Based on Blood Profiles in Canadian Arctic Populations

Project leader

Ih Chu, Environmental and Occupational Toxicology Division, Healthy Environments and Consumer Safety Branch, Health Canada, Environmental Health Centre, Postal Locator 0803B, Tunney's Pasture, Ottawa, ON K1A 0L2; phone: (613) 957-1837; fax: (613) 957-8800; e-mail: Ih_Chu@hc-sc.gc.ca

Project team

Wayne Bowers, Jamie Nakai, David Moir, Mike Wade and Al Yagminas, Environmental and Occupational Toxicology Division, Healthy Environments and Consumer Safety Branch; Doug Arnold, Santokh Gill, Rudi Mueller and Olga Pulido, Food Directorate, Health Products and Food Branch, Health Canada, Ottawa, Ontario K1A 0L2.

Abstract

This project investigated developmental and neurological effects of a reconstituted pollutant mixture based on blood profiles of humans in the Canadian Arctic. Pregnant Sprague Dawley rats were dosed orally with 0, 0.05, 0.5 and 5.0 $mg \cdot kg^{-1} \cdot day^{-1}$ of a mixture of pollutants during the gestational and lactational period. A positive control group was treated in the same manner with 15 $mg \cdot kg^{-1} \cdot day^{-1}$ of Aroclor 1254 (Aroclor). Treatment with the 5.0 $mg \cdot kg^{-1}$ mixture and Aroclor caused decreased litter weight and pup weight gain without affecting maternal weight gain. While 5.0 mixture and Aroclor delayed the appearance of ear opening, they accelerated eye opening. Decreased grip strength was observed in the 0.05 0.5, 5.0 $mg \cdot kg^{-1}$ mixture and positive control. Aroclor and 5.0 mixture altered motor activity and rearing at PND 17 but the effects of these abated as animals matured. Effects of lower doses of the mixture on activity and rearing emerged as animals matured and females appeared more sensitive than males. At PND 17 Aroclor decreased startle responding but the lowest mixture dose affected pre-pulse inhibition responding, suggesting altered sensorimotor gating. The effect of the two highest mixture doses on startle responding emerged as animals matured (PND 44) as did gender differences in the effects of the mixture. The highest dose of the mixture delayed puberty in male pups, and decreased body weights at puberty in both sexes. Brain neurochemical changes were observed in treated rats at the lowest dose of the Arctic mixture. These results demonstrate that perinatal exposure to this mixture of pollutants elicited early developmental and neurological changes at doses where other toxicological signs were not evident, and that the effects of lower doses of the mixture may become more apparent as animals mature. Gender differences in the behavioral effects of the mixture emerge as normal gender difference in behavior become apparent as animals mature.

Key Project Messages

1. A mixture of persistent organochlorines was tested in pregnant rats for toxic effects.
2. The highest dose of the mixture (5 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$) resulted in decreased litter weight and weight gains of pups without affecting maternal weight.
3. Exposure to the mixture altered normal appearance of eye and ear opening, and decreased grip strength but had no effect on the development of negative geotaxis.
4. The lowest mixture dose altered acoustic startle and motor activity and gender differences in the effect of the mixture emerge as animals mature.
5. The highest dose of the mixture delayed puberty in male, but not in female pups.
6. Exposure to the mixture elicited developmental changes in the rat pups at dose levels where no toxicological signs were observed in dams.
7. Exposure to the mixture caused changes in the brain levels of serotonin and dopaminergic neurotransmitters.

Objectives

1. This project investigates the early developmental effects of exposure to persistent organochlorine pollutants found in humans residing in the Canadian Arctic.
2. This project will investigate a broad range of toxicological endpoints including neurobehavioral, neurochemical, endocrine, reproductive, biochemical, neuropathological and systemic effects.
3. This project will examine the relationship between blood levels measured in perinatally exposed animals and toxicological effects, allowing the results to be directly compared with ongoing studies in Arctic populations that examine blood levels in humans.
4. The long-term consequences of gestational and lactational exposure will also be studied by examining neurotoxicological effects in the offspring during their infancy, and juvenile and adult age.
5. When completed, this study will provide public health officials with a better understanding of the potential health effects of exposure to mixtures of persistent environmental pollutants relevant to Arctic populations.

Introduction

There is an increasing concern that the health of people living in the Canadian Arctic may be compromised by exposure to a wide variety of persistent environmental pollutants. Infants and fetuses are thought to be more susceptible to insults from toxic chemicals because their exposure occurs during the period of rapid neural system development. Most toxicological studies investigate effects of single compounds or simple mixtures. For instance, neurological effects including learning and memory deficits have been reported in laboratory rats treated with polychlorinated biphenyls (Aroclor 1254) (Geller et al., 2001; Roegge et al., 2000; Widholm et al., 2001). Epidemiological studies have also revealed that infants born from mothers consuming large amounts of contaminated fish exhibit disturbances such as decreased intellectual capacity, altered attention and memory processes, and developmental effects (Gladen et al., 1088; Goldey et al., 1995; Jacobson et al., 1990, 1993; Lonkey et al., 1996). However, there is little information on the effects of exposure to mixtures of pollutants at low levels during the sensitive neurodevelopmental stage. This study was therefore carried out to investigate the neurological and related toxicological effects in the rat model, and to provide the public with a better understanding of the potential effects of persistent environmental pollutants on Arctic population.

Activities

In 2001–2003

Activities in 2001–2002 consisted of preparation and analysis of the reconstituted mixture of persistent pollutants; breeding and treatment of animals; and conduct of tests for early neurodevelopmental and reproductive effects.

All dosing, behavioral testing and tissue collection have been completed. Available behavioral data, reproductive data and initial neurochemistry data are reported below.

The reconstituted mixture was prepared based on maternal blood levels from a series of studies on Inuit populations (Baffin Regional Health & Social Service Board, 1997). Except for toxaphene, which is of a technical grade, the following chemicals had a purity of 99% and were procured commercially: Aldrin, β-hexachlorocyclohexane (β-HCH), *cis*-nonachlor, p,p'-DDE , p,p'-DDT, dieldrin, hexachlorobenzene (HCB), heptachlor epoxide (β-isomer), mirex, *trans*-nonachlor, and methylmercury chloride (MeHgCl), and PCB Congeners 28, 52, 99, 101, 105, 118, 128, 138, 153, 156, 170, 180, 183 and 187. Oxychlordane was generously donated by Julie Fillion of the Pest Management

Regulatory Agency (Ottawa, ON). The dose of each chemical selected in this project is based on the relative amounts of each chemical found in blood samples from Canadian Arctic populations. Except for mercury, the mixture was prepared by quantitatively dissolving individual compounds separately into diethyl ether and mixing individual ethereal solutions with corn oil followed by evaporating of the ether. The concentration of each chemical in the PCB/OC mixture was then verified by Wellington Laboratories (Guelph, ON) using high resolution GC-MS analysis.

Methyl mercury chloride was first dissolved in corn oil, and mixed with that of the organochlorine mixture. The actual concentration of each component as determined with GC-MS is shown in Table 1. All compounds are between 85 and 115% of the nominal concentrations (except for dieldrin (83%), heptachlor epoxide (84%), oxychlordane (62%), toxaphene (61%), mirex (116%) and PCB 28 (122%)).

Seventy-seven nulliparious female Sprague Dawley rats weighing 200–230 g and 38 males weighing 320–350 g were purchased from Charles River Laboratories, St. Constant, Quebec. Upon arrival, females were housed 2 per cage while males were individually caged. Room temperature and humidity were maintained at 22±2°C and 50±10%, respectively. Food and water were made available to the animals *ad libitum* throughout the study except where operant testing was conducted. The lighting was gradually switched to a reverse light cycle with the dark cycle being advanced 1 hour per day. Once the light cycle shift was completed (On at 8 pm and Off at 8 am) the animals remained on this reverse light cycle throughout the study. After 3 weeks of habituation to the housing conditions, breeding was conducted by transferring 2 females into 1 male cage. Females were monitored twice daily for vaginal plugs. Once a vaginal plug was detected, the female was removed from the male cage and housed individually with shaved wood bedding. The day of detection of a vaginal plug was denoted as gestation day (GD) 0. Dosing started on GD 1 with a measured amount of the mixture in the corn oil solutions deposited on Teddy Graham cookies (Nabisco Ltd., Toronto, ON) and the dosed cookies were provided to the pregnant dams. A pilot study was conducted in which dams were given the mixture up to 20 $mg \cdot kg^{-1}$ to establish the appropriate dose range for the main study. For the main study, the animals were dosed daily at 0, 0.05, 0.5, 5.0 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$ from gestation day 1 to postnatal day (PND) 23, while the positive control group was given 15 $mg \cdot kg^{-1}$ Aroclor 1254 in the same manner. This dosing method permitted administration of controlled doses of the mixture that were adjusted daily on the basis of body weight. The dams were monitored for parturition, and pups were counted immediately after birth. Litters were culled to 4 males and 4 females on PND 4, and pups were individually identified and weighed daily thereafter.

Table 1. Chemical constituents of the mixture. The quantity of each chemical for the 5.0 $mg \cdot kg^{-1}$ dose group shown is the actual concentrations measured in dosing solutions. Animals were dosed at 1 $ml \cdot kg^{-1}$

PCB Congener	mg	Organochlorines	mg
28	0.0072	Aldrin	0.0049
52	0.0154	β-HCH	0.0746
99	0.0973	*cis*-Nonachlor	0.0525
101	0.0145	p,p'-DDE	0.9187
105	0.0165	p,p'-DDT	0.0569
118	0.0727	Dieldrin	0.0223
128	0.0071	Hexachlorobenzene	0.2961
138	0.2146	Heptachlor epoxide	0.0232
153	0.3177	Mirex	0.0291
156	0.029	Oxychlordane	0.1359
170	0.0562	Toxaphene	0.0699
180	0.1522	*trans*-Nonachlor	0.2203
183	0.0193	Methylmercury Cl	1.9965
187	0.0795		
Sum PCB	1.0992	Sum Non-PCB	3.9009
% PCB	22.0%	% non-PCB	78.0%
Total Dose			**5.0001**

One male and 1 female pup from a litter were assigned to 1 of 4 groups which were either designated for subsequent behavioral testing and necropsies on PND 37, 75, and 250. One male and 1 female from each litter were assigned for neuropathology analysis with half the litters from this group killed on PND 37, and the remainder killed on PND 75. Neuropathology results will be reported separately. Measurements of reproductive success and growth included number of litters, number of pups, males/females ratio, uterine implantation sites, litter weights (PND 1–4), pup weights by sex (PND 4–23), weight gain, litter mortality rates (before PND 4), pup mortality rates (after PND 4), and number of litters with mortality. In addition to the analysis of reproductive endpoints, the following neurodevelopmental landmarks were measured in all pups:

Negative Geotaxis: Beginning on PND 6, pups were gently placed snout downward on a 25° inclined surface covered with a computer mouse pad. The time required (up to 60 sec) for the pups to rotate such that its snout pointed upward was recorded. Failure to re-orient on

Table 2. Total blood mercury levels ($\mu g \cdot L^{-1}$ ± s.e.m) in dams and offspring

	Vehicle	Aroclor	0.05 $mg \cdot kg^{-1}$	0.5 $mg \cdot kg^{-1}$	5.0 $mg \cdot kg^{-1}$
Maternal Blood	30.3 (±3.03)	26.4 (±1.71)	511.7 (±49)	5658 (±357)	46369 (±5473)
Maternal Brain	0.05 (.05)	0.007 (.005)	0.061 (.030)	0.623 (.030)	5.32 (.367)
Offspring Blood	9.4 (±0.87)	10.6 (±0.48)	12.8 (±1.05)	36.9 (±2.47)	249.3 (±28.04)

the inclined plane was scored as a failure and the pups were retested the following day.

Eye and Ear Opening: Eye opening and ear opening were checked daily starting on PND 10 until their occurrence.

Grip Strength: Grip strength testing was conducted on PND 10, 12 and 14. Each pup was removed from its home cage and the front paws were gently placed on a 3 mm wire suspended 20 cm above a one-inch layer of wood shavings. The length of time (to a maximum of 60 sec) that the pups held themselves suspended from the wire was recorded. Pups that did not grasp the wire when the paws were placed in contact with the wire were given a score of 0 and scored as absent for the grasping reflex.

Other behavioral measurements including activity testing, holeboard exploration, light-dark emergence testing, acquisition of a visual discrimination, partial reinforcement extinction testing and delayed spatial alternation testing are in progress and will be reported later.

Seven to 10 days after weaning, the dams were killed by guillotine and brains were rapidly removed and frozen on dry ice for subsequent mercury analysis. Liver, kidney, adrenal glands, lungs, heart and reproductive organs were excised and weighed. The tissues were kept in phosphate buffered formalin for histopathological analysis if deemed necessary. Liver homogenates were made for microsomal enzyme activity assays. Blood was collected for serum biochemistry and residue analysis. Biochemical, neuropathology, molecular biology, neurochemical and endocrine assays are in progress and will be reported separately.

Statistical analysis: Both parametric (analysis of variance, ANOVA) and non-parametric statistical tests (Kruskal-Wallis; Mann-Whitney U tests) were used depending on the specific type of data being analyzed.

Results

Mercury Residue Levels: Blood residue levels of mercury analyzed in dams and offspring sacrificed at PND 35. As shown in Table 2, blood mercury concentrations increased in approximate proportion to the dose included in the mixture. Doses of methylmercury were 0.02, 0.2 and 2.0 $mg \cdot kg^{-1} \cdot day^{-1}$ for doses of 0.05, 0.5 and 5.0 $mg \cdot kg^{-1}$ of the mixture. All mixture treated groups had significantly higher levels of blood mercury than vehicle or Aroclor-treated animals. Moreover, mercury blood levels in all mixture dose groups were significantly different from each other. Blood mercury levels in Aroclor treated dams were not different from vehicle controls. Maternal brain levels of mercury were also elevated in mixture treated groups but only at mixture doses of 0.5 and 5.0 $mg \cdot kg^{-1}$. Brain levels of mercury in Aroclor treated and 0.05 mixture animals were not different from vehicle controls.

Blood total mercury levels in offspring were also elevated in all mixture dosed groups but not Aroclor treated animals. Like dams, blood levels were also significantly different between all mixture dose groups. Mercury residue levels in brain of 35 day old offspring are not available.

It is interesting to note that in dams both blood and brain mercury levels increased 100 fold with a 100 fold increase in mercury dose. In contrast, a 100 fold increase in dose produce a 19 fold increase in offspring residue levels, probably reflecting that the transfer of maternal blood mercury to offspring is distributed among the entire litter. More importantly, blood levels in the lowest mixture dose group is approximately equal to the levels recently reported in cord blood in Inuit infants (Muckle reference).

Reproductive Outcomes: Treatment of rats with the mixture had no effects on litter size ($F_{4,47}$ = .392, p = .813), and number of implantation sites ($F_{4,47}$ = .456, p = .768) (Table 3). Similarly, there were no significant group differences in gestation period ($F_{4,47}$ = .449, p = .773), sex ratio of the offspring (χ^2_4 = 5.26, p = .262) and the ratio of pups born to implantation sites ($F_{4,47}$ = .466, p = .760).

There was a small increase in pup mortality in the Aroclor treated group, however, non parametric analysis indicated no significant differences between groups for either litter mortality (χ^2_4 = 2.85, p = 0.583) or pup mortality (χ^2_4 = 577, p = .217). Except for the Aroclor and 5.0 mixture groups, post-culling (PND 4) mortalities occurred in only one litter of each treatment group. All of the pup mortalities in the vehicle group occurred in one litter and are most likely a reflection of an idiosyncratic response in this litter. The

Table 3. Reproductive data and mortality rates

		Vehicle		0.05		0.5		5		Aroclor	
Number of litters		10		9		10		12		11	
Number of Pups		149		139		147		170		168	
Number of Implantation sites		156		147		1554		179		175	
Mean Number of pups		14.9 (.837)		15.4 (.882)		14.7 (.837)		14.2 (.764)		15.27 (.798)	
Mean Implant sites (sem)		15.6 (.808)		16.3 (.851)		15.4 (.808)		14.9 (.737)		15.9 (.770)	
Mean Gestation days		22.6		22.6		22.5		22.5		22.1	
Ratio Pups Born/Implant Sites		95.7.0%		94.4%		95.5%		91.8%		95.3%	
Sex ratio at birth (% male)		48.6%		57.3%		51.1%		53.7%		55.7%	
		N[a]	%[b]	N	%	N	%	N	%	N	%
Number of Pup Deaths and % of pups that died	≤ PND 4	3	2%	5	4%	4	3%	9	5%	4	2%
	>PND 4[c]	8	10%	1	1%	1	1%	7	7%	13	15%
Number of Litters with Mortality and % litters with mortality	≤ PND 4	3	30.0%	4	44.4%	4	40.0%	6	50.0%	3	27.3%
	> PND 4	1	10.0%	1	11.0%	1	10.0%	3	25.0%	5	45.5%

a. Number of pups (or litters) with deaths

b. Percent mortality in total pup sample or percent of litters with any mortality

c. Because litters were culled to 4 male and 4 female pups at PND 4, the percent mortality after PND 4 is based on the percent of the pups available after culling

small increase in mortality in the Aroclor-treated offspring was associated with mortalities in almost half the litters.

Figure 1 shows maternal weight gain during gestation. As shown in the figure, body weights increased in all groups over days ($F_{4,44} = 680.2$, $P < .001$) and treatment had no effect on weight gain. Although 5.0 mg·kg^{-1} of the mixture produced a small decrease in maternal weight gain, the effect did not reach statistical significance ($F_{4,47} = 2.203$, $p = .083$) and the interaction between time and treatment was not significant ($F_{16,188} = 1.31$, $p = .200$). Litter weight was increased for all groups between PND 1 and PND 4 (Figure 2). Although there was little difference in the average pup weight on PND 1, growth rate was decreased in offspring exposed to the 5.0 mg·kg^{-1} mixture and Aroclor. As revealed in Figure 3, the difference in weight gain between the control and Aroclor and 5.0 mg·kg^{-1} mixture groups became more pronounced over the first 23 days of life. Repeated measures of ANOVA on the transformed body weights confirmed the effect of the treatment ($F_{4,369} = 46.95$, $p < .001$) and that the effect of treatment varied over days ($F_{24,1271} = 21.17$, $p < .001$). Follow-up simple contrast tests revealed that the weights of offspring exposed to Aroclor or 5.0 mg·kg^{-1} mixture were significantly smaller than control animals on PND 5, 8, 11, 14, 17, 20, and 23 (t's > 2.6, p's < .04). Analysis also confirmed that there was a sex difference in body weight ($F_{4,369} = 10.78$, $p = .001$) with males being slightly larger than females. There was no indication, however, that the effect of treatment was influenced by gender ($F_{4,369} = .179$, $p = .949$) or that gender influenced the interaction between age and treatment ($F_{24,1271} = .598$, $p = .937$).

Figure 1. Body weights in dams treated with the mixture and Aroclor. No treatment significantly altered maternal weight gain during pregnancy

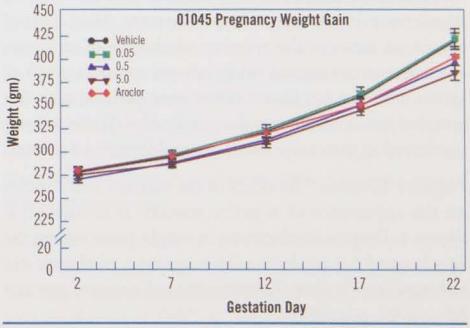


Figure 2. Body weights of litters exposed to the mixture or Aroclor. Both Aroclor and 5.0 mixture decreased litter weights

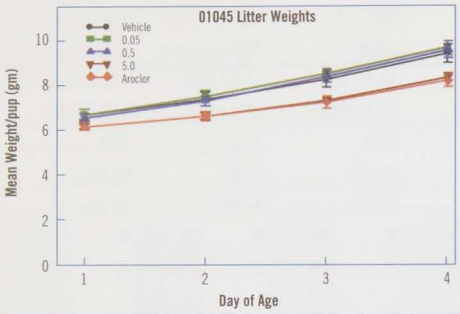


Figure 3. Weight gains in offspring to the mixture or Aroclor. Both Aroclor and 5.0 mixture significantly reduced weight gain until weaning

Figure 4. Negative geotaxis in rat pups was not affected by Aroclor or the mixture

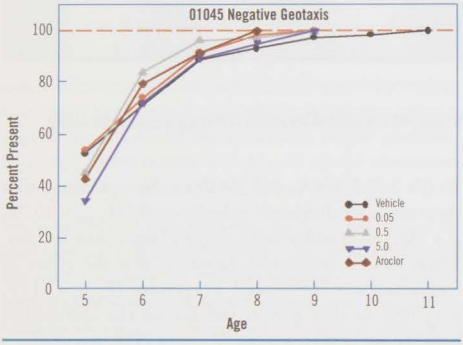
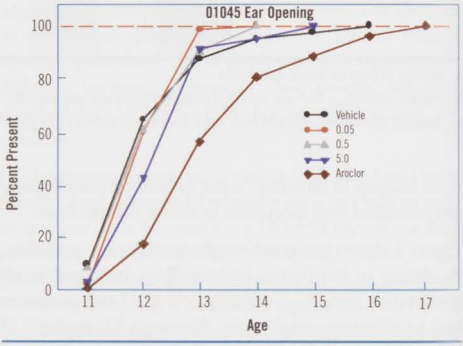


Figure 5. Ear opening was delayed by Aroclor but the mixture had only minor effects on ear opening



Developmental Landmarks

A number of developmental landmarks that normally emerge according to a precise timetable after birth were evaluated. These landmarks provide indications of the normal pattern of development of the neural system. Delays in the occurrence of these landmarks may indicate treatment related impairments in neural system development. Since most of these tests measure the presence or absence of an event, analyses were conducted using non-parametric analysis of variance. Where significant effects were detected with this omnibus test, a subsequent discrete Kruskal-Wallis test was conducted to determine where group differences occurred.

Negative Geotaxis: The effect of the mixture and Aroclor on the appearance of negative geotaxis is illustrated in Figure 4. Despite the decreases in weight gains among the Aroclor and 5.0 mg·kg^{-1} mixture groups, treatment did not significantly alter the appearance of negative geotaxis ($\chi^2_4 = 4.99$, $p = .289$).

Ear Opening: Figure 5 shows the proportion of animal in each treatment group exhibiting ear opening between PND 11 and 17. An overall Kruskal-Wallis analysis indicated that there was a significant treatment effect ($\chi^2_4 = 67.72$, $p < .001$). A subsequent pair-wise test indicated that Aroclor significantly delayed the onset of ear opening (Mann-Whitney $U = 1370$, $p < .001$) as did 5.0 mg·kg^{-1} of the mixture (Mann-Whitney $U = 2526$, $p = .018$). On PND 12 ear opening was present in more than 60% of vehicle treated animal but in less than 20% and 40% of Aroclor and 5.0 mg mixture treated groups, respectively.

Eye Opening: Figure 6 shows the impact of treatment on the onset of eye opening. As can be seen, both Aroclor and 5.0 mg·kg^{-1} of the mixture decreased the days to the appearance of eye opening. Kruskal-Wallis ANOVA confirmed the treatment effect ($\chi^2_4 = 141.45$, $p < .001$) and follow-up pairwise comparisons confirmed that the

Figure 6. Both Aroclor and 5.0 mixture accelerated eye opening while the lowest mixture dose produced a small delay in eye opening

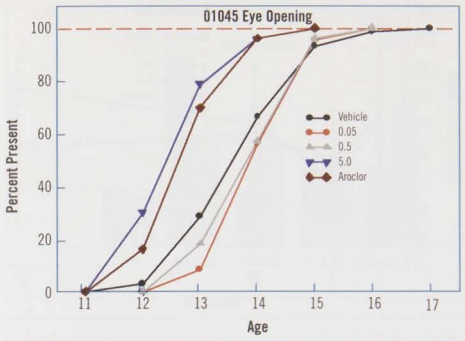
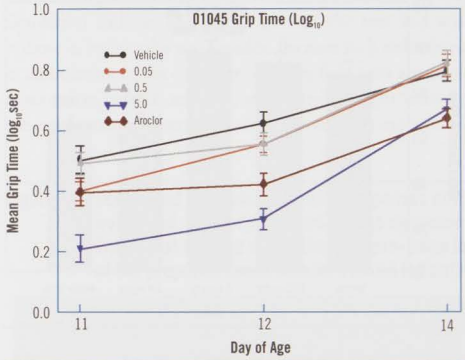


Figure 7. Aroclor and the highest mixture dose reduced grip pre-weaning strength



vehicle group was significantly different from the Aroclor (Mann-Whitney U = 1419, p <.001) and 5.0 mg·kg^{-1} mixture group (Mann-Whitney U = 1139, P < .001). In both cases, the proportion of animals with detectable eye opening was increased relative to vehicle control groups from PND 12 to 14. Pairwise comparisons also revealed that the lowest dose of the mixture (0.05 mg/kg) produced a small but significant delay in eye opening (Mann-Whitney U = 2130, p = .036) that is associated primarily with a decrease in the proportion of animals exhibiting eye opening on PND 13 and 14. The cause of this reversal of eye opening at the high dose of the mixture and Aroclor is not clear though others have reported similar results following perinatal exposure to Aroclor 1254 (Goldey et al., 1995).

Grip Strength was determined by measuring the time that animals maintained grip on the suspended bar on PND days 10, 12 and 14 (Figure 7). Time values were initially analyzed with repeated measures of ANOVA. But because of violations of assumptions of homogeneity of variance and circularity, a log10 transformation was conducted on grip times and the transformed values analyzed with repeated measures of ANOVA. Grip time, while increased over days for all groups ($F_{2,246}$ = 127.1, p < .001), was affected by treatment ($F_{4,47}$ = 10.3, p < .01). Follow-up contrasts revealed that Aroclor and 0.5 and 5.0 mg·kg^{-1} mixture decreased grip time (p's < 0.05). The impact of chemical treatment, however, differed over test days as revealed by a significant days by treatment interaction ($F_{8,494}$ = 2.37, p = .016). Follow-up tests indicated that Aroclor decreased grip time on PND 12 and 14 (t's > 2.99, p's < .004). In contrast, 5.0 mg·kg^{-1} of the mixture decreased grip time on PND 10 and 12 (t's > 4.4, p's <.001). There were no differences between male and females nor were there any indications that gender influenced grip times.

Behavioral and Functional Results

Motor activity

Motor activity at PND 17 was affected by both Aroclor and the mixture. While Aroclor significantly reduced ambulation and rearing (a measure of exploration of the environment), the lowest mixture dose (0.05 mg·kg^{-1}) significantly reduced ambulation but had no effect on rearing. In contrast, the highest mixture dose (5.0 mg·kg^{-1}) did not alter total ambulation but significantly decreased rearing. The lack of habituation (a form of non-associative learning) in PND 17 offspring is evident from the relatively constant ambulation over the course of the 30 min test.

Motor activity in juvenile offspring at PND 30 was decreased by Aroclor but not by any mixture dose. Similar to results at PND 17, Aroclor also decreased rearing as did the highest mixture dose. The decrease in ambulation in all dose groups over the course of the 30 min test confirms the normal occurrence of habituation at this age. Because rodents normally avoid open spaces, the proportion of time spent in the central area of the chamber versus the safer area near the periphery of the chamber provides indications of reactivity to the open field chamber. The two lowest mixture doses altered the distribution of time spent in the central area of the chamber. Similarly, Aroclor increased the amount of time spent in the outer area of the activity chamber.

Motor activity in adults at PND 68 was altered by the intermediate dose of the mixture (0.5 mg·kg^{-1}) but not by Aroclor or any other mixture dose. Unlike motor activity tests conducted at PND 17 and 30, the effect of Aroclor

Figure 8. Rearing at PND 17. Both Aroclor and 5.0 mg/kg^{-1} mixture decreased rearing

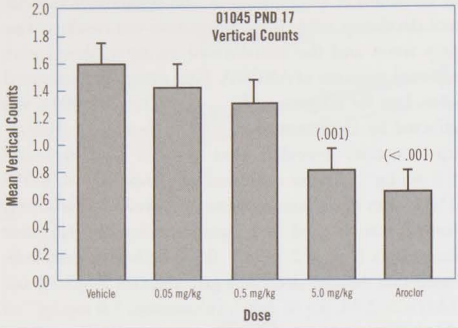


Figure 9. Ambulation at PND 17. Both Aroclor and 0.05 mg/kg^{-1} mixture decreased ambulation

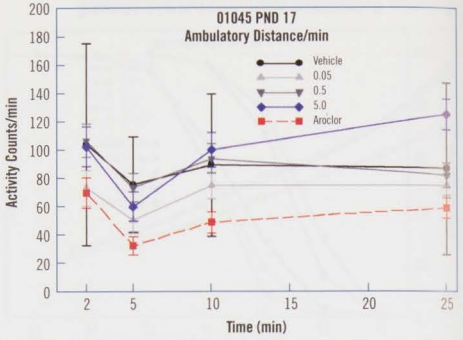


Figure 10. Ambulation at PND 30. Aroclor decreased ambulation but the mixture had no effect

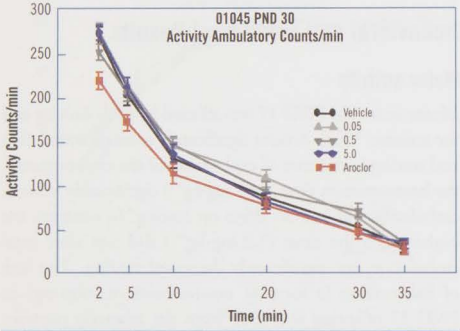


Figure 11. Rearing at PND 30. Both Aroclor and 5.0 mixture decreased rearing

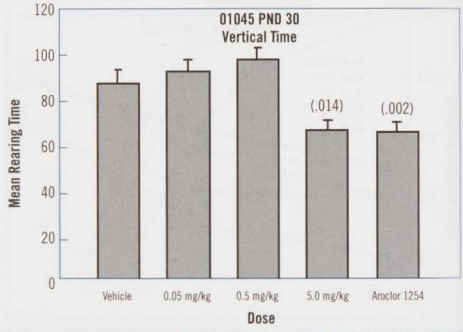


Figure 12. Time spent in the outer area of open field. Both Aroclor and the two lowest mixture doses increased the time spent in outer area

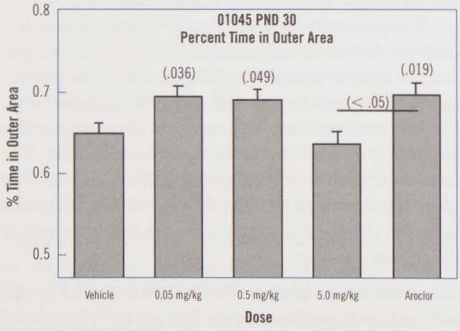


Figure 13. Ambulation at PND 68. 0.5 mg/kg mixture decreased ambulation only in the early part of the test

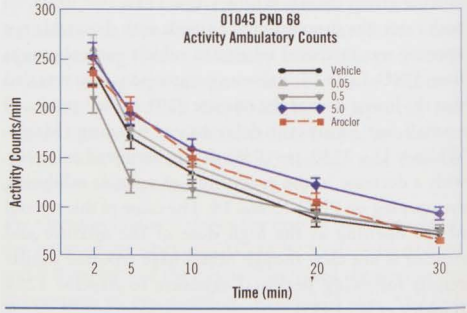
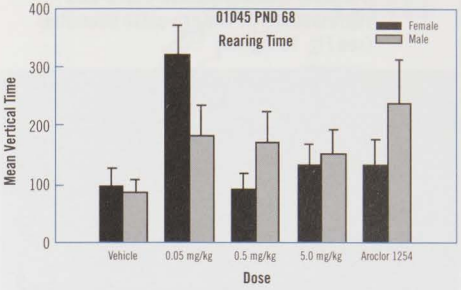


Figure 14. Rearing time of rats exposed to NCP mixture. Only the lowest mixture dose increased rearing and only in female



on ambulation was no longer evident at PND 68. Similarly, rearing was no longer affected in animals exposed to Aroclor or 5.0 mg·kg^{-1} of the mixture. The decrease in ambulation produced by the intermediate mixture dose was significant only in the first 5 min of the test and was evident in both males and females. Because such reductions in ambulation in the early part of open field tests are often observed in stressed animals, these results might indicate the emergence of altered reactivity in animals exposed to the intermediate dose of the mixture as they mature. While females exhibited significantly more ambulation than males, there was no indication that gender influenced the effect of the mixture on ambulation. The mixture also affected rearing in adult animals. Only the lowest dose of the mixture altered rearing. This dose produced a significant increase in rearing in females. An analysis of the time course of rearing indicated that this increased rearing in females was due to the elimination of normal habituation in females exposed to the lowest mixture dose. Except for rearing in these animals, normal habituation was evident for both ambulation and rearing. Unlike rearing results at PND 17 and 30, the effect of Aroclor and 5.0 mixture were no longer evident in adults animals tested at 68 days of age. Results on time spent in the central area of the chamber are not yet available.

Acoustic startle

Startle and pre-pulse inhibition curves using three startle intensities (95, 105 and 115 db) and four pre-pulse intensities (50, 60, 70 and 80 db) were evaluated at PND 21. Aroclor produced a large suppression in startle responding on both startle only and pre-pulse trials. In addition, Aroclor attenuated the ability of pre-pulses to reduce startle magnitude. This attenuation of pre-pulse effectiveness probably

Figure 15. Startle and pre-pulse inhibition responses at PND 21. Three startle intensities and four pre-pulse intensities were used. Aroclor produced a large decrease in the startle response and reduced pre-pulse inhibition. The lowest mixture dose attenuate pre-pulse inhibition but had little effect on startle response in the absence of the prepulse. Lower numbers in red indicate pre-pulse intensities

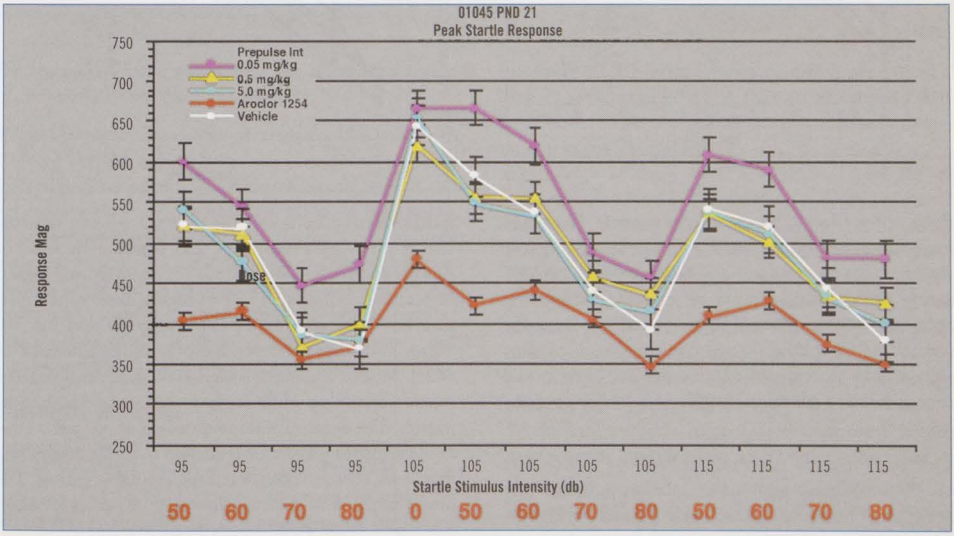


Figure 16. Startle and PPI in females at PND 44. The two highest mixture doses increased startle responding but this varied with startle and pre-pulse intensity. Numbers on X axis represent startle intensity (95, 105, 115 db) and pre-pulse intensity (50, 60, 70, 80 db)

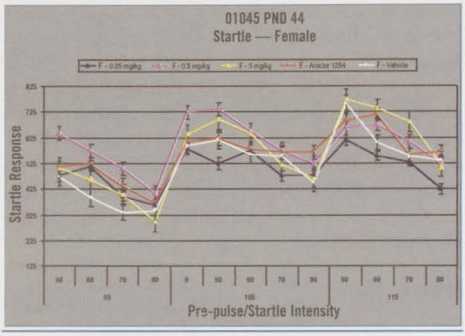


Figure 17. Startle and PPI in males at PND 44. Aroclor and the two highest mixture doses reduced startle responding independent of startle or pre-pulse intensity. Numbers on X-axis represent startle and pre-pulse intensities (see Fig. 16 legend)

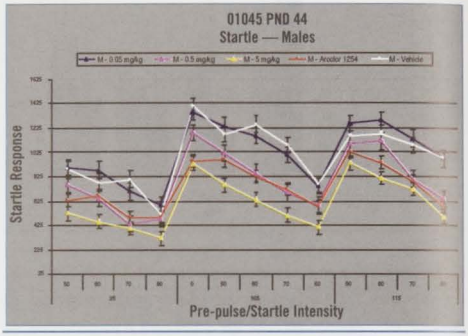


Figure 18. Percent correct responses during visual discrimination learning in male offspring. The highest mixture dose increased choice errors but males eventually reached levels of correct responding comparable to control animals

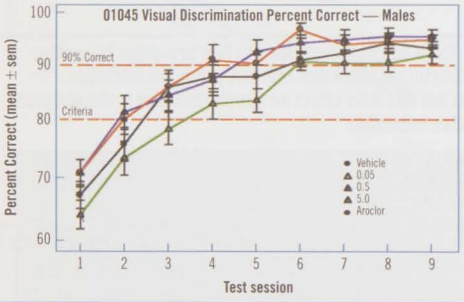
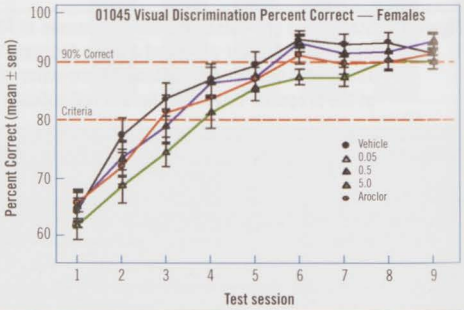


Figure 19. Percent correct responses during visual discrimination learning in female offspring. The highest mixture dose increased choice errors but these animals did eventually reach level of correct responding seen in control animal



reflects a floor effect in Aroclor treated animals. The lowest mixture dose had no effect on startle responding on startle only trials (pre-pulse value = 0). However, 0.05 mg·kg^{-1} mixture attenuated the efficacy of pre-pulses in reducing startle responses regardless of startle intensity or pre-pulse intensity. No other dose affected startle responding. These results suggest that the lowest mixture dose alters neural systems mediating sensorimotor gating assessed by pre-pulse inhibition.

Startle and pre-pulse inhibition at PND 44. While data analysis in ongoing, preliminary analysis indicates that the effects of both the chemical mixture and Aroclor on startle responding is evident at PND 44 and that the effects differ between males and females. In females, Aroclor and 0.05 mixture produce relatively little impact on startle responding. The two higher doses of the mixture however, attenuate pre-pulse inhibition but the degree of disruption depends on the startle intensity. In males, Aroclor and the two highest mixture doses reduced startle responding while the lowest mixture dose had no impact. The decrease was independent of pre-pulse inhibition suggesting a general reduction in startle responding that is independent of altered sensorimotor gating. The downward shift in the intensity-response curves for males

Figure 20. Age at puberty A) in female and B) in male pups

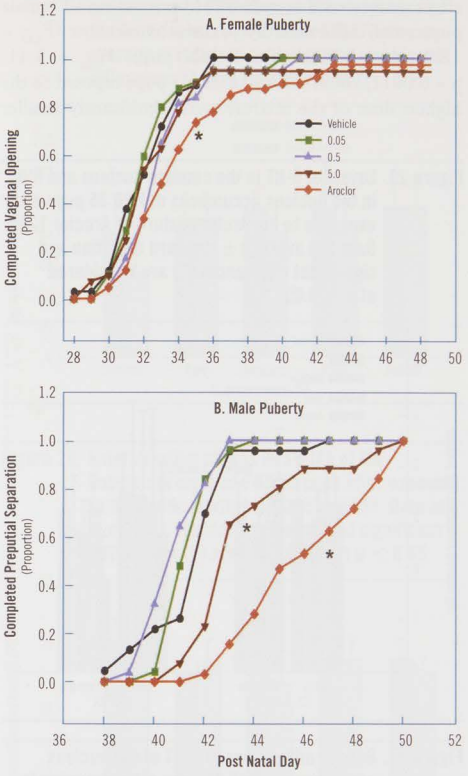
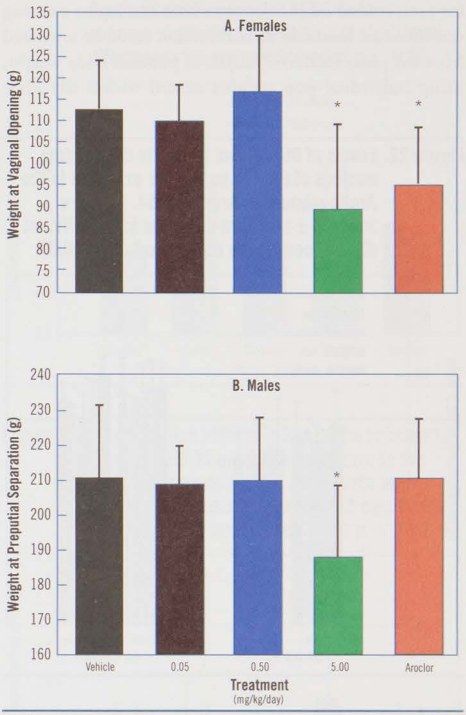


Figure 21. Body weight at puberty for (A) female and (B) male pups



indicates that startle responding was affected regardless of the startle or pre-pulse intensity.

Visual Discrimination learning was tested at PND 120–135. Aroclor exerted no effect on the acquisition of visual discrimination responding, a relatively simple operant task for rodents. However, offspring exposed to the highest dose of the mixture were slower to learn the task (more errors in early test sessions) but did achieve control levels of percent correct by the end of training. Females consistently made fewer errors than males throughout the entire training period. These results indicate that the highest mixture dose affect learning but that the impact appears to be transient.

Reproductive effects

To assess mixture effects on reproductive maturation, all female pups were monitored for vaginal opening beginning on PND 27 while male pups were examined for separation of the foreskin from the prepuce beginning on PND 37. Univariate survival analysis of data for the day at which puberty was first observed indicated a significant difference between treatments for both males and females (Log-Rank $\chi^2_4 = 87.9$, $p < 0.0001$ for males; $\chi^2_4 = 14.2$, $p = 0.007$ for females; Figure 20). The greatest delay for both sexes was clearly due to Aroclor treatment as the proportion of pups attaining puberty in this group was always less than the proportion of vehicle-treated pups throughout the monitoring period for both sexes. When data for Aroclor treated pups were excluded and re-analyzed there was no significant effect of any treatment for female pups (Log-Rank $\chi^2_3 = 3.06$, $p = 0.38$) while there was still a significant treatment effect for male pups (Log-Rank $\chi^2_3 = 32.9$, $p < 0.0001$). When data for male pups treated with the 5 $mg \cdot kg^{-1}$ mixture were also excluded no treatment effect was seen (Log-Rank $\chi^2_2 = 4.59$, $p = 0.1$) suggesting that the highest dose of the mixture significantly delayed puberty

in male, but not female pups. Body weight was recorded for each animal on the day on which the vagina opening was observed (females) or the foreskin could be separated from the penis (males). Analysis of pubertal body weight, using individual pup weights nested within the litter effect, indicated that values for both male and female pups were influenced by perinatal treatment ($F_{4,47}$ = 18.8, $p < 0.0001$, for female pups: $F_{4,48}$ = 5.41, $p = 0.0011$). Both male and female pups exposed to the highest dose of the mixture were significantly smaller

Figure 22. Levels of DOPAC and 5-HIAA in the caudate nucleus of PND 35 pups after exposure to the Arctic mixture or Aroclor 1254. Data are average ± standard deviation and significant differences (*) are considered at $p < 0.05$

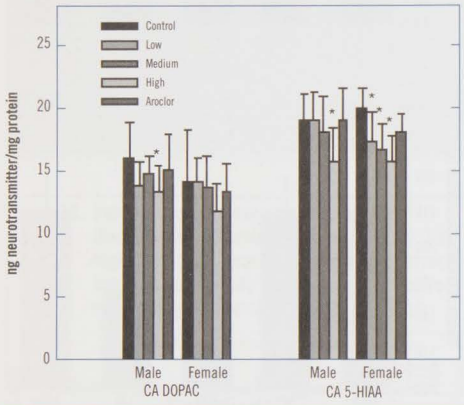


Figure 23. Levels of 5-HT in the caudate nucleus and HVA in the nucleus accumbens of PND 35 pups after exposure to the Arctic mixture or Aroclor 1254. Data are average ± standard deviation and significant differences (*) are considered at $p < 0.05$

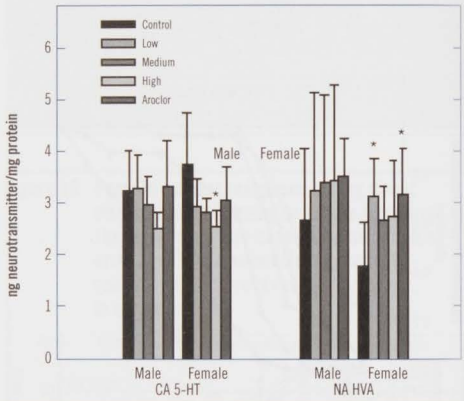


Figure 24. Levels of 5-HT in the substantia nigra and DA in the nucleus accumbens of PND 35 pups after exposure to the Arctic mixture or Aroclor 1254. Data are average ± standard deviation and significant differences (*) are considered at $p < 0.05$

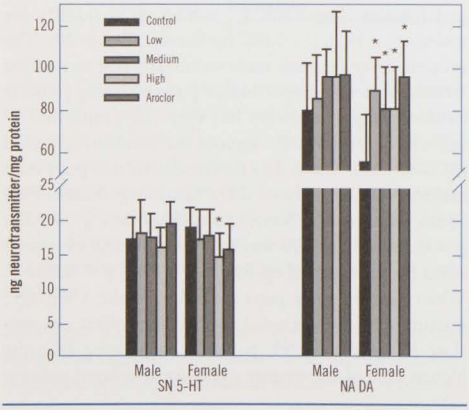


Figure 25. Gender differences in 5-HT of the nucleus accumbens of PND 35 pups after exposure to the Arctic mixture or Aroclor 1254. Data are average ± standard deviation and significant differences (*) are considered at $p < 0.05$

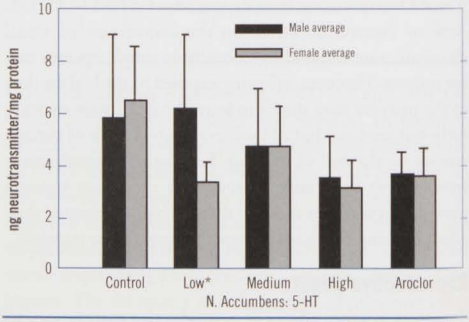


Figure 26. Gender differences in DA of the nucleus accumbens of PND 35 pups after exposure to the Arctic mixture or Aroclor 1254. Data are average ± standard deviation and significant differences (*) are considered at $p < 0.05$.

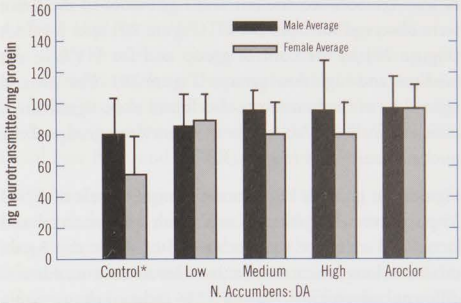


Figure 27. Lateralization effects in 3-MT of the substantia nigra of PND 35 pups after exposure to the Arctic mixture or Aroclor 1254. Data are average ± standard deviation and significant differences (*) are considered at $p < 0.05$.

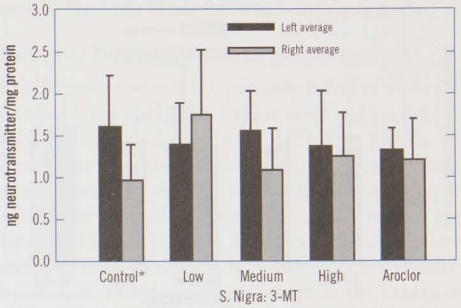


Figure 28. Lateralization effects in 5-HIAA of the substantia nigra of PND 35 pups after exposure to the Arctic mixture or Aroclor 1254. Data are average ± standard deviation and significant differences (*) are considered at $p < 0.05$

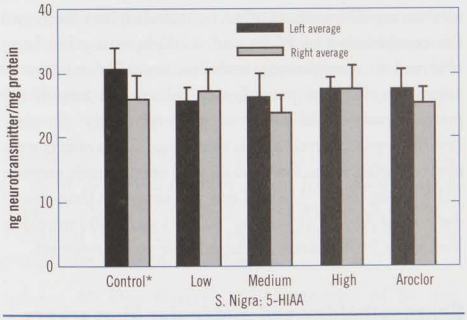
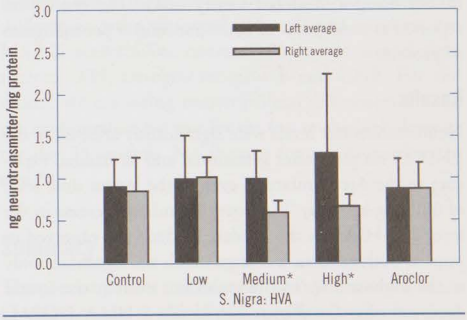


Figure 29. Lateralization effects in HVA of the substantia nigra of PND 35 pups after exposure to the Arctic mixture or Aroclor 1254. Data are average ± standard deviation and significant differences (*) are considered at $p < 0.05$



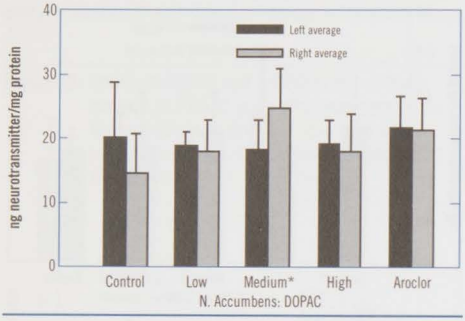
than vehicle exposed pups of the same gender on the day of puberty as determined by Tukey's post hoc test (Figure 21). Aroclor treatment also caused a reduction in age at vaginal opening in female pups while weight at preputial separation was not affected by this treatment. These results suggest that the mixture does influence reproductive development but only at the highest dose tested.

Neurochemical Results — Day 35 Pups

Methods

The neurochemical analysis involves examining the effect of perinatal exposure of rat pups to the POP mixture on the level of specific neurotransmitters in selected brain regions. The methodology is described briefly as follows. Immediately after decapitation of the rat, the brain is removed quickly, rinsed with ice-cold phosphate-buffered saline and weighed. The brain is then carefully cut in half along the sagittal plane with one half being assigned for neurochemistry and the other half for biomarker analysis (Santokh Gill). The assignment of the left or right side of the brain for neurochemistry and biomarker analysis was balanced between dose groups and sexes to address potential lateralization effects. The portion of the brain for neurochemistry is snap frozen on powdered dry ice and stored at −80°C until analysis. Frozen brain halves used for neurochemistry are sectioned and specific brain regions are then "punched" from the 750 μm slices. The

Figure 30. Lateralization effects in DOPAC of the nucleus accumbens of PND 35 pups after exposure to the Arctic mixture or Aroclor 1254. Data are average ± standard deviation and significant differences (*) are considered at $p < 0.05$



tissue punches are subjected to ultrasonic disruption in perchloric acid, which precipitates the proteins. The proteins are precipitated by spinning in a microfuge and the supernatant is analyzed by HPLC with electrochemical detection; the protein content of the pellet is determined using a modified Lowry assay. The results are reported as nanograms of neurotransmitter per milligram of protein.

Results

Neurotransmitter levels were significantly affected in the PND 35 rat pups after gestational and lactational exposure to the Arctic mixture, even at the lowest dose level of 0.05 $mg \cdot kg^{-1} \cdot day^{-1}$. A dose-dependent decrease in the level of 5-HIAA in the caudate nucleus was observed in pups of both genders, a change which was significant only at the highest dose in the males but even at the lowest dose in the females (Figure 22). Unlike 5-HIAA, DOPAC in the caudate nucleus was significantly decreased by treatment with the Arctic mixture only in the male pups (Figure 22) while 5-HT was significantly affected only in the females (Figure 23). Both HVA (Figure 23) and DA (Figure 24) were significantly elevated relative to the controls in the nucleus accumbens, but only for the female pups. In the substantia nigra, 5-HT was significantly decreased but again, only for the female pups (Figure 24). In all cases, similar trends were evident for the opposite sex but the changes were not statistically significant (Figures 22–24). No other significant dose-related changes were observed for any of the neurotransmitters in any region of the brain.

Gender differences in neurotransmitter levels were observed only in the nucleus accumbens for 5-HT in the low dose group (Figure 25) and for DA in the control group (Figure 26). In both cases, the levels in the females were lower than that for the males. Lateralization effects were only observed in the nucleus accumbens and in the substantia nigra. In the substantia nigra, significant differences between the left and right sides of the brain were observed for both 3-MT (Figure 27) and 5-HIAA (Figure 28) in the control group and for HVA in the medium and high dose groups (Figure 29). The left and right sides of the brain were also found to be significantly different for DOPAC in the medium dose group of the nucleus accumbens (Figure 30).

Significant changes in neurotransmitter levels of PND 35 pups were also observed as a result of gestational and lactational exposure to Aroclor 1254. While the Arctic mixture altered neurotransmitter levels in a number of different brain regions, Aroclor 1254 induced changes only in the nucleus accumbens. Aroclor treatment elevated both HVA (Figure 23) and DA (Figure 24) relative to the controls, as did exposure to the Arctic mixture. In contrast to the Arctic mixture, no significant gender differences or lateralization effects were observed after exposure to Aroclor.

The PCBs, organochlorines and mercury in the Arctic mixture are all known to affect neurotransmitter levels and the combination of PCBs and methylmercury has been observed to synergistically lower rat brain DA content *in vitro*. It is therefore possible that the components of the mixture work additively or synergistically to alter neurotransmitter levels in this work. Significant effects were observed even at the lowest dose level of the Arctic mixture (0.05 $mg \cdot kg^{-1} \cdot day^{-1}$), which was 300 times less than that of the dose of Aroclor (15 $mg \cdot kg^{-1} \cdot day^{-1}$) and 1,400 times less if only the PCB content of the mixture was considered.

Neuropathology and molecular biomarkers

A detailed gross examination of the rats was done at the 35 and 70 day kill dates (35 day pups 50 animals, 70 day pups 52 animals). All animals were perfuse with 4% PFA and allowed to post 'immersion' fix, processed for paraffin embedding, sectioned and stained for light microscopic evaluation.

The brains were processed following our standard procedures used for developmental neuropathology. Briefly outlined here. Brains were weighed and measurements were taken before tissue slices were processed for paraffin embedding. Specific brain regions were selected as per Paxinos atlas of the rat brain. All brains were sectioned using the 'brain matrix', to include B1 plates 16/17; B2 18/30; B3 plates 31/32; B4 Left Cerebellum mid

sagittal section; B5 Right Cerebellum mid saggital section; B6 Frontal lobes. Sections stained with H&E will be used for Tier 1 histopathology evaluation and for Tier 2 including morphometric measurements of the hippocampus, the cortex, the corpus callosum. Apoptosis:mitosis ratio will be assessed within the anterior subventricular zone at the level of plates 16/17. The neuropathology portion of this study is still in progress for data gathering and morphometric analysis. Unstained sections were prepared for future histochemical and immunohistochemical stains used as biomarkers of neural injury including Bodian, Luxol Fast Blue, and GFAP immunohistochemistry.

For general pathology assessment the following tissues were examined: thyroid, parathyroid, esophagus, stomach, heart, lung, thymus, mesenteric and popliteal lymph node, spleen, ileum, femoral bone marrow, adrenal, colon, pancreas, liver, kidney, ovary, uterus, vagina, testis, epididymis, prostate, and seminal vesicle. Significant lesions were found in a few organs and these will be briefly outlined.

Liver: 35 Day Groups. Mild hepatocellular hypertrophy is prevalent in all groups but controls. There is mild multi focal hepatitis in controls; in the .05, .5, and 5.0 mg·kg^{-1} groups the severity of this change is mildly increased. In the Aroclor animals there is a spectrum of changes including: hepatocellular fatty change, atrophy and apoptosis, fibrosis, limited hepatocellular regeneration, cirrhosis, bile duct hyperplasia and cholangiofibrosis. 70 Day Groups. The only lesion is mild hepatocellular hypertrophy.

Thymus: 35 Day Groups. 4 of 10 in the 5 mg·kg^{-1} and all (9 of 9) in the Aroclor group have mild cortical atrophy. 70 Day Groups. 3 of 12 in the .5 mg·kg^{-1}, 2 of 10 in the 5 mg·kg^{-1}, and 7 of 12 in the Aroclor groups have mild cortical atrophy.

Spleen: 35 Day Groups. Mild atrophy of B- and T-dependent regions is common in all groups but controls. 70 Day Groups. Mild cortical atrophy is common in all groups but controls.

Mesenteric Lymph Node: 35 Day Groups. 4 of 9 in the 5 mg·kg^{-1} have mild B- or T-dependent atrophy. 11 of 12 in the Aroclor group have mild to moderate atrophy of B- and T-dependent regions. 70 Day Groups. No lesions.

Kidney: 35 Day Groups. 3 of 11 in the .5 mg·kg^{-1}, 1 of 10 in the 5 mg·kg^{-1}, and 2 of 12 in the Aroclor group have rare to few basophilic tubules in medulla. Multi focal mild cortical chronic interstitial nephritis is common in all animals. 70 Day Groups. No basophilic tubules are present. Chronic interstitial nephritis is common in all.

Thyroid: 35 Day Groups. Mild follicular hypertrophy and hyperplasia are present in 6 of 11 in the .5 mg·kg^{-1}, 7 of 10 in the 5 mg·kg^{-1}, and 9 of 9 in the Aroclor group. 70 Day Groups. These are all within normal limits. Additional sections were prepared and stained with PAS to be used by Dr. Mike Wade for morphometric analysis.

Molecular biomarkers (transcriptional analysis)

For the transcriptional analysis, only halves of the brain were used and total RNA was extracted and pooled for each individual dose group. Different groups of biomarkers were monitored, including the early injury markers such as c-fos, c-jun and Hsp 72 and specific markers for each cell type in the CNS. Some of these are GFAP, S100, NSE, MAP 2, muscarinic acetycholine receptors, estrogen receptor B, GABA receptors, tyrosine hydroxlase, PCNA and the markers in the oxidative pathways such as superoxidase dismutase (SOD-Zn and SOD-Mn) and mitochondrial cytochrome oxidase 3 (Cox-3). These were monitored for both males and females, left and right hemipshere. Hence, approximately 20 biomarkers were tested in triplicate for each sample. The transcriptional changes observed at day 35 were most predominant in the males but not females, no hemispheric differences were observed. The altered markers are MAP-2, acetycholine esterase, muscarinic acetycholine receptor M5, estrogen receptor B and CNP. For the results, we are seeing transcriptional differences for the the medium dose but not for the low or the high doses in the day 35 animals. No changes for any biomarkers in day 70.

Summary

The present project demonstrates that perinatal exposure of pregnant rats to the mixture produced early developmental effects on weight gain, ear opening, and grip strength in the offspring. Startle response and motor activity were also affected by treatment. It also caused neurochemical changes in the brain of the pups. Exposure to the mixture caused delayed puberty in males, and decreased body weights at puberty in both sexes of pups. While a broad range of other assays are being pursued, it is worth noting that the effects were observed at dose levels where no maternal effects were evident. Further laboratory analyses including molecular and neuropathology are being carried out to evaluate comprehensively the developmental effects of the Arctic mixture.

Expected Completion Date

October 2004.

References

Baffin Regional Health & Social Service Board. 1997. Baffin Region Blood Monitoring Program Results. Environment and Lifestyle Monitoring Project.

Geller, A.M., W.M. Oshiro, N. Haykal-Coates, P.R. Kodavanti, and P.J. Bushnell. 2001. Gender-dependent behavioral and sensory effects of a commercial mixture of polychlorinated biphenyls (Aroclor 1254) in rats. *Toxicol. Sci.* 59:268–277.

Gladen, B.C and W.J. Rogan.1988. Decrements on six-month and one-year Bayley scores and prenatal polychlorinated biphenyls (PCBs) exposure. *Am. J. Epidemiol.* 128:912.

Goldey, E.S., L.S. Kehn, C. Lau, G.L. Rehnberg, and K.M. Crofton. 1995. Developmental exposure to polychlorinated biphenyls (Aroclor 1254) reduces circulating thyroid hormone concentrations and causes hearing deficits in rats. *Toxicol. Appl. Pharmacol.* 135: 77–88.

Jacobson, J.L., S.W. Jacobson, and H.E. Humphrey. 1990. Effects of exposure to PCBs and related compounds on growth and activity in children. *Neurotoxicol. Teratol.* 12:319–326.

Jacobson, J.L., and S.W. Jacobson. 1993. A 4 year followup study of children born to consumers of Lake Michigan fish. *Journal of Great Lakes Research.* 19: 776–783.

Lonkey, E., J. Reihman, T. Darvill, J. Mather, and H.B. Daly. 1996. Neonatal Behavioral Assessment Scale performance in humans influenced by maternal consumption of environmentally contaminated Lake Ontario fish. *Journal of Great Lakes Research.* 22:198–212.

Morse, D.C., R.F. Seegal, K.O. Borsch, and A. Brouwer. 1996. Long term alterations in regional brain serotonin metabolism following maternal polychlorinated biphenyl exposure in the rat. *Neurotox.* 17:631–638.

Roegge, C.S., B.W. Seo, K.M. Crofton, and S.L. Schantz. 2000. Gestational-lactational exposure to Aroclor 1254 impairs radial-arm maze performance in male rats. *Toxicol. Sci.* 57:121–130.

Widholm, J.J., G.B. Clarkson, B.J. Strupp, K.M. Crofton, R.F. Seegal, and S.L. Schantz. 2001. Spatial reversal learning in Aroclor 1254-exposed rats: sex-specific deficits in associative ability and inhibitory control. *Toxicol. Appl. Pharmacol.* 174:188–198.

Effects of Exposure to Organochlorines, Chlorinated Pesticides and Heavy Metals on the Infectious Diseases Incidence of Inuit Preschool Children

Project leader

Éric Dewailly, Public Health Research Unit, Laval University, Centre Hospitalier Universitaire de Québec (CHUQ), 2400 d'Estimauville, Beauport (Qc), G1E 7G9; phone: (418) 666-7000; fax: (418) 666 2776, e-mail: Eric.Dewailly@crchul.ulaval.ca

Project team

Frédéric Dallaire, Carole Vézina, Gina Muckle, Pierre Ayotte, Gaston de Serres, Public Health Research Unit, Laval University Medical Research Center (CHUQ), Quebec City, Quebec.

Abstract

The purpose of this study is to clarify the role played by chlorinated pesticides, PCBs and heavy metals on the high incidence of infections in Nunavik. These substances accumulate in the body of Inuit women in part due to their consumption of sea mammal fat and can be transferred to the fetus during pregnancy and to the infant during breast-feeding. To determine if there is a relation between contaminants and infection rates, we are reviewing the medical charts of 480 children between 5 and 7 years old to record the number of infections during the first 5 years of life. Some characteristics of the immune system (complement and cellular immunity) are also being evaluated.

Key Project Messages

1. This study investigates possible detrimental effects on the immune system of Inuit preschool children that may be induced by prenatal and postnatal exposure to persistent environmental contaminants such as organochlorine compounds and heavy metals.
2. The medical charts of 450 preschool children will be reviewed and the relation between the incidence of infections and contaminants will be evaluated.

Objectives

Main objective

The main objective of this project is to evaluate the effect of exposure to organochlorines and heavy metals on the infectious diseases incidence of Inuit preschool children.

Specific objectives

1. To determine the incidence of infectious diseases during the first 5 years of life.
2. To assess the impact of pre- and post-natal exposure to OCs and heavy metals on the incidence of infections.

3. To evaluate the status of some components of the immune system (complement and cellular immunity).
4. To assess the vitamin A status and its influence on the incidence of infections.

Introduction

The high incidence of infectious diseases (in particular meningitis, broncho-pulmonary and middle ear infections) in native infants and children from Nunavik has been known for many years (Dufour 1988, Proulx 1988). The high exposure to OCs could be in part responsible for the high incidence of infectious diseases in Nunavik (Dewailly et al. 2000). Children exposed *in-utero* to PCBs (born from mothers accidentally exposed to PCBs) were found to have more episodes of influenza (Yu et al. 1998), bronchitis, pneumonia (Rogan et al. 1988) and middle ear diseases associated with clinical complications (Chao et al. 1997) than non-exposed matched controls. Unfortunately, very few studies have been done on the immunotoxic effects of environmental exposure of OCs. Nevertheless, there is growing evidence that high maternal exposition to these substance through the environment could influence some T-cell subsets as well as increase the incidence of infectious diseases of the newborns (Swain 1991, Weisglas-Kuperus et al. 1995, Rylander et al. 1998, Dewailly et al. 2000, Weisglas-Kuperus et al. 2000).

While data on environmental effects of OCs on the human immune system are scarce, several immunotoxicological studies on laboratory animals have been conducted (reviewed by Safe (1994)). Immunotoxic properties of dioxin-like compounds (myelosuppression, thymus atrophy, immunosuppression, decreased IgA and IgM concentrations, complement inhibition and T-cell subset alteration) have been observed in rodents and non-human primates (Thomas and Hinsdill 1979, Holsapple et al. 1984, White et al. 1986, Tryphonas et al. 1991, Tryphonas et al. 1991, Neubert et al. 1992, Esser and Welzel 1993). The immune system is particularly vulnerable to immunotoxic agents during its development *in-utero* and during the infancy. High maternal burden during pregnancy and lactation could lead to permanent defects on the infant's immune system (Barnett et al. 1987, Badesha et al. 1995). Perhaps the most valuable data on immunotoxic properties of dioxin-like compounds on humans were provided through the evaluation of a population accidentally exposed to PCB in Taiwan (Yu-Cheng disease). Patients who had consumed PCB contaminated rice oil had decreased total T-cell and activated T-cell counts (Chang et al. 1981), decreased lymphocyte spontaneous and PHA-stimulated proliferation (Lu and Wu 1985) and lower serum IgA and IgM concentrations (Chang et al. 1981, Lu and Wu 1985). Positive responses to delayed-type hypersensibility (DTH) test was less frequent and the size of indurations was smaller (Chang et al. 1982).

This project was designed to assess the effect of OCs and heavy metals on the incidence of infectious diseases in Inuit preschool children of Nunavik. The project is still ongoing and no results are available yet. This report describes the progression of our work as of May 2002.

Activities

In 2001–2002

Evaluation of prenatal exposure

Between 1993 and 1996, an extensive monitoring of the level of OCs and heavy metals in cord blood took place in Nunavik (Dewailly et al. 1998). This study was funded by the ministry of Indian and Northern Affairs (AES) and by Health Canada. We are using these data to evaluate the prenatal exposure to OCs and heavy metals for these children who are now between 5 and 8 years old. Contaminants levels are available for 484 children.

Review of medical charts

The main component of this project is to review the charts of approximately 450 children. We are recording every health problem for which medical attention was sought during the first 5 years of life. This has proven to be a long and painstaking exercise. Nevertheless, the review should be completed by the end of Summer 2002.

Laboratory analyses

Vitamin A levels in cord blood were available for only 134 children out of 484. We wanted to evaluate vitamin A level in archived cord blood samples to increase this number. We first reanalyzed 30 samples for which vitamin A level was already known to make sure that the new analysis yielded comparable results and that the vitamin A level in frozen samples had not been altered during the years. The results of the 2 series of analyses were very similar. We then went on with the analysis of the 286 archived samples for which vitamin A had not been evaluated previously. We now have vitamin A concentrations for 420 samples.

Subgroup of the preschool children neurodevelopmental study

A children subgroup of the present project is nested in the preschool children neurodevelopmental study (already funded through the NCP program). Approximately 110 children have been seen at 5 years of age and blood samples have been drawn. The results of these analyses

will be used to evaluate the relation between the actual OCs burden and the infectious diseases incidence for these children. Information on tobacco, crowding, breast-feeding and socioeconomic status have also been gathered and will be used for the evaluation of confounding factors in the statistical analysis of the present study.

References

Badesha, J.S., G. Maliji and B. Flaks. 1995. Immunotoxic effects of exposure of rats to xenobiotics via maternal lactation. Part I 2,3,7,8-tetrachlorodibenzo-p-dioxin. *Int J Exp Pathol.* 76(6):425–439.

Barnett, J.B., L. Barfield, R. Walls, R. Joyner, R. Owens and L.S. Soderberg. 1987. The effect of in utero exposure to hexachlorobenzene on the developing immune response of BALB/c mice. *Toxicol Lett.* 39(2–3):263–274.

Chang, K.J., K.H. Hsieh, T.P. Lee, S.Y. Tang and T.C. Tung. 1981. Immunologic evaluation of patients with polychlorinated biphenyl poisoning: determination of lymphocyte subpopulations. *Toxicol Appl Pharmacol.* 61(1):58–63.

Chang, K.J., K.H. Hsieh, S.Y. Tang, T.C. Tung and T.P. Lee. 1982. Immunologic evaluation of patients with polychlorinated biphenyl poisoning: evaluation of delayed-type skin hypersensitive response and its relation to clinical studies. *J Toxicol Environ Health.* 9(2):217–223.

Chao, W.Y., C.C. Hsu and Y.L. Guo. 1997. Middle-ear disease in children exposed prenatally to polychlorinated biphenyls and polychlorinated dibenzofurans. *Arch Environ Health.* 52(4):257–262.

Dewailly, E., S. Bruneau, P. Ayotte, G. Lebel, G. Muckle and M. Rhainds. 1998. *Évaluation de l'exposition prénatale aux organochlorés et aux métaux lourds chez les nouveau-nés du Nunavik*, 1993–1996. Beauport: Centre de santé publique de Québec, Université Laval, 74.

Dewailly, E., P. Ayotte, S. Bruneau, S. Gingras, M. Belles-Isles and R. Roy. 2000. Susceptibility to infections and immune status in inuit infants exposed to organochlorines. *Environ Health Perspect.* 108(3):205–211.

Dufour, R. 1988. The otitis media among Inuit children. *Arctic Medical Research.* 47(1):659–665.

Esser, C. and M. Welzel. 1993. Ontogenic development of murine fetal thymocytes is accelerated by 3,3',4,4'-tetrachlorobiphenyl. *Int J Immunopharmacol.* 15(8): 841–852.

Holsapple, M.P., P.J. McNerney, D. W. Barnes and K.L. White, Jr. 1984. Suppression of humoral antibody production by exposure to 1,2,3,6,7,8-hexachlorodibenzo-p-dioxin. *J Pharmacol Exp Ther.* 231(3):518–526.

Lu, Y.C. and Y.C. Wu. 1985. Clinical findings and immunological abnormalities in Yu-Cheng patients. *Environ Health Perspect.* 59:17–29.

Neubert, R., G. Golor, R. Stahlmann, H. Helge and D. Neubert. 1992. Polyhalogenated dibenzo-p-dioxins and dibenzofurans and the immune system. 4. Effects of multiple-dose treatment with 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) on peripheral lymphocyte subpopulations of a non-human primate (*Callithrix jacchus*). *Arch Toxicol.* 66(4):250–259.

Proulx, J.F. 1988. Meningitis in Hudson's Bay, Northern Quebec, Canada. *Arctic Medical Research.* 47(1): 686–687.

Rogan, W.J., B.C. Gladen, K.L. Hung, S.L. Koong, L.Y. Shih, J.S. Taylor, et al. 1988. Congenital poisoning by polychlorinated biphenyls and their contaminants in Taiwan. *Science.* 241(4863):334–336.

Rylander, L., U. Stromberg, E. Dyremark, C. Ostman, P. Nilsson-Ehle and L. Hagmar. 1998. Polychlorinated biphenyls in blood plasma among Swedish female fish consumers in relation to low birth weight. *Am J Epidemiol.* 147(5):493–502.

Safe, S.H. 1994. Polychlorinated biphenyls (PCBs): environmental impact, biochemical and toxic responses, and implications for risk assessment. *Crit Rev Toxicol.* 24(2):87–149.

Swain, W.R. 1991. Effects of organochlorine chemicals on the reproductive outcome of humans who consumed contaminated Great Lakes fish: an epidemiologic consideration. *J Toxicol Environ Health.* 33(4):587–639.

Thomas, P.T. and R.D. Hinsdill. 1979. The effect of perinatal exposure to tetrachlorodibenzo-p-dioxin on the immune response of young mice. *Drug Chem Toxicol.* 2(1–2):77–98.

Tryphonas, H., M.I. Luster, G. Schiffman, L.L. Dawson, M. Hodgen, D. Germolec, et al. 1991. Effect of chronic exposure of PCB (Aroclor 1254) on specific and nonspecific immune parameters in the rhesus (*Macaca mulatta*) monkey. *Fundam Appl Toxicol.* 16(4): 773–786.

Tryphonas, H., M.I. Luster, K.L. White, Jr., P.H. Naylor, M.R. Erdos, G.R. Burleson, et al. 1991. Effects of PCB

(Aroclor 1254) on non-specific immune parameters in rhesus (*Macaca mulatta*) monkeys. *Int J Immunopharmacol.* 13(6):639–648.

Weisglas-Kuperus, N., T.C.J. Sas, C. Koopman-Esseboom, C.W. Van Der Zwan, M.A.J. De Ridder, A. Beishuizen, et al. 1995. Immunologic effects of background prenatal and posnatal exposure to dioxins and polychlorinated biphenyls in Dutch infants. *Ped Res.* 38(3): 404–410.

Weisglas-Kuperus, N., S. Patandin, G.A. Berbers, T.C. Sas, P.G. Mulder, P.J. Sauer, et al. 2000. Immunologic effects of background exposure to polychlorinated biphenyls and dioxins in Dutch preschool children. *Environ Health Perspect.* 108(12):1203–1207.

White, K.L., Jr., H.H. Lysy, J.A. McCay and A.C. Anderson 1986. Modulation of serum complement levels following exposure to polychlorinated dibenzo-p-dioxins. *Toxicol Appl Pharmacol.* 84(2) 209–219.

Yu, M.L., J.W. Hsin, C.C. Hsu, W.C. Chan and Y.L. Guo. 1998. The immunologic evaluation of the Yucheng children. *Chemosphere.* 37(9–12):1855–1865.

Effects of Prenatal Exposure to Organochlorines and Mercury on the Immune System of Inuit Infants

Project leader

Éric Dewailly, Public Health Research Unit-CHUQ (CHUL), 945, Wolfe, 2nd floor, Sainte-Foy, QC G1V 5B3; phone: (418) 650-5115 (ext. 5240); fax: (418) 654-3132; e-mail: Eric.Dewailly@crchul.ulaval.ca

Project team

Frédéric Dallaire, Carole Vézina, Gina Muckle, Pierre Ayotte, and Gaston de Serres, Public Health Research Unit-CHUQ (CHUL) and Laval University, Beauport, QC; Jean Philippe Weber, Direction et laboratoire de toxicologie humaine, Institut national de santé publique du Québec–Ste-Foy, QC; Claire Infante-Rivard, McGill University, Montréal, QC; Joseph Jacobson, Wayne State University, Detroit, MI; Houda Bilrha, Raynald Roy, and Marthe Belles-Iles, Rhumatology-Immunology Research Unit-CHUQ (CHUL), Ste-Foy, QC.

Abstract

Many persistent organic pollutants affect the immune system. The immunotoxic effects of environmental exposure to organochlorines and heavy metals in young children are of great concern since the immune system is especially vulnerable during its development in-utero. The medical charts of 199 Inuit infants from Nunavik were reviewed from birth to 12 months. The incidences of infections were calculated and put in relation with organochlorines and heavy metals exposure. A subgroup of 115 infants was selected for the immunological analyses (cytokines, complement, and antibody titer). Environmental prenatal exposure to OCs was associated with a higher incidence of infections during the first 6 months of life. This increased incidence was mostly observed during the first 6 months of life and the association was much weaker when infections during the first 12 months of life were considered. The contaminant burden in infant blood at 6 months was not associated with infection incidence. These results support the hypothesis of an adverse effect of prenatal exposure to OCs on infection susceptibility in Inuit infants.

Key Project Messages

1. This study investigates possible detrimental effects on the immune system of Inuit infants that may be induced by prenatal and postnatal exposure to persistent environmental contaminants such as organochlorine compounds and heavy metals.
2. A total of 199 infants' medical charts were reviewed to assess infectious disease incidence rate during the first 6 months of life.
3. It was shown that environmental prenatal exposure to OCs is associated with a higher incidence of infections during the first 6 months of life. Although the associations were not always statistically significant,

infants in the higher quartiles of exposure to PCBs and DDE had systematically more episodes of infections than their counterparts in the first quartile of exposure.

Objectives

The main objective of this project is to examine the effects of prenatal and postnatal exposure to organochlorines (OCs) and mercury on the immune system of Inuit infants from birth to 12 months of age. The specific objectives include:

1. Assessment of the prenatal and postnatal exposure to OCs and mercury.
2. Measurement of some immunological parameters (humoral and cellular immunity).
3. Determination of the incidence of infections.

Introduction

Substantial information concerning the contamination of northern marine food by persistent organic pollutants (POPs) and heavy metals is now available (Barrie et al. 1992, Braune et al. 1999, Bright et al. 1995, Burkow and Kallenborn 2000, Lockhart et al. 1992, Muir et al. 1999, Muir et al. 1992, Thomas et al. 1992). Chemicals such as pesticides [dieldrin, mirex, toxaphene], industrial compounds and by-products of industrial processes [hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs), polychlorodibenzo-p-dioxins (PCDDs), and polychlorodibenzofurans (PCDFs)], as well as heavy metals [inorganic and organic mercury, lead, cadmium] have been emitted by industrial countries for many years. Regulatory actions have been taken since the late 1970s to limit their emission but they are still released into the environment due to improper storage and ongoing use in certain parts of the world.

Exposure to some OCs, in particular dioxin-like compounds, produces a wide variety of immunotoxic effects on animals and humans. Alterations of T-cell subsets, of serum IgA and IgM concentrations, of delayed-type hypersensibility (DTH), and of complement activation have all been documented in rodents, primates and human (Belles-Isles et al. 2002, Chang et al. 1982, Esser and Welzel 1993, Hoffman et al. 1986, Holsapple et al. 1984, Lu and Wu 1985, Neubert et al. 1992, Thomas and Hinsdill 1979, Tryphonas et al. 1991a, Tryphonas et al. 1991b, White et al. 1986). The development of the immune system *in-utero* and during the infancy is particularly sensitive to immunotoxic agents such as OCs. High exposure during the early life could lead to permanent defects of the immune system and thus decrease resistance to infectious agents (Badesha et al. 1995).

Organic and inorganic mercury possess cytotoxic activities for cellular components of the immune system in several species of rodents. Methylmercury, a form of organic mercury, can alter non-specific defense mechanisms such as inhibition of natural killer (NK) cell activity in rats and mice. It also decreases the expression of certain activation markers of T cells (HLA-Dr, IL-2R) (Moszczynski 1997). Moreover, it was shown that methylmercury can affect the functions of B cells and therefore reduce the humoral mediated response (Moszczynski 1997). Exposure to inorganic mercury induces allergies and autoimmune problems in hypersensitive individuals (Bagenstose et al. 1999).

The high incidence of infectious diseases (in particular meningitis, broncho-pulmonary and middle ear infections) in infants and children from Nunavik has been known for many years (Bruneau et al. 2001, Dufour 1988, Proulx 1988). Because of the immunotoxic effects of OCs and methylmercury, particularly after perinatal exposure, we hypothesized that part of the high incidence of infections among Inuit infants could be related to the high maternal body burden of these contaminants.

This study is nested in the ongoing PCBs and infant development study and involves 248 Inuit mothers and their newborns. We investigated possible detrimental effects on the immune system of Inuit infants that may be induced by prenatal and postnatal (breast feeding) exposure to OCs and mercury. We evaluated incidence of infections through an extensive medical chart review. The immune system status was also evaluated using immunological markers including the level of antibody produced by the infant following *Haemophilus influenza* immunization, the level of complement components, and the level of some cytokines. Vitamin A concentration was also evaluated in mothers and infants since striking similarities exist between symptoms of high dioxin-like compound exposure and vitamin A deficiency.

Activities

In 2001–2003

The recruitment ended in April 2001 and the collection of sample was completed in March 2002. A total of 248 mothers have accepted to participate in the study. Considering miscarriages, mortality and withdrawal from the study; we were able to included 199 infants in the final analyses for infection incidence. Due to technical and logistic problems, 62 infant's samples were included in the final biological analysis. The number of participants

for whom vitamin A levels were available was insufficient to conduct the analysis that was originally planned. This arm of the project was abandoned.

In 2002 and 2003, we performed all the database management, the statistical programming, and the final statistical analyses. The redaction of reports and of a scientific paper should be completed by the end of summer 2003. Most results are already available.

Results

2001–2002

We performed preliminary analyses for the 144 infants for whom the incidence of infection was available. The geometric mean concentration for the sum of the 14 PCB congeners was 308.9μg·kg^{-1}. PCB-153 was the most abundant congener detected in maternal and cord blood samples. It was strongly correlated with other PCB congeners and was used as a surrogate for PCB exposure. Children born to mothers who were above the median concentration for congener 153 (311.2μg·kg^{-1}) were included in the "high exposure" group. The remaining children were included in the "low exposure" group. The mean infection incidence rates are presented in Table 1.

We used Poisson regression to evaluate the ratio of the incidence rate of the high exposure group over that of the low exposure group. Table 2 shows the crude and adjusted rate ratio. The multivariate model of the adjusted rate ratio included breastfeeding duration, cigarette smoking during pregnancy, number of smokers in the house where the child lived, crowding (number of residents divided by the number of rooms), the number of children under 6 years old living with the participant, the sex of the child and the age of the mother.

Table 1. Incidence rates of infectious diseases according to exposure status

	Mean incidence rate (episode · person^{-1} year^{-1})		
Infection	Total (n =144)	Low exposure (n = 72)	High exposure (n = 72)
URTI[a]	2.3 ± 1.7	2.3 ± 1.8	2.3 ± 1.7
Otitis media	3.0 ± 1.8	3.2 ± 1.9	2.8 ± 1.7
Bronchitis	1.1 ± 1.3	0.9 ± 1.1	1.3 ± 1.4
Pneumonia	0.6 ± 0.9	0.4 ± 0.7	0.8 ± 1.0
GI infection[a]	1.0 ± 1.2	1.0 ± 1.1	1.1 ± 1.2

[a] URTI = upper respiratory tract infection; GI infection = gastro-intestinal infection

Table 2. Infectious diseases incidence rate ratios (high exposure group: low exposure group)

	Incidence rate ratio			
Infection	Crude ratio (n = 144)		Adjusted ratio[b] (n = 126)	
URTI[a]	1.01	[0.82–1.25]	1.08	[0.85–1.37]
Otitis media	0.87	[0.72–1.05]	0.87	[0.70–1.08]
Bronchitis	1.34	[0.98–1.83]	1.28	[0.89–1.83]
Pneumonia	1.69	[1.09–2.61]	1.63	[1.00–2.64]
GI infection[a]	1.10	[0.80–1.52]	1.18	[0.83–1.69]

[a] URTI = upper respiratory tract infection; GI infection = gastro-intestinal infection

[b] Adjusted for breastfeeding duration, cigarette smoking during pregnancy, number of smokers in the house where the child lived, crowding (number of residents divided by the number of rooms), the number of children under 6 years old living with the child, the sex of the child and the age of the mother

2002–2003

Recruitment and participation

During the study period, 417 pregnancies were identified in the targeted communities. Of them, we excluded 47 (11.3%) pregnant women because they had been already enrolled in the study during a previous pregnancy and 3 women (0.7%) because of miscarriage. We were unable to contact 9 (2.2%) women. Three hundred and fifty eight eligible women were thus asked to participate and 110 (30.7%) refused. Of the 248 women willing to participate, we were unable to review the medical chart of the 43 infants for the following reasons: 10 (4.0%) moved to another village, 14 (5.6%) were adopted in another village, 11 (4.4%) because of miscarriage or perinatal mortality and 8 (3.2%) because the mother decided to withdraw from the study. Finally, we excluded 6 (2.4%) participants because no biological samples were available for exposure analysis. A total of 199 participants were included in the final analyses.

Population characteristics

The characteristics of the mothers and their infant are shown in Table 4. The mothers included in the analysis were mostly from Puvirnituq (45.4%) and Inukjuaq (39.3%). The mean age at delivery was 25.2 years and most of the mothers smoked during pregnancy (91.4% declared smoking at least one cigarette a day with a mean of 10.6 cigarettes a day). Only 2.6% of the infants were not exposed to secondhand smoke during their first year of life. Breastfeeding was very common and only 12.2% were not breastfed. Adoption was the main reason for exclusive bottle-feeding (83.3%). The mean birth weight was 3454.4 g.

Table 3. Description of infection categories

Category	*Code ICPC-2*	Code ICD-10	Infection
Upper respiratory tract infections (URTI)	R74	B00.2, B08.5, J00, J02.8, J02.9, J06	Acute upper respiratory tract infection Acute rhinitis Head cold Nasopharyngitis Pharyngitis Coryza
	R72	J02.0, J03.0	Streptococcal pharyngitis or tonsillitis
Otitis media	H71	H66.0, H66.4, H66.9, H73.0	Acute suppurative otitis media Otitis media NOS Acute tympanitis
	H72	H65	Otitis media with effusion Serous otitis media Glue ear
Gastro-intestinal (GI) infections	D70	A00 to A08	Gastrointestinal infection or dysentery with specified organism
	D73	A09	Diarrhea or vomiting presumed to be infective Dysentery NOS Gastric flu
Lower respiratory tract infections (LRTI)	R78	J20 to J22, J40	Acute bronchitis or bronchiolitis Acute lower respiratory infection NOS Chest infection NOS Laryngotracheobronchitis Tracheobronchitis
	R81	A48.1, J10.0, J11.0, J12 to J16, J18	Bacterial and viral pneumonia Bronchopneumonia Influenzal pneumonia Legionnaire's disease Pneumonitis

NOS = Not otherwise specified; ICPC-2 = International classification of primary care, 2nd edition; ICD-10 = International classification of diseases, 10th edition

Incidence of infections

Infections incidence proportions and rates are detailed in Table 5. Otitis media was the most frequent infection diagnosed with a mean of 2.8 episodes per infant per year, followed by URTI with 2.4 episodes per infant per year. Almost all infants have had at least one episode of otitis (96.0%) and 17.1% have had 5 episodes or more. LRTI and urinary tract infection (UTI) required hospitalization 31.4% and 26.3% of the time, respectively. More than half of the infants (56.8%) were hospitalized at least once during their first year of life. Only the infection categories with a mean incidence rate higher than 1.0 episode per infant per year yielded sufficient statistical power to be included in further analyses.

Contaminants burden

Table 6 shows the concentration of contaminants in maternal and infant blood. The geometric mean concentration, for the sum of the 14 PCB congeners in maternal blood, was 308μg·kg^{-1}, ranging from 60 to 1951μg·kg^{-1}. The concentration of the sum of the PCB congeners was highly correlated with the congener PCB 153 in maternal blood (R^2 = 0.985). The correlation between cord blood and maternal blood was also excellent both for the sum of the PCB congener and for the congener PCB 153 (R^2 = 0.905 and R^2 = 0.885, respectively). The geometric mean concentration of DDE in maternal blood was 294μg·kg^{-1}, ranging from 54 to 2269μg·kg^{-1}. The correlation between cord blood and maternal blood for DDE was also very good (R^2 = 0.887). The congener PCB 153 and DDE were detected in all samples analyzed. Mean concentrations of PCBs and DDE were lower in infant blood than in maternal blood. Means concentration in infant blood was 259μg·kg^{-1} and 256μg·kg^{-1} for the sum of PCBs and DDE, respectively.

Lead concentration in maternal blood ranged from 0.05 to 1.25μmol·L^{-1} with a geometric mean of 0.25μmol·L^{-1}. Mean mercury concentrations were 49.6nmol·L^{-1} in blood and 3.37μg·g^{-1} in hair. Mercury and lead were detected in all samples analyzed.

Table 4. Characteristics of participants

Characteristics	Mean value (± standard deviation) or proportion (%)
Mothers	
Village of residence (n = 196)	
Puvirnituq	45.4%
Inukjuaq	39.3%
Kuujjuarapik	15.3%
Age (n = 199)	25.2 ± 5.8 years
Smoking during pregnancy (n = 198)	91.4%
Nb of cigarettes smoked per day (n = 181)	10.6 ± 5.6 cig.
Parity (n = 199)	2.1 ± 1.9
Infants	
Sex (males) (n = 199)	57.6%
Weight (n = 199)	3454.4 ± 573.4 g
Height (n = 183)	50.3 ± 2.2 cm
Breastfeeding status (n = 180)	
Never breastfed	12.2%
Breastfed between 1 and 60 days	16.7%
Breastfed between 61 and 120 days	12.8%
Breastfed more than 121 days	58.3%

PCBs prenatal exposure and infections

The relation between PCBs prenatal exposure and incidence rates is shown in Table 7. In preliminary analyses, we found that the association between OCs and incidence rates was somewhat stronger during the first 6 months of life. Although this study was designed for a 12 months follow-up, we also present the results for the first 6 months of life. For PCBs exposure, during the first 6 months of life, we observed a statistically significant association only for LRTI (RR = 1.70, 3rd quartile) in the adjusted model. Although not statistically significant, almost all others associations were above the unity. When the 4 types of infections were combined (labeled all infections in the tables), the relative rates varied from 1.19 to 1.20 in the unadjusted model and from 1.17 to 1.29 in the adjusted model. The trend was significant in the adjusted model (P = 0.04).

For the 12-month follow-up, most associations were weaker that the 6-month follow-up and only GI infection still pointed towards a positive association. The association was significant for the 3rd quartile in the adjusted

Figure 1. Adjusted incidence rate ratios of the four types of infection combined for prenatal exposure to selected OCs during the first 6 months of life.
Dots represent point estimates and lines represent 95% confidence intervals of rate ratios of the 2nd (Q2), 3rd (Q3), and 4th (Q4) quartiles when compared to corresponding first quartile.

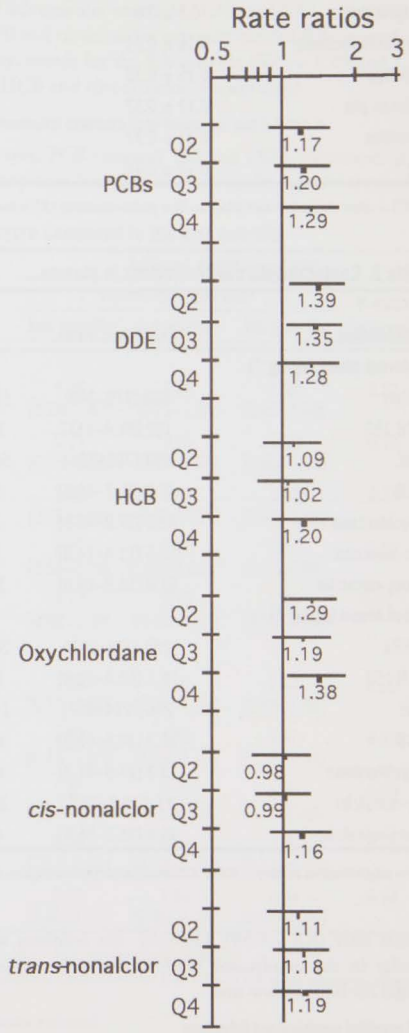


Table 5. Incidence proportion and mean infection incidence for all participants (n = 199)

Infection	Mean Incidence (episodes/person · year)	Proportion of episodes requiring hospitalization	Proportion of participants who had at least...		
			1 episode	3 episodes	5 episodes
URTI *	2.4 ± 1.7	1.3%	90.0%	42.7%	12.6%
Otitis media	2.8 ± 1.7	0%	96.0%	52.8%	17.1%
GI infections	1.0 ± 1.1	3.4%	58.8%	10.6%	0.5%
LRTI *	1.8 ± 1.7	31.4%	73.9%	28.1%	6.0%
Conjunctivitis	0.3 ± 0.6	0%	26.1%	1.0%	0.0%
Dermatitis/eczema	0.16 ± 0.61	0%	10.1%	1.5%	0.5%
Impetigo	0.15 ± 0.39	0%	13.1%	0%	0%
Chicken pox	0.12 ± 0.32	0%	12.1%	0%	0%
Tonsilitis	0.11 ± 0.37	0%	9.5%	0.5%	0%
UTI *	0.10 ± 0.42	26.3%	6.0%	1.0%	0%

* URTI = upper respiratory tract infection; GI = gastro-intestinal; LRTI = lower respiratory tract infection; UTI = urinary tract infection

Table 6. Contaminants concentrations in plasma

Contaminant	Geometric mean	Range	Quartile boundaries			
			1st	2nd	3rd	4th
Maternal blood ($\mu g \cdot kg^{-1}$)						
(PCBs	308 [279–340]	59.6–1951	< 190	[190–296]	[296–500]	(500
PCB 153	102 [91.4–113]	14.6–709	< 57.6	[57.6–98.4]	[98.4–170]	(170
DDE	294 [267–324]	54.3–2269	< 183	[183–281]	[281–472]	≥ 472
HCB	40.0 [36.7–43.6]	6.7–352	< 27.0	[27.0–39.7]	[39.7–57.9]	≥ 57.9
Oxychlordane	41.2 [37.0–45.9]	7.0–390	< 24.8	[24.8–40.5]	[40.5–66.5]	≥ 66.5
cis-nonalclor	12.6 [11.4–14.0]	1.7–114	< 9.1	[9.1–12.8]	[12.8–20.2]	≥ 20.2
trans-nonalclor	62.6 [56.8–69.0]	11.5–578	< 43.3	[43.3–64.9]	[64.9–94.7]	≥ 94.7
Infant blood ($\mu g \cdot kg^{-1}$)						
(PCBs	259 [218–307]	26.9–3801	< 99.0	[99.0–283]	[283–609]	(609
PCB 153	76.1 [62.4–92.9]	1.9–1441	< 28.0	[28.0–95.3]	[95.3–199]	(199
DDE	256 [214–307]	15.6–4386	< 100	[100–355]	[355–618]	(618
HCB	36.3 [30.5–43.2]	n.d.–446	< 16.2	[16.2–44.5]	[44.5–88.5]	(88.5
Oxychlordane	33.9 [27.8–41.3]	n.d.–881	< 12.8	[12.8–42.0]	[42.0–88.3]	(88.3
cis-nonalclor	11.7 [9.9–13.9]	3.1–169.4	< 4.6	[4.6–13.9]	[13.9–27.7]	≥ 27.7
trans-nonalclor	46.4 [38.1–56.5]	n.d.–798	< 17.0	[17.0–62.6]	[62.6–126]	≥ 126

PCB = polychlorinated biphenyls; DDE = dichlorodiphenyl trichloroethylene; HCB = hexachlorobenzene; n.d. = not detected

model only (RR = 1.59). Globally, the relations were similar in the unadjusted model and in the adjusted model for both follow-ups.

DDE prenatal exposure and infections

The relation between infection incidence and DDE exposure seemed stronger than that of PCBs exposure (Table 6). For the 6-month follow-up, we detected significant associations with otitis (RR = 1.63, 3rd quartile) in the unadjusted model and with URTI (RR = 1.56, 2nd quartile) and otitis (RR = 1.83, 3rd quartile) in the adjusted model. The trend P value was significant for otitis in the unadjusted model (P = 0.04) and borderline significant for the adjusted model

(P = 0.07). When the four types of infections were combined, we observed significant association for the 2nd (RR = 1.50) and 4th (RR = 1.25) quartiles in the unadjusted model, and for the 2nd (RR = 1.39) and 3rd (RR = 1.35) quartile in the adjusted model. The P value for trend was borderline significant in the adjusted model (P = 0.09). Similar to what was observed for PCB exposure, almost all associations were above the unity.

For the 12-month follow-up, we observed significant associations for GI infections (RR = 1.49, 2nd quartile) in the unadjusted model and for URTI (RR = 1.34, 2nd quartile) and GI infections (RR = 1.59, 2nd quartile) in the adjusted model. For all infections combined, the association reached statistical significance only for the 2nd quartile in the unadjusted model (RR = 1.16).

Other chlorinated pesticides prenatal exposure and infections

Figure 1 shows the effect of prenatal exposure to PCBs, DDE, HCB, oxychlordane, *cis*-nonalclor, and *trans*-nonalclor on infection incidence. Results are shown for the 6-month follow-up in the adjusted model. With the exception of PCBs and DDE, the strongest effect was observed with oxychlordane exposure (RRs for the 2nd, 3rd and 4th quartiles were 1.29, 1.19, and 1.38, respectively), followed by *trans*-nonalclor (RRs for the 2nd, 3rd and 4th quartiles were 1.11, 1.18, and 1.19, respectively). HCB and *cis*-nonalclor exposure yielded RRs around the unity, except for the 4th quartile (RRs = 1.20 and 1.16 for HCB and *cis*-nonalclor, respectively).

OCs postnatal exposure (mid follow-up) and infections

We used PCB congener 153 and DDE concentration in infant plasma (sampling done at a median age of 7.0 months)

Table 7. Incidence rate ratio of each PCB quartile of prenatal exposure compared to the first quartile

	Unadjusted model (n = 199)				Adjusted model (n = 177)[a]			
	Incidence rate ratio[b]			P value	Incidence rate ratio[b]			P value
Infection type	2nd quartile	3rd quartile	4th quartile	for trend[c]	2nd quartile	3rd quartile	4th quartile	for trend[c]
6-month follow-up								
URTI	1.08 [0.76–1.55]	0.98 [0.68–1.41]	1.19 [0.84–1.68]	0.69	1.08 [0.69–1.67]	1.08 [0.71–1.65]	1.32 [0.87–2.00]	0.22
Otitis media	1.33 [0.85–2.07]	1.15 [0.73–1.82]	1.30 [0.83–2.02]	0.17	1.11 [0.65–1.89]	0.99 [0.59–1.66]	1.39 [0.82–2.35]	0.17
GI infections	1.63 [0.80–3.34]	1.31 [0.62–2.76]	1.55 [0.75–3.20]	0.33	1.89 [0.78–4.56]	1.52 [0.65–3.54]	1.54 [0.66–3.60]	0.38
LRTI	1.11 [0.72–1.73]	1.51 [1.00–2.28]	1.01 [0.64–1.58]	0.56	1.23 [0.69–2.18]	1.70 [1.02–2.84] *	1.21 [0.70–2.08]	0.32
All infections[d]	1.20 [0.96–1.50]	1.19 [0.95–1.49]	1.20 [0.96–1.50]	0.12	1.17 [0.89–1.55]	1.20 [0.93–1.55]	1.29 [0.99–1.68]	0.04 *
12-month follow-up								
URTI	0.93 [0.72–1.20]	0.87 [0.67–1.13]	1.12 [0.88–1.43]	0.81	0.99 [0.71–1.36]	0.96 [0.71–1.29]	1.23 [0.92–1.65]	0.29
Otitis media	1.05 [0.83–1.32]	0.97 [0.76–1.22]	0.94 [0.75–1.20]	0.89	1.02 [0.77–1.35]	0.89 [0.68–1.17]	0.97 [0.73–1.28]	0.89
GI infections	1.27 [0.86–1.88]	1.22 [0.82–1.82]	1.05 [0.69–1.58]	0.81	1.53 [0.94–2.49]	1.59 [1.01–2.49] *	1.26 [0.78–2.04]	0.29
LRTI	0.87 [0.64–1.18]	1.05 [0.78–1.33]	0.95 [0.71–1.27]	0.52	0.88 [0.59–1.30]	1.07 [0.76–1.50]	1.05 [0.73–1.47]	0.36
All infections[d]	1.00 [0.87–1.15]	0.99 [0.86–1.13]	1.01 [0.88–1.16]	0.66	1.02 [0.86–1.21]	1.01 [0.86–1.18]	1.08 [0.92–1.28]	0.24

PCB = polychlorinated biphenyl; URTI = upper respiratory tract infections; GI = gastro-intestinal; LRTI = lower respiratory tract infections

[a] Model included mother's age, season of birth, year of birth, breastfeeding duration, sex, socioeconomic status of the care giver, tobacco use during pregnancy, village of residence and number of children living with the participant

[b] Incidence rate ratio when the given quartiles are compared to the first quartile of exposure (Poisson regression)

[c] P values for trends were calculated by multivariate regression in which the contaminants concentration (log-transformed) is a continuous variable

[d] We only considered infections with a mean incidence superior to 1.0 episode per year per infant (see methods)

* $P < 0.05$

Table 8. Incidence rate ratio of each DDE quartile of prenatal exposure compared to the first quartile

	Unadjusted model (n = 199)				Adjusted model (n = 177)[a]			
	Incidence rate ratio[b]			P value	Incidence rate ratio[b]			P value
Infection type	2nd quartile	3rd quartile	4th quartile	for trend[c]	2nd quartile	3rd quartile	4th quartile	for trend[c]
6-month follow-up								
URTI	1.50 [1.05–2.13]	1.06 [0.72–1.55]	1.19 [0.82–1.73]	0.91	1.56 [1.05–2.33] *	1.15 [0.75–1.75]	1.40 [0.90–2.16]	0.24
Otitis media	1.27 [0.79–2.05]	1.63 [1.04–2.57] *	1.50 [0.95–2.38]	0.04 *	1.03 [0.59–1.77]	1.83 [1.09–3.07] *	1.55 [0.90–2.68]	0.07
GI infections	2.16 [1.02–4.55] *	1.76 [0.81–3.82]	1.67 [0.76–3.64]	0.34	1.91 [0.84–4.35]	1.66 [0.69–3.97]	1.35 [0.54–3.42]	0.58
LRTI	1.50 [0.99–2.27]	0.98 [0.63–1.54]	1.03 [0.66–1.61]	0.92	1.41 [0.87–2.30]	1.23 [0.74–2.06]	0.99 [0.57–1.71]	0.98
All infections[d]	1.50 [1.20–1.87] *	1.22 [0.97–1.54]	1.25 [1.00–1.58] *	0.17	1.39 [1.08–1.79] *	1.35 [1.04–1.75] *	1.28 [0.97–1.68]	0.09
12-month follow-up								
URTI	1.27 [0.98–1.63]	1.03 [0.79–1.34]	1.11 [0.85–1.44]	0.85	1.34 [1.00–1.78] *	1.09 [0.81–1.47]	1.30 [0.96–1.78]	0.27
Otitis media	1.00 [0.79–1.27]	1.12 [0.89–1.42]	1.08 [0.85–1.36]	0.36	0.89 [0.68–1.17]	1.08 [0.83–1.41]	1.02 [0.76–1.35]	0.72
GI infections	1.49 [1.00–2.23] *	1.30 [0.86–1.96]	1.20 [0.79–1.82]	0.98	1.59 [1.03–2.47] *	1.27 [0.81–2.00]	1.43 [0.87–2.34]	0.59
LRTI	1.11 [0.83–1.48]	0.96 [0.71–1.29]	1.03 [0.76–1.38]	0.91	1.06 [0.75–1.49]	1.00 [0.71–1.41]	1.00 [0.69–1.42]	0.99
All infections[d]	1.16 [1.01–1.33] *	1.07 [0.93–1.24]	1.09 [0.94–1.25]	0.61	1.13 [0.96–1.32]	1.08 [0.92–1.26]	1.12 [0.95–1.33]	0.40

DDE = dichlorodiphenyl trichloroethylene; URTI = upper respiratory tract infections; GI = gastro-intestinal; LRTI = lower respiratory tract infections

[a] Model included mother's age, season of birth, year of birth, breastfeeding duration, sex, socioeconomic status of the care giver, tobacco use during pregnancy, village of residence and number of children living with the participant

[b] Incidence rate ratio when the given quartiles are compared to the first quartile of exposure (Poisson regression)

[c] P values for trends were calculated by multivariate regression in which the contaminants concentration (log-transformed) is a continuous variable

[d] We only considered infections with a mean incidence superior to 1.0 episode per year per infant (see methods)

* $P < 0.05$

to evaluate the effect of postnatal exposure on infection incidence. Table 9 shows the incidence rate ratios of all four types of infections combined according to the exposure quartiles. Results are shown for the first six months of life, from 7 to 12 months and for the entire 12-month follow-up. We observed no obvious trend with postnatal exposure. Only one association was significant for PCBs (0 to 12 months follow-up, 2nd quartile, RR = 1.19) in the unadjusted model but the statistical significance was lost when we adjusted for confounding factors.

OCs exposure and hospitalization rate

Neither contaminants studied was associated with the incidence of hospitalization for LRTI or for hospitalization for any infection type (results not shown). Unfortunately, our study design did not yield enough statistical power to investigate properly if contaminant exposure increased the risk of being hospitalized in the group of infants who had had episodes of LRTI.

Mercury prenatal exposure and infections

We investigated the relation between infection incidence rates and mercury using blood mercury and mercury in hair. Mercury in hair represents the average exposure across the pregnancy whereas blood mercury reflects the exposure of the previous 2 months. No statistically significant association could be detected and no clear pattern was apparent both for blood and hair mercury. Using blood mercury, slight negative associations were seen for GI infection and otitis but this was not true using hair mercury.

Table 9. Incidence rate ratio of all four types of infection combined for each quartile of postnatal exposure compared to the first quartile

	Unadjusted model (n = 176)				Adjusted model (n = 162)[a]			
	Incidence rate ratio[b]			P value	Incidence rate ratio[b]			P value
Contaminant	2nd quartile	3rd quartile	4th quartile	for trend[c]	2nd quartile	3rd quartile	4th quartile	for trend[c]
0 to 6 months								
PCB 153	1.18 [0.94–1.49]	1.14 [0.90–1.45]	1.03 [0.81–1.30]	0.40	1.10 [0.79–1.51]	1.17 [0.79–1.74]	1.20 [0.80–1.81]	0.07
DDE	0.96 [0.75–1.21]	1.16 [0.92–1.46]	0.99 [0.78–1.25]	0.55	0.90 [0.65–1.26]	1.27 [0.85–1.90]	1.28 [0.85–1.93]	0.13
7 to 12 months								
PCB 153	1.19 [0.99–1.44]	0.95 [0.78–1.17]	0.93 [0.77–1.14]	0.14	1.17 [0.90–1.51]	0.91 [0.66–1.27]	0.96 [0.68–1.35]	0.33
DDE	1.19 [0.98–1.44]	1.04 [0.85–1.27]	0.92 [0.75–1.13]	0.15	1.22 [0.93–1.58]	1.03 [0.74–1.44]	1.05 [0.73–1.50]	0.40
0 to 12 months								
PCB 153	1.19 [1.03–1.38] *	1.03 [0.88–1.20]	0.97 [0.83–1.13]	0.56	1.13 [0.92–1.38]	1.01 [0.78–1.30]	1.04 [0.80–1.35]	0.74
DDE	1.09 [0.94–1.26]	1.09 [0.94–1.29]	0.95 [0.81–1.11]	0.48	1.06 [0.88–1.33]	1.12 [0.87–1.45]	1.14 [0.87–1.49]	0.80

PCB = polychlorinated biphenyls; DDE = dichlorodiphenyl trichloroethylene

[a] Model included mother's age, season of birth, year of birth, breastfeeding duration, sex, socioeconomic status of the care giver, tobacco use during pregnancy, village of residence, number of children living with the participant and age when blood sample was drawn

[b] Incidence rate ratio when the given quartiles are compared to the first quartile of exposure (Poisson regression)

[c] P values for trends were calculated by multivariate regression in which the contaminants concentration (log-transformed) is a continuous variable

* $P < 0.05$

Parameters of immune system function

Parameters of immune system function were assayed using interleukin (IL)-10, tumor necrosis factor (TNF), and complement components (C3 and C4) in cord blood and infant blood (Table 10). Unfortunately, we were not able to evaluate these markers in a great proportion of the samples because the volume of blood collected was insufficient. Person correlation analysis yielded statistically significant results for IL-10 and HCB in cord blood and for C4 and HCB in infant blood. However, correlations with IL-10 and C4 were not constant across the different contaminants. These results are hard to interpret because of the small number of samples involved and further studies are needed to identify the effect of contaminants on immune biomarkers in this population.

Discussion

2001–2002

The results presented in this synopsis of research are preliminary. We shall be cautious when interpreting the results since many factors can influence the immune system function. Before speculating on the effects of PCBs on the immune system, one should await the results of a more thorough statistical analysis with careful attention being paid to other potential confounders and co-variables (seasonality, vaccination, small outbreaks, methods of diagnostic, vitamin A status, village of residence, reviewer of the medical chart, etc.)

The infants included in this study show a very high rate of infections. On average, they have had 3 episodes of otitis media and 2.3 upper respiratory tract infections (URTI) that were serious enough to seek medical attention. As many as 43% of the infants included have had at least 1 episode of pneumonia in the first 12 months of life. This high incidence of infectious diseases is preoccupying and deserves a lot of attention from public health authorities.

Our results show that prenatal PCB exposure tended to be associated with a higher rate of infections, especially lower respiratory tract infections. The association was statistically significant only for pneumonia. We did not expect to observe

Table 10. Pearsons' correlation between contaminants and selected immune system function in cord blood and infant blood

Immune system marker	Pearson correlation coefficient (p-value)							
	∑PCB	PCB-153	DDE	HCB	*Trans*-nonalclor	Oxychlordane	Mirex	Mercury
Cord blood								
IL-10 (n = 37)	0.063	−0.041	−0.031	−0.034	−0.071	−0.090	−0.115	−0.014
	(0.71)	(0.81)	(0.85)	(0.84)	(0.67)	(0.59)	(0.49)	(0.93)
TNF-α (n = 38)	0.117	0.140	0.060	0.024	0.061	0.144	0.011	−0.042
	(0.48)	(0.40)	(0.72)	(0.88)	(0.71)	(0.39)	(0.95)	(0.79)
Complement C2 (n = 20)	0.293	0.280	0.263	0.061	0.259	0.162	0.195	0.167
	(0.21)	(0.23)	(0.26)	(0.79)	(0.27)	(0.49)	(0.41)	(0.42)
Complement C4 (n = 20)	−0.092	−0.055	0.115	0.453	0.225	0.170	−0.163	0.015
	(0.69)	(0.82)	(0.63)	(0.04) *	(0.34)	(0.47)	(0.49)	(0.94)
Infant blood								
IL-10 (n = 37)	0.110	0.117	0.155	0.362	0.288	0.270	0.009	na
	(0.56)	(0.49)	(0.36)	(0.03) *	(0.08)	(0.11)	(0.96)	
TNF-α (n = 34)	−0.094	−0.112	−0.132	−0.133	−0.219	−0.233	−0.247	na
	(0.59)	(0.53)	(0.46)	(0.46)	(0.21)	(0.18)	(0.17)	
C2 (n = 40)	−0.183	−0.164	−0.172	−0.172	−0.193	−0.210	−0.109	na
	(0.26)	(0.31)	(0.29)	(0.28)	(0.23)	(0.22)	(0.50)	
C4 (n = 40)	0.121	0.083	0.083	0.055	−0.003	0.053	−0.040	na
	(0.91)	(0.61)	(0.62)	(0.73)	(0.98)	(0.76)	(0.80)	
Anti-Hib[a] (n = 62)	−0.015	−0.019	0.014	−0.036	−0.001	0.008	−0.036	na
	(0.90)	(0.88)	(0.91)	(0.78)	(0.95)	(0.95)	(0.78)	

* Statistically significant ($p < 0.05$)

na = not available

[a] Humoral response following Hib vaccine challenge

a large increase in the incidence of benign infections such as commons colds. The subtle effects of OCs will most likely compromise the ability of the immune system to quickly eradicate minor infections, thus increasing the probability of deteriorating into a more serious condition like bronchitis or pneumonia. Our results support this hypothesis since PCB exposure was more strongly associated with serious respiratory conditions.

2002–2003

In this study, we have shown that environmental prenatal exposure to some OCs is associated with a higher incidence of infections during the first 6 months of life. Although the associations were not always statistically significant, infants in the higher quartiles of exposure to PCBs and DDE had systematically more episodes of infections than their counterparts in the first quartile of exposure. This increased incidence was mostly observed during the first 6 months of life and the association was much weaker when infections during the first 12 months of life were considered. Furthermore, the contaminants burden in infant blood at mid follow-up was no longer associated with infection incidence.

Accidental and occupational exposure to PCBs has already been associated with adverse effect on infection susceptibility in infants. Rogan et al. (1988) observed those mothers who were exposed to PCBs through the consumption of contaminated rice oil (Yu-Cheng accident) reported a higher rate of bronchitis than controls. After examination

by two otolaryngologists, the same children were also shown to have a higher prevalence of middle-ear diseases than matched controls (Chao et al. 1997). In Japan, Hara (1985) noted that infants born from women who had handled PCBs in a capacitor manufacturer had a higher incidence of colds and gastrointestinal complains.

Evidences of an effect of environmental exposure to OCs on infection susceptibility in children are scarce and inconsistent. To our knowledge, the first study addressing the question was done in the Great Lakes area. The Wisconsin Maternal/Infant cohort was designed to evaluate the effect upon infant health status as a result of exposure to PCBs through maternal fish consumption. The authors observed that fish consumption during pregnancy was positively associated with colds, earaches and flu symptoms in infants (Smith 1984). Between 1978 and 1982, Rogan et al. (1987) followed around 900 families in North-Carolina (USA). They reviewed the medical charts of the children and did not find any evidence of harmful effects of PCBs or DDE in the first year of life. In the Netherlands, Weisglas-Kuperus et al. (1995) observed no association between PCBs and the number of episodes of rhinitis, bronchitis, tonsillitis, and otitis, during the first 18 months of life. However, the same group of children was seen at 42 months and current PCB burden was associated with a higher prevalence of recurrent middle-ear infections and of chicken pox (Weisglas-Kuperus et al. 2000). Karmaus et al. (2001) also observed a higher risk for otitis media, but the relation was only present with the combined exposure to DDE and PCBs. Finally, our group previously showed that exposed Inuit infants had a higher risk of acute otitis media during the first year of life (3rd tertile of exposure compared to the first). The relation was significant with exposure to DDE and HCB but remained above the unity for PCBs, dieldrin and mirex (Dewailly et al. 2000).

Because evaluations of both exposure and infectious episodes frequency varied among studies, it is hazardous to directly compare previously published results with our results. Nevertheless, our results support the hypothesis that the immunotoxic properties of OCs could affect the health status of prenatally exposed children, as did some of the above-mentioned studies on accidental (Chao et al. 1997, Rogan et al. 1988), occupational (Hara 1985), and environmental (Karmaus et al. 2001, Smith 1984, Weisglas-Kuperus et al. 2000) exposure. In the literature, a middle-ear infection is the most consistently reported infection associated with prenatal exposure to OCs. In our study, the strongest dose-response relationship was seen with ear infections. However, it is likely that OCs' insults on the developing immune system would result in the increase of incidence of many different types of acute infections, and not only ear infections. Coherent with that assumption, our results showed a higher rate of medical consultations for the 4 most frequent infections in infants in the higher exposure groups, and the rate ratios were similar to that observed for otitis. Furthermore, when these 4 types of infections were combined, the association was more stable and the magnitude of a dose-response relationship was increased, compared to that of the four types of infection taken separately.

Although it was not in our original study objectives, we have shown that the effect of prenatal exposure was mostly present in the first few months, and that this effect seemed to vanish after six months of life. Furthermore, we found no effect of post-natal exposure to OCs with infections. It has already been suggested that the immune system is vulnerable to immunotoxic products during its development and that high maternal burden during pregnancy and lactation could lead to permanent defects on the infant's immune system (Badesha et al. 1995, Barnett et al. 1987). If our results support the hypothesis of a stronger effect during early infancy, we were not able to clearly identify any harmful affect after the age of 6 months. After a few months of life, cumulative environmental influences on the immune system may begin to play a larger role, thus increasing the variably of response to infections. Furthermore, contributions of OCs burden by breast milk entangled with the beneficial effect of breast-feeding on infections might have masked the effect. This could explain in parts the discrepancies in the results of other studies on OCs and infections, since the age of children during disease and exposure assessment varied considerably among studies. Further studies are needed to clarify the period during which environmental exposure to OCs have a detrimental effect on childrens' health.

In this population, most of the OCs included in this analysis are strongly correlated. Muckle et al. (2001) already published correlation analyses for a proportion of infants included in this cohort. They have shown that PCB congeners and chlorinated pesticides are correlated with each other, and that cord blood, maternal blood and breast milk samples are also well correlated. It is not therefore possible to attribute the effect observed to one specific OC, nor are we able to unravel the specific contribution of each substance studied.

In this study, a review of the medical charts was used to evaluate disease frequency. There is only one health center in each of the 3 Inuit communities included in this study. Participants almost always go to that health center when they seek medical attention and copies of consultations done elsewhere are routinely requested to complete the charts when needed. We are therefore confident to have reviewed a great proportion of the medical consultations

sought by the participants. Nevertheless, we did not attempt to verify every diagnosis, nor did we try to inquire about infections for which medical attention was not sought by the parents. Furthermore, we did not find a suitable surrogate for the propensity to go to the clinic when infants had symptoms. Our results are therefore an underestimation of the true incidence, especially for benign infections. It is possible that this underestimation was associated with traditional lifestyle, and thus with OCs exposure, but the direction of the bias is unknown. However, if such a bias was present, we could assume that it would have persisted past 6 months of age. Since results for the following 12 months are close, such a bias seemed to have little effect on our results.

The high rate of infectious episodes in young Inuit children has been observed in Northern Canada, the United States (Alaska) and Greenland (Banerji et al. 2001, Holman et al. 2001, Koch et al. 2002, Proulx 1988, Wainwright 1996). Many cultural, environmental and economical factors contribute to this situation and our study population is no exception with a mean of almost 9 infection-related medical consultations per infant in the first 12 months of life. In the context of such a high rate of infections, rate ratios of around 1.25, like the ones observed in this study, could have a tremendous impact on the public health of this population. Evidence grows stronger for the adverse effect of OCs on infection susceptibly in infants of environmentally exposed populations. Awareness and caution in the selection of food items before and during pregnancies is warranted. Further studies will help clarifying the potential contribution of persisting contaminants in the high infection rate of these children.

References

Badesha, J.S., G. Maliji, and B. Flaks. 1995. Immunotoxic effects of exposure of rats to xenobiotics via maternal lactation. Part I 2,3,7,8-tetrachlorodibenzo-p-dioxin. *Int J Exp Pathol.* 76(6):425–439.

Bagenstose, L.M., P. Salgame, and M. Monestier. 1999. Murine mercury-induced autoimmunity: a model of chemically related autoimmunity in humans. *Immunol Res.* 20(1):67–78.

Banerji, A., A. Bell, E.L. Mills, J. McDonald, K. Subbarao, and G. Stark. 2001. Lower respiratory tract infections in Inuit infants on Baffin Island. *Cmaj.* 164(13):1847–1850.

Barnett, J.B., L. Barfield, R. Walls, R. Joyner, R. Owens, and L.S. Soderberg. 1987. The effect of in utero exposure to hexachlorobenzene on the developing immune response of BALB/c mice. *Toxicol Lett.* 39(2–3):263–274.

Barrie, L.A., D. Gregor, B. Hargrave, R. Lake, D. Muir, and R. Shearer. 1992. Arctic contaminants: sources, occurrence and pathways. *Sci Total Environ.* 122(1–2): 1–74.

Belles-Isles, M., P. Ayotte, É. Dewailly, J.P. Weber, and R. Roy. 2002. Cord blood lymphocyte functions in newborns from a remote maritime population exposed to organochlorines and methylmercury. *J Toxicol Environ Health A.* 65(2):165–182.

Braune, B., D. Muir, B. DeMarch, M. Gamberg, K. Poole, and R. Currie. 1999. Spatial and temporal trends of contaminants in Canadian Arctic freshwater and terrestrial ecosystems: a review. *Sci Total Environ.* 230(1–3):145–207.

Bright, D.A., W.T. Dushenko, S.L. Grundy, K.J. Reimer. 1995. Effects of local and distant contaminant sources: polychlorinated biphenyls and other organochlorines in bottom-dwelling animals from an Arctic estuary. *Sci Total Environ.* 160–161:265–283.

Bruneau, S., H. Ayukawa, J.F. Proulx, J.D. Baxter, and K. Kost. 2001. Longitudinal observations (1987–1997) on the prevalence of middle ear disease and associated risk factors among Inuit children of Inukjuak, Nunavik, Quebec, Canada. *Int J Circumpolar Health.* 60(4): 632–639.

Burkow, I.C., and R. Kallenborn. 2000. Sources and transport of persistent pollutants to the Arctic. *Toxicol Lett.* 112–113:87–92.

Chang, K.J., K.H. Hsieh, S.Y. Tang, T.C. Tung, and T.P. Lee. 1982. Immunologic evaluation of patients with polychlorinated biphenyl poisoning: evaluation of delayed-type skin hypersensitive response and its relation to clinical studies. *J Toxicol Environ Health.* 9(2): 217–223.

Chao, W.Y., C.C. Hsu, and Y.L. Guo. 1997. Middle-ear disease in children exposed prenatally to polychlorinated biphenyls and polychlorinated dibenzofurans. *Arch Environ Health.* 52(4):257–262.

Dewailly, É., P. Ayotte, S. Bruneau, S. Gingras, M. Belles-Isles, and R. Roy. 2000. Susceptibility to infections and immune status in inuit infants exposed to organochlorines. *Environ Health Perspect.* 108(3):205–211.

Dufour, R. 1988. The otitis media among Inuit children. *Arctic Medical Research.* 47(1):659–665.

Esser, C., and M. Welzel. 1993. Ontogenic development of murine fetal thymocytes is accelerated by 3,3',4,4'-tetrachlorobiphenyl. *Int J Immunopharmacol.* 15(8): 841–852.

Hara, I. 1985. Health status and PCBs in blood of workers exposed to PCBs and of their children. *Environ Health Perspect.* 59:85–90.

Hoffman, R.E., P.A. Stehr-Green, K.B. Webb, R.G. Evans, A.P. Knutsen, and W.F. Schramm. 1986. Health effects of long-term exposure to 2,3,7,8-tetrachlorodibenzo-p-dioxin. *Jama.* 255(15):2031–2038.

Holman, R.C., A.T. Curns, S.F. Kaufman, J.E. Cheek, R.W. Pinner, and L.B. Schonberger. 2001. Trends in infectious disease hospitalizations among American Indians and Alaska Natives. *Am J Public Health.* 91(3): 425–431.

Holsapple, M.P., P.J. McNerney, D.W. Barnes, and K.L. White Jr. 1984. Suppression of humoral antibody production by exposure to 1,2,3,6,7,8-hexachlorodibenzo-p-dioxin. *J Pharmacol Exp Ther.* 231(3):518–526.

Julien, G., J.D. Baxter, M. Grago, H.J. Ilecki and F. Therien. 1987. Chronic otitis media and hearing deficit among native children of Kuujjuaraapik (Northern Quebec): a pilot project. Canadian Journal of Public Health. 78 (Jan-Feb): 57–62.

Karmaus, W., J. Kuehr, and H. Kruse. 2001. Infections and atopic disorders in childhood and organochlorine exposure. *Arch Environ Health.* 56(6):485–492.

Koch, A., P. Sorensen, P. Homoe, K. Molbak, F.K. Pedersen, and T. Mortensen. 2002. Population-based study of acute respiratory infections in children, Greenland. *Emerg Infect Dis.* 8(6):586–593.

Lockhart, W.L., R. Wagemann, B. Tracey, D. Sutherland, and D.J. Thomas. 1992. Presence and implications of chemical contaminants in the freshwaters of the Canadian Arctic. *Sci Total Environ.* 122(1–2):165–245.

Lu, Y.C., and Y.C. Wu. 1985. Clinical findings and immunological abnormalities in Yu-Cheng patients. *Environ Health Perspect.* 59:17–29.

Moszczynski, P. 1997. Mercury compounds and the immune system: a review. *Int J Occup Med Environ Health.* 10(3):247–258.

Muckle, G., P. Ayotte, É. Dewailly, S.W. Jacobson, and J.L. Jacobson. 2001. Prenatal exposure of the northern Quebec Inuit infants to environmental contaminants. *Environ Health Perspect.* 109(12):1291–1299.

Muir, D., B. Braune, B. DeMarch, R. Norstrom, R. Wagemann, and L. Lockhart. 1999. Spatial and temporal trends and effects of contaminants in the Canadian Arctic marine ecosystem: a review. *Sci Total Environ.* 230(1–3):83–144.

Muir, D.C., R. Wagemann, B.T. Hargrave, D.J. Thomas, D.B. Peakall, and R.J. Norstrom. 1992. Arctic marine ecosystem contamination. *Sci Total Environ.* 122(1–2): 75–134.

Neubert, R., G. Golor, R. Stahlmann, H. Helge, and D. Neubert. 1992. Polyhalogenated dibenzo-p-dioxins and dibenzofurans and the immune system. 4. Effects of multiple-dose treatment with 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) on peripheral lymphocyte subpopulations of a non-human primate (*Callithrix jacchus*). Arch Toxicol. 66(4):250–259.

Proulx, J.F. 1988. Meningitis in Hudson's Bay, Northern Quebec, Canada. *Arctic Medical Research.* 47(1): 686–687.

Rogan, W.J., B.C. Gladen, K.L. Hung, S.L. Koong, L.Y. Shih, and J.S. Taylor. 1988. Congenital poisoning by polychlorinated biphenyls and their contaminants in Taiwan. *Science.* 241(4863):334–336.

Rogan, W.J., B.C. Gladen, J.D. McKinney, N. Carreras, P. Hardy, and J. Thullen. 1987. Polychlorinated biphenyls (PCBs) and dichlorodiphenyl dichloroethene (DDE) in human milk: effects on growth, morbidity, and duration of lactation. *Am J Public Health.* 77(10): 1294–1297.

Smith, B.J. 1984. *PCB levels in human fluids: Sheboygan case study. Technical report WIS-SG-83-240.* Madison, Wisconsin: University of Wisconsin Sea Grant Institute.

Thomas, D.J., B. Tracey, H. Marshall, and R.J. Norstrom. 1992. Arctic terrestrial ecosystem contamination. *Sci Total Environ.* 122(1–2):135–164.

Thomas, P.T., and R.D. Hinsdill. 1979. The effect of perinatal exposure to tetrachlorodibenzo-p-dioxin on the immune response of young mice. *Drug Chem Toxicol.* 2(1–2):77–98.

Tryphonas, H., M.I. Luster, G. Schiffman, L.L. Dawson, M. Hodgen, and D. Germolec. 1991a. Effect of chronic exposure of PCB (Aroclor 1254) on specific and nonspecific immune parameters in the rhesus (*Macaca mulatta*) monkey. *Fundam Appl Toxicol.* 16(4): 773–786.

Tryphonas, H., M.I. Luster, K.L. White Jr., P.H. Naylor, M.R. Erdos, and G.R. Burleson. 1991b. Effects of PCB (Aroclor 1254) on non-specific immune parameters in rhesus (*Macaca mulatta*) monkeys. *Int J Immunopharmacol.* 13(6):639–648.

Wainwright, R.B. 1996. The US Arctic Investigations Program: infectious disease prevention and control research in Alaska. *Lancet.* 347(9000):517–520.

Weisglas-Kuperus, N., S. Patandin, G.A. Berbers, T.C. Sas, P.G. Mulder, and P.J. Sauer. 2000. Immunologic effects of background exposure to polychlorinated biphenyls and dioxins in Dutch preschool children. *Environ Health Perspect.* 108(12):1203–1207.

Weisglas-Kuperus, N., T.C.J. Sas, C. Koopman-Esseboom, C.W. Van Der Zwan, M.A.J. De Ridder, and A. Beishuizen. 1995. Immunologic effects of background prenatal and postnatal exposure to dioxins and polychlorinated biphenyls in Dutch infants. *Ped Res.* 38(3): 404–410.

White, K.L. Jr., H.H. Lysy, J.A. McCay, and A.C. Anderson. 1986. Modulation of serum complement levels following exposure to polychlorinated dibenzo-p-dioxins. *Toxicol Appl Pharmacol.* 84(2):209–219.

Evaluation of a Risk Management Strategy to Protect Pregnant Women from Contaminant Exposure in Nunavik

Project leader

Éric Dewailly, Public Health Research Unit, CHUQ, 945 Wolfe, Sainte-Foy,(Quebec) G1V 5B3; phone: (418) 650-5115 ext. 5240, eric.dewailly@inspq.qc.ca

Project team members

Carole Blanchet, Suzanne Bruneau, Chris Furgal, and Carole Vézina, Public Health Research Unit, Laval University Research Centre-CHUQ, Ste-Foy, Quebec; Serge Dery, Nunavik Regional Board of Health and Social Services, Kuujjuaq, Quebec; Minnie Grey, Nunavik Nutrition and Health Committee.

Abstract

The objective of this research project is to evaluate a risk reduction program for pregnant women exposed to food chain contaminants in Nunavik. This program will promote the consumption of Arctic char among pregnant women living in three selected communities in Nunavik. Arctic char contains very few contaminants and is very nutritious. We will evaluate to what extent pregnant women participate in the program and how efficient the program is in reducing contaminant intake (especially mercury) while maintaining or improving nutritional status during pregnancy. Results of this project will help regional public health authorities to assess and implement risk management actions including, but not limited to this one in Nunavik communities.

Key Project Messages

1. One of the most vulnerable groups for exposure to contaminants is pregnant women and their foetus.
2. Arctic char is a healthy country food item to promote to women during pregnancy, providing significant benefits, while at the same time reducing exposure, for the mother and developing foetus, to some important environment contaminants present in other country food species (e.g. mercury and POP's in marine mammal meat and blubber).
3. This project is collecting information on the feasibility and challenges of implementing a promotion program to distribute free char to all pregnant women in Nunavik.

Introduction

It is well accepted that solutions must be found to address the issue of contaminants in the Arctic food chain. One of the most logical and sustained solutions is the ban of production and use of these chemicals throughout the world. International conventions (POPs and mercury) are currently in various phases of development and implementation to achieve this goal. Nevertheless, we also know that it will take many years to see a substantial improvement of the environmental situation. Ethically, this raises the question of the need, feasibility and efficacy of an immediate dietary intervention to decrease exposure to these chemicals among the population. Certainly, one of the most vulnerable groups for exposure to these contaminants is pregnant women and their foetus (Muckle, 2001). POPs (especially PCBs) and methylmercury (MeHg) are toxic for the foetus and may affect the development of the central nervous and the immune systems. In the Faroe Islands, dietary advice has been released in order to reduce pilot whale meat consumption during pregnancy and thus decrease prenatal exposure to methyl mercury (AMAP, 2002). In this case, virtually a single source (pilot whale meat) and unique contaminant with a relatively short half life (MeHg) supported public health authorities in advising pregnant women to stop consumption of pilot whale during pregnancy (at that time, it was believed that only mercury was associated with effects; later, PCBs were reported to have a possible interaction in the high mercury exposed group). In Nunavik, there are multiple contaminants (metals and POPs) coming from the consumption of various country food items (whale and seal blubber and meat, lake trout, etc) and no restrictive dietary advice could be proposed without imposing risks related to nutritional, social and cultural disruption. One way to avoid such difficulties is to promote the consumption of a nutritionally rich and relatively contaminant-free species such as Arctic char (*Salvelinus alpinus*), as an alternative to other country food items during pregnancy.

The Nunavik Nutrition and Health Committee (NNHC) is the recognized and authorized committee for the region on health and environment issues and one of its mandates is related to directing the orientation of regional policies on nutrition and health. Information gathered by researchers involved in Nunavik and communicated to the committee has shown that Arctic char is a healthy country food item to promote to women during pregnancy, providing significant benefits, while at the same time reducing exposure, for the mother and developing foetus, to some important environment contaminants in other country food species (e.g. mercury and POPs in marine mammal meat and blubber). Recently, the Nunavik Board of Health and Social Services (Public Health Department) disseminated a message to all communities suggesting that women of childbearing age (13–45), whenever possible, select country foods that are rich in fatty acids and less contaminated with PCBs (Arctic char, misiraq made from seal blubber instead of beluga).

Eating Arctic char can have many benefits for the health of pregnant women and their foetus. For example, it is an important source of protein and excellent source of vitamin D and phosphorus. Furthermore, significant amounts of selenium are found in Arctic char and it is the best source of omega-3 fatty acids among northern fishes.

It is for these reasons that the NNHC has recommended the development and implementation of a program promoting the consumption of Arctic char among pregnant women in the region for some time. Research has shown that health advice related to consumption habits is more closely followed when viable alternatives are provided, and one of the important barriers to country food consumption is access — that is why free distribution of char to pregnant women is proposed by the committee. Also, it is argued that the promotion of a contaminant-low, nutrient-rich country food species is less disruptive than banning a contaminant high species and still in line with the same desirable toxicological and nutritional results.

Objectives

1. To conduct a pilot study of the distribution of Arctic char to pregnant Inuit women in 3 Nunavik communities;
2. To assess the feasibility, and identify challenges to the program by collecting qualitative data on issues related to fish collection, storage and distribution as well as the receptability of the program by the pilot communities and participants;
3. To collect quantitative data on the health benefits and reduction of risks associated with such a promotion program. Blood and hair samples will be collected for analysis of contaminants, nutrients and fatty acids analysis and for the detection of the anaemia.

Activities

In 2002–2003

The following activities were completed between April 2002 and March 2003:

Three communities have been chosen to participate in the pilot project: Kuujjuarapik, Salluit and Kuujjuaq. The

choice of these communities was based on the differences in diet and socio-demographic characteristics providing a good cross sectional representation of differences among communities in the region. Nevertheless, the CLSC of Salluit has withdrawn from the project because of a lack of staff to support the conduct of the project. The committee decided to offer the pilot project to the Municipality of Quaqtaq and we are now in discussion with the Municipal Office so that the recruitment of pregnant women starts as soon as possible.

In summary, the following activities were completed:

1. The Municipal Council of the 4 communities contacted to participate in this pilot project were consulted and have all supported the project with great enthusiasm. As described earlier, in Salluit, the collaboration was more difficult with the CLSC and we had to abandon the idea of doing the project in that community.

2. In co-operation with local Hunter Support Program coordinators and Municipal Office representatives, the char collection, storage and distribution processes of 2 arctic chars per week to each of the 10 pregnant women (per community) has been organized in each community. Arrangements have been made with communities where Arctic char are abundant and the fish is sent by plane on a regular basis to two participating municipalities (the other one having char available near the community) to be distributed to the pregnant women (2 to 3 char per week for the duration of their pregnancy).

3. All documents (information sheet, consent form, questionnaire) have been submitted and approved by the Ethical Committee of Laval University as well as both CPDP of Inuulitsivik and Tullatavik Health Centres.

4. Consent forms and general information documents for participating women have been developed as well as the laboratory procedure and questionnaires. In collaboration with the Health Centre laboratories and the CLSCs nursing personnel, a blood and hair sampling protocol for contaminants and nutrients was set up.

In each community the CLSCs or the Health Centre staff and the Community Health Representative (CHR) are sharing responsibilities of running the program:

1. Recruiting pregnant women, informing them about the program, and interviewing participants regarding the program efficiency and its desirability is being done by the CHR in 2 communities and the community Health nurse in 1 community.

2. In two communities the CHR is also responsible for managing the distribution of Arctic char. The Hunters Support Program coordinator is managing this function in the other community.

3. Sampling of blood (at onset and end of pregnancy) and hair (end of pregnancy) is being performed by the CLSCs or Hospital Centre nurse.

Hair and blood sampling analysis is being performed for POPs, mercury, selenium and Omega-3 fatty acids and for the detection of anaemia.

Conclusion

This project has experienced delays in its implementation mostly associated with the technical and logistical aspects (staff shortages, char supplying, storage and transportation) but is on-going in 2 communities and is in the initial stages in the third community. The project will be completed regardless of delays as the Nunavik Regional Health Board has committed to finance the project to its end. Since pregnant women will be followed for the duration of their pregnancy, final results are not yet available.

To date, a qualitative assessment of the program indicates that the logistical operation of this program is far more difficult than previously thought. The project has been strongly supported by the participating and authorizing agencies in the regions and communities (Municipal Councils, Regional Hunter and Trappers Organization, Regional Health Board), yet the operation of the program has still experienced the above mentioned challenges. We feel that this is associated with a number of factors. Challenges faced to date have included the securing of an adequate source of char either in close proximity to a participating community or the arrangement of transportation and storage of this char from another location. The management of the char storage and then its distribution in each community to the participants has also required significant effort. Although the project is supported with great interest and many individuals are volunteering time to operate the program by adding it to their regular work responsibilities, many of these individuals (although they are the proper individuals to be involved in the program) are already extremely busy and the addition of another task has been difficult (e.g., one of the main reasons the program is not operating in Salluit is related to a shortage of staff). Time is required to recruit women, meet, inform and interview them, ensure they have access to the char on a continuing basis, etc. During the duration of this program, interviews with individuals in participating communities as well as those individuals helping operate

the program will provide valuable information regarding the feasibility of expanding such a program to other communities, and its sustainability over a long period of time into the future.

References

Muckle, G., P. Ayotte, É. Dewailly, S. Jacobson, and J.L. Jacobson. 2001. Determinants of polychlorinated biphenyls and methylmercury exposure in Inuit women of childbearing age. *Env Health Perspect.* (109):957–963.

Arctic Pollution 2002, Arctic Monito ring and Assessement Program, AMAP, Oslo, Norway

Mercury in Salluit: Effects of Mercury on Oxydative Status and Sensorimotor Functions

Project leader

Éric Dewailly, Public Health Research Unit-CHUQ (CHUL), 945, Wolfe, 2nd floor, Sainte-Foy, QC G1V 5B3; phone: (418) 650-5115 (ext. 5240); fax: (418) 654-3132; e-mail : Eric.Dewailly@crchul.ulaval.ca

Project team

Anne Beuter, Cognitive Neuroscience Laboratory, University of Québec at Montreal; Michel Plante, Hydro-Québec; Pierre Ayotte and Suzanne Bruneau, Public Health Research Unit CHUQ-CHUL Beauport, Québec; Marc Édouard Mirault, Health and Environment Research Unit CHUQ-CHUL; Minnie Grey, Nutrition and Health Committee, Kuujjuaq, Québec; Jean-Philippe Weber, Quebec Toxicology Centre, Québec National Institute of Public Health, Ste-Foy, Québec.

Abstract

Among all contaminants present in different aquatic ecosystems in Canada, methylmercury (MeHg) is a major source of concern for public health. Some studies suggest that MeHg toxicity can be detected at levels far below the minimal level proposed by the World Health Organization (10–15 ppm in maternal hair). Thus, it seems important to determine with precision the minimal dose at which oxidative stress and neurotoxic effects can be identified. The main goal of this project is to investigate the effects of mercury on sensorimotor functions and on markers of oxidative stress in the population of Salluit, Nunavik, Canada. A total of 113 individuals were tested for neuromotor performances and also agreed to provide a sample of urine, blood and hair. Specific recommendations based on quantitative evidence will be made to the concerned populations so as to diminish long-term risk on health.

Key Project Messages

1. This study aims at studying subtle effects mercury can have on brain functions.
2. Measures done in the blood will tell us more about early sign of mercury toxicity particularly concerning cardiovascular disease.

Objectives

1. Evaluate the oxidative status of Sallumiut exposed to mercury.
2. Quantify the effects of mercury on sensorimotor functions with highly sensitive measures.

Introduction

Mercury is an environmental contaminant originating from both anthropogenic and natural sources. It can be transported from distant sources to the Arctic by oceanic and atmospheric transport. Mercury has been found in all components of the Arctic ecosystem (Barrie et al. 1992; Muir et al. 1992) and is mainly present as methylmercury in fish and marine mammals. Their consumption constitutes an important source of exposure, especially in sustenance populations such as the Inuit. Although the underlying biochemical and molecular mechanisms that lead to impaired cell function and nerve cell degeneration are not well understood, there is abundant evidence supporting the hypothesis that a major mechanism of MeHg neurotoxicity involves an oxidative stress (Sarafian, 1991; Yee, 1996). Mercury increases production of reactive oxygen species (ROS) via deregulation of mitochondrial electron transport as well as through glutathione (GSH) depletion (Lund, 1993). The oxidative stress hypothesis is clearly supported by the finding that MeHg neurotoxicity can be inhibited by various antioxidants including selenium (Park, 1996) and N-acetyl-L-cysteine a precursor of GSH (Ornaghi, 1993).

Homocysteine plasma concentration is a well-known risk factor for cardiovascular diseases, in particular stroke (see review by Gerhard & Duell, 1999). Homocysteine auto-oxidation generates free radicals that can in turn oxidize LDL and promote arteriosclerosis. Methylene tetrahydrofolate reductase (MTHFR) is involved in the biotransformation homocysteine to methionine, which is catalyzed by methionine synthase. Individuals homozygous for a mutation in MTHFR (cytosine to thymidine) display high levels of plasma homocysteine. Interestingly, methylmercury was shown to inhibit methionine synthase in several tissues including the brain and could therefore increase plasma homocysteine concentration.

Neuromotor functions are particularly vulnerable to neurotoxic damage including those associated with MeHg. Several studies have demonstrated that chronic exposure to methylmercury may cause a wide variety of well known neurological impairments including: prickling, paresthesia, impaired peripheral vision, hearing, taste and smell, slurred speech, paraplegia, muscle weakness, irritability, memory loss, depression, sleeping difficulties, cerebellar ataxia, tremors, etc. (ATSDR, 1994). Other studies have suggested that low-level exposure to MeHg was associated with changes in neuromotor functions (Beuter, 1996; Beuter, 1999a,b; Rice, 1996a,b). Neurologic dysfunctions have been reported with exposure levels much lower than what has been considered acceptable by the WHO, which indicates that these functions are sensitive to low levels of neurotoxicity. MeHg is also suspected to be toxic for children during prenatal development. However, results from ongoing research in Faeroe and Seychelles islands are not conclusive at this point. In addition, no study dealing specifically with the protecting role of selenium on neuromotor functions was found in the literature searched.

Currently, it is difficult to reliably determine the threshold of MeHg concentration at which functional changes will occur in humans. Since some studies suggest that MeHg toxicity can be detected at levels far below the minimal exposure level proposed by the World Health Organization, it seems important to determine more precisely the minimal dose at which oxidative stress and neurotoxic effects can be identified.

General Objectives

1. Evaluate the oxidative status of Sallumiut exposed to mercury.
2. Quantify the effects of mercury on neuromotor functions with highly sensitive measures.

Activities

In 2000–2001

A total of 125 Salluit residents signed the consent form and participated to the present study. Of these, 85 (68%) individuals had taken part in the 1999 study on temporal trends of mercury exposure in Nunavik. As described in Table 1, a total of 113 participants completed all steps of the study: 1) providing biological samples; 2) fill in a short questionnaire; 3) allowing the nurse to review his/her medical file; 4) completion of neuromotor tests.

Fieldwork was carried out in Salluit, Nunavik from February 5 to April 20, 2001. Two fieldworkers were based in Salluit for the whole time of data collection. Three local research assistants were hired and trained to second the field workers. Their tasks included recruiting participants, translating collection tools, interviewing

Table 1. Number of participants according to tests completion and gender

	Number of participants at each test				Number of participants that completed all tests
	Hair	Blood	Urine	Neuro.	
Men	39	35	35	35	33
Women	84	83	83	81	80
Total	123	118	118	116	113

participants and assisting the field workers in their respective tasks. To recruit participants, the team: 1) held a radio-show and informed the population about the research; 2) met with the Local Health Committee to discuss research objectives; 3) displayed posters in strategic areas to stir up the population interest; 4) sent personal invitation letters to Salluit residents. The first individuals contacted by the research assistants were those who participated in a 1999 study on temporal trends of mercury exposure in Nunavik, then participants were randomly chosen from the population list.

Data collection was performed in four steps: Firstly, participants met with the field workers and their assistants to receive information about the research and to sign a consent form. At that time, a hair sample was taken and the participant was interviewed. Furthermore, participants of the 1999 study were given the possibility to look at and discuss their last mercury results with the nurse. Secondly, participants were asked to come back the next morning after fasting since midnight and to bring their urine sample. A blood sample was then taken. Finally, another appointment for neuromotor tests was scheduled.

A questionnaire documenting current health status, lifestyle, and past medical history was administered to participants with the help of an interviewer. The section on lifestyle included questions on smoking, drinking and drugs consumption habits while the section on health status included questions on past neurological problems, past trauma and actual health problems and medication. Most of these questions were used to identify individuals to be excluded from the study because of the presence of external factors influencing neuromotor tests. Revision of medical files was not done for all participants but only for the ones who needed more information on medical history and actual medication.

Biological assessment

Hair samples were stapled in a plastic case to avoid any moving during transportation and manipulation and sent to the Quebec Toxicology Centre for mercury analysis.

A total of four 10ml tubes (EDTA lavender) were sampled from participants using venous puncture technique. Samples were sent from Salluit to the Quebec Toxicology Centre (CHUL–CHUQ) three times during the fieldwork. The tests to be performed were as follows:

1) Total blood analysis was performed to assess short-term mercury exposure and selenium exposure.

2) Assessment of the oxidative/antioxidant status was performed by measuring glutathione peroxidase and glutathione reductase activity levels in blood, and homocystein and oxidized LDL in plasma.

3) Because of potential confounding effects on neuromotor endpoints, PCBs and pesticides were measured in plasma.

4) Lipid profiles (VLDL, LDL, HDL, apolipoprotein B and A) and fatty acid profiles were also determined using plasma and erythrocyte membranes respectively.

5) Furthermore, since *cannabis* consumption is relatively frequent in Nunavik and because it could interfere with neuromotor tests acuity, Cannabinol levels in urine were measured.

Neuromotor tests procedures

In order to objectively quantify pre-clinical alterations of neuromotor functions, a series of non-invasive portable test battery was developed to measure involuntary and voluntary movements. (Beuter et al., 1996; Beuter et al., 1998; Beuter, et al. 1999a; Beuter et al., 1999b; Beuter et al., 1999c; Beuter et al., 1999d; Edwards et al., 1999; Beuter & Edwards., 2002) The use of sophisticated technologies (laser, infrared, optical encoder systems, CCD sensors, etc) coupled with continuous recordings of various neurophysiological signals provided a detailed neuromotor profile for all participants. The tests selected for this study included a tremor-recording test using lasers and accelerometer, quantitative analysis of rapid pointing movements (Diadochokinesia), quantitative analysis of alternating movements (Eurythmokinesia), postural sway and a simple reaction time task. The total duration of the evaluation including the questionnaire, clinical evaluation and the quantitative measurement of neuromotor function was 90 minutes.

Laboratory analysis

Toxicology Laboratory Centre of the National Public Health Institute of Québec

1. **Hair mercury analysis** was performed by cold vapor atomic absorption after nitric acid digestion.

2. **Blood mercury analysis** was carried out by cold vapor atomic absorption.

3. **Selenium** was analyzed by graphite furnace atomic absorption after nitric acid digestion.

4. **PCBs and pesticides** were measured using high-resolution gas chromatography.

5. **Cannabinol** was measured using ADX screening followed by a mass spectrometry confirmation.

Table 2. Proportion of participants by gender and age group

	18–39 years		40–59 years		60 -+ years		
	N	%	N	%	N	%	Total
Women	35	77.8	30	73.2	16	59.3	81
Men	10	22.2	11	26.8	11	40.7	32
Total	45	100	41	100	27	100	113

Environmental Health Unit laboratory and Lipidic Diseases Research Centre

1. **Glutathione reductase and glutathione peroxidase** activity levels were measured in total blood.
2. **Oxidized LDL (LDLox)** was measured in plasma by ELISA (Mercodia).
3. **Plasma total homocysteine (tHcy)** was measured by capillary high-performance liquid chromatography.
4. **Urinary F2-isoprostanes:** the objective for measuring urinary F2-isoprostanes, which result from *in vivo* lipid peroxidation, was to provide an additional index of oxidative stress. It was attempted to measure urinary isoprostane $iPF_{2\alpha}$-III as a biological index of lipid peroxidation, using a commercially available kit from Cayman. Despite many attempts with various extraction methods and ranges of urine dilutions from control individuals, we could not overcome an interference problem that appears to be inherent to the assay. Although the $iPF2_{2\alpha}$-III concentrations were within the limits of the Cayman standard curve, their determinations inconsistently increased with increased dilution, suggesting that there was a contaminant(s) in the urine extract that interfered with the assay, or that the antibody was not specific enough for an isoprostane epitope. In addition, up to 25% differences were observed between duplicates and seven Cayman kits were used without significant success. In agreement with several other laboratories which used this kit, we concluded that the Cayman $iPF2_{2\alpha}$-III assay is unreliable. Moreover, this assay measures $iPF2_{2\alpha}$-III (formely known as 8-iso-$PGF2_{2\alpha}$), a compound that is not only formed by direct oxidation of fatty acids by oxygen free radicals but may also be formed by normal metabolism of arachidonic acid via the prostaglandin G/H synthase (cyclooxygenase (COX) isoenzymes). A posteriori, the most relevant form of isoprostane to be determined for our study would be $iPF2_{2\alpha}$-VI, which is several fold more abundant in urine than $iPF2_{2\alpha}$-III, and a more specific index of lipid peroxidation. This isoprostane could be measured in our urinary sample collection by tandem mass spectrometry using homologous internal standards (Meagher & FitzGerald 2000; Li, H et al. 1999) as soon as these internal standards are commercially available.
5. **The lipoproteins** were fractionated by ultracentrifugation. Cholesterol (C) and triacyglycerols (Tg) were measured by enzymatic method. **Apoprotein B and A1** was measured by immunonephelometry.
6. **The fatty acid** composition of membrane erythrocyte was determined by gas chromatography.

Discussion and Conclusions

Description of the population under study

A total of 125 individuals have accepted to participate in this study. Table 2 shows the distribution of participants by gender and age group. Seventy-two percent of the participants were female and the mean age of participants is 44 years old (from 17 to 77 years old). Furthermore, 32% of the participants are single, 56% are either married or living with a partner; 6% are separated or divorced and finally, 6% are widowed. As for schooling, 25% of participants never attended school, 25% have 7 or less years of schooling and 50% have 8 to 13 years of school. Questions on lifestyle revealed that 68% of the participants are smokers but surprisingly women have a higher proportion of smokers, with 72%, while the men smoke in a proportion of 28% (45% and 18%, respectively, declared they were non or ex smokers).

As shown above in Table 1, 12 individuals had to be excluded from the study because they did not complete all tests.

Mercury, organochlorines and selenium concentrations according to gender and age of participants

Figures 1, 2 and 3 present the distribution (%) of mercury, PCB'S and selenium concentration in participants. Figures 1 and 2 show that only a weak percentage of participants are presenting high concentrations of mercury and PCB's in their blood. As regards selenium, one can observe than 50% of participants have concentration of selenium in their blood between 5 and 10 nmol/L.

Figure 1. Distribution of Mercury in Sallumiut

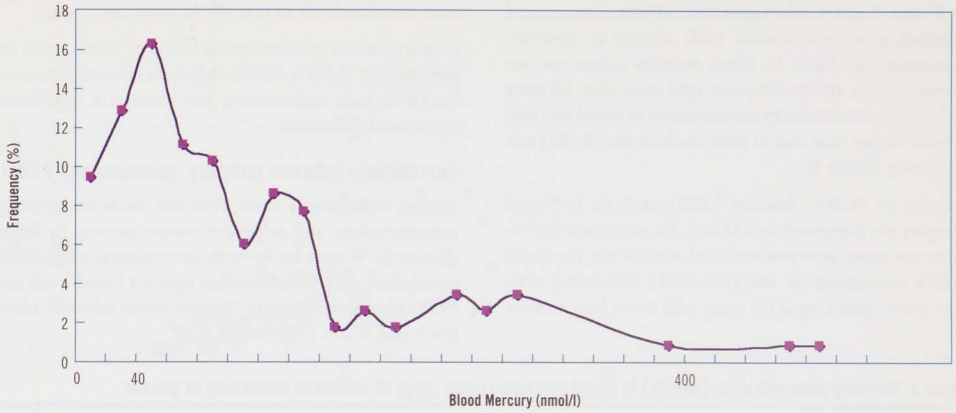


Figure 2. Distribution of PCB's in Sallumiut

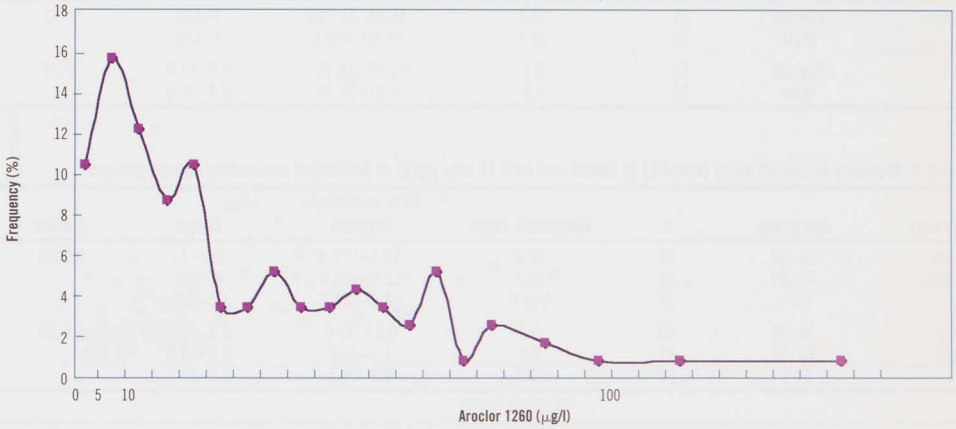
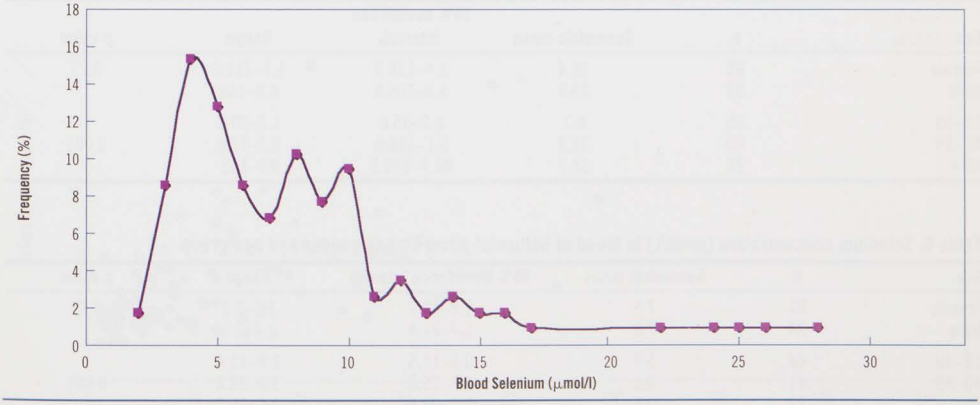


Figure 3. Distribution of Selenium in Sallumiut



Results of mercury analysis in blood samples are presented in Tables 3 and 4. No significant difference was noted between men and women with regards to mercury concentration (Table 3). Mean mercury concentrations increased with age; participants aged more than 60 years had a mean total mercury concentration in blood and hair 3 times higher than that of individuals in the 18–39 years age group (Table 4).

Results of PCB's (Aroclor 1260) analysis in blood samples are presented in Table 5. No statistical difference was noted between men and women but the mean PCB's concentration is significantly increasing with age; participants aged 60 years and more had a mean concentration in blood more than 6 times higher than that of individuals in the 18–39 years age group.

Concentrations of selenium in blood of participants are presented in Table 6. Similar selenium concentrations are found in men and women but there is a significant age-related difference.

Correlations between mercury, selenium and PCB's

Strong correlations were observed between mercury concentrations and selenium concentrations in blood (Figure 4). Weaker but nevertheless statistically significant correlations were noted between mercury blood levels and PCB's blood levels (Figure 5) and between selenium blood levels and PCB's (Figure 6).

Table 3. Mercury concentration (nmol/L) in blood and hair (1 cm; µg/g) of Sallumiut according to gender

Mercury	Sex	n	Geometric mean	95% confidence interval	Range	p value
Blood	Female	81	79.4	15.08–417.68	7–469	0.53
	Male	34	70.7	10.02–498.6	6–480	
Hair	Female	82	5.8	1.08–31.35	0.2–24.8	0.34
	Male	34	4.8	0.61–38.76	0.4–38.8	

Table 4. Mercury concentration (nmol/L) in blood and hair (1 cm; µg/g) of Sallumiut according to age groups

Mercury	Age group	n	Geometric mean	95% confidence interval	Range	p value
Blood	18–39	44	47.9	13.3–173.4	13–171	0.0001
nmol/L	40–59	41	89.4	12.7–633.6	7–480	
	60+	27	143.6	64.6–319.0	52–273	
Hair	18–39	45	3.2	0.67–15.6	0.2–12.3	0.0001
µg/g	40–59	41	6.8	1.2–36.7	0.8–38.8	
	60+	27	10.6	4.0–28.5	2.9–23.1	

Table 5. PCB'S (Aroclor 1260) concentration (µg/L) in blood of Sallumiut according to gender and age group

Sex	n	Geometric mean	95% confidence interval	Range	p value
Female	80	18.4	2.4–138.9	1.7–111.0	0.27
Male	33	23.3	3.3–165.0	4.1–143	
18–39	45	8.7	2.2–35.0	1.7–29.0	
40–59	40	24.3	5.1–116.5	2.2–77.0	0.001
60+	26	58.7	26.7–129.5	20–143	

Table 6. Selenium concentration (µmol/L) in blood of Sallumiut according to gender and age group

Sex	n	Geometric mean	95% confidence interval	Range	p value
Female	81	7.5	2.8–19.7	1.2–3.2	0.84
Male	34	7.6	2.7–21.4	1.4–3.5	
18–39	44	5.9	3.0–11.5	2.9–11.4	
40–59	41	8.4	2.7–25.8	3.0–28.4	0.001
60+	27	9.6	3.9–23.5	3.6–26.2	

Figure 4. Correlation between Mercury and Selenium

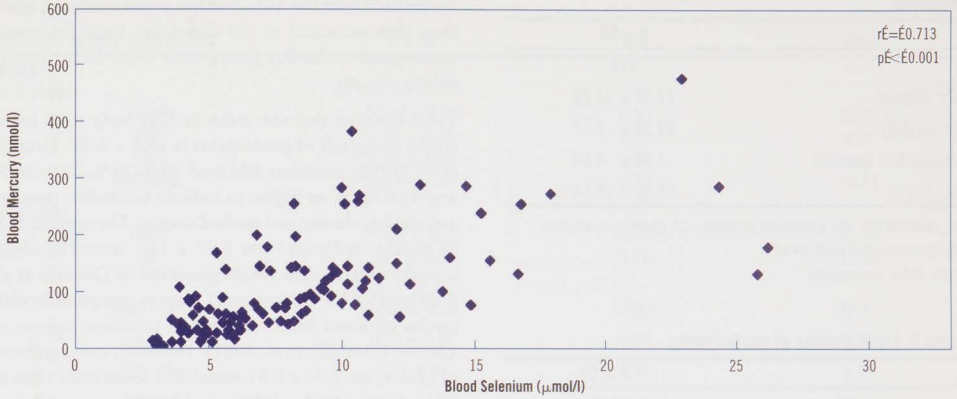


Figure 5. Correlation between Mercury and PCB's

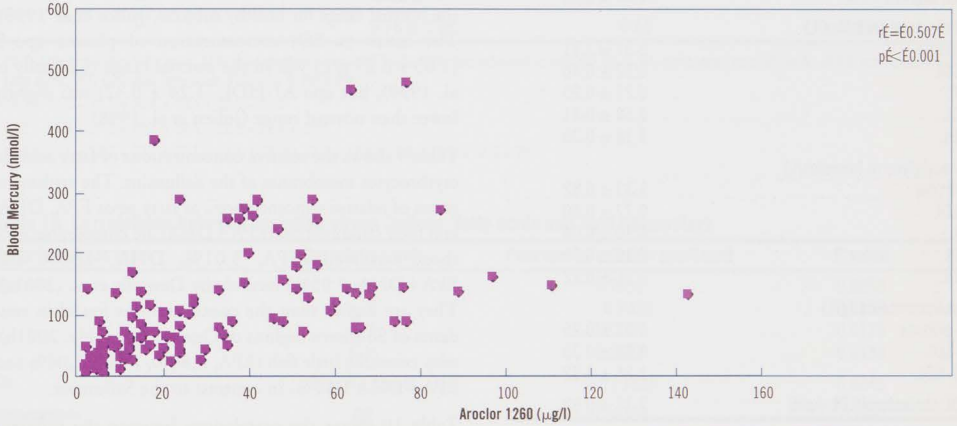


Figure 6. Correlation between PCB's and Selenium

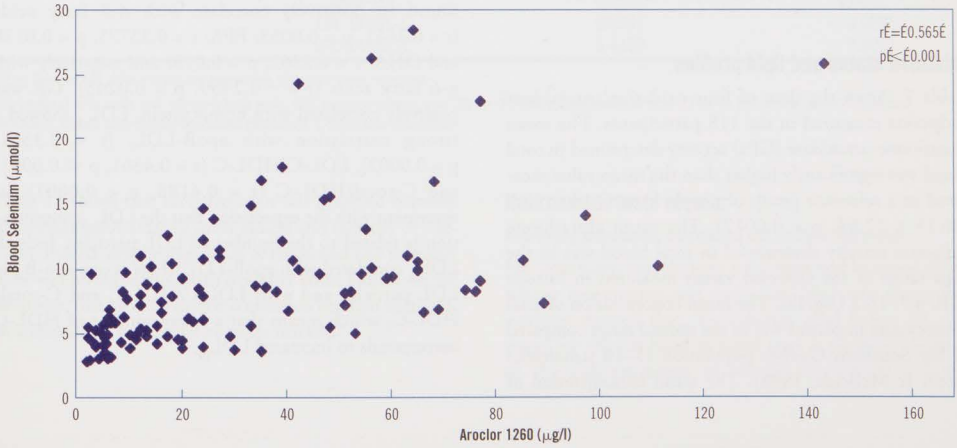


Table 7. Oxidative stress markers measured in Salluit residents

	X ± SD
N	118
GPx[2] (U/gHb)	77.47 ± 14.29
GR[3] (U/gHb)	13.57 ± 2.07
Homocystein (µmol/L)	7.96 ± 4.04
LDL_{ox}[1] (U/L)	45.20 ± 18.14

LDL_{ox}: Oxidized LDL, GPx: glutathione peroxidase, GR: glutathione reductase
U/L: standard unit of the ELISA kit/L
U/gHb: Unit/g haemoglobin

Table 8. Lipid profiles of participants

	X ± SD
N	125
BMI (kg/m^2)	29.4 ± 6.61
Cholesterol (mmoles/L)	
Plasma	5.57 ± 1.11
VLDL	0.52 ± 0.46
IDL	0.27 ± 0.25
LDL	2.58 ± 0.81
HDL	1.18 ± 0.35
Triacylglycerol (mmoles/L)	
Plasma	1.33 ± 0.82
VLDL	0.77 ± 0.60
IDL	0.10 ± 0.04
LDL	0.18 ± 0.06
HDL	0.11 ± 0.12
Apolipoproteins (g/L)	
B-plasma	1.03 ± 0.25
B-LDL	0.63 ± 0.25
A1-HDL	1.24 ± 0.32
LDL cholesterol/LDL-ApoB	2.34 ± 0.92

BMI: body mass index, VLDL: very low density lipoprotein, IDL: intermediate density lipoprotein, LDL: low density lipoprotein, HDL: high density lipoprotein

Oxidative status and lipid profiles

Table 7 shows the data of four oxidative/antioxidant endpoints measured in the 118 participants. The mean glutathione peroxidase (GPx) activity determined in total blood was significantly higher than the mean value measured in a reference group of people from Québec City (60.15 ± 17.84; p = 0.0017). The mean glutathione reductase activity determined in total blood was in the high range of the expected values measured in Europe (GR: 4.7–13.2 U/gHb). The mean concentration of total homocystein in plasma was in the normal range compared to the Southern Québec population (5–10 µmoles/L) (Stein & McBride, 1998). The mean concentration of LDL_{ox} was lower than the mean expected value provided by the ELISA kit (61 U/L, Swedish population) and lower than that measured in the Caucasian sport fishermen investigated in the Bay James study (52.6 U/L after the fishing season).

Table 8 shows that the mean (± SD) body mass index (BMI; in kg/m^2) of participants is 29.4 ± 6.61. Grundy et al. (1998) considers BMIs of 25.0–26.9, 27.0–30.9, and 31.0 kg/m^2 or higher to indicate borderline (moderate) obesity, obesity, and marked obesity. The mean (± SD) of plasma cholesterol was 5.57 ± 1.11 mmol/L, which is slightly higher than results presented by Dewailly et al. (2001a) (5.07 ± 0.05 mmol/L) but is comparable with results obtained from residents of southern regions of Quebec (Dewailly et al. 2001). However, concentration of LDL-C are 2.58 ± 0.81 mmol/L, a lower value than in other Inuits (3.67 ± 0.06 mmol/L). The mean plasma triacylglycerol concentration was 1.33 ± 0.82 mmol/L, in the normal range for healthy subjects (Julien et al. 1998). The mean (± SD) concentration of plasma apo-B (1.03 ± 0.25 g/L) was in the normal range (Connelly et al. 1999), but apo-A1-HDL (1.24 ± 0.32) was slightly lower than normal range (Julien et al. 1998).

Table 9 shows the relative concentrations of fatty acids in erythrocytes membranes of the Sallumiut. The arithmetic mean of relative concentrations of fatty acids EPA, DHA, and their combination (EPA+DHA) are comparable with those observed (EPA, 3.01%, DHA, 4.95% and EPA+DHA, 7.95%) recently by Dewailly et al. (2001a). They are higher than the concentrations found in residents of Southern regions of Quebec (Dewailly, 2001b), who consume little fish (EPA, 0.44%, DHA, 1.04% and EPA+DHA 1.51%) in contrast to the Sallumiut.

Table 10 shows the correlations between the different oxidative stress indices and lipid parameters. GPx was found to positively correlate with n-3 fatty acids (r = 0.2651, p = 0.0053; EPA: r = 0.23775, p = 0.0128 and DHA: r = 0.2262, p = 0.018) and negatively with n-6 fatty acids (r = −0.2439, p = 0.0245). GR was positvely correlated with homocystein. LDL_{ox} showed a strong correlation with apoB-LDL, (r = 0.3361, p = 0.0002), LDL-C/HDL-C (r = 0.4361, p < 0.0001) and C-total/HDL-C (r = 0.4188, p < 0.0001), in agreement with the expectation that the LDL_{ox} concentration is related to the number of LDL particles. Indeed, LDL_{ox} correlated with apoB-LDL (there is one apo-B per LDL particle) and with LDL-C/HDL-C and C-total/HDL-C, which means that a lower content of HDL-C corresponds to increased LDL_{ox}.

Table 9. Relative concentrations of fatty acids in erythrocytes membranes of Salluit residents

Fatty acids *(% by wt of total fatty acids)*	X ± SD	Min	Max
PUFA			
n-3 series			
Total[2]	11.34 ± 2.69	6.85	18.59
EPA	2.92 ± 1.43	0.70	6.94
DHA	5.81 ± 1.06	4.34	8.17
EPA+DHA	8.74 ± 2.31	5.13	15.11
n-6 series			
Total[3]	21.53 ± 3.66	12.84	29.00
AA	9.26 ± 1.99	3.10	13.12
Total PUFA	32.88 ± 2.76	19.97	36.87
n-3 :n-6	0.56 ± 0.21	0.24	1.25
EPA :AA	0.34 :0.21	0.06	1.09
MUFA[4]	24.53 ± 1.97	20.71	27.85
SFA[5]	42.31 ± 1.44	39.76	46.34
P :S	0.78 ± 0.08	0.44	0.87

[1] PUFA: polyinsaturated fatty acids, EPA: eicosapentaenoic acid(20:5n-3); DHA: docosahexaenoic acid (22:6n-3); AA: arachjdonic acid (20:4n-6); MUFA: monounsaturated fatty acids, SFA: saturated fatty acids; P:S: ratio de PUFA:SFA

[2] 18:3 + 18:4 + 20:3 + 20:4 + 20:5 + 22:5 + 22:6

[3] 18:2 + 18:3 + 20:2 + 20:3 + 20:4 + 22:2 + 22:4 + 22:5

[4] 14:1 + 16:1 + 18:1 + 20:1 + 22:1 + 24:1; 5 14:0 + 16:0 + 17:0 + 18:0 + 20:0 + 22:0 + 24:0

Table 10. Correlations between oxidative stress indices, fatty acids and lipid parameters

Oxidative stress index	Correlation with	Pearson correlation coefficent	P value
GPx	n-3	0.2651	0.0053
	n-6	−0.2439	0.0106
	EPA	0.23775	0.0128
	DHA	0.2262	0.0180
GR	Plasma Apo-B	−0.21635	0.0245
Homocystein	GR	0.26168	0.006
LDL_{ox}	n-6	−0.2120	0.0223
	ApoB-LDL	0.3361	0.0002
	LDL-C/HDL-C	0.4361	< 0.0001
	C-total/HDL-C	0.4188	< 0.0001

LDLox: Oxidized LDL, GPx: glutathione peroxidase, GR: glutathione reductase

n-3: omega-3 fatty acids, n-6: omega-6 fatty acids, EPA: eicosapentaenoic acid (20 :5n-3), DHA: docosahexaenoic acid (22:6n-3), LDL-C: low-density lipoprotein cholesterol, HDL-C: high-density lipoprotein cholesterol, C-total: total cholesterol

Table 11 shows that no correlation was observed between the antioxidant/oxidative stress indices and mercury or selenium. Indeed, despite high levels of blood and hair mercury, there was no correlation with oxidative stress indices. In the same way, there was no inverse correlation between selenium, an antioxidant, and oxidative stress markers.

Neuromotor tests results

Alternating movements: Correlation and multiple regression

No significant correlations were observed between alternating movements and exposure. Multiple regression analyses showed that, for subjects aged below 45, the range for the left hand at rapid pace is positively related to the concentration of Hg in hair ($t(52) = 2.59$;

Table 11. Correlations between oxidative stress indices, selenium and mercury

Oxidative stress marker	Correlation with blood mercury	Correlation with hair mercury	Correlation with Selenium
GPx	ns	ns	ns
GR	ns	ns	ns
Homocystein	ns	ns	ns
LDL_{ox}	ns	ns	ns

ns: no significant correlation

$p < 0.01$) and negatively related to the concentration of PCBs ($t(52) = -2.88$; $p < 0.01$). This relation is explaining 21% of the variance.

Pointing movements: Correlations and multiple regressions

In pointing movements, the Fitt's constant measure (right: $r = 0.31$; $p < 0.001$; left: $r = 0.32$; $p < 0.001$) was significantly correlated with age. Also, a small correlation was observed between the Fitt's constant for the left hand and PCB concentration ($r = 0.18$; $p < 0.05$). Multiple regression analyses show a relationship between the Fitt's constant for the right hand and age ($t(102) = 4.33$; $p < 0.001$) and a tendency for hair Hg concentration ($t(102) = -1.70$; $p < 0.1$). For participants aged below 45, it reaches significant level for hair Hg concentration ($t(55) = -2.01$; $p < 0.05$). Therefore, it seems that the effects of Hg exposure on neuromotor functions are more efficiently detected with participants aged below 45 years old whereas with participants aged over 45, the oxidative effect of mercury exposure is merged with the natural effects of aging. As for the left hand, results for the Fitt's constant tend to be related to the age of the subjects for both younger and older participants.

Postural finger tremor (Laser-based system): Regression analyses

Multiple regression analyses showed a link between proportional power in the 3–4 Hz band for the right hand and PCB concentration ($t(105) = 2.18$; $p < 0.05$).

Postural arm tremor (Catsys system): Correlations and regression analysis

For postural arm tremor (DPD Tremor pen), median frequency (right hand) was correlated with blood Hg level: ($r = -0.19$; $p < 0.05$). Correlations with covariates show that PCB levels ($r = -0.20$; $p < 0.05$), selenium concentration ($r = -0.20$; $p < 0.01$) and age ($r = -0.22$; $p < 0.01$) are also related to the median frequency of the right hand. Also, PCB levels ($r = 0.22$; $p < 0.05$) and age ($r = -0.29$; $p < 0.01$) are both correlated with the harmonic index results for the right hand.

The median frequency of arm tremor for the right hand was predicted by Se concentration ($t(103) = -1.94$; $p < 0.05$). A significant relation for the harmonic index (right hand) was also found with age ($F(4,99) = 2.93$; $p < 0.02$) as a predictor. However, for participants below 45 years old, performance was significantly related to age ($t(55) = 2.52$; $p < 0.01$) and Se concentration ($t(55) = -1.95$; $p < 0.05$).

Reaction time: Correlation and regression analyses

No significant correlations were observed between Hg concentration and reaction time. Multiple regression analyses did not identify any significant predictor for the reaction time task.

Inverted aiming movements (Graphics tablet): Correlation and regression analyses

Results reveal a relation between both the Hg concentration in hair ($r = 0.28$; $p < 0.01$) and in blood ($r = 0.26$; $p < 0.05$) and the precision of trajectories in inverted aiming. Also, the precision of trajectories was significantly linked to the level of PCBs ($r = 0.25$; $p < 0.05$) and age ($r = 0.23$; $p < 0.05$). When controlling for PCBs concentration, the relation between Hg concentration in hair and the precision of trajectories is still significant ($r = 0.20$; $p < 0.1$). When controlling for Se, trajectory precision is still related to Hg concentration ($r = 0.26$; $p < 0.05$).

Multiple regression analyses reveals a trend for hair Hg concentration in the prediction of trajectory precision in the whole sample ($t(67) = 1.88$; $p = 0.06$). Again, when results are examined in two age groups, (below and over 45 years old) it shows that results for participants aged below 45 years old are significantly related to the hair Hg concentration ($t(42) = 2.42$; $p < 0.05$) and Se concentration ($t(42) = -2.83$; $p < 0.01$). Thus, the effects of Hg exposures on neuromotor functions are one more time more efficiently detected with participants aged below 45 years old.

Discussion and Conclusions

One of the objectives of the study was to quantify the effects of mercury on neuromotor functions of adults

exposed to high levels of mercury with highly sensitive measures. If recent data from the Faeroe Islands suggest that the neurologic status of children can be affected by low-level prenatal exposure to mercury (Grandjean et al., 1997), to our knowledge, no study has yet looked at subtle effects of mercury concentrations on neuromotor functions of Inuit adults.

As regards mercury exposure among Sallumiut, results presented here are similar to data presented in another study done in Salluit in 1999 where the mean mercury concentration in hair was 6,1 ppm. Results obtained to date indicate that there are large differences between age groups with regard to mercury and selenium exposure in Sallumiut. The strong correlation (r = 0.71) noted between mercury and selenium concentrations suggests that both substances originate from common dietary sources. This may be of utmost importance in assessing the health risk associated with mercury exposure in this population because selenium may counteract methylmercury-induced toxicity. Seafood is a good source of selenium, an essential trace element that has been shown to provide some protection against methylmercury-induced neurotoxicity in various experimental systems (WHO, 1990, Whanger, 1992). Mattak (beluga skin) consumption is part of the traditional diet in Nunavik. Mattak generally contains between 4 and 10 µg/g of selenium (wet weight) (AMAP, 1998) and is the most important source of selenium among all traditional foods in Nunavik (Blanchet et al., 2000).

PCB's and pesticides concentrations were measured because of potential confounding effects on neuromotor endpoints. Results show that older participants aged 60 years and more had a mean concentration in blood more than 6 times higher than that of individuals in the 18–39 years age group.

In this population, PCBs, mercury and selenium concentrations are around 10 times higher of what is observed in background Canadian populations.

As regard the oxidative status, none of the four indices of oxidative/antioxidant status investigated showed in preliminary statistical analysis any evidence of oxidative stress associated with mercury exposure in the Sallumiut group. The GPx and GR data indicated that both antioxidant activities were more elevated than in two Caucasian reference groups, one in Québec City and the second in the James Bay area (Hydro-Québec workers and sport fishermen). The basis for increased antioxidant activities in the Sallumiut is not known. Of interest, the increase in GPx activity was correlated with n-3 fatty acid content of erythrocytes membranes. Several rodent studies (Takahashi et al., 2002; Venkatraman et al., 1994) showed that fish oil-enriched diets increased antioxidant activities in liver, and suggested that enhanced lipid peroxidation associated with elevated n-3 fatty acids contents induced antioxidant activities as a defence mechanism. By analogy, it is thus possible that the observed increase in antioxidant activities in Sallumiut resulted from their fish-based diet, which is rich in n-3 fatty acids. In contrast, the average level of plasmatic LDL_{ox} in Sallumiut was lower than that determined in the sport fisherman Bay James study, which does not suggest enhanced lipid peroxidation in plasma. It should be emphasized, however, that this investigation did not address the difficult problem of assessing oxidative stress in brain, which can so far only be investigated in animal studies.

As regards to neuromotor tests, the results of the present study indicate that low-level chronic exposure to mercury can produce pre-clinical alterations in sensitive neuromotor measures. Results show that mercury concentration was related most importantly to alternating movements, pointing movements and inverted aiming task. Age was found to be the best predictor in pointing movements and postural arm tremor. Finally, Selenium concentration was mainly related to the postural arm tremor and inverted movements for participants aged below 45 years old.

It must be noted that age also predicts performance in many measures confirming our previous data (Després et al., 2000). Indeed, performance in participants aged below 45 are best predicted by exposure concentration and age whereas participants aged over 50 years old, performance is best explained by age alone. Yee et al. (1996) demonstrated the effect of oxidative stress following MeHg exposure in brain cells. In that sense, one explanation for this observation could be the additive effects of aging and neurotoxic exposure on oxidative stress in the brain. It appears that neurotoxic exposure is more readily detected in participants aged below 45 years old in whom oxidative stress is less intermingled with normal aging effects. Further multi variate statistical analysis will be conducted shortly.

References

ATSDR, (1994) *Toxicological Profile for Mercury.* U.S. Department of Health and Human Services, TP-93/10.

Barrie, L.A., D. Gregor, B. Hargrave, R. Lake, D. Muir, R. Shearer, B. Tracey, and T. Bidleman. 1992. Arctic contaminants: sources, occurrence and pathways. *Sci Total Environ.* Jul 15;122(1–2):1–74.

Beuter, A. and A. de Geoffroy. 1996. Can tremor be used to measure the effect of chronic mercury exposure in human subjects? *NeuroToxicology.* 17, 1:213–228.

Beuter, A. and R. Edwards. 1998. Tremor in Cree subjects exposed to methylmercury: A preliminary study. *Neurotoxicology and Teratology.* 20, 6:581–589.

Beuter, A. and R. Edwards. 1999a. Using frequency domain characteristics to discriminate physiological and parkinsonian tremors. *Journal of Clinical Neurophysiology.* 16(5):484–494.

Beuter, A., R. Edwards, A. de Geoffroy, D. Mergler, and K. Hudnell. 1999b. Quantification of neuromotor function for detection of the effects of manganese exposure. *NeuroToxicology.* 20(2–3):355–366.

Beuter, A., A. de Geoffroy, and R. Edwards. 1999c. Analysis of rapid alternating movements in Cree subjects exposed to methylmercury and in subjects with neurological deficits. *Environmental Research.* 80:64–79.

Beuter, A., A. de Geoffroy, and R. Edwards. 1999d. Quantitative analysis of rapid pointing movements in Cree subjects exposed to methylmercury and in subjects with neurological deficits. *Environmental Research.* 80:50–63.

Beuter, A. and R. Edwards. 2002. Kinetic tremor during tracking movements in patients with Parkinson's disease. *Parkinsonism & Related Disorders.* June 8(5): 366–368.

Blanchet C., É. Dewailly, P. Ayotte, S. Bruneau, O. Receveur, and B.J. Holub. 2000. Contribution of Selected Traditional and Market Foods to the Diet of Nunavik Inuit Women. *Can J Diet Pract Res.* Summer;61(2):50–59.

Connelly, P.W., M. Poapst, J. Davignon, S. Lussier-Cacan, B. Reeder, R. Lessard, R.A. Hegele, and A. Csima. 1999. Reference values of plasma apolipoproteins A-I and B, and association with nonlipid risk factors in the populations of two Canadian provinces: Quebec and Saskatchewan. Canadian Heart Health Surveys Research Group. *Can J Cardiol.* 15(4):409–18.

Després, C., D. Lamoureux, and A. Beuter. 2000. Standardization of a Neuromotor Test Battery: The Catsys System. *NeuroToxicology.* Oct;21(5):725–35.

Dewailly, É., C. Blanchet, S. Lemieux, and L. Sauvé. 2001a. n-3 Fatty acids and cardiovascular disease risk factors among the Inuit of Nunavik. *Am J Clin Nutr.* 74(4):464–73.

Dewailly, É. S. Gingras, S. Lemieux, L. Sauvé, P. Ayotte, and B.J. Holub. 2001b. Relations between n-3 fatty acid status and cardiovascular disease risk factors among Quebecers. *Am J Clin Nutr.* 74(5):603–11.

Gerhard, G.T., and P.B. Duell. 1999. Homocysteine and atherosclerosis, *Curr Opin Lipidol.* Oct;10(5):417–28.

Grandjean, P., P. Weihe, R.F. White, F. Debes, S. Araki, K. Yokohama, K. Murata, N. Sorensen, R. Dahl, and P.J. Jorgensen. 1997. Cognitive deficit in 7-year-old children with prenatal exposure to methylmercury. *Neurotoxicol Teratol.* Nov–Dec;19(6):417–28.

Grundy, S.M. 1998. Multifactorial causation of obesity: implications for prevention. *Am J Clin Nutr.* 67(3 Suppl):563S–72S.

Julien, P., C. Gagné, M.R. Murphy, G. Levesque, S. Mooriani, F. Cadelis, M.R. Hayden, and P.J. Lupien. 1998. Dyslipidemias associated with heterozygous lipoprotein lipase mutations in the French-Canadian population. *Hum Mutat Suppl.* (1):S148–53.

Li, H., J.A. Lawson, M. Reilly, M. Adiyaman, S.W. Hwang, J. Rokach, and G.A. FitzGerald. 1999. Quantitative high performance liquid chromatography/ tandem mass spectrometric analysis of the four classes of F(2)-isoprostanes in human urine. *Proc Natl Acad Sci.* USA. 96:13381–13386.

Lund, B.O., D.M. Miller, and J.S. Woods. 1993. Studies on Hg(II)-induced H2O2 formation and oxidative stress in vivo and in vitro in rat kidney mitochondria. *Biochem Pharmacol.* 45:2017–2024.

Meagher E.A., and G.A. FitzGerald. 2000. Indices of lipid peroxidation in vivo: strengths and limitations. *Free Radic Biol Med.* Jun 15;28(12):1745–50.

Muir, D.C.G., R. Wagemann, B.T. Hargrave, D.J. Thomas, D.B. Peakall, and R.J. Norstrom. 1992. Arctic marine ecosystem contamination. *Sci Tot Environ.* 122:75–134.

Ornaghi, F., S. Ferrini, M. Prati, and E. Giavini. 1993. The protective effects of N-acetyl-L-cysteine against methyl mercury embryotoxicity in mice. *Fundam Appl Toxicol.* 20:437–445.

Park, S.T., K.T. Lim, Y.T. Chung, and S.U. Kim. 1996. Methylmercury-induced neurotoxicity in cerebral neuron culture is blocked by antioxidants and NMDA receptor antagonists. *Neurotoxicology.* 17:37–45.

Sarafian, T., and M.A. Verity. 1991. Oxidative mechanisms underlying methyl mercury neurotoxicity. *Int J Dev Neurosci.* 9:147–153.

Stein J.H., P.E. McBride. 1998. Hyperhomocysteinemia and atherosclerotic vascular disease: pathophysiology, screening, and treatment. *Arch Intern Med.* Jun 22;158(12):1301–6.

Takahashi, M., N. Tsuboyama-Kasaoka, T. Nakatani, M. Ishii, S. Tsutsumi, H. Aburatani, and O. Ezaki. 2002. Fish oil feeding alters liver gene expressions to defend against PPARalpha activation and ROS production. *Am J Physiol Gastrointest Liver Physiol.* 282(2):G338–48.

Venkatraman, J.T., B. Chandrasekar, J.D. Kim, and G. Fernandes. 1994. Effects of n-3 and n-6 fatty acids on the activities and expression of hepatic antioxidant enzymes in autoimmune-prone NZBxNZW F1 mice. *Lipids.* 29(8):561–8.

Whanger, P.D. 1992. Selenium in the treatment of heavy metal poisoning and chemical carcinogenesis. *J Trace Elem Electrolytes Health Dis.* 6:209–221.

W.H.O. 1990. Environmental Health Criteria 101. *Methylmercury.* World Health Organization, Geneva.

Yee, S., and B.H. Choi. 1996. Oxidative stress in neurotoxic effects of methylmercury poisoning. *Neurotoxicology.* 17: 17–26.

Determinants of Food Choices in Labrador

Project leader

Christopher Furgal, Public Health Research Unit, CHUL Research Centre (CHUQ), 945 Ave Wolfe, Ste-Foy, Québec, G1V 5B3, tel: (418) 650-5115, ext. 5260; fax: (418) 654-3132; e-mail: christopher.furgal@crchul.ulaval.ca

Project team members

Susie Bernier, Public Health Research Unit, CHUL Research Centre (CHUQ), Québec; Gaston Godin, Research Group for the Study of Health-Related Behaviours, Laval University, Québec; Éric Dewailly, Public Health Research Unit, CHUL Research Centre, Québec.

Abstract

This project addresses a gap in our understanding of determinants of food choices that should contribute to the management of wild food (WF) and contaminant issues in the North. A culturally specific questionnaire was developed, tested and applied to 251 Labrador Inuit Association (LIA) members of Nain, Labrador to provide a quantitative assessment of determinants of food choices. Results on intention to eat wild food show that the most influential determinants were: ease or difficulty of access, beliefs about the consequences of eating wild food and personal values. Results on intention to eat store food (SF) show that the most influential determinants were: ease or difficulty of access, beliefs about specific roles, perception that a certain type of people eats store food, and barriers/facilitating factors. Knowledge of contaminants was not found to be a major determinant of intention to eat wild food. This is the second quantitative data on this topic in the North to date (see Furgal et al. 2001). Results on the determinants of food choices in Kuujjuaq, were very similar to results for Nain, Labrador. This suggests that implementation of intervention and promotion programs related to wild foods and contaminants in the Canadian North could share a similar form, as ease of access was an important significant determinant of wild food use in both regions. Data also suggests that many questions used in both surveys were similar and supports our hypothesis that a core set of questions could be used across the Canadian North in similar surveys on this subject.

Key Project Messages

1. Knowledge of contaminants was not found to be a major determinant of the intention to eat wild food in Nain (Labrador).
2. How easy or difficult a person thought eating wild food three times a week or more would be, was the strongest determinant of intention to eat wild food, followed by beliefs about the consequences of eating wild food and personal values.
3. The most important factors influencing intention to eat store food every day were ease or difficulty of access, beliefs about specific roles, perception that a certain type/group of people eats store food, and barriers/facilitating factors.

Objectives

Specifically, this project aimed to:

1. Develop and apply a survey tool to increase our understanding of the determinants of food choices.
2. Compare the results and the methods with similar efforts conducted in Nunavik and Alaska.
3. Make recommendations for a general food determinants survey to be adapted to other regions of the Canadian North.

Introduction

Our understanding of the associated risks and benefits related to the Inuit traditional diet has expanded significantly within the last decade. The many physical health benefits of a traditional diet have been reported by a number of researchers (e.g. Dewailly 1996; Kuhnlein 1997). A low incidence of cardiovascular heart disease, diabetes and some cancers in Inuit populations has been attributed, in part, to traditional food consumption (Bang 1971, 1980; Bjerregaard 1997). At the same time, our understanding of the potential public health risks related to the presence of environmental contaminants in northern wildlife has increased significantly in the last ten years (Indian and Northern Affairs Canada 1997). Recent work conducted under the *Avativut/Ilusivut* Eco-Research Program in Nunavik and Labrador has described the economic costs and benefits associated with traditional foods and food-related activities, and evaluated the impact of potential food-related advisories.

For decades, researchers have been documenting changes in consumption of traditional food among Inuit populations. Inuit have been replacing and/or supplementing their traditional diet by some nutrient-poor imported store foods (Lawn 1993). We know that these changes affect Inuit health by the increasing occurrence of diabetes, cardiovascular heart disease and other diet-related nutritional deficiencies (Kuhnlein 1997, Schaefer 1980). The prevalence of these diseases can be expected to continue to increase and cause health problems in the future (Thouez 1990). Fortunately, diet behaviour is a modifiable risk behaviour (Elford 1991, Krondl 1978). Therefore, a better understanding of the factors influencing diet choice will help northern health professionals and decision makers to better understand diet trends and support activities to protect and promote nutritional health and well being. Health promotion professionals, such as the Labrador Inuit Health Commission (LIHC), as well as educators, can be better equipped to develop programs targeted to specific at-risk populations such as women of childbearing age, who are more prone to suffer from nutritional deficiencies (e.g. iron, calcium) and are of utmost importance due to the influence they have on their infant's nutritional health, and teenagers who are known to be less inclined to prefer nutrient rich traditional foods and more inclined and prompted to consume nutrient-poor store foods (Kuhnlein 1997, Dewailly 1998).

Although economic, contaminant-related and some social factors have been identified to explain associated changes in the consumption of traditional country foods, few studies have looked at nutritional knowledge, food preferences and other personal factors influencing individual food choices. Some studies do mention social and cultural factors related to changes in traditional food consumption (in particular food availability, harvesting time, costs of equipment for hunting/fishing, etc.). However, to date, no comprehensive study has been done to assess the actual impact these factors have on individual consumption-related behaviour, and the relative bearing of modernity, contaminants information or social and individual preferences of food choice is not known.

This research project addresses the needs of northern health professionals in promoting healthy food choices through organizing and presenting the factors influencing northerners' food habits in a comprehensive and understandable way. It supports the role of Inuit health organizations, government agencies, and advisory bodies in providing balanced and accessible information to Inuit and other northerners on traditional/wild foods, nutrition and health.

While western science has recently recognized the biological and economic benefits and risks related to traditional/wild foods, traditional knowledge has long since recognized the many benefits of a traditional diet in terms of physical, social, and spiritual well-being (Borré 1991, 1994; Egede 1995). Others have reported on the loss or disruption of these social and cultural components through associated confusion and concern over food safety related to reports of environmental contamination (Santé Québec 1992; Wheatley 1981; Wenzel 1986). Northern health professionals, government representatives and advisory bodies have had the responsibility to "manage", through the balancing of available information, the provision of advice and in some cases intervention, as well as the protection and promotion of public health in the North and its relationship to local resource use. This has proven to be a difficult, and at times, challenging exercise, in particular because the population's needs, expectations and preferences have not always been considered.

It is argued here that an organization and presentation of this information is of value to northern managers and

health professionals as it allows for ordered consideration of the reported influence of psycho-social factors on personal food choices in the development of interventions and promotions to support nutritional health and well-being. The balanced consideration of these components of a traditional diet are vitally important to any decisions regarding traditional/wild food protection and promotion, as they too directly impact individual's health and well-being and determine the extent to which the population is able and willing to comply to health policies, programs and interventions. Those responsible for the protection and promotion of public health in the North must consider and have access to all available information in order to make informed decisions. This is becoming increasingly more important as the issues surrounding traditional/wild foods in the North are becoming increasingly complex.

Activities

In 2001–2002

The development of the survey tool to identify and assess determinants of diet behaviour was completed through a number of activities. First, consultations with local researchers were held to discuss the proposed ways to conduct the research and methods to be used, and to review and adjust the focus group guide for the community. The project was also presented to the LIHC health promotion and nursing team at this time.

Second, group discussions (focus groups) were conducted with a sample of Nain residents representing a range of different socio-economic and demographic characteristics among the general population. There were eleven (11) group discussions (n = 66) with 4 groups of men (13–75 years old), 6 groups of women (13–75 years old) and 1 group of teenagers composed of girls and boys.

Content analysis of the data from the discussion groups was based on Gagné and Godin's guide (1999). Influences on traditional food and store food consumption were categorized according to 6 groups: 1. Behavioural beliefs (advantages/disadvantages), 2. Normative forces, 3. Behavioural norms, 4. Facilitating factors/barriers, 5. Affect, and 6. Others. Questions were then drafted and organized in the questionnaire based on the results of this analysis. Then, a first draft of the questionnaire was discussed and reviewed by the Labrador Inuit Association Research Office, Labrador Inuit Health Commission representatives, local translators and people randomly selected in the community. Adjustments were made for clarity and comprehension resulting from these conversations. The second version of the questionnaire was then translated from English to Inuktituut and back-translated from Inuktituut to English by a second translator. Both versions were reviewed and adjusted accordingly.

Finally, the questionnaire was tested for its clarity, comprehension and reliability with representatives of different socio-demographic groups of the population of Nain. These individuals were asked to complete the survey and then duplicate this exercise between 10 and 19 days later. A total of 40 participants (divided into 2 groups) completed the test and 39 completed the retest. Group 1 tested the English version at Time 1 and at Time 2 (10–19-day interval). Group 2 tested the Inuktituut version at Time 1 and at Time 2 (12–29-day interval). Only one participant was not available for the retest.

Verification of the internal consistency of the theoretical variables by means of Cronbach's Alpha (Cronbach 1951), and testing of the stability of the instruments over time by means of the intra-class correlation coefficient (Shroutte 1979) are being conducted.

The questionnaire developed for the test-retest was based on the emic content (as elicited from the population through group interviews) of the etically defined constructs of Triandis' theory of interpersonal behaviour (1980). (A copy of the questionnaire is in appendice.)

Activities

In 2002–2003

The application of the survey tool developed in year 1 was successfully completed in the fall of 2002. One member of our research team and nine locally-hired and trained interviewers, completed 251 face to face interviews with LIA members of Nain (Labrador), 13 years of age and older. The questionnaire had been tested and retested in both English and Inuktituut with 40 residents of Nain the previous spring and was then further adapted following statistical analysis for each question's validity and the survey's reliability. Composed of 50 questions, it measured frequency of use of foods, constructs of Triandis' (1977) theory for use of wild food three times a week or more, use of store food every day, degree of liking of foods, as well as basic socio-demographic information (see Table 4). The project and consent forms were reviewed and approved by the Ethics Committee of Laval University and by the LIA Research Office and LIHC. Informed consent was obtained from all participants after having explained the objectives of the survey.

Table 1: Categorized content of focus groups responses (TRADITIONAL FOOD)*

Potential determinants of decreased use	Potential determinants of increased use	Uncertain effects on use
Affect	**Affect**	**Behavioural norms (reference groups)**
• Don't like it	• Like it, prefer it, love it	• Older people
• Sick/tired of it	• Crave/want it bad/need it	• Teens
Behavioural beliefs/preferences	• Happy	• Low income people
• Can make you sick (food poisoning, eating too much, mixing foods)	**Behavioural beliefs/preferences**	• Everyone eats some
• Hard to get/find	• Available/around/abundant	**Other influences**
• Expensive (need equipment)	• Healthy	• Culture
• Strong taste	• Tasty	• Identity (in our blood, part of you)
• Preparation/cooking	• Simple/convenient	• Celebrations (holidays, birthdays, etc.)
• Lack of variety/boring	• Strength/feel better	• Being raised on it
Normative forces	**Normative forces**	• Way of life
• Children	• Parents & elders	• Habit
• Health professionals	• Health professionals	• Being a parent
Barriers	**Facilitating factors**	
• Lack of access/availability	• Availability (around community, in home)	
• Lack of equipment	• Sharing (family, friends)	
• Lack of hunter/fisher in home	• Donations	
• Lack of time (employment)	• Storage/freezers	
• Season	• Equipment	
• Cost of equipment	• Variety/choices	
	• Hunting	
	• Time (to prepare, to harvest)	
	• Already cooked, prepared	
	• Municipal freezer	
	• Money	

* Top 75% of most frequently mentioned reasons for eating traditional food (except for the "other influences" category)

Table 2: Categorized content of focus groups (STORE FOOD)*

Potential determinants of decreased use	Potential determinants of increased use	Uncertain effects on use
Affect	**Affect**	**Behavioural norms (reference groups)**
• Tired/sick of it	• Like it/love it	• Kids/youth
Behavioural beliefs/preferences	• Crave it	• Everyone eats it
• Lack of freshness	**Behavioural beliefs/preferences**	• Teachers/nurses/RCMP not used to lifestyle
• Expensive	• Taste	**Other influences**
• Can make you sick (food poisoning)	• Variety, choices	• Habit
• Unfulfilling	• Available (just there)	• Celebrations (holidays, birthdays, etc.)
Barriers	• Quick and convenient	• Being raised on it
• Cost	• As substitute for traditional food	• Being a parent
• Availability	**Normative forces**	• Hunger
• Lack of quality	• Children	
• Fattening	• TV/commercials	
	• Parents	
	Facilitating factors	
	• Money	
	• Availability	
	• Sharing with family & friends	
	• Better quality	
	• Food banks	
	• Lack of choice (no TF)	

* Top 75% of most frequently mentioned reasons for eating store food (except for the "other influences" category)

Table 3: Characteristics of participants in test-retest

Characteristic		n = 40	%
Age	13–19	9	22.5
	20–30	8	20.0
	31–40	11	27.5
	41–59	8	20.0
	60+	4	10.0
Gender	M	21	52.5
	F	19	47.5
Mean # of children in home		2.5	
Mean # of adults in home		2.7	
Hunt or fish	Yes	32	80.0
	No	8	20.0
Interview conducted in:			
English		20	50.0
Inuktituut		20	50.0
Level of education attained:			
Teens (in school)	Junior	5	12.5
	Senior	3	7.5
	ABE (Adult Basic Education)	3	7.5
Adults	Elementary	3	7.5
	Junior	13	32.5
	Senior	7	17.5
	Post secondary	2	5.0
	No schooling	4	10.0
	Secondary complete	***5***	***12.5***
Occupation*	Unemployed	13	32.5
	Student	11	27.5
	Retired	4	10.0
	Professional occupation in culture	4	10.0
	Elementary sales and service occupation	4	10.0
	Trades and equipment operators	2	5.0
	Intermediate sales and service occupation	1	2.5
	Elementary occupations in primary industry	1	2.5

* Major groups of the National Occupation Classification (NOC) (Employment and Immigration Canada, 1992)

All questionnaire forms were reviewed and validated to eliminate logic or coding errors and all data for statistical analysis were captured twice. Statistical analysis was conducted using Statistical Analysis System (SAS) software (Statistical Analysis System Institute Inc.1999). The relationship between the intention to eat wild food and the Triandis theory's constructs was evaluated via logistic regression. The relationship between intention to eat store food and the Triandis theory's constructs was evaluated via multiple regression analysis (Kleinbaum 1988).

Results

Descriptive

The participation rate for the final survey was 94%. Stratified random sampling gave us the distribution presented in Table 2, according to age and gender. More than half the sample was represented by men. Mean age of the group was 35 years old. Ninety percent (90%) of the sample completed the survey in English, while 7% in Inuktitut and 3% in a combination of both languages.

Overall, 88% of participants reported an intention to eat wild food three times a week or more over the next month. Results for regular consumption of wild food were: 39% eat wild food more than 4 times a week; 41% eat wild food from one to three times a week. Sixty percent (60%) of participants had eaten wild food the day before participating in the survey. In regards to store food, 53% of participants reported an intention to eat store food every day over the next month, while 66% mentioned eating it 4 times a week or more, and 24% from one to three times a week. Participants having eaten store

Table 4. Summary of questionnaire used in final survey of food choices in Labrador

Constructs	WF[1]	SF[2]	Example
Normative belief*	5	4	Would the following people approve/disapprove of you eating WF ≥ 3/week? (e.g. elders) (5-point scale: Totally disapprove – Totally approve)
Affect*	3	3	If you ate WF ≥ 3 times per week, would you get tired of it? (5-point probability scale, no – yes)
Attitude*	5	5	If you ate SF every day, would it be very unsafe – very safe? (5-point semantic differential scale)
Intention*	2	2	Over the next month, do you plan on eating WF ≥ 3 times/week? (5-point probability scale, no – yes)
Perceived behavioural control	3	3	How easy would it be for you to eat WF ≥ 3 times/week? (5-point semantic differential scale)
Personal normative beliefs*	2	2	Do you feel you should eat SF every day? (5-point scale, Totally disagree – Totally agree)
Behavioural beliefs*	5	7	If you ate WF ≥ 3 times per week, do you believe it would save you money? (5-point no – yes scale)
Self-efficacy*	17	11	If SF made you gain weight would that prevent you from eating it every day? (5-point no – yes scale)
Role Belief*	3	3	As a parent, do you think you should eat WF? (5-point scale, Totally disagree – Totally agree)
Perceived behavioural norm	1	1	In your community, how many people do you think eat SF every day? (5-point scale: 0% – 100%)
Degree of liking	1	1	How do you like the taste of WF? (10-point scale, not at all – like very much)
Habit*	1	1	Usually: Frequency of use of WF (6-point frequency scale: never – every day)
Use of foods	1 1	1 1	Yesterday: Did you eat SF? (Dichotomous: yes/no), What did you eat? Last week: Frequency of use of SF (4-point frequency scale: 0 – every day)
Place of use and frequency	5	5	Place foods are consumed. (E.g. at home, in restaurant) (4-point scale: rarely/never – most of the time)
One (1) open question on other reasons for eating wild food and store food			

* Constructs of Triandis's theory; [1]Number of items (questions) used to measure each construct in relation to wild food (WF); [2]Number of items (questions) used to measure each construct in relation to store food (SF)

Table 5. Composition of participants in final food choice survey in Nain, Labrador, according to age and gender

Age group	Male	% of sample	Female	% of sample	Total	% of sample
13–19	30	11.95	29	11.55	59	23.51
20–30	32	12.75	32	12.75	64	25.50
31–40	25	9.96	21	8.37	46	18.33
41–59	33	13.15	25	9.96	58	23.11
60+	13	5.18	11	4.38	24	9.56
TOTAL	133	52.99	118	47.01	251	100.00

food the day before the survey represented 88% of the sample. Also, 78% of adult participants in the final survey responded that they participated in harvesting activities and 79% had a hunter/fisherman that shared wild foods with them. Ninety-five percent (95%) of youth reported that their parents hunt and/or fish[1].

[1] Calculations of mean frequency of harvesting activity could not be made as answers varied from "sometimes" to "twice a month", "weekends and all summer", "on holidays", etc.

Questions related to health and safety value of traditional/wild food

When asked if "eating wild food three times per week or more over the next month would be the healthiest thing for you" (one measure of behavioural belief), 99% of participants responded probably/yes. When asked if eating wild food three times/week or more over the next month would be unhealthy/healthy (one measure of attitude), 96% of participants thought it would be healthy/very healthy. When asked if this behaviour was unsafe or safe, 97% responded that they thought it would be safe/very safe (one measure of attitude).

Analytical

Results on intention to eat wild food 3 times a week or more over the next month show that the most influential factors were ease or difficulty of access, beliefs about the consequences of eating wild food (e.g. "I believe eating wild food saves me lots of money") and personal values (e.g. "I think I should eat wild food three times a week or more"). Participants in the survey who perceived eating wild food three times a week or more as being easy, had 14 times more chance of reporting a strong intention to eat it than those who perceived it as being difficult. Participants who had strong beliefs about the consequences of eating wild food had 4.6 times more chance of reporting a strong intention to eat wild food. People who believed that they should eat wild food three times a week or more had 4.5 times more chance of reporting a strong intention to eat wild food. Table 6 presents the logistic regressions of intention to eat wild food on the statistically significant predictor variables.

Results on intention to eat store food every day over the next month show that the most influential factors were ease or difficulty of access (e.g. "If I wanted to, I could eat store food every day"), beliefs about specific roles (e.g. "I think that a person my age should eat store food every day"), perception that a certain type of people eat it every day (e.g. "In my community, I believe that 75% of people eat store food every day") and barriers/facilitating factors to eating store food every day ("If it was too long to cook/prepare, it would/would not stop me from eating store food every day). Table 7 presents the multiple regressions of intention to eat store food on the statistically significant predictor variables.

Of the 12 constructs examined for their part in predicting intention to eat wild food and store food, three play a significant role in the intention to eat wild food three times/week or more over the next month, while 4 of them explain 60% of the variance in intention to eat store food every day over the next month.

Discussion

The methods used in the first year of this study, to elicit the emic views of the etic constructs, contributed to the quality of our questions in the year 2 survey. The questionnaire was built from local knowledge and language, tested and retested, and further adjusted so it was easy to understand and answer. No questions in the applied survey were considered inappropriate or irrelevant by participants and thus the number of non-responses was very low as only 7 questionnaires were dropped in the final analysis. Also, including an open-ended question at the end of the questionnaire allowed us to further ensure that we covered all possible answers in the previous questions as no new or different attributes were reported.

In our survey, only three questions addressed the issue of the effect of contaminants on food choices and our results indicate that there is no effect. Two of the three questions on this issue were included in the composite measure of attitude and one was included in the measure of behavioural beliefs. Although these were not specific questions on contaminants, we believe the fear, or lack of fear of contaminants in wild foods is filtered through the measure of attitude which was included in this study. It must also be emphasized that the methods used to build the survey aimed to elicit, through focus group interviews, *salient beliefs* about the consumption of wild food and store food. This was done using very general elicitation questions during the focus group process. Therefore, if contaminants was not brought up by participants, it was not

Table 6. Logistic regression model predicting intention to eat wild food 3 times a week or more over the next month in Nain, Labrador (n = 244)

Variables	Parameter estimate	Standard error	OR	$CI_{95\%}$	p
Perceived behavioural control	2.67	0.37	14.44	6.95–29.97	< .0001
Behavioural beliefs	1.53	0.49	4.62	1.76–12.16	< .0004
Personal normative belief	1.51	0.43	4.53	1.96–10.43	< .0001

OR = Odds ratio; $CI_{95\%}$ = 95% Confidence interval

Table 7. Multiple regression model predicting of intention to eat store food (SF) every day over the next month (n = 244)

Constructs of Triandis' theory of interpersonal behaviour, modified	Eating SF every day over the next month (n = 244)	
	B	R^2 adjusted
Perceived behavioural control	0.46**	
Role belief	0.09**	
Perceived behavioural norm	0.04**	
Self-efficacy (barriers/facilitating factors)	0.01*	0.60[1]

* $p < .01$; ** $p < .001$; To be included, a variable must add at least 1% of variance to the model

[1] For the behaviour to eat store food every day, 60% of the variance observed is explained by the 4 significant constructs

considered a salient concern and therefore not included as a specific question in the questionnaire (this protected the researcher from the situation of "suggesting" responses to the participants).

With this study, we aimed to go beyond asking people to agree with predetermined or preconceived statements about wild food consumption. Comments made regarding disadvantages of wild food in this study mainly concerned food poisoning from zoonoses in raw meat and botulism. Only four out of 288 mentions of advantages/disadvantages of wild food during our focus groups concerned contaminants (cadmium and PCBs). However, none of these mentions were expressed as barriers to wild food consumption. Participants were much more expressive of their fear of store foods in Labrador. Furthermore, participants had multiple opportunities to express their concerns during the test-retest phase also since, for each question, precise reasons for answering in one way or another were requested. Although we recognize that all methods have limits in what information they elicit, we believe that if concern for contaminants was an issue *when faced with the intention to eat wild food or not (as the question was posed in this survey)*, it would have come out more often in participants' responses.

Conclusions

This study addressed two identified gaps or challenges in the effective management and communications related to contaminants and traditional/wild food in the North. Additionally, it has provided a basis of understanding of diet related behaviour in a northern community. This is the second quantitative data of its kind in a region where significant influences to, and changes in, diet have been observed in the last few decades and appear to be continuing into the future. Some of these shifts in diet have significant health implications. These results are intended to help health and environment officials in managing contaminants and health issues and in planning promotion or prevention activities to effectively target specific groups based on specific diet-related behaviours. If the objective of health advice and advisories is to simply inform people of the potential human health effects of exposure to certain contaminants through the consumption of traditional/wild foods, general communication methods are most appropriate. However, if the desired effect is to change behaviour based on these results, planning an intervention based on changing the perception people have of how easy or difficult it is to increase or decrease their consumption of a certain traditional/wild food will have a greater chance of achieving the program goal. An example of this might be the hypothetical case of a recommendation to decrease consumption of a specific traditional/wild food that is met with non-compliance. The results of this study suggest that an argument based on the provision of health information alone would have little chance in changing behaviour if this traditional/wild food was available for free through sharing networks or other sources in the community (i.e. people do not choose their food solely on the basis of their value to health). The issue of ease of access would need to be considered in the development of the intervention strategy or release of health advice and expected outcomes.

Results on the determinants of food choice in Kuujjuaq, were very similar to results for Nain, Labrador (Table 5). This may suggest that implementation of intervention and promotion programs related to wild foods and contaminants in the Canadian North could take a similar form in many regions (results here are from two Inuit regions only and application to other Aboriginal groups must be evaluated) as ease of access was an important determinant of wild food use in both regions. Data also suggest that questions used in both survey tools were very similar and support our hypothesis that a core set of questions could be used across the Canadian North. Both questionnaires used in Kuujjuaq (Nunavik) and

Table 8. Comparison of results between Kuujjuaq (Nunavik) and Nain (Labrador) of the significant determinants[1] of intention to eat traditional/wild food and store food reported in each community

	Kuujjuaq (Nunavik)		Nain (Labrador)	
Determinants of intention	Traditional Inuit Food[2]	Store-Bought Food[2]	Wild Food[2]	Store Food[2]
	PBC	PNB	PBC	PBC
	AFF	AFF	BB	RB
	PNB	PBC	PNB	PBN
	AACT	HAB		SE
	HAB	Taste		
		SE		

[1] In order of decreasing importance; [2] Different terms were used in the different regions (traditional Inuit food and wild food are the same thing, and store-bought food and store food are the same thing)

PBC = Perceived behavioural control; AFF = Affect; PNB = Personal normative belief; AACT = Attitude; HAB = Habit; Taste; SE = Self-efficacy; BB = Behavioural beliefs; RB = Role beliefs; PBN = Perceived behavioural norm

Nain (Labrador) are included in appendix A. As only qualitative data is available for Barrow (Alaska), we can not compare our questionnaires with our work from that region at this time.

Expected Completion Date

This project is now complete.

Acknowledgments

We would like to thank the Labrador Inuit Health Commission and Labrador Inuit Association for their support and assistance. We are also most grateful to our interviewers and the population of Nain for their active participation in this project.

References

Borré, K.S. 1994. The healing power of the seal: The meaning of Inuit health practice and belief. *Arctic Anthropology*, 31(1):1–15.

Borré, K. 1991. Seal Blood, Inuit Blood and Diet: A Biocultural Model of Physiology and Cultural Identity. *Medical Anthropology Quarterly*, 5(1):48–62.

Cronbach, L.J. 1951. Coefficient Alpha and the Internal Structure of Tests. Psychometrika, 16:297–334.

Dewailly, É. et al. 1998. The Eco-Researach Avativut/ Ilusivut Research Program, Final report presented to the Tri-Council Eco-Research Program. Institute for Risk Research, Waterloo and Québec Public Health Centre, Beauport. 114 pp.

Dewailly, É., P. Ayotte, C. Blanchet, J. Grondin, S. Bruneau, B. Holub, and G. Carrier. 1996. Weighing contaminant risks and nutrient benefits of country food in Nunavik. Arctic Medical Research, 55(Suppl. 1):13–19.

Egede, I. 1995. Inuit food and Inuit health: Contaminants in perspective. In: Inuit Circumpolar Conference, 7th General Assembly, Panel of Environmental Contamination, July 27, 1995.

Furgal, C., S. Bernier, G. Godin, S. Gingras, D. Laverdière, J. Grondin, and É. Dewailly. 2001. Decision-making and diet in the North: Balancing the Physical, Economic and Social Components (Year 2). *Synopsis of Research Conducted under the 2000–2001 Northern Contaminants Program*, (Ed. Sarah Kalhok), 42–53.

Gagné, C. and G. Godin. 1999. Les théories sociales cognitives: Guide pour la mesure des variables et le développement de questionnaire. Québec: Université Laval.

Kleinbaum, D.G., L.L. Kupper, and K.E. Muller. 1988. *Applied Regression Analysis and Other Multivariable Methods*. Boston: PWS-KENT Publishing Company.

Miles, M.D. and A.M. Huberman. 1984. Qualitative Data Analysis: A Source Book of New Methods. Beverly Hills, California: Sage Publications.

Patton, M.Q. 1990. Qualitative Evaluation and Research Methods. Sage Publications: Newbury Park, California.

Santé Québec. 1992–1995. A health Profile of the Inuit: A report of the Santé Québec Health Survey among the Inuit of Nunavik, Volumes 1–3. Québec: Santé Québec.

Shroutte, P.E. and J.L. Fleiss. 1979. Intraclass correlations: Uses in assessing rater reliability. Psychological Bulletin, 86:420–428.

Statistical Analysis Systems Institute Inc. 1999. *The SAS System for Windows.* 8.00 Edition. Vol. NC27513. Cary, USA.

Tesch, R. 1990. Qualitative Research: Analysis, Types and Software Tools. New York, New York: Falmer.

Triandis, H.C. 1980. Values, attitudes and interpersonal behaviour. In M.M. Page (Ed.), *Nebraska Symposium on Motivation, Beliefs, Attitudes and Values,* 1:195–259. Lincoln, NE: University of Nebraska.

Wenzel, G.W. 1986. Canadian Inuit in a Mixed Economy: Thoughts of Seals, Snowmobiles and Animal Rights. *Native Studies Review,* 2(1):69–82.

Wheatley, M.A. and B. Wheatley. 1981. The effects of eating habits on mercury levels among Inuit residents of Sugluk, P.Q. *Études/Inuit/Studies,* 5(1):27–43.

Appendix A:

Food Choice Questionnaires Used in Nain (Labrador) and Kuujjuaq (Nunavik)

Food Choices in Nain

Survey Introduction

This short survey is a collection of personal opinions and attitudes towards STORE (MARKET) FOODS and WILD FOODS.

By STORE FOOD, we mean any food produced outside of the region (like canned food, meat, fruit, vegetables, pasta, rice and other staples), including ingredients to make panitsiak, food eaten in restaurants (hotel, Jenkins, other restaurants out of town) and take-out food.

By WILD FOOD, we mean all plants and animals (from land and water), and includes resources that you get from other communities (example: wild food sent by friends or relatives from outside of Nain).

For each question or statement, more than one answer is offered. I will read the question and the answers. You tell me which answer is the one that best describes what you think or feel at this moment. Here is an example:

"WILD FOOD is good for your body". Do you:

INTERVIEWER: Read all answers and check only one box (√)

Totally disagree	Disagree	Neither agree/ disagree	Agree	Totally agree
☐	☐	☐	☑	☐

Remember: THERE ARE NO RIGHT NOR WRONG ANSWERS.
THIS IS NOT A NUTRITION SURVEY. PLEASE ANSWER AS TRUTHFULLY AS POSSIBLE ACCORDING TO WHAT YOU THINK AT THIS MOMENT.

Date of interview: /_____/_____/_____/
Month Day Year

Start of interview (time): /_____:_____/ End of interview: /_____:_____/
Hour Minutes Hour Minutes

Name of interviewer: /_____/

Place of interview (home, workplace, LIA office, specify other place): /_____/

Wild Food

1. How often do you usually eat WILD FOOD?

- Never ☐ ➪ Why not? _____
- Less than once a month ☐ _____
- 1–3 times a month ☐ _____
- 1–3 times a week ☐
- 4–6 times a week ☐
- Every day ☐

2. Last week, how many times did you eat WILD FOOD?

- 0 times ☐ ➪ Why not? _____
- 1–3 times ☐ _____
- 4–6 times ☐ _____
- Every day ☐

3. Did you eat WILD FOOD yesterday?

- Yes (write down all foods eaten) ☐ ➪ What did you eat? _____
- No ☐ _____
- _____
- _____

4. Where do you usually eat WILD FOOD and how often?

	N/A	Rarely/never	Sometimes	Often	Most of the time
a) At home (where you live presently)		☐	☐	☐	☐
b) At friends' homes		☐	☐	☐	☐
c) At parent's/relative's homes	☐	☐	☐	☐	☐
d) At camp (out on the land)		☐	☐	☐	☐
e) Other: (_____ write down name of place)		☐	☐	☐	☐

5. Over the next month, is it possible for you to eat WILD FOOD 3 times a week or more?

No	Probably not	Maybe/ Maybe not	Probably	Yes
☐	☐	☐	☐	☐

6. How would you feel about eating WILD FOOD 3 times a week or more over the next month?

	No	Probably not	Maybe/ Maybe not	Probably	Yes
a) Would you be satisfied?	☐	☐	☐	☐	☐
b) Would you get tired or sick of it?	☐	☐	☐	☐	☐
c) Would you be happy about it?	☐	☐	☐	☐	☐

7. "I feel I should eat WILD FOOD 3 times a week or more as part of my values". Do you:

Totally disagree?	Disagree?	Neither agree or disagree?	Agree?	Totally agree?
☐	☐	☐	☐	☐

8. If you ate WILD FOOD 3 times a week or more over the next month, do you think it would:

	No	Probably not	Maybe/ Maybe not	Probably	Yes
a) Be the healthiest thing for you?	☐	☐	☐	☐	☐
b) Save you lots of money?	☐	☐	☐	☐	☐
c) Make you stronger than eating STORE FOOD?	☐	☐	☐	☐	☐
d) Increase your risk of getting food poisoning?	☐	☐	☐	☐	☐
e) Make you feel better?	☐	☐	☐	☐	☐

9. Over the next month, do you plan on eating WILD FOOD 3 times a week or more?

No	Probably not	Maybe/ Maybe not	Probably	Yes
☐	☐	☐	☐	☐

10. How easy would it be for you to eat WILD FOOD 3 times a week or more over the next month?

Very Hard	Hard	N/either	Easy	Very easy
☐	☐	☐	☐	☐

11. "I feel that a person my age should eat WILD FOOD 3 times a week or more". Do you:

Totally disagree?	Disagree?	N/either agree or disagree?	Agree?	Totally agree?
☐	☐	☐	☐	☐

12. In your community, how many people, do you think, eat WILD FOOD 3 times a week or more?

0% None	25% A few	50% About half	75% Most	100% Everyone
☐	☐	☐	☐	☐

13. If you ate WILD FOOD 3 times a week or more, over the next month, would it be:

a)	Not tasty at all?	Not tasty?	N/either?	Tasty?	Very tasty?
	☐	☐	☐	☐	☐
b)	Very unsatisfying?	Unsatisfying?	N/either?	Satisfying?	Very satisfying?
	☐	☐	☐	☐	☐
c)	Very bad?	Bad?	N/either?	Good?	Very good?
	☐	☐	☐	☐	☐
d)	Very unhealthy?	Unhealthy?	N/either?	Healthy?	Very healthy?
	☐	☐	☐	☐	☐
e)	Very unsafe?	Unsafe?	N/either?	Safe?	Very safe?
	☐	☐	☐	☐	☐

14. "As a Labradorimiuk, I feel I should eat WILD FOOD 3 times a week or more". Do you:

Totally disagree?	Disagree?	N/either agree or disagree?	Agree?	Totally agree?
☐	☐	☐	☐	☐

15. If you wanted to, could you eat WILD FOOD 3 times a week or more, over the next month?

No	Probably not	Maybe/ Maybe not	Probably	Yes
☐	☐	☐	☐	☐

16. "I feel I should eat WILD FOOD 3 times a week or more because it's part of who I am". Do you:

Totally disagree?	Disagree?	N/either agree or disagree?	Agree?	Totally agree?
☐	☐	☐	☐	☐

17. Over the next month, will you eat WILD FOOD 3 times a week or more?

No	Probably not	Maybe/ Maybe not	Probably	Yes
☐	☐	☐	☐	☐

18. Would you eat WILD FOOD 3 times a week or more, over the next month:

		No	Probably not	Maybe/ Maybe not	Probably	Yes
a)	If it was prepared in a new or different way (new recipes)?	☐	☐	☐	☐	☐
b)	If family members gave it to you?	☐	☐	☐	☐	☐
c)	If you had more time?	☐	☐	☐	☐	☐
d)	If you had some in your freezer/stocked up?	☐	☐	☐	☐	☐
e)	If there was a community freezer in Nain?	☐	☐	☐	☐	☐
f)	If you could buy it in a local store?	☐	☐	☐	☐	☐
g)	If it was cut up/packaged in small pieces in your freezer?	☐	☐	☐	☐	☐
h)	If it was already cooked/prepared for you at home?	☐	☐	☐	☐	☐
i)	If you could have it all ready over at someone's place?	☐	☐	☐	☐	☐
j)	Even if it was the same kind every time?	☐	☐	☐	☐	☐

19. Over the next month, what would stop/prevent you from eating WILD FOOD 3 times a week or more?

	No	Probably not	Maybe/ Maybe not	Probably	Yes
a) If you had to ask around for it, would that stop you?	☐	☐	☐	☐	☐
b) If you had to hunt/fish for it, would that stop you?	☐	☐	☐	☐	☐
c) If you had to work (and had less time), would that stop you?	☐	☐	☐	☐	☐
d) If you had no money to go fishing/hunting, would that stop you?	☐	☐	☐	☐	☐
e) If it made you gain weight, would that stop you?	☐	☐	☐	☐	☐
f) If you had no equipment (boat, skidoo), would that stop you ?	☐	☐	☐	☐	☐
g) If you had to travel far to get it, would that stop you?	☐	☐	☐	☐	☐

20. On a scale of 1 to 10, how do you like the taste of WILD FOOD? (circle only one number)

Not at all — Like very much

0 1 2 3 4 5 6 7 8 9 10

21. In your opinion, would the following people approve or disapprove of you eating WILD FOOD 3 times a week or more over the next month?

	N/A	Totally disapprove	Disapprove	N/either	Approve	Totally approve
a) Elders	☐	☐	☐	☐	☐	☐
b) Health professionals (doctor/ nurse/nutritionist)	☐	☐	☐	☐	☐	☐
c) Your parents	☐	☐	☐	☐	☐	☐
d) Your children	☐	☐	☐	☐	☐	☐
e) Your husband/wife/partner	☐	☐	☐	☐	☐	☐

22. "As a parent, I feel that I should eat WILD FOOD 3 times a week or more", do you:

N/A	Totally disagree?	Disagree?	N/either agree or disagree?	Agree?	Totally agree?
☐	☐	☐	☐	☐	☐

INTERVIEWER: NOW LET'S TALK ABOUT STORE FOOD ONLY

Store Food

23. How often do you usually eat STORE FOOD?

- Never ☐ ➪ Why not? _____
- Less than once a month ☐ _____
- 1–3 times a month ☐ _____
- 1–3 times a week ☐
- 4–6 times a week ☐
- Every day ☐

24. Last week, how many times did you eat STORE FOOD?

- 0 times ☐ ➪ Why not? _____
- 1–3 times ☐ _____
- 4–6 times ☐ _____
- Every day ☐

25. Did you eat STORE FOOD yesterday?

- Yes (write down all foods eaten) ☐ ➪ What did you eat? _____
- No ☐ _____
_____

26. Where do you usually eat STORE FOOD and how often?

		N/A	Rarely/never	Sometimes	Often	Most of the time
a)	At home (where you live presently)	☐	☐	☐	☐	☐
b)	At friends' homes	☐	☐	☐	☐	☐
c)	At parent's/relative's homes	☐	☐	☐	☐	☐
d)	At camp (out on the land)	☐	☐	☐	☐	☐
e)	Hotel/take-out	☐	☐	☐	☐	☐
f)	Other: (_____ write down name of place)	☐	☐	☐	☐	☐

27. "Personally, I feel that I should eat STORE FOOD every day?". Do you:

Totally disagree?	Disagree?	N/either agree or disagree?	Agree?	Totally agree?
☐	☐	☐	☐	☐

28. How would you feel about eating STORE FOOD every day over the next month?

		No	Probably not	Maybe/ Maybe not	Probably	Yes
a)	Would you be satisfied?	☐	☐	☐	☐	☐
b)	Would you get tired or sick of it?	☐	☐	☐	☐	☐
c)	Would you be happy about it?	☐	☐	☐	☐	☐

29. If you ate STORE FOOD every day over the next month, do you think it would:

	No	Probably not	Maybe/ Maybe not	Probably	Yes
a) Be good for your health?	☐	☐	☐	☐	☐
b) Be very expensive?	☐	☐	☐	☐	☐
c) Save you time?	☐	☐	☐	☐	☐
d) Taste good?	☐	☐	☐	☐	☐
e) Make you full/be fulfilling?	☐	☐	☐	☐	☐
f) Increase your risk of getting food poisoning?	☐	☐	☐	☐	☐
g) Be different?	☐	☐	☐	☐	☐

30. "As a Labradorimiuk, I feel I should eat STORE FOOD every day". Do you:

Totally disagree?	Disagree?	N/either agree or disagree?	Agree?	Totally agree?
☐	☐	☐	☐	☐

31. If you ate STORE FOOD every day, over the next month, would it be:

a)	Not tasty at all?	Not tasty?	N/either?	Tasty?	Very tasty?
	☐	☐	☐	☐	☐
b)	Very bad?	Bad?	N/either?	Good?	Very good?
	☐	☐	☐	☐	☐
c)	Very unsatisfying?	Unsatisfying?	N/either?	Satisfying?	Very satisfying?
	☐	☐	☐	☐	☐
d)	Very unhealthy?	Unhealthy?	N/either?	Healthy?	Very Healthy?
	☐	☐	☐	☐	☐
e)	Very unsafe?	Unsafe?	N/either?	Safe?	Very safe?
	☐	☐	☐	☐	☐

32. Over the next month, will you eat STORE FOOD every day?

No	Probably not	Maybe/ Maybe not	Probably	Yes
☐	☐	☐	☐	☐

33. In your community, how many people, do you think, eat STORE FOOD every day?

0% None	25% A few	50% About half	75% Most	100% Everyone
☐	☐	☐	☐	☐

34. In your opinion, would the following people approve or disapprove of you eating STORE FOOD every day over the next month?

	N/A	Totally disapprove	Disapprove	N/either	Approve	Totally approve
a) Your kids?	☐	☐	☐	☐	☐	☐
b) Your parents?	☐	☐	☐	☐	☐	☐
c) Your husband/wife/partner?	☐	☐	☐	☐	☐	☐

	No	Probably not	Maybe/ maybe not		Probably	Yes
d) Does TV influence you to eat more SF?	☐	☐	☐	☐	☐	☐

35. "I feel that a person my age should eat STORE FOOD every day". Do you:

Totally disagree?	Disagree?	N/either agree or disagree?	Agree?	Totally agree?
☐	☐	☐	☐	☐

36. If you wanted to, could you eat STORE FOOD every day, over the next month?

No	Probably not	Maybe/ Maybe not	Probably	Yes
☐	☐	☐	☐	☐

37. Would you eat STORE FOOD every day, over the next month:

	No	Probably not	Maybe/ Maybe not	Probably	Yes
a) If people shared it with you?	☐	☐	☐	☐	☐
b) If you had it in your home or freezer?	☐	☐	☐	☐	☐
c) If you could order it from Murray's?	☐	☐	☐	☐	☐
d) If it was cheaper?	☐	☐	☐	☐	☐

38. Over the next month, what would stop/prevent you from eating STORE FOOD every day?

	No	Probably not	Maybe/ Maybe not	Probably	Yes
a) If it was expensive, would that stop you?	☐	☐	☐	☐	☐
b) If there were less choices (less variety)	☐	☐	☐	☐	☐
c) If it was not fresh/outdated, would that stop you?	☐	☐	☐	☐	☐
d) If it was too long to cook/prepare?	☐	☐	☐	☐	☐
e) If it was not in stores & restaurants locally?	☐	☐	☐	☐	☐
f) If there was more WILD FOOD?	☐	☐	☐	☐	☐
g) If it made you gain weight, would that stop you?	☐	☐	☐	☐	☐

39. How easy would it be for you to eat STORE FOOD every day, over the next month?

Very hard	Hard	N/either	Easy	Very easy
☐	☐	☐	☐	☐

40. "i feel I should eat STORE FOOD every day because it's part of who I am". Do you:

Totally disagree?	Disagree?	N/either agree or disagree?	Agree?	Totally agree?
☐	☐	☐	☐	☐

41. Over the next month, do you plan on eating STORE FOOD every day?

No	Probably not	Maybe/ Maybe not	Probably	Yes
☐	☐	☐	☐	☐

42. Over the next month, is it possible for you to eat STORE FOOD every day?

No	Probably not	Maybe/ Maybe not	Probably	Yes
☐	☐	☐	☐	☐

43. "As a parent, I feel that I should eat STORE FOOD every day", do you:

N/A	Totally disagree?	Disagree?	N/either agree or disagree?	Agree?	Totally agree?
	☐	☐	☐	☐	☐

44. On a scale of 1 to 10, how do you like the taste of STORE FOOD? (circle only one number)

Not at all — Like very much

0 1 2 3 4 5 6 7 8 9 10

45. Can you tell me anything else about why you eat WILD FOOD? (other reason/influence?)

46. Can you tell me anything else about why you eat STORE FOOD? (other reason/influence?)

Socio-economic Information

SE1. Gender: Male ☐ Female ☐

SE2. What is your date of birth? /_____/_____/_____/
Day Month Year

SE3. What grade did you complete in school?
/_____/

SE4. ***Teens (or adults still in school): What grade are you in school?***
/_____/

SE5. What do you do for a living (work)?

..... Unemployed ☐

a) **Is it:**..... part time? ☐ **or** full time? ☐
b) **Is it:**..... seasonal? ☐ **or** year round? ☐

SE7. ***Teens: What do your parents/guardians do for a living?***

1) Mother/guardian: ..... Unemployed ☐

a) **Is it:**..... part time? ☐ **or** full time? ☐
b) **Is it:**..... seasonal? ☐ **or** year round? ☐

2) Father/guardian: ..... Unemployed ☐

a) **Is it:**..... part time? ☐ **or** full time? ☐
b) **Is it:**..... seasonal? ☐ **or** year round? ☐

SE8. How many children (under 18) besides yourself live in your home?
/_____/ (number)

SE9. How many adults (over 18) besides yourself live in your home?
/_____/ (number)

SE10. How many of these people living in your home have a job?

INTERVIEWER: Write what each person does and if they are part-time or full-time and year round or seasonal

Example:
1. My sister: waitress, part-time, year round
2. My cousin: hunter, full-time, seasonal

1. _____ **a) Is it:** part time? ☐ **or** full time? ☐
b) Is it: seasonal? ☐ **or** year round? ☐

2. _____ **a) Is it:** part time? ☐ **or** full time? ☐
b) Is it: seasonal? ☐ **or** year round? ☐

3. _____ **a) Is it:** part time? ☐ **or** full time? ☐
b) Is it: seasonal? ☐ **or** year round? ☐

4. _____ **a) Is it:** part time? ☐ **or** full time? ☐
b) Is it: seasonal? ☐ **or** year round? ☐

5. _____ **a) Is it:** part time? ☐ **or** full time? ☐
b) Is it: seasonal? ☐ **or** year round? ☐

SE11A. Do you hunt or fish?

Yes ☐ ➪ How often?

Spring _____ (number)
Summer _____ (number)
Fall _____ (number)
No ☐ Winter _____ (number)

(Interviewer: Don't take vague, general answers for an answer, like: «seasonally», «once in a while», «when I get the chance». We want an average or number of times. E.g. 3 times in winter, never in summer, every weekend in Fall, once a month in Spring, etc.)

SE11B. Do you have a hunter/fisherman in your family that hunts/fishes for you or shares with you?

Yes ☐ No ☐

SE12. *Teens: Do your parents/guardians hunt or fish?*

Yes ☐ ➪ How often?

Spring _____ (number)
Summer _____ (number)
Fall _____ (number)
No ☐ Winter _____ (number)

(Interviewer: Don't take vague, general answers for an answer, like: «seasonally», «once in a while», «when I get the chance». We want an average or number of times. E.g. 3 times in winter, never in summer, every weekend in Fall, once a month in Spring, etc.)

Thank you very much for your help.

(Pay and have him/her sign the receipt. Before leaving, check that all the questions were answered.)

The interview was conducted in: English ☐ Inuktituut ☐ Both ☐

Food Choices in Nunavik

Survey Introduction

This short survey is a collection of opinions and attitudes towards IMPORTED FOOD (QALLUNAAT FOOD) and TRADITIONAL INUIT FOOD.

By IMPORTED FOOD, we mean any food produced outside of the region and imported into the North (like meat, fruit, vegetables, pasta, rice and other staples), including ingredients to make bannick, food eaten in restaurants (JD's, Kuujjuaq Inn, Quick Stop, etc.) and take-out food.

By TRADITIONAL INUIT FOOD, we mean all regional plants and animals (from the land and the water), including resources that you get from other communities.

For each question or statement, more than one answer is offered. I will read the question and the answers. You tell me which answer is the best one that describes what you think or feel at this moment. Here is an example:

"TRADITIONAL INUIT FOOD is good for your body". Do you:

INTERVIEWER: Read all answers and check only one box (√)

Totally disagree	Disagree	Neither agree/ disagree	Agree	Totally agree
☐	☐	☐	☑	☐

Remember: THERE ARE NO RIGHT NOR WRONG ANSWERS.
THIS IS NOT A NUTRITION SURVEY. PLEASE ANSWER AS TRUTHFULLY AS POSSIBLE ACCORDING TO WHAT YOU THINK AT THIS MOMENT.

Some questions may sound the same, but it is important to answer every one of them.

Date of interview: /_____/_____/_____/
Month Day Year

Start of interview (time): /_____:_____/ End of interview: /_____:_____/

ID number: /_____:_____/

Name of interviewer: /_____/

Place of interview (home, workplace, LIA office, specify other place): /_____/

Traditional Inuit Food (TIF)

1. How often do you usually eat TRADITIONAL INUIT FOOD?

- Never ☐ ➪ IF NEVER, GO TO QUESTION 6, PAGE 3
- Less than once a month ☐
- 1–3 times a month ☐
- 1–3 times a week ☐
- 4–6 times a week ☐
- Once or more per day ☐

2. Where do you usually eat TRADITIONAL INUIT FOOD and how often?

		Rarely/never	Sometimes	Often	Most of the time
a)	At home (your own house)	☐	☐	☐	☐
b)	At your friends' house	☐	☐	☐	☐
c)	At parents house	☐	☐	☐	☐
d)	At camp	☐	☐	☐	☐
e)	Other: (_____ write down name of place)	☐	☐	☐	☐

3. Last week, how many times did you eat TRADITIONAL INUIT FOOD?

- 0 times ☐
- 1–3 times ☐
- 4–6 times ☐
- Every day ☐

4. Yesterday, did you eat TRADITIONAL INUIT FOOD?

- No ☐
- Yes ☐ ➪ What did you eat? _____

5. How often do you get TRADITIONAL INUIT FOOD from the community freezer (Hunter Support)?

- Rarely/Never ☐
- Sometimes ☐
- Often ☐
- Most of the time ☐

6. Over the next month, if you ate TRADITIONAL INUIT FOOD 3 times a week or more, would you:

		No	Probably not	Maybe/ Maybe not	Probably	Yes
a)	Like it?	☐	☐	☐	☐	☐
b)	Get tired of it?	☐	☐	☐	☐	☐

7. As part of being Inuk, do you think you should eat TRADITIONAL INUIT FOOD?

Totally disagree?	Disagree?	N/either agree or disagree?	Agree?	Totally agree?
☐	☐	☐	☐	☐

8. Over the next month, if you ate TRADITIONAL INUIT FOOD 3 times/week or more, do you believe it would:

	No	Probably not	Maybe/ Maybe not	Probably	Yes
a) Be very good for your health?	☐	☐	☐	☐	☐
b) Be less expensive ($$) than IMPORTED FOOD?	☐	☐	☐	☐	☐
c) Give you more strength and energy than IMPORTED FOOD?	☐	☐	☐	☐	☐
d) Keep you full longer than IMPORTED FOOD?	☐	☐	☐	☐	☐
e) Make you feel sick (heartburn, upset stomach)?	☐	☐	☐	☐	☐
f) Keep you warm?	☐	☐	☐	☐	☐

9. Over the next month, do you plan to eat TRADITIONAL INUIT FOOD 3 times a week or more?

No	Probably not	Maybe/ Maybe not	Probably	Yes
☐	☐	☐	☐	☐

10. Over the next month, how easy would it be for you to eat TRADITIONAL INUIT FOOD 3 times/week or more?

Very Easy	Easy	Neither	Hard	Very Hard
☐	☐	☐	☐	☐

11. Do you think you should eat TRADITIONAL INUIT FOOD because you grew up with it?

Totally disagree?	Disagree?	N/either agree or disagree?	Agree?	Totally agree?
☐	☐	☐	☐	☐

12. Over the next month, is it possible for you to eat TRADITIONAL INUIT FOOD 3 times a week or more?

No	Probably not	Maybe/ Maybe not	Probably	Yes
☐	☐	☐	☐	☐

13. Over the next month, if you ate TRADITIONAL INUIT FOOD 3 times a week or more, would it be:

Very pleasant	Pleasant	Neither	Unpleasant	Very unpleasant
☐	☐	☐	☐	☐
Very good	Good	Neither	Bad	Very bad
☐	☐	☐	☐	☐
Very healthy	Healthy	Neither	Unhealthy	Very unhealthy
☐	☐	☐	☐	☐
Very tasty	Tasty	Neither	Not tasty	Not tasty at all
☐	☐	☐	☐	☐
Very satisfying	Satisfying	Neither	Unsatisfying	Very unsatisfying
☐	☐	☐	☐	☐
Very safe	Safe	Neither	Unsafe	Very unsafe
☐	☐	☐	☐	☐

14. In your community, how often do you think the following people eat TRADITIONAL INUIT FOOD?

	Rarely/never	Sometimes	Often	Most of the time
a) Elders	☐	☐	☐	☐
b) People your own age	☐	☐	☐	☐
c) People with no income	☐	☐	☐	☐
d) People who fish and hunt	☐	☐	☐	☐
e) Inuit	☐	☐	☐	☐
f) People who work full-time	☐	☐	☐	☐

15. Over the next month, if you wanted to, could you eat TRADITIONAL INUIT FOOD 3 times a week or more?

No	Probably not	Maybe/ Maybe not	Probably	Yes
☐	☐	☐	☐	☐

16. Over the next month, will you eat TRADITIONAL INUIT FOOD 3 times a week or more?

No	Probably not	Maybe/ Maybe not	Probably	Yes
☐	☐	☐	☐	☐

17. Over the next month, would you eat TRADITIONAL INUIT FOOD 3 times a week or more:

	No	Probably not	Maybe/ Maybe not	Probably	Yes
a) If it was prepared in a new way (e.g. new recipes)?	☐	☐	☐	☐	☐
b) If someone shared it with you?	☐	☐	☐	☐	☐
c) If you got some from other communities?	☐	☐	☐	☐	☐
d) If there was some at the community freezer?	☐	☐	☐	☐	☐
e) If someone went hunting/fishing for you?	☐	☐	☐	☐	☐

18. Over the next month, what would stop you from eating TRADITIONAL INUIT FOOD 3 times/week or more?

		No	Probably not	Maybe/ Maybe not	Probably	Yes
a)	If you had to pay for it	☐	☐	☐	☐	☐
b)	If you had to hunt/fish for it	☐	☐	☐	☐	☐
c)	If it was too expensive	☐	☐	☐	☐	☐
d)	If you had no money to go fishing/hunting	☐	☐	☐	☐	☐
e)	If you had to travel far to get it	☐	☐	☐	☐	☐
f)	If it was not available that season	☐	☐	☐	☐	☐
g)	If it made you gain weight	☐	☐	☐	☐	☐

19. Do the following people tell you that you should eat TRADITIONAL INUIT FOOD?

		Rarely/Never	Sometimes	Often	Most of the time	N/A
a)	Elders	☐	☐	☐	☐	☐
b)	Health professionals (doctor/nurse/dentist)	☐	☐	☐	☐	☐
c)	Your parents	☐	☐	☐	☐	☐
d)	Friends	☐	☐	☐	☐	☐
e)	Wife/husband/significant other/partner	☐	☐	☐	☐	☐
f)	Your children	☐	☐	☐	☐	☐

20. On a scale of 1 to 10, how do you like the taste of TRADITIONAL INUIT FOOD?

Not at all — Like very much

0 1 2 3 4 5 6 7 8 9 10

NOW LET'S TALK ABOUT IMPORTED (QALLUNAAT) FOOD

Imported Food (IF)

21. How often do you usually eat IMPORTED FOOD?

- Never ☐ ➪ IF NEVER, GO TO QUESTION 25, PAGE 7
- Less than once a month ☐
- 1–3 times a month ☐
- 1–3 times a week ☐
- 4–6 times a week ☐
- Once or more per day ☐

22. Where do you usually eat IMPORTED FOOD and how often?

		Rarely/never	Sometimes	Often	Most of the time
a)	At home	☐	☐	☐	☐
b)	At your friends's place	☐	☐	☐	☐
c)	At your parents house	☐	☐	☐	☐
d)	At camp	☐	☐	☐	☐
e)	At a restaurant (JD's, Kuujjuaq Inn, Quickstop)	☐	☐	☐	☐
f)	Other: (_____write down name of place)	☐	☐	☐	☐

23. Last week, how many times did you eat IMPORTED FOOD?

- 0 times ☐
- 1–3 times ☐
- 4–6 times ☐
- Every day ☐

24. Yesterday, did you eat IMPORTED FOOD?

- No ☐
- Yes ☐ ➪ What did you eat? _____

25. As part of being Inuk, do you think you should eat IMPORTED FOOD every day?

Totally disagree?	Disagree?	N/either agree or disagree?	Agree?	Totally agree?
☐	☐	☐	☐	☐

26. Over the next month, if you ate IMPORTED FOOD every day, would you:

		No	Probably not	Maybe/ Maybe not	Probably	Yes
a)	Like it?	☐	☐	☐	☐	☐
b)	Get tired of it?	☐	☐	☐	☐	☐
c)	Crave TRADITIONAL INUIT FOOD?	☐	☐	☐	☐	☐

27. Over the next month, if you ate IMPORTED FOOD every day, do you believe it would:

	No	Probably not	Maybe/ Maybe not	Probably	Yes
a) Be bad for your health?	☐	☐	☐	☐	☐
b) Be more expensive than TRADITIONAL INUIT FOOD?	☐	☐	☐	☐	☐
c) Take less time to prepare than TRADITIONAL INUIT FOOD	☐	☐	☐	☐	☐
d) Be easier to prepare than TRADITIONAL INUIT FOOD?	☐	☐	☐	☐	☐
e) Keep you as full as TRADITIONAL INUIT FOOD?	☐	☐	☐	☐	☐
f) Make you feel sick (heartburn, upset stomach)?	☐	☐	☐	☐	☐
g) Keep you warm?	☐	☐	☐	☐	☐

28. Over the next month, will you eat IMPORTED FOOD every day?

No	Probably not	Maybe/ Maybe not	Probably	Yes
☐	☐	☐	☐	☐

29. Over the next month, if you wanted to, could you eat IMPORTED FOOD every day?

No	Probably not	Maybe/ Maybe not	Probably	Yes
☐	☐	☐	☐	☐

30. Personally, do you believe in eating IMPORTED FOOD every day?

No	Probably not	Maybe/ Maybe not	Probably	Yes
☐	☐	☐	☐	☐

31. Over the next month, if you ate IMPORTED FOOD every day would it be:

Very pleasant	Pleasant	Neither	Unpleasant	Very unpleasant
☐	☐	☐	☐	☐
Very good	Good	Neither	Bad	Very bad
☐	☐	☐	☐	☐
Very healthy	Healthy	Neither	Unhealthy	Very unhealthy
☐	☐	☐	☐	☐
Very tasty	Tasty	Neither	Not tasty	Not tasty at all
☐	☐	☐	☐	☐
Very satistfying	Satisfying	Neither	Unsatisfying	Very unsatisfying
☐	☐	☐	☐	☐
Very safe	Safe	Neither	Unsafe	Very unsafe
☐	☐	☐	☐	☐

32. Do the following people tell you that you should eat IMPORTED FOOD?

	Rarely/never	Sometimes	Often	Most of the time	N/A
a) Friends	☐	☐	☐	☐	☐
b) Health professionals (doctor/nurse/dentist)	☐	☐	☐	☐	☐
c) Your parents	☐	☐	☐	☐	☐
d) Television commercials	☐	☐	☐	☐	☐
e) Husband/wife/significant other/partner	☐	☐	☐	☐	☐
f) Your children	☐	☐	☐	☐	☐

33. Over the next month, how easy would it be for you to eat IMPORTED FOOD every day?

Very easy	Easy	Neither	Hard	Very hard
☐	☐	☐	☐	☐

34. Over the next month, do you plan to eat IMPORTED FOOD every day?

No	Probably not	Maybe/ Maybe not	Probably	Yes
☐	☐	☐	☐	☐

35. In your community, how often do you think the following people eat IMPORTED FOOD?

	Rarely/never	Sometimes	Often	Most of the time
a) Parents	☐	☐	☐	☐
b) Elders	☐	☐	☐	☐
c) People that have an income	☐	☐	☐	☐
d) Youth (kids and teenagers)	☐	☐	☐	☐
e) Inuit	☐	☐	☐	☐
f) People your own age	☐	☐	☐	☐
g) People who work full-time	☐	☐	☐	☐

36. Over the next month, what would stop you from eating IMPORTED FOOD every day?

	No	Probably not	Maybe/ Maybe not	Probably	Yes
a) High cost	☐	☐	☐	☐	☐
b) If there were less choices (less variety)	☐	☐	☐	☐	☐
c) If it was not fresh/outdated	☐	☐	☐	☐	☐
d) If it was too long to cook/prepare	☐	☐	☐	☐	☐
e) If it was not in stores and restaurants	☐	☐	☐	☐	☐
f) If you had more TRADITIONAL INUIT FOOD	☐	☐	☐	☐	☐
g) If it made you gain weight	☐	☐	☐	☐	☐
h) Because it's not healthy	☐	☐	☐	☐	☐

37. On a scale of 1 to 10, how do you like the taste of IMPORTED FOOD?

Not at all — Like very much

0 1 2 3 4 5 6 7 8 9 10

38. What other reasons make you choose to eat TRADITIONAL INUIT FOOD OR IMPORTED FOOD?

Socio-economic Information

39. Gender: Male ☐ Female ☐

40. What is your date of birth? /_____/_____/_____/
Day Month Year

41. What grade did you complete in school?
/_____/

42. Teens: What grade are you in school?
/_____/

43. What do you do for a living (work)?
/_____/

Is it: part time? ☐ full time? ☐
Is it: seasonal? ☐ year round? ☐

44. What does your significant other (husband/wife) do for a living?
/_____/

Is it: part time? ☐ full time? ☐
Is it: seasonal? ☐ year round? ☐
Don't have a partner ☐

45. *Teens: What do your parents do for a living?*

a) Mother: /_____/
Is it: part time? ☐ full time? ☐
Is it: seasonal? ☐ year round? ☐
Don't have a mother ☐

a) Father: /_____/
Is it: part time? ☐ full time? ☐
Is it: seasonal? ☐ year round? ☐
Don't have a father ☐

46. How many children besides yourself live in your home?

/_____/ (number)

47. How many adults besides yourself live in your home?

/_____/ (number)

48. How many of these people living in your home have a job?

INTERVIEWER: Write what each person does and if they are part-time or full-time and year round or seasonal

Example:
1. My sister: waitress, part-time, year round
2. My cousin: hunter, full-time, seasonal

1. _____	**a) Is it:** part time? ☐	**or**	full time? ☐
	b) Is it: seasonal? ☐	**or**	year round? ☐
2. _____	**a) Is it:** part time? ☐	**or**	full time? ☐
	b) Is it: seasonal? ☐	**or**	year round? ☐
3. _____	**a) Is it:** part time? ☐	**or**	full time? ☐
	b) Is it: seasonal? ☐	**or**	year round? ☐
4. _____	**a) Is it:** part time? ☐	**or**	full time? ☐
	b) Is it: seasonal? ☐	**or**	year round? ☐
5. _____	**a) Is it:** part time? ☐	**or**	full time? ☐
	b) Is it: seasonal? ☐	**or**	year round? ☐

49. Do you hunt or fish? Yes ☐ No ☐ How often? /_____/

50. Teens: Do your parents hunt or fish? Yes ☐ No ☐ How often? /_____/

End of the interview.

Thank the participant. Pay him/her and have him/her sign the receipt.

Before leaving, check that all the questions were answered.

The interview was conducted in: English ☐ Inuktituut ☐ Both ☐

Completing CINE Data and Reports for Three Major Dietary Studies

Project leader

Harriet V. Kuhnlein, Centre for Indigenous Peoples' Nutrition and Environment (CINE), Macdonald Campus of McGill University, 21,111 Lakeshore Rd., Ste. Anne de Bellevue, Quebec, H9X 1R9; phone: (514) 398-7671; harriet.kuhnlein@mcgill.ca

Project team

Grace Egeland (CINE), Olivier Receveur (University of Montreal), Peter Berti (Path Canada).

Abstract

Data bases of nutrient composition for both traditional Arctic food and market food have been updated and compiled with all existing information from CINE and Health Canada nutrient laboratories. Dietary data for nutrient intake have been merged with these data for assessment of inadequacy of nutrients. The new Dietary Reference Intakes for protein and fat, as well as other nutrients, are still being completed by the National Academy of Sciences in cooperation with Health Canada. The data analyses are still incomplete, but will be finished by the end of this year.

Key Project Messages

The three major dietary studies completed by CINE in the Canadian Arctic are now being finalized with revision of data bases using the latest information from Health Canada for nutrient reference intakes. This project has involved extensive revision of nutrient and dietary intake data bases.

Objectives

1. To review and revise data bases of traditional food composition and market food composition in light of the new Health Canada dietary reference intakes requirements for food data bases.
2. To incorporate recent laboratory data into the traditional food composition data base.
3. To re-run the 24-hour recall dietary intake data for three studies incorporating the new dietary reference intakes.
4. To review and revise the extensive data bases for frequency and seasonality of food use.
5. To prepare the data, harmonized across the three studies, for a series of publications for the peer-reviewed literature.

Introduction

Extensive data were collected on nutrient and contaminant exposure in the three major cultural areas of the Canadian Arctic (Dene/Métis, Yukon First Nations and Inuit) by CINE in the last 10 years. More than 750 food samples were collected and analyzed during the course of these studies for analysis of a variety of nutrients. Resulting data were incorporated into a traditional food data base that can be used together with a market food data base for complex dietary data analysis. Considerable work remained to place this key information in the peer-reviewed literature (laboratory analysis of nutrients and compilation, update with new information from Health Canada on dietary data analysis, adjusting files for compatibility).

Activities

In 2002–2003

1. An arctic nutrient composition database was created that included all the food samples collected by CINE since 1987. Since its purpose was for nutrient intake analysis, a vast amount of time was required to complete, compile, search for substitutions, merge and assess variance in sample data for a total of 28 nutrients for approximately 200 food samples. Table 1 shows new nutrient composition data from CINE and

Table 1. New data for vitamins in traditional Arctic foods

Food sample										
Species and part	Preparation	n[a]	Mean retinol (μg)	Mean VitE (μg)[b]	n[c]	Mean VitB2 (mg)	Mean VitB6 (μg)	Mean folate (μg)	n[d]	Mean VitC (mg)
Arctic char, flesh	raw	2	41	nd[e]	2	0.16	607	70.2	5	1.2
Caribou, bone grease	boiled	1	27	nd	1	0.03	90	tr[f]	1	0.0
Caribou, bone marrow	aged	2	278	nd	na[g]	–	–	–	2	0.0
Caribou, bone marrow	raw	3	47	nd	na	–	–	–	2	0.0
Caribou, brain	roasted	2	5.8	nd	2	0.459	132	10.4	2	4.5
Caribou, meat	raw	2	72	nd	5	1.29	423	11.8	5	1.0
Grizzly bear, grease	boiled	1	107	nd	1	0.03	102	nd	1	0.0
Lake trout, flesh	raw	3	77	nd	2	0.15	526	70.2	na	–
Moose, liver	raw	1	4608	nd	1	6.51	575	268	1	22.0
Polar bear, meat	raw	1	508	915	1	0.42	192	7.45	na	–
Ringed seal, liver	raw	na	–	–	1	2.88	907	655	1	18.0
Ringed seal, meat	raw	na	–	–	na	–	–	–	2	0.0
Spruce sap	dried	na	–	–	1	0.12	nd	3.05	1	0.0
Walrus, blubber	aged	1	255	nd	na	–	–	–	na	–
Walrus, blubber	raw	3	99	nd	na	–	–	–	4	0.0
Walrus, liver	raw	1	4283	nd	4	2.54	1087	918	4	8.5
Walrus, meat	aged	na	–	–	1	0.59	191	3.40	na	–
Walrus, meat	raw	1	264	nd	1	0.34	131	9.10	na	–
Whitefish, flesh	dried	na	–	–	1	0.07	1007	21.9	1	0.0
White-winged scoter, flesh	raw	na	–	–	1	3.62	721	26.4	1	1.0

[a] N samples for VitA and VitE [b] alpha-tocopherol [c] N samples for VitB2, B6 and folate [d] N samples for VitC [e] Not detected [f] Trace [g] Not analyzed

Table 2a. Categories of supplements used by adults and teens in the three surveys

		Dene/Métis[a]	Yukon	Inuit
Supplement Category	N[b]	N recalls		
Vitamins/Minerals	25	26	63	29
Vitamins only	24	36	78	26
Minerals only	6	12	8	5
Cod liver oil	12	3	7	2
Unknown[c]	30	3	15	15

[a] Total N recalls: Dene/Métis = 1007, Yukon = 797, Inuit = 1758

[b] Number of types/brands mentioned within each category, in all 3 surveys

[c] Examples: ABC 1200, Adults, Essential, Nobites, Trophic, etc...

Table 2b. Categories of supplements used by Western Arctic children (total N recalls = 222)[d]

Supplement Category	N[b]	N recalls[d]
Vitamins/Minerals	–	–[e]
Vitamins only	8	49[e]
Minerals only	1	1
Cod liver oil	1	2

[d] Excluding repeat recalls in each season

[e] There are 34 recalls that had one of 3 supplements that could possibly be categorized under 'Vitamins/Minerals' or 'Vitamins only', the 3 supplements being Flintstones, Pokemon and Chewable

Health Canada laboratories that were incorporated into the final traditional food composition data.

2. Requirements of the new procedures for computing dietary assessments (IOM, 2000; Barr et al., 2002) were met by revising the data bases for both traditional and market food for folic acid (using dietary folate equivalents), vitamin E (using only mg alpha-tocopherol), and vitamin A (using retinol activity equivalents), selenium and manganese (Murphy, 2001).
3. Release of draft dietary reference intakes for protein, energy and carbohydrate (IOM, 2002) and other nutrients (IOM, 2001) were incorporated into dietary analysis procedures.
4. Interview data from pregnant and lactating women have been separated from the main files; nutrient supplement use for all interviewees have been compiled (Tables 2a and 2b).
5. Highlights of the preliminary findings were presented at the NCP symposium in Ottawa in March 2003.

All activities on this project have been, and continue to be, conducted in the CINE facilities. The extensive data set management and analysis was not possible to complete during the time period of the one-year program.

Results

Table 3 shows similarities of market food items consumed across the Arctic as food type and percent of recalls mentioning the item.

Table 4 gives the contribution of market and traditional food groups to total energy intake. In all three surveys, land animals were the highest contributors among traditional foods, whereas grains and sweet/fat were the highest contributors of market food.

Discussion and Conclusions

The project has been very useful and productive, although we are still constrained with late release of important

Table 3. Top 20 market foods mentioned consumed by adults in the three surveys

Dene/Métis (N = 1007 recalls)		Yukon (N = 797 recalls)		Inuit (N = 1604 recalls)	
Food item	**%[a]**	**Food item**	**%[a]**	**Food item**	**%[a]**
Sugar	82	Coffee	77	Sugar	74
Coffee	76	Sugar	72	Coffee	63
Bread, white, enriched	64	Tea	47	Tea	53
Tea	59	Bread, white, enriched	43	Bread, white, enriched	50
Potatoes[b]	47	Butter	43	Crystal drinks	34
Butter	45	Potatoes[b]	42	Soft drinks	33
Lard	45	Eggs, hard boiled or scrambled	37	Cream, light or powdered	30
Eggs, hard boiled or scrambled	42	Rice, white	32	Margarine	27
Cream, light or powdered	42	Lard	25	Potatoes[b]	26
Crystal drinks	29	Milk, partly skimmed (2%)	23	Butter	22
Bannock	27	Onions, boiled	23	Rice, white	21
Margarine	24	Bread, whole wheat	23	Bannock	20
Bacon, cooked, drained	23	Milk, evaporated, canned	21	Milk, evaporated, canned	19
Milk, partly skimmed (2%)	21	Carrots	20	Eggs, hard boiled or scrambled	18
Milk, evaporated, canned	21	Bacon, cooked, drained	19	Chicken	16
Chicken	21	Cream, light or powdered	18	Spaghetti, enriched, cooked	16
Rice, white	20	Beef, hamburger	17	Beef, hamburger	16
Soft drinks	19	Margarine	17	Soup, chicken noodle	14
Frankfurters, cooked	15	Spaghetti, enriched, cooked	17	Potato chips	13
Beef, hamburger	14	Chicken	15	Crackers, saltine	13

[a] Percent of recalls that mentioned the corresponding food item [b] Baked, boiled or mashed with milk and fat added

Table 4. Percent of total energy intake from market and traditional food groups, by gender and age, adjusted for season, site and day of week[a]

	Market food groups							Traditional food groups				
	Dairy	Fruits and vegetables	Grains	Meat alternates	Meat	Mixed dishes	Sweet and fat	Berries	Birds	Fish	Land animals	Sea mammals
Dene/Métis												
Women												
20–40 y (n = 276)	5.8 ± 0.5	12.1 ± 0.9	19.8 ± 1.1	4.0 ± 0.4	16.3 ± 1.3	4.7 ± 0.9	25.6 ± 1.2	0	0.1 ± 0.1	1.4 ± 0.5	10.2 ± 1.0	0
41–60 (n = 135)	4.3 ± 0.7	8.1 ± 1.0	25.9 ± 1.9	4.0 ± 0.7	12.1 ± 2.1	3.0 ± 0.8	18.2 ± 1.5	0.01 ± 0.09	0.1 ± 0.8	5.7 ± 1.5	18.7 ± 2.4	0
61 + (n = 95)	3.9 ± 0.9	9.2 ± 1.2	32.7 ± 2.4	2.5 ± 0.7	10.8 ± 2.5	4.0 ± 0.8	13.7 ± 1.9	0.06 ± 0.04	0.2 ± 0.4	3.6 ± 1.6	19.1 ± 3.8	0.1 ± 0.4
Men												
20–40 y (n = 248)	4.7 ± 0.5	8.2 ± 0.8	20.0 ± 1.1	5.0 ± 0.7	19.0 ± 1.4	4.0 ± 0.6	22.3 ± 1.0	0	0.01 ± 0.2	2.1 ± 0.6	14.5 ± 1.3	0
41–60 y (n = 162)	4.4 ± 0.9	10.6 ± 1.2	21.6 ± 1.5	4.3 ± 0.6	17.1 ± 1.8	1.8 ± 0.7	17.9 ± 1.2	0	0.2 ± 0.2	5.4 ± 1.0	16.6 ± 1.9	0
61+ y (n = 91)	2.5 ± 0.5	6.3 ± 0.9	21.5 ± 2.8	3.6 ± 0.7	18.0 ± 2.8	3.4 ± 1.0	16.5 ± 2.3	0.01 ± 0.04	0.3 ± 0.5	4.7 ± 1.7	23.2 ± 2.8	0
Yukon												
Women												
20–40 y (n = 248)	6.8 ± 0.6	14.0 ± 1.0	17.8 ± 1.0	4.5 ± 0.6	21.1 ± 1.3	5.0 ± 0.8	20.6 ± 0.9	0.07 ± 0.04	0.03 ± 0.05	1.7 ± 0.4	8.4 ± 1.0	0
41–60 y (n = 102)	6.1 ± 0.9	9.6 ± 1.2	23.1 ± 1.8	3.7 ± 0.8	18.9 ± 2.0	3.3 ± 0.9	18.8 ± 1.6	0.06 ± 0.06	0	1.7 ± 0.9	14.7 ± 2.1	0
61+ y (n = 67)	5.4 ± 1.3	10.9 ± 1.4	20.0 ± 1.9	3.4 ± 0.7	15.2 ± 2.5	2.9 ± 1.3	16.2 ± 1.3	0.03 ± 0.1	0	2.0 ± 0.9	24.0 ± 2.4	0
Men												
20–40 y (n = 221)	5.6 ± 0.5	13.9 ± 1.1	18.0 ± 1.0	4.2 ± 0.6	22.7 ± 1.4	5.4 ± 0.8	18.5 ± 0.8	0.01 ± 0.01	0.1 ± 0.1	0.7 ± 0.3	10.8 ± 1.4	0
41–60 y (n = 103)	4.7 ± 0.8	10.8 ± 1.2	20.3 ± 1.7	6.3 ± 1.1	19.9 ± 2.1	3.1 ± 1.2	16.6 ± 1.1	0.07 ± 0.03	0	2.0 ± 1.2	16.2 ± 2.2	0
61 + y (n = 56)	5.9 ± 1.9	10.2 ± 1.9	21.4 ± 3.0	4.1 ± 1.3	10.0 ± 3.8	4.1 ± 1.3	16.0 ± 2.5	0	0.3 ± 0.6	2.1 ± 1.7	26.0 ± 3.5	0
Inuit												
Women												
20–40 y (n = 482)	4.3 ± 0.3	8.9 ± 0.6	17.1 ± 0.7	2.2 ± 0.3	16.5 ± 0.9	6.9 ± 0.6	28.2 ± 0.8	0.05 ± 0.02	0.4 ± 0.2	1.8 ± 0.4	10.5 ± 0.9	3.0 ± 0.5
41–60 y (n = 283)	3.8 ± 0.5	6.6 ± 0.6	21.7 ± 1.0	2.8 ± 0.4	13.5 ± 1.2	4.5 ± 0.6	18.7 ± 0.9	0.05 ± 0.03	1.2 ± 0.4	4.8 ± 0.8	16.4 ± 1.4	6.1 ± 1.0
61 + y (n = 98)	3.7 ± 0.8	8.0 ± 1.2	21.6 ± 3.0	1.8 ± 0.6	6.9 ± 1.5	2.3 ± 1.0	16.5 ± 1.7	0.1 ± 0.07	0.7 ± 0.8	11.8 ± 1.9	21.0 ± 3.1	5.5 ± 2.2
Men												
20–40 y (n = 424)	3.6 ± 0.4	7.6 ± 0.6	18.1 ± 0.7	3.2 ± 0.3	16.7 ± 1.0	6.6 ± 0.6	27.0 ± 0.8	0.01 ± 0.003	0.5 ± 0.2	2.0 ± 0.4	11.9 ± 1.1	2.9 ± 0.6
41–60 y (n = 240)	3.7 ± 0.5	5.0 ± 0.7	19.5 ± 1.2	3.2 ± 0.5	10.6 ± 1.4	5.7 ± 0.8	18.5 ± 1.2	0.06 ± 0.03	0.7 ± 0.4	6.3 ± 1.1	18.8 ± 1.8	7.6 ± 1.3
61+ y (n = 77)	3.9 ± 0.9	4.1 ± 1.2	22.1 ± 3.2	1.5 ± 0.7	17.2 ± 2.6	3.2 ± 0.8	14.0 ± 1.5	0.09 ± 0.07	1.4 ± 1.3	11.6 ± 2.4	15.0 ± 3.4	5.9 ± 2.4

[a] Values are lsmeans ± SE

Dietary Reference Intakes, such as those for protein and fat. The extensive final data sets are being analyzed and brought to completion. Tables presented here are important components. We anticipate peer-review publications to be submitted during the fall and winter 2004.

Acknowledgments

We thank the CINE staff and collaborators for their continued good work. The majority of this project has been conducted by Rula Soueida in consultation with the project team members, most importantly Dr. Peter Berti. We were fortunate to have assistance of students, Tomoko Nakano and Amira Kassis. We also thank the CINE Governing Board members for their patience as we complete these analyses with reduced staff.

References

Barr, S.I., S.P. Murphy, and M.I. Poos. (2002). Interpreting and using the Dietary Reference Intakes in dietary assessment of individuals and groups. *J Am Diet Assoc.* 102:780–788.

IOM (Institute of Medicine). 2000. *Dietary Reference Intakes. Applications in Dietary Assessment.* National Academy Press, Washington, D.C.

IOM (Institute of Medicine). 2001. *Dietary Reference Intakes. Vitamin A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium, and Zinc.* National Academy Press, Washington, D.C.

IOM (Institute of Medicine). 2002. *Dietary Reference Intakes. Energy, Carbohydrate, Fiber, Fat, Fatty acids, Cholesterol, Protein and Amino Acids.* National Academy Press, Washington, D.C. www.nap.edu

Murphy, S.P. (2001) Changes in dietary guidance: Implications for food and nutrient databases. *Journal of Food Composition and Analysis.*14:269–278.

Food Choice Decisions by Western Arctic Aboriginal Women and Children, Year 2

Project leader

Harriet Kuhnlein, Centre for Indigenous Peoples' Nutrition and Environment, Macdonald Campus, McGill University, 21,111 Lakeshore Rd., Ste. Anne de Bellevue, QC H9X 3V9; phone: (514) 398-7671; fax: (514) 398-1020; e-mail: harriet.kuhnlein@mcgill.ca

Project team

Cindy Dickson, Council of Yukon First Nations, Whitehorse, YT;
Allison Armstrong and Chris Paci, Dene Nation, Yellowknife, NT.

Abstract

Following on the extensive dietary and socio-cultural information resulting from the CINE studies in Dene/Métis and Yukon First Nation communities, this study addressed the context of food choice decisions in the community setting. Three Dene/Métis communities (Fort McPherson, Tulita, Fort Resolution) and two Yukon First Nations (Old Crow and Carcross) were selected by the Dene Nation and the Council of Yukon First Nations to represent the Western Arctic. Focus groups of women and interviews of children 10–12 years old, and their mothers were conducted over a 2 year time period. 409 24-hour recalls of children and 49 women's interviews were conducted. Results indicate that these children are eating smaller quantities of traditional food than women reported earlier. However, days with traditional food were superior in nutrient content (protein, iron, zinc) than were days without traditional food. Vitamin A and calcium were nutrients of low intakes. Days without traditional food were higher in carbohydrates, including sucrose, and fat. Women gave several factors that influenced food choices for their families. Most significant were those of cost and availability of traditional food. Several strategies were suggested by women to improve availability and use of better food for themselves and their children.

Key Project Messages

1. Children's traditional food use in Dene/Métis and Yukon First Nation communities is less than that reported by adult women in earlier studies.
2. Children's nutrient intake patterns show that days when traditional food is consumed are superior in nutritional quality than days without traditional food. Nutrients of low intake are vitamin A and calcium. Others may be reported with additional analysis.
3. Women who were mothers of the children interviewed reported several factors that influenced family food availability and food choices. Most important were costs associated with market food and availability of traditional food.
4. Several strategies were suggested to improve children's knowledge on good food choices and better availability of food in communities.

5. Concerns for contaminants and other factors of food safety in traditional food were listed by more than 40% of women interviewed; however, more than 70% said they wanted community activities leading to greater use of traditional food.
6. Education strategies for children's food should emphasize suitability for increasing traditional food use because of its nutritional and cultural values. Both adults and children should receive education activities that their traditional food contains low levels of contaminants, and that concern for contaminants should not inhibit their selection of traditional food.

Objective

1. The overall objective was to understand the larger picture of factors influencing food choice decisions by Arctic women and children so that risks and benefits messages can be placed in relevant and appropriate context for effective education purposes.
2. To understand the factors involved in making choices among traditional and market food.
3. To better understand children's traditional and market food use in Dene/Métis and Yukon First Nation communities, and children's food preference factors.
4. The long-term goal is to develop relevant food education strategies for women and children that will guide family food choices.

Improved knowledge of how nutrient and sociocultural benefits and contaminant risk information affects the food decision process will lead to more effective communication efforts. This project provides essential information for the success of these initiatives.

Introduction

At the heart of the risk/benefit discourse about contaminants and traditional foods is the process of personal decision-making. People living in the North must ultimately decide what foods, market or traditional, to consume based on information they receive from various sources. Contaminant information is one of many factors influencing food choice decisions in the Arctic.

Research literature in the area of personal food choice is complex and scattered across various disciplines (Rappaport et al., 1992). Contributions from the areas of anthropology, sociology, marketing research, and psychology, as well as nutrition have contributed to existing knowledge in this area. Factors influencing personal food choice are numerous and can be categorized as ecological (e.g., geography, climate), biological (e.g., nutrient requirements, taste, health status), cultural (e.g., identity, values, beliefs, customs, symbolisms), societal (e.g., economy, politics, technology) and individual (e.g., income, education, attitudes, preferences, nutrition knowledge) (Parraga, 1990; Bisogni et al., 2002). The factors within these categories can vary within and among individuals.

Various models have been proposed in an effort to simplify and explain the complex process of human food selection (Furst et al., 1996; Parraga, 1990; Khan, 1981; Winter Falk et al., 1996). In addition, many theoretical approaches and methods have been used to investigate factors that influence food choice. Researchers have focused on psychological perspectives, measuring attitudes, beliefs and motives (Owen et al., 1997; Bell, 1981; Steptoe et al., 1995). Other studies have used sociological perspectives (Murcott, 1982) or combined sociological and anthropological perspectives (Murcott, 1988). Finally, nutrition researchers have utilized multi-disciplinary approaches to investigate food choice (Winter Falk et al., 1996; Chapman and Maclean, 1993; Stewart and Tinsley, 1995).

Both qualitative and quantitative methods have been employed to measure and identify food choice factors. Qualitative methodology, including focus groups and semi-structured interviews, has been used extensively (Winter Falk et al., 1996; Chapman and Maclean, 1993; Furst et al., 1996). As well, various quantitative methods such as questionnaires, repertory grid techniques and cognitive mapping have been utilized (Rappaport et al., 1992; Owen et al., 1997; Bell et al., 1981; Steptoe et al., 1995). In addition, investigators have used a combination of qualitative methods to develop a quantitative instrument that measures food choice influences (Stewart and Tinsley, 1995). There has been an appeal for further qualitative methodology in the investigation of food choice (Milburn, 1995). Researchers acknowledge that qualitative methods are particularly useful in illuminating the social and cultural context of factors involved in food choice decisions. Moreover, new research tools, such as pile sorts and stacking box methods, are being recognized as useful methodology to measure food attributes and gain a greater understanding of the meanings attached to foods (Gittelsohn et al., 1996; Jonsson et al., 1998).

Investigations of food choice among specific cultural groups are limited, as research has focused on adults and children from "westernized" societies. However, culture has been identified as a prime factor affecting food choice (Parraga, 1990). Among Canadian Aboriginal populations, research has focused on the measurement of food preferences as well as food health beliefs (Wein and Freeman, 1992; Wein et al.,

1993; Wein, 1996; Simoneau, 1997). Anderson (1999) and O'Neill et al. (1997) reported on Arctic food risks and communications, and a concurrent study on social and cultural factors associated with traditional/country food related activities was conducted with Inuit of Kuujjuaq (Furgal, 2001).

There is a need to develop research tools to identify the important food decision factors among people living in the North. In particular, an examination of factors affecting women and children's food choices is necessary. Women of childbearing age and children are more susceptible to nutritionally compromised status, and possibly to the risks of contaminants. As well, studies have reported that young women and children living in the Western Artic consume smaller amounts of traditional foods than men and elders living in their communities (Morrison, 1995). These findings are disturbing because of current knowledge about the nutritional and sociocultural benefits of traditional foods.

A substantial amount of knowledge now exists identifying food species and parts consumed by Aboriginal Peoples in the Western Arctic (Kuhnlein et al., 1994; Kuhnlein et al., 1995a; Kuhnlein et al., 1995b; Morrison et al., 1995; Receveur et al., 1996; Receveur et al., 1998; Berti et al., 1998; Receveur et al., 1998; Van Oostdam et al., 1999). However, little is known about the various reasons why individuals select particular foods. Inadequate knowledge of the factors influencing food choice restricts the success of nutrition and diet education (Krondl and Lau, 1978). A greater understanding of the decision making process, including how contaminant information affects this process, will improve existing educational efforts in local communities. Moreover, future educational strategies could incorporate results from this project to develop and target more effective nutrition information for Aboriginal People in the North. This would enable them to make better, more informed choices about their food, thereby leading to improved health, and reduced risk of contaminant exposure.

This project is built upon the basic knowledge of traditional food use in the Western Arctic obtained during the interview studies of 18 Dene/Métis and 10 Yukon First Nation communities conducted from 1994–1998, in which consumption of traditional and market food was determined for adult women and men.

During the first year of the project (2000–2001) data were reviewed from recent discussion groups held in Whitehorse and Yellowknife. This was the first round of gathering women's ideas on the major and minor factors contributing to food choices of women and children. CYFN and Dene Nation selected 5 communities to represent Yukon First Nation and Dene women and children: Fort McPherson, Tulita, Fort Resolution, Carcross and Old Crow. Research agreements were made with each community. Human ethics research approval was given from McGill University and science licenses obtained. Following this, the first year (2000–2001) of fieldwork in each community resulted in completion of focus groups, preliminary interviews with women, and children's 24-hour dietary recalls during the late winter season. Focus group transcripts were analyzed to further refine the list of factors contributing to food use, and the final interview protocol was prepared.

Activities

In 2001–2002

During summer of 2001, the five communities were given progress reports from the first year of the project, and interviews were conducted with 49 women who were mothers of 10–12-year-old children in the 5 communities, and 24-hour recalls were conducted with 118 children in the 10–12-year age range. Numbers of interview participants are shown in Table 1.

Interview data were coded and analyzed using standard procedures. A series of 13 questions on determinants of food choice was prepared, and is shown in Table 2. The interview protocol included the multiple possible answers derived from the focus group transcripts; relevant responses were selected by the interviewee, and these were then ranked in order of importance.

Results

Traditional food consumed

The extent of traditional food consumed (g traditional food per child per day) by 10–12-year-old children is shown in Table 3. The overall average of female and male traditional food use was from 40–50 g per day. There was no significant difference between the two seasons (not shown). When the amount of traditional food was con-

Table 1. Interview participants

	Season 1 Nov–Jan 2000–01	Season 2 Aug–Oct 2002
Focus groups	5	N/A
Women's interviews	13	49
Children interviewed	105	118
# with 2 recalls	89	98

sidered for only those children who actually used traditional food during the recall day, the amount of food was 80–90 g, approximately 3 ounces. The data reflect that on any one day during the two seasons, about one-half of the children in this age group would consume traditional food of various kinds.

The second section of Table 3 demonstrates the amount of traditional food reported consumed by Dene/Métis and Yukon women in two age categories. It can be seen that average intake was from 111 to 340 g per day. Adult women are therefore consuming at least twice as much traditional food as do children 10–12 years old.

Nutrient intakes by 10–12 year old children

Table 4 shows preliminary analysis of nutrient intake of 10–12-year-old female and male children. Data are presented for the two seasons separately and combined, and for both genders and combined. There were few differences in nutrient intake between the genders. The late summer season, when more traditional and market food was consumed (Table 3) results in intake of more energy (kcal), protein, carbohydrate, calcium and sucrose consumption, particularly for girls. As reported earlier for

Table 2. Questions in women's interviews: Factors influencing food choices

When you are deciding what to buy at the store, you mainly think about:
The main factors that affect what you eat in your house from day to day are:
At meal time(s) your main concern(s) is (are):
The main influence(s) on the foods that you and your family have at meals is (are):
The main reasons that influence how often you serve traditional food (meat, fish, birds) at home are:
I would serve more traditional food if:
Your family does not eat more traditional food in your household because:
What makes a difference in the amount of traditional food I have at home is:
I think what really affects what women eat is:
What children want to eat is mainly influenced by:
Children eat less wild meat than we did growing up because:
In order for families to eat better we need:
I would like to see the following things initiated in our community to improve our food:

Table 3. Traditional (TF) and market food (MF) consumed* by 10–12-year-old children and women (24 h recalls)

	Mean TF g/24hr		Mean MF g/24hr	
	Season 1	Season 2	Season 1	Season 2
	$\bar{X}$ ± SE (range)	$\bar{X}$ ± SE (range)	$\bar{X}$ ± SE (range)	$\bar{X}$ ± SE (range)
Females	74 ± 13 (0–380)	66 ± 14 (0–333)	1503 ± 122 (807–4162)	1770 ± 136 (315–4059)
Males	48 ± 18 (0–295)	75 ± 17 (0–410)	1708 ± 205 (935–4327)	1624 ± 118 (880–3220)
Total	38 ± 11 (0–380)	63 ± 15 (0–410)	1549 ± 106 (807–4327)	1746 ± 122 (315–4059)
TF Consumers Only	100 ± 16 (23–380) n = 50	89 ± 23 (15–410) n = 67	1523 ± 151 (935–4162) n = 50	1770 ± 173 (315–4059) n = 67

* Preliminary analysis, adjusted for site and day of week, for children

Traditional food consumed by western arctic women averaged over two seasons**

	Dene / Métis	Yukon
	$\bar{X}$ ± SE	$\bar{X}$ ± SE
20–40	144 ± 13 (n = 280)	111 ± 12 (n = 253)
41–60	340 ± 33 (n = 136)	153 ± 22 (n = 102)

**Combined days with and days without traditional food, adjusted for season, site and day of week

Data from Receveur et al., 1996; Receveur et al., 1998

the case of Dene/Métis, and Yukon women, mean protein, iron and zinc levels were close to the recommended intakes, whereas mean intakes of vitamin A and calcium were far below recommended intake levels. Further analysis will discern the numbers of children who are not meeting the new dietary reference intakes.

Table 5 shows nutrient and sucrose intakes for the children on days with traditional food reported being consumed in contrast to days without traditional food. There were no significant differences (NS) for intakes of energy, vitamin A, calcium or sucrose. Days with traditional food had significantly more protein, iron and zinc; days without traditional food had significantly more carbohydrate and fat, and a trend to more sucrose.

Interviews with mothers of 10–12-year-old children

Women participating in the interviews were from 27–64 years of age, and had been community residents for a mean duration of 34.9 years. The number of household members ranged from 2 to 7 members, with a mean household density of 4.9 persons. Sixty percent of the women interviewed reported that they were the

Table 4. Nutrient intake of 10–12-year-old children[a]

	Season 1[b]		Season 2[b]		Combined Seasons[c]		Both[c]
	Female $\bar{x}$ ± SE (n = 62)	Male $\bar{x}$ ± SE (n = 43)	Female $\bar{x}$ ± SE (n = 65)	Male $\bar{x}$ ± SE (n = 52)	Female $\bar{x}$ ± SE (n = 127)	Male $\bar{x}$ ± SE (n = 95)	All $\bar{x}$ ± SE (n = 222)
Kcal	1771 ± 127	1969 ± 178	2269 ± 130	2028 ± 132	2008 ± 81	2052 ± 127	1976 ± 66
Protein (g)	72 ± 5	71 ± 8	81 ± 6	80 ± 8	77 ± 3	75 ± 7	74 ± 3
CHO (g)	240 ± 22	258 ± 26	316 ± 19	281 ± 18	277 ± 13	278 ± 18	273 ± 10
Fat (g)	61 ± 5	76 ± 9	80 ± 6	67 ± 7	69 ± 3	74 ± 7	69 ± 3
Vit A (RAE)	419 ± 52	468 ± 76	450 ± 68	501 ± 61	446 ± 37	564 ± 59	471 ± 29
Fe (mg)	15 ± 1	14 ± 2	16 ± 1	17 ± 2	16 ± 0.7	16 ± 1	15 ± 0.6
Zn (mg)	10 ± 0.7	11 ± 1	13 ± 0.8	12 ± 1	11 ± 0.5	12 ± 1	11 ± 0.5
Ca (mg)	587 ± 102	744 ± 150	896 ± 77	757 ± 89	739 ± 57	777 ± 95	750 ± 46
Sucrose (g)	68 ± 12	82 ± 14	101 ± 9	81 ± 8	83 ± 6	81 ± 10	81 ± 5

[a] Preliminary analysis; adjusted for site and day of week

[b] Mean of 2 days per individual per season considered when applicable (i.e. when a repeat recall was provided)

[c] Repeating recalls across seasons were not averaged

Table 5. Nutrients on days with and days without traditional food*

Nutrients	Mean ± SE Both seasons / All children / 409 recalls		
	Days with (n = 148)	Days without (n = 261)	Sig.**
Kcal	1856 ± 67	1926 ± 52	NS
Protein (g)	83 ± 3	63 ± 2	**
CHO (g)	249 ± 10	270 ± 8	**
Fat (g)	62 ± 3	70 ± 3	**
Vit A (RAE)	470 ± 31	461 ± 24	NS
Fe (mg)	16 ± 0.6	14 ± 0.5	**
Zn (mg)	12 ± 0.5	10 ± 0.4	**
Ca (mg)	669 ± 47	736 ± 36	NS
Sucrose (g)	77 ± 5	85 ± 4	NS

*Adjusted for season, site and day of week

**$p \leq 0.05$

primary shopper for household food supplies (market food). Twenty-five percent of interviewees reported weekly use of traditional food, a similar percentage reported seldom having traditional food at home, and the remaining 50% varied between the two. Approximately 70% of respondents reported satisfaction with traditional food availability and variety. Approximately 60% of respondents reported satisfaction with market food variety and quality.

When asked about decision-making of market food, "cost" was the most important factor influencing choices, followed by considerations about "what would go with the traditional food available at home," whether they thought "the food was healthy", and "whether or not the children would like it." Women would serve more traditional food at home "if they had more of it," "if it was easier to get," and "if they were less concerned about contaminants." Forty-two percent of women listed "concern for contaminants" as a reason why they did not serve traditional food more often, and 16/49 women gave this reason as the first, second or third most important consideration.

"Concerns for food safety" were also reiterated when women were asked why the family does not eat more traditional food (59%), with 28% of respondents listing this as the first, second or third most important factor. "Food safety" was also a factor when women were asked what made a difference in the amount of traditional food served at home, and 36% of interviewees gave this as an important reason. When asked what affects women's diets, the most important factor was "knowledge of what is nutritious" (73%), general "concerns for their health" (83%), and "what they grew up with" (67%).

When asked what were the most important influences in what children eat, women replied that children eat "what their bodies need" (69%, with 51% giving this as the first, second, or third most important reason) and "what parents/grandparents prepare for them" (69%, with 46% stating this was first, second or third most important). The "appearance of the food" (67%), "what they see on TV" (63%) were also important. When asked "why children are eating less wild meat today that they themselves did", 55% of women reported that it was "because children are spending more time in town" (51% reported this as the first, second or third most important reason). Two other important factors were that "children had less opportunity to participate in hunting and learning to prepare traditional food" (73%, with 42% giving this as first, second or third most important) and "women working outside of the home with less time to prepare traditional food" (71% with 40% giving it as a most important reason).

During the focus group discussions about how to improve children's food use by community access to better traditional and market food, several factors surfaced, and were incorporated into the later interviews. All women had opinions on how to do this, with only 5 women (10%) reporting that things were "good as they are" at the time of the interview. For families to eat better, 87% of women wanted "more information for parents and children about healthy food choices", and 87% desired "more teaching in schools about healthy food choices." Eighty five percent said they wanted "more access to traditional food," with 77% giving this as the first, second or third most important factor. Women reported they would like to see initiation of "community gardens" (83%), "workshops on healthy eating" (79%), "programs to teach how to preserve and prepare traditional food" (77%), "community organized hunting" (75%), "availability of equipment for preserving and preparing traditional food (canners, sausage makers, etc.)" (73%), "more subsidies for hunting" (67%), "a school lunch program" (69%), "a school breakfast program" (63%), and "a ban on junk food in schools" (63%).

Discussion and Conclusions

This project provided valuable new data on the food and nutrient intake of 10–12-year-old children in the Western Arctic. While children are reporting eating less quantities of traditional food than women reported in earlier studies, this quantity of nutrient dense food is important to fulfill nutrient needs. Protein, iron and zinc were especially provided by the traditional food consumed. Days without traditional food were higher in carbohydrate, including sucrose, and fat. It is thus clear that traditional food provisioning for children is important for their health.

Children are receiving adequate food; that is, they receive sufficient dietary energy. However, given that children of this age require similar levels of energy in their food as do adult women, it is of note and concern that their traditional food intake is approximately half of that of adult women. Market food selected is known to be high in fat, carbohydrate and sucrose, and low in key nutrients such as vitamin A and calcium. This is reflected in the low intakes of these two nutrients by children interviewed.

Parents and their children need to be guided through education activities to select more traditional food, and less energy as market food. Market food selected can be chosen to be of higher nutrient density, particularly micronutrients, with less energy — such as whole grains, fat reduced dairy products, lean meats, and minimally processed fruit and vegetables.

The women interviewed in this study were mothers of the children completing the food use interviews. They noted that concern for contaminants and food safety in general was an important factor in choosing what to prepare for their families; however, they also noted that they wanted more traditional food than they now have for themselves and their children. Education and health promotion activities should be provided which stress the low levels of contaminants found in traditional food consumed in the Western Arctic, and their general high nutritional quality and safety.

Several strategies were suggested for improving community availability and use of both traditional and market food. In particular, women suggested more education in the form of workshops and school activities regarding healthy food choices. Initiation of community gardens, community organized hunting and availability of equipment for food preservation, and hunting subsidies were suggested. It is evident that the ideas and will for implementing community change to improve children's diets exist among residents in Western Arctic communities. Resources and facilitators for these activities would bring positive dietary change for all family members.

Social and cultural values related to traditional food use have been important findings of many Arctic studies. It is clear from this project that parents want to protect the use of traditional food for their children, and that this food is important for nutritional health and community well-being.

Acknowledgements

Special thanks to the children and women who contributed the valuable data in this study from the communities of Fort McPherson, Tulita, Fort Resolution, Carcross and Old Crow. Karen Fediuk and Norma Kassi are especially thanked for their community organization and interviewing skills. Rula Soueida, Tomoko Nakano and Lindi Sibeko are thanked for data management and analysis. The Dene Nation and the Council of Yukon First Nations are thanked for their facilitation of this project.

References

Andersen, F., J. Lampe, F. Murphy, C.M. Furgal, and L. Craig. 1999. Country food, nutrition and health: developing effective communication strategies in Labrador. Synopsis of research conducted under the 1998/99 Northern Contaminants Program. Department of Indian Affairs and Northern Development. Ottawa, pp.291–294.

Bell, A.C., A.M. Stewart, A.J. Radford, and P.T. Cairney. 1981. A method for describing beliefs which may predict personal food choice. *Journal of Nutrition Education.* 13(1):22–26.

Berti, P.R., H.M. Chan, O. Receveur, C.R. Macdonald, and H.V. Kuhnlein. 1998. Population exposure to radioactivity from consumption of caribou among the Dene/Métis of Denendeh (Western Northwest Territories, Canada). *J Exposure Anal and Env Epidem.* 8: 145–158.

Bisogni, C.A., M. Connors, C.M. Devine, and J. Sobal. 2002. Who we are and how we eat: A qualitative study of identities in food choice. *J Nutr Educ Behav.* 34: 128–139.

Chapmen, G. and H. Maclean. 1993. Junk food and healthy food: meanings of food in adolescent culture. *Journal of Nutrition Education.* 25(3):108–113.

Furgal, C. 2001. Decision making and diet in the North: Balancing the physical, economic and social components. Synopsis of research conducted under the 2000–2001 Northern Contaminants Program. Minister of Indian Affairs and Northern Development, Ottawa, Minister of Public Works and Government Services Canada. Pp 42–53.

Furst, T., M. Connors, C.A. Bisogni, J. Sobal, and L. Winter Falk. 1996. Food choice: a conceptual model of the process. *Appetite.* 26:247–266.

Gittelsohn, J., S.B. Harris, K.L. Burris, L. Kakegamic, L.T. Landman, A. Sharma, T.M.S. Wolever, A. Logan, A. Barnie, and B. Zinman. 1996. Use of ethnographic methods for applied research on diabietes among the Ojibway-Cree in northern Ontario. *Health Education Quarterly.* 23(3):365–382.

Jonnsson, I., L. Gummeson, M. Conner, and E. Scensson. 1998. Assessing food choice in school children: reliability and contruct validity of a method stacking food photographs. *Appetite.* 30:25–37.

Khan, M.A. 1981. Evaluation of food selection patterns and preferences. *Critical Reviews in Food Science and Nutrition.* October:129–153.

Krondl, K.K. and D. Lau. 1978. Food habit modification as a public health measure. *Canadian Journal of Public Health.* 69(Jan/Feb):39–44.

Kuhnlein, H.V., D. Appavoo, N. Morrison, R. Soueida, and P. Pierrot. 1994. Use and nutrient composition of traditional Sahtu (Hareskin) Dene/Métis foods. *J Food Comp and Anal.* 7:144–157.

Kuhnlein, H.V., O. Receveur, D.C.G. Muir, H.M. Chan, and R. Soueida. 1995a. Arctic indigenous women consume greater than acceptable levels of organochlorines. *J Nutr.* 125:2501–2510.

Kuhnlein, H.V., O. Receveur, N.E. Morrison, D.M. Appavoo, R. Soueida, and P. Pierrot. 1995b. Dietary nutrients of Sahtu Dene/Métis vary by food source, season and age. *Ecol Food Nutr.* 34:183–195.

Milburn, K. 1995. Never mind the quantity, investigate the depth. *British Food Journal.* 97(7):36–38.

Morrison, N.E., O. Receveur, H.V. Kuhnlein, D.M. Appavoo, R. Soueida, and P. Pierrot. 1995. Contemporary Sahtu Dene/Métis use of traditional and market food. *Ecology Food Nutr.* 34:197–210.

Murcott, A. 1982. The cultural significance of food and eating. *Proceedings of the Nutrition Society.* 41:203–210.

Murcott, A. 1988. Sociological and social anthropological approaches to food and eating. *World Reviews of Nutrition and Dietetics.* 55:1–40.

O'Neil, J.D., B. Elias, and A. Yassi. 1997. Poisoned food: cultural resistance to the contaminants discourse in Nunavik. *Arctic Anthropology.* 34(1):29–40.

Owen, S., P. Schickler, and J. Davies. 1997. Food choice: how to assess attitudes of pre-adolescent children. *British Food Journal.* 99(4):148–153.

Parraga, I.M. 1990. Determinants of food consumption. *Journal of the American Dietetic Association.* 90(5): 661–663.

Rappaport, L.H., G.R. Peters, L. Huff-Corzine, and R.G. Downey. 1992. Reasons for eating: an exploratory cognitive analysis. *Ecology Food Nutr.* 28:171–189.

Receveur, O., M. Boulay, C. Mills, W. Carpenter, and H.V. Kuhnlein. 1996. Variance in food use in Dene/Métis communities. Research report. Centre for Indigenous Peoples' Nutrition and Environment (CINE). Macdonald Campus, McGill University. Ste. Anne de Bellevue, QC.

Receveur, O., N. Kassi, H.M. Chan, P.R. Berti, H.V. Kuhnlein. 1998. Yukon First Nations' assessment of dietary benefit/risk research report. Centre for Indigenous Peoples' Nutrition and Environment (CINE). Macdonald Campus, McGill University, Ste. Anne de Bellevue, QC.

Receveur, O., M. Boulay, and H.V. Kuhnlein. 1997. Decreasing traditional food use affects diet quality for adult Dene/Métis in 16 communities of the Canadian Northwest Territories. *J Nutr.* 127:2179–2186.

Ross, S. 1995. 'Do I really have to eat that?': A qualitative study of schoolchildren's food choices and preferences. *Health Education Journal.* 54:312–321.

Simoneau, N. 1997. Attributes of Vitamin A and calcium-rich foods consumed in K'Asho Go'tine, NWT. M.Sc. Thesis. School of Dietetics and Human Nutrition, McGill University.

Steptoe, A., T.M. Pollard, and J. Wardle. 1995. Development of a measure of the motives underlying the selection of food: the food choice questionnaire. *Appetite.* 25:267–284.

Stewart, B. and A. Tinsley. 1995. From qualitative to quantitative: development of an instrument to assess food choice influences of young adults. *Ecology Food Nutr.* 34:171–181.

Tracy, B., M. Feeley, V. Jerome, and B. Kwavnick. 1999. Human health implications of environmental contaminants in Arctic Canada: a review. *The Science of the Total Environment.* 230:1–82.

Van Oostdam, J., A. Gilman, É. Dewailly, P. Usher, B. Wheatley, H. Kuhnlein, S. Neve, J. Walker, B. Tracy, M. Feeley, V. Jerome, and B. Kwavnick. 1999. Human health implications of environmental contaminants in Arctic Canada: a review. *Sci Total Environ.* 230:1–82.

Wein, E.E. 1996. Foods and nutrients in reported diets versus perceived ideal diets of Yukon Indian people. *Journal of Nutrition Education.* 28(4):203–208.

Wein, E.E. and M.M.R. Freeman. 1992. Inuvialuit food use and food preferences in Aklavik, Northwest Territories, Canada. *Arctic Medical Research.* 51:159–172.

Wein, E.E., Z.J. Hawrysh, and M.I. Gee. 1993. Food preferences and food health beliefs of native school children and mothers in northern Alberta. *Ecology Food Nutr.* 29:259–273.

Wheatley, M.A. 1998. Social and cultural impacts of environmental change on Aboriginal peoples in Canada. In R. Fortuine and G.A. Conway (eds.) *Proceedings of the Tenth International Congress on Circumpolar Health.* American Society for Circumpolar Health. Anchorage, Alaska, pp. 537–542.

Winter Falk, L., C.A. Bisogni, and J. Sobal. 1996. Food choice processes of older adults: a qualitative investigation. *J Nutr Educ.* 28(5):257–265.

Follow-up of Preschool Aged Children Exposed to PCBs and Mercury Through Fish and Marine Mammal Consumption

Program leader

Gina Muckle, Unité de recherche en santé publique, Centre Hospitalier Universitaire de Québec (CHUQ), Pavillon CHUL et Département de médecine préventive de l'Université Laval. 2400 rue D'Estimauville, Beauport, QC G1E 7G9; phone: (418) 666-7000 (ext. 360); fax: (418) 666-2776; e-mail: gmuckle@cspq.qc.ca

Researchers

Éric Dewailly and Pierre Ayotte, Unité de recherche en santé publique, Centre Hospitalier Universitaire de Québec (CHUQ), Pavillon CHUL et Département de médecine préventive de l'Université Laval, Beauport, QC; Célyne H. Bastien, École de psychologie, Université Laval, Beauport, QC; Anne Beuter, Centre de neuroscience de la cognition, Université du Québec à Montréal, Montreal, QC; Marie-Sylvie Roy, Département d'ophtalmologie, Université de Montréal, Montreal, QC; Annie Veilleux, Département de pédiatrie, Université de Montréal, Montreal, QC.

Project team

Karine Poitras and Carole Vézina, Unité de recherche en santé publique, Centre Hospitalier Universitaire de Québec (CHUQ), Pavillon CHUL, Beauport, QC; Christine Després, Centre de neuroscience de la cognition, Université du Québec à Montréal, Montreal, QC; Dave Saint-Amour, Département de psychologie, Université de Montréal, Montreal, QC.

Abstract

As projected originally, during the year 2001–2002, two data collection trips were performed. Each of these trips lasted about 3–4 weeks, and they allowed testing 51 children, thus the final sample size is 110. Recruitment of study participants, coding of maternal interviews and child testing protocols, laboratory analysis of blood and hair samples, and data entry are the activities carried out during year 2001–2002.

During year 2002–2003, the activities planned were essentially related to the analyses of the data collected during previous years and the publication as well as the communication of results. The statistical analyses phase turned out to be much longer than anticipated due to the complexity of the data involved. Study results will be available for communication to the population and publication at end of year 2003–2004.

Key Project Messages

2001–2002

1. As projected originally, during the year 2001–2002, two data collection trips were performed and allowed to test 51 children, for a sample size of 110.
2. Data are available to describe the participation rate, socio-demographic characteristics of the sample, country food consumption, prenatal and contemporaneous exposure to PCBs and Hg.

2002–2003

3. Analysis of results are ongoing.
4. Results will be available for communication to the population and publication at end of year 2003–2004.

Objectives

The general objective of this research is to examine the neurophysiological and neurological long term consequences of prenatal exposure to PCBs and MeHg.

Introduction

The effects of prenatal exposure to polychlorinated biphenyls (PCBs) and methylmercury (MeHg) resulting from fish consumption were studied in fish eating populations from various countries. Prenatal exposures to PCBs and MeHg have been linked to deficits in neurobehavioral development during infancy. However, only two studies provided data for school age children, and neuromotor as well as neurophysiological effects were poorly documented. Although neurophysiological testing was performed in one of these studies with school aged children exposed to MeHg, the study remained incomplete. Furthermore, no study has been aimed at investigating cognitive deficits under MeHg exposure using event-related potentials. The purpose of this research is to examine the long-term consequences of prenatal exposure to PCBs and MeHg. This project is designed to extend previous findings by studying domains of effects that have been overlooked in most of the previous studies (neurophysiological and neurological endpoints) that could be related to learning difficulties and disabilities. The large number of highly exposed Aboriginal children in Northern Quebec provides a unique opportunity to: 1) study the impact of PCBs and MeHg on child development; 2) provide the information required for the development of blood guidelines, no effect thresholds, acceptable daily intakes, and health advisories for Canadian children and women of reproductive age; and 3) broaden our knowledge on the nature of specific deficits associated with the exposure to these environmental contaminants. The sample will comprise 100 Nunavik Inuit children aged between five and six years. According to *in utero* PCBs and MeHg exposure levels (low and high), two subsets of 50 children will be formed. Prenatal exposure to PCBs and MeHg was documented from cord blood analysis at birth. Groups will be comparable regarding the socio-economic status. A neurological exam will be performed; the fine and gross neuromotor function as well as the visual system and the cognitive and attentional functions will be assessed. Demographic, socio-familial and biological potential confounds will be assessed via maternal interviews and blood sample analysis.

Activities

In 2001–2003

Two data collection trips were planned for year 2001–2002. These two trips were performed and allowed testing of 51 children.

The activities planned were essentially related to the analyses of the data collected during previous years and the publication as well as the communication of results. Four set of analysis were scheduled: the association between prenatal exposure to environmental contaminants and 1) neuromotor function, 2) cognitive evoked potentials and 3) visual evoked potentials, as well as the 4) description of the cohort study and the exposures — prenatal and postnatal — to environmental contaminants.

Results and Discussion

There are no results to present at this stage in relation to the study objectives. Nevertheless, data are available to describe the participation rate, socio-demographic characteristics of the sample, country food consumption, and prenatal and contemporaneous exposure to PCBs and Hg.

Research procedures, participation rate and sample characteristics

Inuit women from Northern Quebec (Nunavik) were invited to participate in this study. The study is the continuation of the Cord Blood Monitoring Program in which they had participated at the birth of their child. The Nunavik region is located north of the 55th parallel; 7660 Inuit are scattered along a 2000-km seashore line along Hudson Bay, Hudson Strait, and Ungava Bay, about 1500 km from Montreal and 2000 km from the Great Lakes in the United States. The Nunavik Inuit live in 14 villages, ranging from 125 to 1300 inhabitants per

village. The study participants were living in villages from Hudson Coast (48.2%) and Ungava Coast (51.8%).

From the 484 participants of the Cord Blood Monitoring Program, 298 were eligible for this study (Table 1). The main reason of exclusion was that the child was adopted at birth: given that the consent to participate in the Cord Blood Monitoring Program was obtained for the biological mothers, we were not authorized to invite the adoptive mothers to participate in this follow-up study. A significant number of children had to be discarded because they were not in the age range for testing at the time of the data collection. Since the data collection was done during five trips to Nunavik, some eligible participants couldn't be reached by us. From the eligible participants, 110 children were evaluated (51 during year 2001–2002) and 108 mothers and 2 fathers were interviewed to get information about their child and their family. About 25.7% refused to participate and the main reason for refusal to participate was the obligation to travel to another community in order to meet our research assistants.

The data collection was conducted by 3 research assistants and one Inuit interpreter between January 2000 and October 2001 (2 trips during year 2001–2002). Five one-month trips to Nunavik allowed evaluations of the children and conduction of the maternal interviews. Two research assistants started the evaluation of the child in the presence of the mother. The mother was interviewed by the third research assistant during the last part of the child's evaluation. Children's mothers were located with the help of the information available in the Cord Blood Surveillance Program database, and key informants like nurses and community workers. Evaluations were done by two graduated students with the help of the Inuit research assistant. Child's blood and hair samples were taken in order to test for contemporaneous PCBs and MeHg exposure. Socio-demographic and personal characteristics were documented from interviews conducted by a highly experienced research assistant, and are summarized in Table 2.

Table 1. Participation and attrition rates

Potential participants (N = 484)[1]		
Exclusions:		
Adoption (117/484)	117	24.2
Death of the mother (2/484)	2	0.4
Death of the child (7/484)	7	1.4
Moved outside the visited villages (7/484)	7	1.4
Missing information (exposure or identification) (48/484)	48	9.9
Health problems (3/484)	3	0.6
Non Inuit mother (2/484)	2	0.4
Out of the age limit when we were travelling (70/484)	70	14.5
Eligible children (N = 228)		
Unable to contact (68/228)	68	29.8
Out of town when we were travelling (7/228)	7	3.1
Contacted children (N = 153)		
Travel problems (3/153)	3	2.0
Impossible to test (2/153)	2	1.3
Refusal rate (38/148)	38	25.7
Refuse to being interviewed (1/148)	1	0.4
Never come to the appointments (10/148)	10	6.8
Not available to come in the same village (10/148)	10	6.8
Not available to travel (17/148)	17	11.5
Participation rate (110/148)	110	74.3

[1] Children who have participated in the cord blood monitoring

Table 2. Characteristics of participants

	Total N	Mean	SD	Range	N	%
Marital status (% single)	110				23	20.9
Mother age	110	30.2	5.4	21.4–45.1		
Child age	110	5.4	0.4	4.8–6.2		
Parity	109	4.3	2.0	1.0–10.0		
Crowding	108	1.0	0.3	0.5–2.0		
Education	110	9.0	2.2	5.0–16.0		
Socioeconomic status[1]	107	28.4	1.2	8.0–57.0		
Proportion of working mothers	110				74	67.3
Menial service workers	73				8	11.0
Unskilled laborers	73				3	4.1
Semiskilled workers	73				13	17.8
Skilled craftsmen, clerical & sales	73				24	32.9
Technical, small business	73				15	20.5
Minor professionals	73				8	11.0
Administrators, lesser professionals	73				2	2.7
Language of interview	110					
English					93	84.5
French					6	5.5
Inuktituk					11	10.0
Breastfeeding (%)	108				86	79.6
Duration (in months)	86	16.7	1.8	0.1–60.0		

[1] Hollingshead Index for the mother and her partner or, if she was not self-supporting, for her primary source of support (usually her parents)

Exposure to PCBs and MeHg

Since a primary route of exposure to environmental contaminants in the Inuit population is the consumption of traditional food, especially fish and sea mammals, for descriptive purposes, we documented the frequency of traditional food consumption during the child's last year of life (Table 3). The participants were questioned about their consumption of the following fish species: Arctic char, lake trout, salmon, and white fish. Their consumption of beluga, seal, narwhal, whale, walrus, and marine birds' eggs was also evaluated. Fish, beluga, seal and eggs were the most frequently consumed species whereas the consumption of whale, narwhal and walrus was much less common in the selected communities.

A blood sample was obtained from each participating child. One 5 mm diameter hair sample was also collected from the child. PCB congener and chlorinated pesticide concentrations were measured at birth in cord plasma and in the child's plasma collected at the testing session. Hg concentrations were determined in cord and child whole blood as well as in the hair sample collected at testing time. Organochlorine, heavy metals and selenium analyses were performed at the laboratory of the *Centre de Toxicologie du Québec*, which is accredited by the Canadian Association for Environmental Analytical Laboratories. Blood samples containing EDTA as the anticoagulant were centrifuged and the plasma was collected in glass vials pre-washed with hexane. Plasma samples were stored at −20°C until time of analysis. A 1:1:3 mixture of ammonium sulfate/ethanol/hexane was first added to the plasma to extract PCB congeners. The extracts were then concentrated and purified on two Florisil columns. The 14 most prevalent PCB congeners (IUPAC nos. 28, 52, 99, 101, 105, 118, 128, 138, 153, 156, 170, 180, 183, 187) and 11 chlorinated pesticides or their metabolites (aldrin, α-chlordane, γ-chlordane, *p,p'*-DDT, *p,p'*-DDE, HCB, β-HCH, mirex, *cis*-nonachlor, *trans*-nonachlor, oxychlordane) were measured in the purified extracts by high-resolution gas chromatography using two capillary columns (Hewlett-Packard Ultra I and Ultra II) and dual Ni-63 electron capture detectors.

Table 3. Country food consumption during pregnancy

	N	# meals per month	SD	Range	IQR	At least 1 meal/week[3]	At least 1 meal/month[3]
Fish meals[1]	109	10.1	10.9	0.0–52.1	2.0–16.4	54.1	89.9
Beluga meals							
Skin	109	0.7	0.1	0.0–7.5	0.1–0.6	2.7	17.4
Fat	107	2.4	0.6	0.0–30.3	0.0–1.0	15.0	26.2
Meat	109	0.2	0.1	0.0–4.3	0.0–0.2	0.0	5.4
Liver	108	0.0	0.0	0.0–0.6	0.0–0.0	0.0	0.0
Seal meals							
Fat	110	2.4	0.5	0.0–30.3	0.0–1.8	20.0	30.9
Meat	107	0.1	0.0	0.0–4.7	0.0–0.8	1.8	21.5
Liver	108	0.3	0.1	0.0–4.7	0.0–0.1	1.8	12.0
Seabird's eggs	107	0.5	1.0	0.0–7.5	0.0–0.6	0.9	16.8
Birds & waterfowls[2]	105	8.8	10.3	0.0–35.5	0.6–3.7	22.0	62.0
Cariboo	105	8.8	10.3	0.0–52.0	2.0–10.8	61.0	88.6

[1] Artic char, salmon, white fish and lake trout [2] Ptarmigan, geese and duck [3] Percent

Table 4. PCB and mercury concentrations obtained at birth and at 5-year of age

	N	Arithmetic mean	SD	Range	IQR
Mercury					
Cord blood ($nmol \cdot L^{-1}$)	110	111.2	91.9	9.0–520.0	44.5–146.5
5-year blood ($nmol \cdot L^{-1}$)	110	47.8	44.5	1.0–191.0	15.8–69.3
5-year hair ($\mu g \cdot g^{-1}$)	110	2.7	2.6	0.1–13.9	0.9–3.7
PCB Congener 153 ($\mu g \cdot kg^{-1}$)					
Cord blood	109	123.6	95.2	21.6–653.6	63.6–151.6
5-year blood	109	160.5	214.1	7.5–1467.2	35.1–196.2

Quality control procedures were described previously (Rhainds et al., 1999). Percent recovery varied from 89 to 100% and the detection limit was approximately 0.02 $\mu g \cdot L^{-1}$ for all compounds. Coefficients of variation (N = 20, different days) ranged from 2.1 to 9.1% and biases from –10.9 to 3.8%. Since OCs distribute mainly in body fat, concentrations in plasma samples are reported in µg/kg of lipids. Total cholesterol, free cholesterol and triglycerides were measured in plasma samples by standard enzymatic procedures, while phospholipids were determined according to the enzymatic method of Takayama et al. (1977), using a commercial kit (Wako Pure Chemical Industries, Richmond, VA). The concentration of total plasma lipids was estimated according to the formula developed by Phillips et al. (1989). Total mercury concentrations were determined in samples of whole cord and child blood and child hair by cold vapor atomic absorption spectrometry. Samples were digested with nitric acid, reduction of mercury was accomplished using anhydrous stannous chloride ($SnCl_2$) and the reaction was catalyzed with cadmium chloride ($CdCl_2$). Metallic mercury was volatilized and detected by atomic absorption spectrometry (Pharmacia Model 120). The detection limit for blood mercury analysis was 1.0 $nmol \cdot L^{-1}$. Quality control procedures were described previously (Rhainds et al., 1999). Coefficients of variation (N = 50, different days) at levels of 40 and 90 $nmol \cdot L^{-1}$ (in-house reference materials) were 5% and 5.5% respectively. The relative bias of the samples was 2.4% and −0.4% respectively. The detection limit for hair mercury analysis was 1 $nmol \cdot g^{-1}$. Accuracy and precision data were obtained using certified reference material through Health Canada's hair mercury inter-laboratory comparison program. The coefficients of variation (N = 50, different

Table 5. Comparison of Hg concentrations in blood (μg/l) and hair (μg/g)

Cohort	Medium	Years	N	Geometric mean	Range	Interquartile range
Nunavik Inuit	Cord blood[2]	1993–1996	475	14.2	1.0–104.0	8.4–24.8
	5-year blood[3]	2000	58	8.8	0.8–38.2	4.1–18.3
	5-year hair[3]	2000	58	2.2	0.3–8.6	1.2–4.1
Southern Quebec[4]	Cord blood	1993–1995	1108	1.0	0.9–1.0	
Faroe Islands[5]	Cord blood	1986–1987	894	22.9	13.4–41.3	
	Child hair, 7 years	1993–1994	903	3.0	1.7–6.1	
	Child blood, 7 years	1993–1994	672	8.8	4.8–18.2	

[1] 95% confidence interval; [2] Dewailly et al. (1998); [3] Current study; [4] Rhainds et al. (1999); [5] Grandjean et al. (1999)

Table 6. Comparison of PCB concentrations observed in Nunavik Cord Blood samples (μg/l) with those in comparison groups and high levels cohorts using same analytical methods

	Years	N	PCB congener	Arithmetic mean	Range
Canada, Nunavik Inuit[5]	1993–1996	59	Aro 1260[1]	2.7	0.5–8.4
		59	153	0.3	0.5–1.0
		59	ΣPCB[2]	1.3	0.2–4.2
Canada, Southern Quebec[6]	1993–1995	656	Aro 1260[1]	0.5[3]	0.5–0.5[4]
USA, New Bedford[7]	1993–1998	751	153	0.1	0.0–1.3
Netherlands[8]	1990–1992	382	153	0.2	0.0–0.9
Faroe Islands[9]	1994–1995	174	ΣPCB[2]	2.5	0.7–8.7
Greenland, Disco Bay[10]	1994–1996	160	Aro 1260[1]	4.2	[11]

[1] Aro 1260, 5.2 times the sum of PCB congeners 138 and 153; [2] ΣPCB, 2 times the sum of PCB congeners 138, 153, and 180; [3] Geometric mean; [4] 95% Confidence interval; [5] Current study; [6] Rhainds et al. (1999); [7] Korrick et al. (2000); [8] Koopman-Esseboom et al. (1994); [9] Steuerwald et al. (2000); [10] Bjerregaard & Hansen (2000); [11] Not available

days) at levels of 12.3 $\mu g \cdot g^{-1}$ (Bureau of Community Reference) and 4.42 $\mu g \cdot g^{-1}$ (National Institute for Environmental Studies) were 4.8% and 4.3% respectively. The relative biases were –2.2% and +1.9%, respectively. Descriptive statistics of mercury (Hg) concentrations obtained in cord and child blood are presented in Table 4. The average Hg concentration is higher in cord blood than child blood.

Hg concentrations reported in other cohorts are presented in Table 5. The data confirmed that prenatal exposure to Hg among the Inuit of Northern Quebec is higher than that observed in general population sample in Southern Quebec. When compared with the Faroe Islands cohort who has been studied for electrophysiological effects associated with Hg exposure, the Nunavik Inuit Hg range of exposure — cord blood, child blood, and child hair — is very similar.

Cord blood and child blood samples were analyzed for 14 PCB congeners and 11 chlorinated pesticides. Table 4 shows the descriptive statistics for these compounds in cord blood and child blood. PCB congener 153, the most prevalent congener, was used as a marker variable to reflect exposure to the moderate-to-heavily chlorinated PCB congeners. With regard to PCB exposure, it is difficult to compare the data in the present study with those from the first PCB neurobehavioral studies conducted in Michigan (Jacobson and Jacobson, 1996) and North Carolina (Rogan et al., 1986), which were based on packed columns gas chromatography technology for OCs determination. In Table 6, PCB concentrations observed in the present sample are compared with those from the general Canadian and American populations, and with other cohorts studies using similar analytical methods for PCBs determination (congener specific analysis). For each comparison, the Nunavik PCB concentrations were calculated according to the method used in the comparison study.

Comparison of cord blood PCB levels confirmed that prenatal exposure to PCBs among the Nunavik Inuit is

much higher than that observed in general populations from Southern Quebec in Canada and New Bedford in United States. The Nunavik PCB concentrations are similar to those found in cord blood samples of the Netherlands study, and they are about two times lower than those found in the groups of marine mammal consumers from the Faroe Islands and Greenland cohorts.

Conclusions

As projected originally, during the year 2001–2002, two data collection trips were performed and allowed to test a total of 51 children. The research plans and milestones to be achieved in the next year have not changed, as well as the timetable of activities. No results have been published or communicated to date. Results will be available for publication before the end of year 2003–2004.

Expected Completion Date

March 31, 2004

References

Bjerregaard, P., and J.C. Hansen. 2000. Organochlorines and heavy metals in pregnant women from the Disco Bay area in Greenland. *The Science of the Total Environment.* 245:195–202.

Dewailly, É., S. Bruneau, P. Ayotte, G. Lebel, G. Muckle, and M. Rhainds. 1998. Évaluation de l'exposition prénatale aux organochlorés et aux métaux lourds chez les nouveau-nés du Nunavik, 1993–1996. Unpublished research report.

Grandjean, P., E. Budtz-Jorgensen, R.F. White, P.J. Jorgensen, P. Weihe, F. Debes, and N. Keiding. 1999. Methylmercury exposure biomarkers as indicators of neurotoxicity in children aged 7 years. *American Journal of Epidemiology.* 150:301–305.

Hollingshead, A.B. 1975. Four Factor Index of Social Status. Unpublished manuscript, New Haven, CT: Yale University.

Jacobson, J.L., and S.W. Jacobson. 1996. Intellectual impairment in children exposed to polychlorinated biphenyls *in utero. New England Journal of Medicine.* 335:783–789.

Koopman-Esseboom C., M. Huisman, N. Weisglas-Kuperus, C.G. Van der Paauw, L.G.M.Th. Tuinstra, E.R. Boersma, and P.J.J. Sauer. 1994. PCB and dioxin levels in plasma and human milk of 415 Dutch women and their infants. Predictive value of PCB congener levels in maternal plasma for fetal and infant's exposure to PCBs and dioxins. *Chemosphere.* 28:1721–1732.

Korrick, S.A., L.M. Altshul, P.E. Tolbert, V.W. Burse, L.L. Needham, and R.R. Monson. 2000. Measurement of PCBs, and hexachlorobenzene in cord blood from infants born in towns adjacent to a PCB-contaminated waste site. *Journal of Exposure Analysis and Environmental Epidemiology.* Volume 10 issue 6 (part 2): 742–753.

Phillips, D.L., J.L. Pirkle, V.W. Burse, J.T. Bernert Jr., L.O. Henderson, and L.L. Needham. 1989. Chlorinated hydrocarbon levels in human serum: effects of fasting and feeding. *Arch Environ Contam Toxicol.* 18: 495–500.

Rhainds, M., P. Levallois, É. Dewailly, and P. Ayotte. 1999. Lead, mercury and organochlorine compound levels in cord blood in Québec, Canada. *Archives of Environmental Health.* 54:40-47.

Rogan, W.J., B.C. Gladen, J.D. McKinney, N. Carreras, P. Hardy, J. Thullen, J. Tinglestad, and M. Tully. 1986. Neonatal effects of transplacental exposure to PCBs and DDE. *Journal of Pediatrics.* 109:335–341.

Steuerwald, U., P. Weihe, P.J. Jorgensen, B. Bjerve, and J. Brock. 2000. Maternal seafood diet, methylmercury exposure, and neonatal neurologic funtion. *The Journal of Pediatrics.* 136:599–605.

Takayama, M., S. Itoh, T. Nagasaki, and I. Tanimizu. 1977. A new enzymatic method for determination of serum choline-containing phospholipids. *Clin Chim Acta.* 79:93–98.

Transplacental Exposure to PCBs and Infant Development/ Human Exposure Assessment

Program leader

Gina Muckle, Unité de recherche en santé publique, Centre Hospitalier Universitaire de Québec (CHUQ), Pavillon CHUL and Département de médecine préventive de l'Université Laval, 2400 rue D'Estimauville, Beauport, QC G1E 7G9; phone: (418) 666-7000 (ext. 360); fax: (418) 666-2776; e-mail: Gina.Muckle@crchul.ulaval.ca

Researchers

Éric Dewailly and Pierre Ayotte, Unité de recherche en santé publique, Centre Hospitalier Universitaire de Québec (CHUQ), Pavillon CHUL et Département de médecine préventive de l'Université Laval, Beauport, QC; Joseph L. Jacobson, Psychology Department, Wayne State University; Sandra W. Jacobson, Department of Psychiatry and Behavioral Neurosciences, Wayne State University School of Medicine.

Project team

Jocelyne Gagnon, Carole Vézina, Karine Poitras and Christine Bouffard (2001–02), Unité de recherche en santé publique, Centre Hospitalier Universitaire de Québec (CHUQ), Pavillon CHUL; Lisa Chiodo, Sonia Narang, and Brenda Tuttle, Psychology Department, Wayne State University.

Abstract

The main objective of this study is to examine the consequences of *in utero* and lactational exposure to polychlorinated biphenyls (PCBs) and mercury on Inuit infants, from birth to 12 months of age. Of particular interest is the impact of exposure on newborn thyroid hormone levels and physical growth, on the infant's overall health, mental, psychomotor, and neurobehavioral development, and on visual and spatial information processing abilities.

The data collection of this study started in November 1995 and ended in March 2002. The continuation of data collection was the main activity carried out in 2001–2002. 248 Nunavik mothers have completed the prenatal interview and 216 have completed the postnatal interview; 185 infants were assessed at 6.5 months and 167 were assessed at 11 months of age. There are no results available regarding the effects of exposure to PCBs but two related articles were published during 2002.

Time trend analysis of prenatal exposure to environmental contaminants was also under study. Statistical analysis of collected data was the main activity carried out in 2002–2003. Study results were communicated to the Nunavik population and to the Canadian Arctic Contaminants Assessment Symposium. Manuscripts were submitted to scientific journals and others are under preparation.

Key Project Messages

2001–2002

1. The data collection of this ongoing study started in November 1995 and ended in 2002. The continuation of data collection was the main activity carried out in 2001–2002. To date, 248 Nunavik mothers have completed the prenatal interview and 216 have completed the postnatal interview; 185 infants were assessed at 6.5 months and 167 were assessed at 11 months of age.
2. There are no results available regarding the effects of exposure to PCBs on infant health and development. Effect analysis results are now available.
3. One article recently published corroborated previous findings relating marine mammal and fish consumption to increased Hg and selenium body burden. Despite widespread knowledge regarding the presence of these contaminants in traditional foods, a large proportion of Inuit women increased their consumption of these foods during pregnancy, due primarily to pregnancy-related changes in food preferences and the belief that these foods are beneficial during pregnancy.
4. In that study, cord blood, maternal blood and maternal hair mercury concentrations averaged 18.5 $\mu g \cdot L^{-1}$, 10.4 $\mu g \cdot L^{-1}$ and 3.7 $\mu g \cdot g^{-1}$ respectively, and are similar to those found in the Faroe Islands but lower than those documented in the Seychelles Islands and New Zealand cohorts. Concentrations of PCB congener 153 averaged 86.9, 105.3 and 131.6 $\mu g \cdot kg^{-1}$ (lipids) in cord plasma, maternal plasma and maternal milk, respectively; prenatal exposure to PCBs in the Nunavik cohort is similar to that reported in the Dutch but much lower than those in other Arctic cohorts. Levels of N3-PUFA in plasma phospholipids and selenium in blood are relatively high. The relatively low correlations observed between organochlorine and methylmercury concentrations may make it easier to identify the specific developmental deficits attributable to each toxicant. Similarly, the weak correlations noted between environmental contaminants and nutrients will facilitate the documentation of possible protective effects afforded by either N3-PUFA or selenium against neurotoxic contaminants.

2002–2003

1. Prenatal exposure to PCBs, mercury or lead has no effect on visual acuity, overall mental and motor development.
2. Prenatal exposure to PCBs is associated with subtle effects on duration of pregnancy as well as weight and length at birth.
3. Prenatal exposure to environmental contaminants is associated with poorer memory/attention during infancy; each contaminant has a specific effect on cognitive function.
4. Intake of omega-3 fatty acids during pregnancy has beneficial effects on foetal growth and is associated with more optimal development of infants on virtually all outcomes assessed.
5. The adverse effects of PCB on growth and development remained significant despite the beneficial effects of omega-3 fatty acids.
6. Prenatal exposure to PCBs has significantly decreased over the last decade, and cord blood lead levels have declined drastically since the discontinuation of the use of lead pellets.

Objectives

1. To examine physical growth and developmental effects of *in utero* and lactational exposure to PCBs on Inuit infants from birth to 12 months of age. Of particular interest is the impact of PCBs and Hg exposure on newborn's thyroid hormones, physical growth, physical and central nervous system maturity, on infant's overall health, mental, psychomotor and neurobehavioral development, and on functional and neural impairment in the domains of visual and spatial information processing.
2. To document the exposure to heavy metals, organochlorines and polyunsaturated fatty acids of newborns from selected communities in Nunavik. This ongoing effect study provides the opportunity to continue the cord blood monitoring program financed by NCP since 1993 and as a result, to be able to perform long time trend analysis of human exposure to OCs and heavy metals.

Introduction

The developmental neurotoxicity of MeHg first became evident during the 1950s at Minimata Bay, Japan, which was heavily contaminated with Hg from industrial effluent entering the bay. A second well-documented MeHg poisoning occurred in Iraq in the 1970s when seed grain contaminated with a MeHg fungicide was used to make homemade bread (Amin-Zaki et al. 1976). The neurodevelopmental affects seen in children exposed *in utero* in both Japan and Iraq included severe sensory and central nervous system impairments (Harada 1995; Marsh et al. 1987). Three well-designed, prospective, longitudinal studies that examined the effects of prenatal exposure to lower doses of MeHg on childhood cognitive function were performed in New Zealand, Faroe Islands, and Seychelles Islands (Crump et al. 1998; Kjellstrom et al. 1986; Grandjean et al. 1997; Davidson et al. 1998; Myers et al. 1995a). In the Faroe Islands study, MeHg exposure was found to be related to poorer performance in the domains of fine motor function, attention, language, visual-spatial abilities and verbal memory (Grandjean et al. 1997; Grandjean et al. 1999). Although no adverse effects were found in the Seychelles study (Davidson et al. 1998; Davidson et al. 1995; Myers et al. 1995b), the New Zealand study, which was similar in exposure and research design, found poorer performance in similar domains to those observed in the Faroe study (Crump et al. 1998; Kjellstrom et al. 1986).

The developmental toxicity of heat-degraded PCBs was first recognized in Japan in the late 1960s and in Taiwan in the late 1970s. In both countries, infants born to women who had consumed rice oil contaminated with mixtures of PCBs and polychlorinated dibenzofurans (PCDFs) exhibited skin rashes and poorer intellectual functioning during infancy and childhood (Chen et al. 1992; Yu et al. 1991). The effects of prenatal exposure to background levels of PCBs and other OCs from environmental sources have been studied since the 1980s in prospective longitudinal studies. In Michigan, prenatal PCB exposure was associated with poorer visual recognition memory in infancy (Jacobson et al. 1985; Jacobson et al. 1990a; Jacobson et al. 1992), an effect recently confirmed in the Oswego study (Darvill et al. in press). In North Carolina, deficits in psychomotor development were seen in the most highly exposed children through 24 months of age (Gladen et al. 1988; Rogan et al. 1991). In Michigan, prenatal PCB exposure was linked to poorer intellectual function at 4 and at 11 years (Jacobson et al. 1990a; Jacobson 1996), a finding confirmed at 42 months in the Netherlands (Patandin et al. 1999).

Neurotoxic effects of MeHg might be attenuated by protective effects of nutrients such as selenium (Se), and adverse effects from OCs might be attenuated by a high intake of N-3 polyunsaturated fatty acids (N3-PUFA). Increased intake of Se and N3-PUFA would be expected in a population who consume relatively large quantities of fish and marine mammals. Although the effects of Se on MeHg toxicity have not been well documented in humans, there is evidence from over 40 animal studies that Se can influence the deposition of Hg in the body and protect against its toxicity (National Research Council 2000). N3-PUFA, especially DHA, are essential for brain development (Crawford et al. 1976). DHA deficiency impairs learning and memory in rats (Greiner et al. 1999), and rodents and nonhuman primates fed diets severely deficient in N3-PUFA show altered visual function and behavioral problems (Innis 2000). Supplementation of N3-PUFA can enhance visual acuity and brain development in preterm human infants (Bjerve et al. 1992; Uauy et al. 1990), although it is not clear whether increased levels of these nutrients can benefit full term infants (Uauy and Hoffman 2000). It has been hypothesized that N3-PUFA may protect against neurotoxicity associated with prenatal exposure to environmental contaminants.

The effects of prenatal exposure to polychlorinated biphenyls (PCBs) and other organochlorine compounds (OCs) from environmental sources on growth at birth and duration of pregnancy have been studied in prospective longitudinal studies conducted in the United States and Europe. In Michigan higher cord serum PCB concentrations were associated at birth with lower weight, smaller head circumference and shorter gestation. Similar effects were observed in the Netherlands study but prenatal PCB exposure was not associated with growth in North Carolina, the cohort with the lowest PCB exposure. Prenatal exposure to PCBs and methylmercury have also been linked prospectively to developmental and cognitive deficits in infancy and childhood; the data from at least one important study are difficult to interpret, however, because the children were exposed simultaneously to high levels of both contaminants.

Activities

In 2001–2002

Most of the focus of that year's activity was in data collection. To date, 248 Nunavik mothers have completed the prenatal interview and 216 have completed the postnatal interview; 185 infants were assessed at 6.5 months and 167 were assessed at 11 months of age.

In 2002–2003

Between 1995 and 2002, we conducted a prospective study of Inuit infants in three communities located in northern Québec (Nunavik), where the Inuit population relies on species from the marine food web for subsistence and is therefore exposed to high doses of environmental contaminants such as PCBs and mercury. During year 2002–2003, we conducted time trend analysis of prenatal exposure to environmental contaminants, and statistical analysis aimed to look at the effects of prenatal exposure to environmental contaminants on physical growth at birth and developmental outcomes assessed at 6.5 and 11 months of age. These results were communicated to the Nunavik population.

Results and Discussion

The most prevalent PCB congeners were 153, 138 and 180. These three congeners represent about 66% of the total concentration of the 14 PCB congeners. The intercorrelations among PCB congeners that were detected in at least 70% of cord plasma samples were very high (median $r = 0.90$). The predominant chlorinated pesticides were *p,p'*-DDE, hexachlorobenzene, oxychlordane, and *trans*-nonachlor. The intercorrelations among the chlorinated pesticides detected in at least 70% of samples were strong (median $r = 0.76$). Moreover, the chlorinated pesticides measured were strongly associated with PCB congener 153, except for *p,p'*-DDT where the association was moderate. Based on these data, it seems reasonable to use PCB congener 153, the most prevalent congener, as a marker for exposure to the environmental organochlorine mixture in the Arctic. Cord plasma PCB 153 concentrations averaged 116.0 μg/kg (lipids) (geometric mean 86.9). Prenatal PCB exposure in Nunavik was two to three times higher than that observed in general populations in southern Québec and in Massachusetts (USA), similar to that found in the Netherlands, and about two to three times lower than in the groups of marine mammal consumers from Greenland and Faroe Islands. With regard to PCB exposure in the early neurobehavioral studies conducted in Michigan and North Carolina, prenatal PCB exposure in Nunavik was similar to that observed in the Michigan study, while both were higher than prenatal exposure observed in North Carolina cohort.

Hg concentrations found in cord blood and maternal hair samples averaged 22.7 $\mu g \cdot L^{-1}$ and 4.5 $\mu g \cdot g^{-1}$, respectively (geometric means 18.5 and 3.7). These data confirm that prenatal exposure to Hg in the studied population is higher than that observed in general population samples in Canada and the United States. When compared to cohorts with relatively high concentrations that were studied in relation to neurobehavioral effects of prenatal Hg exposure, the Hg exposure in Nunavik Inuit was similar to that observed in the Faroe Islands' first and second cohorts, slightly lower than in the Seychelles Islands cohorts, and substantially lower than in the highest exposed group in the New Zealand study. Hg exposure in Nunavik Inuit was slightly higher than the average concentration observed in another Canadian aboriginal population, the Cree, in 1992. Compared with Greenlandic Inuit from the Disco Bay region, the Nunavik Hg exposure was lower.

Cord blood lead concentrations averaged 0.2 $\mu mol \cdot L^{-1}$, which corresponds to 41.4 $\mu g \cdot L^{-1}$ (geometric mean 0.2 $\mu mol \cdot L^{-1}$). The average lead concentration obtained in this cohort was two times higher than that found in the general population from Southern Quebec and similar to that reported for the Greenlandic Inuit.

Although the studied infants were exposed transplacentally to both OCs and mercury, exposures were only moderately confounded: cord PCB-cord Hg, $r = 0.24$; cord PCB-average hair Hg, $r = 0.34$. The associations between cord blood lead and Hg concentrations were also low, and the intercorrelations between cord blood lead and OC concentrations were even weaker.

We examined cord plasma PCB 153 concentrations in relation to duration of pregnancy, physical growth at birth and developmental outcomes assessed at 6.5 and 11 months of age using multiple regression analyses. Pearson correlations were performed to select among the control variables those to be included in multivariate analyses. After controlling for potential confounders associated at $p \leq .10$ with the studied outcomes, higher cord plasma PCB 153 concentrations were associated with lower birth weight and marginally related to shorter duration of pregnancy. The magnitude of the negative association between PCB and birth weight was comparable to those noted with prenatal exposure to alcohol or smoking during pregnancy. Cord plasma PCB 153 concentrations were associated with shorter length at birth in girls and were not related to head circumference.

With regard to early cognitive development, each of the major environmental contaminants examined in this study was associated with a specific aspect of early cognitive development. Whereas prenatal PCB exposure was most strongly related to visual recognition memory, cord blood lead concentrations were related to slower speed of processing information, and prenatal mercury exposure — whether assessed in cord blood or maternal hair — to poorer performance on the A-not-B Test, which is

believed to be an early precursor of executive function. Moreover, omega-3 fatty acids was found to be associated with elevated birth weight, longer duration of pregnancy, better visual acuity, and more optimal motor and cognitive development.

Conclusions

These findings are consistent with results of previous epidemiological studies conducted in populations exposed to PCBs through the consumption of contaminated food. The beneficial effects of omega-3 fatty acids intake during pregnancy were seen in a broad range of infant outcomes. In this population, the negative effects of prenatal PCB exposure on duration of pregnancy, physical growth and cognitive function remained significant despite the beneficial effects of omega-3 fatty acids. These data also provide support for the hypothesis that the adverse effects of prenatal exposure to PCBs, mercury and lead do not operate on a common neural pathway but instead impact on very different aspects of cognitive function during infancy.

All the activities planned for this year were performed.

Expected Completion Date

March 2003.

Acknowledgments

We are grateful to the Nunavik population for their participation in this research, and to the medical and health care professionals — midwives, nurses, laboratory technicians, archives technicians and doctors — from the Inuulitsivik Health Center and the nursing stations in Puvirnituk, Inukjuak, and Kuujjuarapik for their assistance. We also acknowledge the administration of the Inuulitsivik Health Center, municipal councils from Puvirnituk, Inukjuak, and Kuujjuarapik, the Nunavik Nutrition and Health Committee, Nunavik Regional Board of Health and Social Services, the Board of the Nunalituqait Ikajuqatigiitut Inuit Association, and the Pauktuutit Inuit Women's Association for their support during the last decade. This study was made possible by yearly grants from Indian and Northern Affairs Canada (Northern Contaminants Program) since 1993, and grant number R01-ES07902 from the National Institute of Environmental Health and Sciences/NIH, Health Canada, FRSQ/Hydro-Québec (Environmental Child Health Initiative) and the Nunavik Regional Board of Health and Social Services.

References

Amin-Zaki, L., S. Elhassani, M.A. Majeed, T.W. Clarkson, R.A. Doherty, M.R. Greenwood, and T. Giovanoli-Jakubczak. 1976. Perinatal methylmercury poisoning in Iraq. *Am J Dis Child.* 130:1070–1076.

Harada, M. 1995. Minamata disease: Methylmercury poisoning in Japan caused by environmental pollution. *Crit Rev Toxicol.* 25:1–24.

Marsh, D.O., T.W. Clarkson, C. Cox, G.J. Myers, L. Amin-Zaki, and S. Al-Tikriti. 1987. Fetal methylmercury poisoning. Relationship between concentration in single strands maternal hair and child effects. *Arch Neurol.* 44:1017–1022.

Crump, K.S., T. Kjellström, A.M. Shipp, A. Silvers, and A. Stewart. 1998. Influence of prenatal mercury exposure upon scholastic and psychological test performance: Benchmark analysis of a New Zealand cohort. *Risk Anal.* 18:701–713.

Kjellstrom, T., P. Kennedy, S. Wallis, and C. Mantell. 1986. Physical and mental development of children with prenatal exposure to mercury from fish. Stage 1: Preliminary test at age 4. Sweden: National Swedish Environmental Protection Board.

Grandjean, P., P. Weihe, R.F. White, F. Debes, S. Araki, K. Yokoyama, K. Murata, N. Sorensen, R. Dahl, and P.J. Jorgensen. 1997. Cognitive deficit in 7-year old children with prenatal exposure to methylmercury. *Neurotoxicol Teratol.* 19:417–428.

Davidson, P.W., G.J. Myers, C.C. Cox, C. Axtell, C. Shamlaye, J. Sloane-Reeves, E. Cernichiari, , L. Needham, A. Choi, and Y.N. Wang. 1998. Effects of prenatal and postnatal methylmercury exposure from fish consumption on neurodevelopment. *JAMA* 280:701–707.

Myers, G.J., D.O. Marsh, C. Cox, P.W. Davidson, C.F. Shamlaye, M.A. Tanner, A. Choi, E. Cernichiari, E. Choisy, and T.W. Clarkson. 1995a. A pilot neurodevelopmental study of Seychellois children following in utero exposure to methylmercury from a maternal fish diet. *Neurotoxicology.* 16:629–638.

Grandjean, P., E. Budtz-Jorgensen, R.F. White, P.J. Jorgensen, P. Weihe, F. Debes, and N. Keiding. 1999. Methylmercury exposure biomarkers as indicators of neurotoxicity in children aged 7 years. *Am J Epidemiol.* 150:301–305.

Davidson, P.W., G.J. Myers, C.C. Cox, C. Shamlaye, D.O. Marsh, M.A. Tanner, M. Berlin, J. Sloane-Reeves, E. Cernichiari, O. Choisy, A. Choi, and T.W. Clarkson.

1995. Longitudinal neurodevelopmental study of Seychellois children following in utero exposure to methylmercury from maternal fish ingestion: Outcomes at 19 and 29 months. *Neurotoxicology.* 16:677–688.

Myers, G.J., D.O. Marsh, P.W. Davidson, C. Cox, C.F. Shamlaye, M.A. Tanner, A. Choi, E. Cernichiari, E. Choisy, and T.W. Clarkson. 1995b. Main neurodevelopmental study of Seychellois children following in utero exposure to methylmercury from a maternal fish diet: Outcome at six months. *Neurotoxicology.* 16: 653–664.

Chen, Y.-C.J., Y.-L. Guo, C.-C. Hsy, and W.J. Rogan. 1992. Cognitive development of Yu-Cheng ("Oil Disease") children prenatally exposed to heat-degraded PCBs. *JAMA.* 268:3213–3218.

Yu, M.L., C.C. Hsu, B.C. Gladen, and W.J. Rogan. 1991. In utero PCB/PCDF exposure: relation to developmental delay to dysmorphy and dose. *Neurotoxicol Teratol.* 13:195–202.

Jacobson, S.W., G.G. Fein, J.L. Jacobson, P.M. Schwartz, and J.K. Dowler. 1985. The effects of intrauterine PCB exposure in visual recognition memory. *Child Dev.* 56: 853–860.

Jacobson, J.L., S.W. Jacobson, and H.E.B. Humphrey. 1990a. Effects of in utero exposure to polychlorinated biphenyls and related contaminants on cognitive functioning in young children. *J Pediatr.* 116:38–45.

Jacobson, J.L., S.W. Jacobson, R.J. Padgett, G.A. Brumitt, and R.L. Billings. 1992. Effects of prenatal PCB exposure on cognitive processing efficiency and sustained attention. *Dev Psychol.* 28:297–306.

Darvill, T., E. Lonky, J. Reihman, P. Stewart, and J. Pagano. Prenatal exposure to PCBs and infant performance on the Fagan Test of Infant Intelligence. *Neurotoxicology.* (In press).

Gladen, B.C., W.J. Rogan, P. Hardy, J. Thullen, J. Tingelstad, and M. Tully. 1988. Development after exposure to polychlorinated biphenyls and dichlorodiphenyl dichloroethene transplacentally and through human milk. *J Pediatr.* 113:991–995.

Rogan, W., and B.C. Gladen. 1991. PCBs, DDE, and child development at 18 and 24 months. *Annals of Epidemiology.* 1:409–413.

Jacobson, J.L., and S.W. Jacobson. 1996. Intellectual impairment in children exposed to polychlorinated biphenyls in utero. *N Engl J Med.* 335:783–789.

Patandin, S., C.I. Lanting, P.G. Mulder, E.R. Boersma, P.J. Sauer, N. Weisglas-Kuperus. 1999. Effects of environmental exposure to polychlorinated biphenyls and dioxins on cognitive abilities in Dutch children at 42 months of age. *J Pediatr.* 134:33–41.

National Research Council. 2000. Toxicological Effects of Methylmercury. Washington, DC: National Academy Press.

Crawford, M.A., A.G. Hassam, G. Williams, and W.E. Whitehouse. 1976. Essential fatty acids and fetal brain. *Lancet* i: 452–453.

Greiner, R.S., T. Morigushi, A. Hutton, B.M. Slotnick, and N. Salem. 1999. Rats with low levels of brain docosahexaenoic acid show impaired performance in olfactory-based and spatial learning tasks. *Lipids.* 34(Suppl.):S239–S243.

Innis, S.M. 2000. Essential fatty acids in infant nutrition: Lessons and limitations from animal studies in relation to studies on infant fatty acid requirements. *Am J Clin Nutr.* 71(suppl):238S–244S.

Bjerve, S.K., L. Thoresen, K. Bonaa, T. Vik, H. Johnsen, and A.M. Brubakk. 1992. Clinical studies with alpha-linolenic acid and long-chain n-3 fatty acids. *Nutrition.* 8(2): 130–132.

Uauy, R., D.G. Birch, E.E. Birch, J.E. Tyson, and D.R. Hoffman. 1990. Effects of dietary omega-3 fatty acids on retinal function of very-low-birth-weight neonates. *Pediatric Research.* 28(5):485–492.

Uauy, R., and D.R. Hoffman. 2000. Essential fat requirements of preterm infants. *Am J Clin Nutr.* 71(suppl): 245S–250S.

Placental Cytochromes P450 as Biomarkers of Adverse Developmental Effects in Inuit Infants

Project leader

Daria Pereg, Public Health Research Unit, CHUQ, CHUL, Institut National de Santé Publique du Québec, Toxicologie Humaine, 945 Wolfe Ave, Ste-Foy, QC G1V 5B3; phone: (418) 650-5115 (ext. 4647); fax: (418) 654-2148; e-mail: daria.pereg@inspq.qc.ca

Project team members

Pierre Ayotte, Gina Muckle and Éric Dewailly, Public Health Research Unit, CHUQ, CHUL, 945 Wolfe Ave, Ste-Foy, QC G1V 5B3.

Abstract

Exposure to selected organochlorines (OCs) was previously linked to adverse developmental effects in animals and humans and it was also shown to increase cytochromes P450 enzymes (CYP) levels in different tissues. The main objective of this project was to relate placental CYP induction in Inuit women of Nunavik to their exposure to environmental OCs and to their life-style habits, as well as to developmental endpoints in their newborn (birth weight, length, head circumference). Immunoblotting analyses on placental microsomes revealed the presence of detectable levels of CYP1A1 and CY2B6, but not CYP1B1 and CYP2E1. Placental pentoxyresorufin *O*-dealkylation (PROD) activity (related to CYP2B6/3A4) was not detected at significant levels in our samples, but ethoxyresorufin *O*-dealkylation (EROD) activity (related to CYP1A1/1A2 and 1B1) was detected and quantified in all samples processed (n = 109). A high proportion of the Inuit population carried the CYP1A1*2c polymorphism, but it didn't significantly influence placental EROD activity. EROD activity was highly correlated with smoking during pregnancy (as estimated by cotinine concentrations in meconium), but it was not related to environmental organochlorine exposure or to the newborn's characteristics at birth (weight, length, head circumference and foetal maturity), hence suggesting that the effects of prenatal exposure to OCs and/or tobacco toxicants on intra-uterine development are not significantly mediated by mechanisms involving the induction of CYP1A1 in the placenta.

Key Project Messages

1. Placental EROD activity (CYP1A1) is primarily modulated by smoking during pregnancy, not by environmental contaminants.
2. The Inuit population of Nunavik shows a proportion higher than expected of people carrying the CYP1A1*2c variant genotype, but this polymorphism does not affect placental EROD activity or newborn's physical characteristics at birth.
3. The newborn's physical characteristics at birth may be affected by smoking during pregnancy and/or by environmental contaminants exposure, but these effects are not significantly mediated by mechanisms involving placental CYP1A1 induction.

Objectives

1. To determine CYP enzyme profiles in placentas of Inuit women of Nunavik and relate them to environmental OCs exposure, lifestyle habits and to developmental endpoints in newborns.
2. To screen for known CYP polymorphisms in order to refine the interpretation of CYP induction as a biomarker of early biochemical effect, and to determine if specific genotypes modify the risk associated with prenatal exposure to xenobiotics in the Nunavik population.

Introduction

The Inuit of Nunavik are exposed to unusually high doses of organochlorines (OCs) due to their traditional consumption of sea mammal fat (Dewailly et al. 1993). Prenatal exposure to OCs was related to adverse developmental effects in different human populations (Gladen et al. 2000; Patandin et al. 1998; Taylor et al. 1989), but the mechanisms underlying this toxicity remain unclear. Several OCs are known inducers of drug-metabolizing enzymes, including cytochromes P450s (CYPs). Dioxins and dioxin-like compounds induce CYP1A1 through a mechanism mediated by the AHR (Okey 1990), while CYP2B and CYP3A are induced by other OCs (ortho-substituted PCBs, some pesticides) through a mechanism mediated by the CAR, PXR and RXR receptors (Zelko and Negishi 2000). Earlier studies have suggested that placental CYP1A1 induction was related to maternal smoking (Boden et al. 1995) and to maternal exposure to dioxin-like compounds (Wong et al. 1985), and high placental CYP1A1 activity was correlated to lower birth weights (Lucier et al. 1987; Pelkonen et al. 1979). Hence, placental CYP1A1 induction by OCs or other xenobiotics may be involved in the mechanism of action leading to adverse developmental effects.

In order to address the effects of prenatal exposure to OCs on the children's physical and neurological development in the Arctic, a cohort study is currently being carried out in the Nunavik population. The present project is nested in this cohort study and aims at including biomarkers of early effects in the study design in order to investigate the mechanisms underlying the prenatal toxicity associated with maternal exposure to xenobiotics, and to add biological plausibility to the associations observed between OCs exposure and adverse effects on children's development. The objective of this project was to determine CYPs induction profiles in placentas of Inuit women of Nunavik and relate them, on the one hand, to environmental OCs exposure and life-style habits, and on the other hand, to developmental endpoints in newborns.

Activities

In 2002–2003

Population description, sample collection, analytical methods

Inuit women residing in Nunavik (Puvirnituk, Inukjuak, Kuujjuaraapik) were recruited in the framework of the Nunavik Infant Development Cohort Study, which is fully described in a report by Muckle et al. (2001b). Briefly, following thorough explanation of the project and after signing a consent form, women answered a questionnaire addressing dietary and life-style habits, and gave their consent for sampling of placenta, maternal blood, umbilical cord blood, infant blood (at 6 months) and milk. Maternal smoking status was ascertained using cotinine concentration in meconium (Ostrea et al. 1994; Pereg et al. 2001). Analytical methods have been fully described in earlier reports (Muckle et al. 2001a; Muckle et al. 2001b; Pereg et al. 2002).

Detection of CYP proteins by immunoblotting

Microsomal fractions were isolated from placental tissue by differential centrifugation and stored in Tris-sucrose buffer (50 mM Tris-0.25 M sucrose, pH 8.0) at −80°C until further processing. Protein concentrations were determined by the bicinchoninic acid assay (Pierce Biotechnology, MJS Biolynx, Brockville, ON). Two pools of placental microsomes were constituted (one for non-smokers, one for smokers) and immunoblotting was carried out to determine which CYP enzymes were detectable at significant levels (CYP1A1, 1B1, 2B6 and 2E1). 3.6 μg placental microsomal proteins were separated by SDS-PAGE. Microsomes from cells over-expressing the CYP protein of interest (CYP1A1, 1A2, 1B1, 2B6 and 2E1) were loaded as positive control and standard reference on every gel in concentrations ranging from 0.03 to 0.25 pmol CYP, according to the standard used (Gentest, Woburn, MA). After electrophoresis, the proteins were electroblotted on PVDF membranes. The latter were blocked in PBS-skim milk (5%), washed in PBS and incubated with one of the following primary antibodies: goat anti-human CYP1A1/2, rabbit anti-human CYP1B1, rabbit anti-human CYP2B6 and goat anti-human CYP2E1 (Gentest, Woburn, MA). After washing the membranes in PBS, they were incubated with a secondary antibody directed against rabbit or goat IgG and conjugated with horseradish peroxidase. Immunoblots were revealed by chemiluminescence with the Immun-Star horseradish peroxidase substrate (BioRad Laboratories, Mississauga, ON) and images were captured and analysed with a digital image analysis system (AlphaInnotech FluorChem 8800).

Table 1. Single nucleotide polymorphisms found on the CYP1A1 gene

SNP	Nucleotide change	Amino acid change	Location	Reference
CYP1A1*2a	3801 T > C MspI restriction site	None	3' flanking region	(Hayashi et al. 1991b)
CYP1A1*2c	2455 A > G	Ile 462 Val	Exon 7	(Hayashi et al. 1991b)
CYP1A1*4	2453 C > A	Thr 461 Asn	Exon 7	(Cascorbi et al. 1996)
CYP1A1*5	2461 C > A	Arg 464 Ser	Exon 7	(Chevalier et al. 2001)
CYP1A1*6	1636 G > T	Met 331 Ile	Exon 4	(Chevalier et al. 2001)

Determination of CYP1A1 and CYP2B6 activity levels

Methods to assess CYP activities on resorufin substrates in 96-well plates have already been described (Lagueux et al. 1997; Lagueux et al. 1999; Pereg et al. 2001; Pereg et al. 2002). EROD and PROD activities were measured in placental microsomes to assess CYP1A and CYP2B activities, respectively (Burke et al. 1994). EROD and PROD activities were expressed in pmoles of resorufin produced·minute^{-1}·mg^{-1} of microsomal proteins.

Genotyping

Genotyping analyses were carried out in Dr. François Rousseau's laboratory (CHUQ-CRSFA). Single nucleotide polymorphisms (SNPs) identified on the CYP1A1 gene (Table 1) were genotyped by allele-specific PCR and a dsDNA-specific dye, according to the method of Moran et al. (1998) with some modifications. The dye used was SYBR Green 1 (Molecular Probes, Eugene, OR) and the results were analysed with software developed in-house. DNA extractions from maternal and cord blood and PCR reactions were performed in 96-well plates.

Statistical analyses

A database was assembled in the framework of the Nunavik Infant Development Cohort Study, which includes data from the questionnaires and analytical data (organochlorines, heavy metals, cotinine, etc.). In order to investigate the relations between CYP enzymes, exposure to environmental contaminants, life-style habits and developmental endpoints (birth weight and length, head circumference) in the present study, biochemical and genetic endpoints (enzyme activities, polymorphisms, etc.) were included in the database of the Nunavik Infant Development Cohort Study.

OCs plasma concentrations, cotinine concentrations in meconium and placental EROD activities followed a log-normal distribution and were normalized through a logarithmic conversion ($\log_{10}$) before further processing. A value equal to half the detection limit was attributed to samples below the detection limit (except EROD activities, for which undetected values were entered as such). Newborns' physical characteristics at birth followed a normal distribution. Means were compared using Student's t tests (2 groups) or one-way analyses of variance (3 groups or more) with Tamhanes's post-hoc procedures. Correlations were tested using Spearman's correlation coefficients. Multiple regression analyses were conducted to test: 1) the effect of OCs exposure and smoking on EROD activity; 2) the effect of CYP1A1 genotypes on EROD activity and on the newborn's physical characteristics at birth; and 3) the effect of EROD activity on the newborn's physical characteristics at birth. For all analyses, the level of significance was set to 0.05. All statistical tests were performed using the SPSS 11.5 for Windows statistical package (SPSS Inc., Chicago, IL).

Results

Organochlorine exposure

Organochlorine measurements in cord plasma were available for 110 subjects (46 for TEQs), and 109 placenta samples were available for biochemical analyses. Detailed exposure analysis for this population is provided in Muckle et al. (2001b). PCBs concentrations were strongly intercorrelated in cord plasma (Spearman's $r > 0.72$, $p < 0.05$) and most PCB congeners showed a significant association with total TEQs measured in milk. PCB 153 was the most abundant congener detected in all samples and it was correlated to other frequently detected PCBs (Correlation coefficients ranging from 0.85 to 0.97, $p < 0.05$) as well as to TEQs in milk (Spearman's $r = 0.50$, $p < 0.05$). Therefore, PCB-153 was selected as the exposure variable in further statistical analyses.

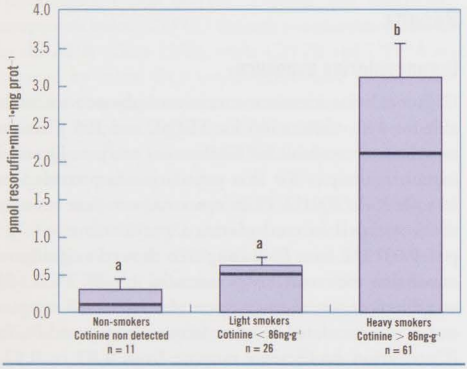
Immunoblotting analyses

Immunoblotting analyses on pooled placental microsomes from Inuit women showed that CYP1A1, CYP2B6 and CYP1A2 (low concentrations), could be detected in placenta. However, CYP1B1 and CYP2E1 could not be detected at significant levels in these samples using this immunoblotting method, and further analyses of these isoforms were not undertaken in the framework of this project.

PROD and EROD activities

PROD activity could not be detected at significant levels in any placental samples, despite the detection of CYP2B6 by immunoblotting in pooled placental microsomes. The limit of detection for resorufin in all EROD and PROD assays was 2.5pmol and for all PROD activity assays, 502 µg placental microsomal proteins were used (3.0mg·ml^{-1} final protein concentration in reaction). All positive controls (phenobarbital-treated rat liver microsomes) showed detectable PROD activity but the coefficient of variation among experimental controls was high (25%). Contrarily to PROD activity, EROD activity was detected in all placenta samples. For EROD assays, 168 and 252 µg placental microsomal proteins were used (1.0 and 1.5mg·ml^{-1} final protein concentration in reaction). All positive controls (pooled placental samples from heavy smokers) showed detectable EROD activity and the coefficient of variation among experimental controls was 14%.

Figure 1. EROD activities in the three smoker categories were based on cotinine concentration in meconium. Statistically significant differences among groups were determined by ANOVA and Tamhane's post-hoc procedure. Bars indicate mean values, error bars indicate standard errors and black lines across bars indicate median values



Cigarette smoke is a known inducer of CYP1A1 (Boden et al. 1995). Cotinine in the meconium was significantly associated with the self-declared cigarette consumption during pregnancy (Spearman's r = 0.45, $p < 0{,}001$) and even more so with placental EROD activity (r = 0.67, $p < 0.001$) and it was shown to be a good biomarker of the foetal exposure to tobacco smoke toxicants. Figure 1 shows the mean (± standard error) and median EROD activities measured in three categories of smokers based on cotinine concentration in the meconium (with a 86 ng·g^{-1} cotinine concentration cut-off to discriminate between women who smoke more or less than 10 cigarettes·day^{-1}) (Pereg et al. 2001). A statistically significant difference was observed between EROD activities measured in placentas from heavy smokers, compared to women who smoked less than 10 cigarettes per day or didn't smoke during pregnancy (ANOVA, $p < 0.001$). Given the lack of effect observed on EROD activities in light smokers, the latter category was merged with the non-smoker category in further analyses involving women's smoking status in order to balance the number of subjects among groups.

Placental EROD activities were also compared between newborn's gender to ensure that this variable did not modify the effect observed. Girls showed a mean EROD value of 1.8 ± 0.3pmol resorufin produced*min^{-1}mg prot^{-1} (median value = 1.2) and boys showed a mean EROD value of 2.6 ± 0.4 (median value = 1.2). No statistically significant difference was found between the two groups (Student's t-test, p = 0.452). This variable was therefore not further considered in multivariate models testing the determinants of placental EROD activity.

The association of placental EROD activity with environmental contaminants was tested while controlling for the

Table 2. Multivariate linear regression analyses testing the association of placental EROD activity with environmental contaminants while controlling for the effect of smoking

EROD (log) = cotinine (log) + PCB-153 (log)	R^2 (std β for variables)	p	n
Model	0.363	< 0.001	93
Cotinine (log)	0.602	< 0.001	
PCB-153 (log)	0.039	0.644	
EROD (log) = cotinine (log) + TEQs milk (log)	**R^2 (std β for variables)**	**P**	**n**
Model	0.390	0.001	31
Cotinine (log)	0.630	< 0.001	
Total TEQs (log)	−0.052	0.732	

effect of smoking. Table 2 shows the results of two multivariate linear regression analyses testing these associations. Analyses were carried out on log-transformed data to account for the log-normal distribution of variables. The results show that EROD activity is primarily modulated by smoking during pregnancy, and that the influence of environmental contaminants on placental EROD activity is not statistically significant.

CYP1A1 genotypes

CYP1A1*4, *5 and *6 polymorphisms showed a very low proportion (or absence) of variants and heterozygotes in the Nunavik population. The frequency of CYP1A1*2a variants was 15.3% (from cord blood). For CYP1A1*2c, the proportion of variants was 23.8%. Placental EROD activity was compared between genotype groups (heterozygotes were pooled with variants and compared to wild-types) while controlling for the smoking status (smoker category) using two-way ANOVAs. No significant effect of CYP1A1 genotypes on placental EROD activity were observed (CYP1A1*2a, $p = 0.121$, and CYP1A1*2c, $p = 0.697$) while the smoker category remained significant in both models ($p < 0.001$).

Newborn's physical characteristics at birth

Correlation analyses and multiple regression analyses were carried out to test the effect of placental EROD on the newborn's physical characteristics at birth. The effect of the variants CYP1A1*2a and *2c on the newborn's physical characteristics at birth were also tested by multiple regression. Known modifying variables such as gestational age, parity, newborn's gender, mother's weight, omega-3 fatty acids, tobacco and alcohol consumption were considered in the regression models. Placental EROD activity was not significantly associated with birth weight (Spearman's $r = 0.240$, $p = 0.803$), birth length ($r = -0.190$, $p = 0.848$) or head circumference ($r = 0.092$, $p = 0.350$). In multiple regression models allowing control for the effect of confounding and/or modifying variables, there was no significant effect of placental EROD on any newborn's physical characteristics at birth and no significant effect of CYP1A1 genotypes could be observed.

Discussion

Foetal growth may be negatively influenced by maternal exposure to environmental contaminants (Lucier et al. 1987) and by maternal smoking during pregnancy (Peacock et al. 1998; Wang et al. 2002). In the Nunavik population, Muckle et al. (2003) report that prenatal exposure to PCBs was associated with subtle effects on duration of pregnancy as well as the newborn's weight and length at birth. However, the effects of maternal smoking on foetal growth remain to be addressed thoroughly in the Nunavik population. Our hypothesis was that the mechanisms of toxicity underlying detrimental effects on foetal growth caused by prenatal exposure to xenobiotics could be related to the induction of P450s in placenta.

The results obtained by immunoblotting showed that CYP1A1, 1A2 and 2B6 could be detected in placenta, whereas CYP2E1 and 1B1 could not. The detection of CYP1A1 and 1A2 and the absence of CYP1B1 in placenta are observations that are consistent with data reported earlier by Hakkola et al. (1996, 1998). However, in the same study, CYP2E1 could be detected at low levels and CYP2B6 could not be detected, while we obtained opposite results. These discrepancies could be attributed to differences in the methods used (RT-PCR vs. immunoblotting), or in the different antibodies used for immunoblotting in both studies.

Our results showed that maternal smoking primarily modulated placental CYP1A1 activity (EROD), while the influence of environmental contaminants on CYP1A1 induction was not significant. This result does not corroborate previous studies carried out in the population affected by the Yu-Cheng syndrome (Lucier et al. 1987; Wong et al. 1985), but it is consistent with data previously published in the Nunavik population with a smaller sample size. This result is fully discussed in a previous publication (Pereg et al. 2002). The frequencies of CYP1A1*2a variants in the Nunavik population (15.3%) is similar to that reported for Asian populations (14%), but surprisingly, the frequency for the CYP1A1*2c polymorphism (23.8% variants) was higher than expected, given the frequencies determined for three ethnic groups in a meta-analysis: Caucasians (0.6% variants), Asians (4.9% variants) and Africans (0% variants) (Garte et al. 2001). However, placental CYP1A1 (EROD) activity was not related to the newborn's characteristics at birth (weight, length, head circumference, foetal maturity), and neither the CYP1A1*2a or *2c variants had a significant effect on EROD activity or on foetal development, as it was suggested by Wang et al. (2002). Nevertheless, the high frequency of CYP1A1*2a and *2c variants in the Inuit population should not be overlooked, given the known effects of these polymorphisms on cancer susceptibility (Hayashi et al. 1991a; Hayashi et al. 1991b; Kawajiri et al. 1993; Moysich et al. 1998).

In summary, these results suggest that the effects of prenatal exposure to OCs and/or tobacco toxicants on intra-uterine development may not be solely mediated by mechanisms involving the induction of CYP1A1 in the placenta, and other pathways leading to toxicity should be investigated.

Unfortunately, the absence of detectable PROD (CYP2B6/3A4) activity in our placenta samples prevents any further interpretation of the significance of placental CYP2B6 induction with regards to environmental contaminants exposure and foetal development. Therefore, further studies are needed to compare our results to similar experiments carried out in other populations (Hakkola et al. 1996; Hakkola, et al. 1998) and to investigate the possible involvement of placental CYP2B6 induction in the mechanism of toxicity underlying the effects of maternal exposure to xenobiotics on foetal growth. These studies should include RT-PCR analyses of CYP mRNA expression in placenta, immunoblotting analyses on individual samples (ongoing) and a better assessment of CYP2B6 activity by the use of a more sensitive and specific technique.

Acknowledgements

We thank Alain Leblanc, Liliane Ferron and Michel Lefebvre from the Institut national de Santé Publique du Québec (INSPQ), Toxicologie Humaine for PCB and cotinine analyses. We thank Nathalie Ouellet (CHUQ-CHUL, URSP) for carrying out immunoblotting analyses. Special thanks are given to Dr. Sylvie Giroux (Laboratoire de génétique, CHUQ-CRSFA) for conducting genotyping analyses as well as for her help in the interpretation of genetic analyses and data.

References

Boden, A.G., P.G. Bush, M.D. Burke, D.R. Abramovich, P. Aggett, T.M. Mayhew, and K.R. Page. 1995. Human placental cytochrome P450 and quinone reductase enzyme induction in relation to maternal smoking. *Reproduction, Fertility, and Development.* 7:1521–24.

Burke, M.D., S. Thomson, R.J. Weaver, C.R. Wolf, and R.T. Mayer. 1994. Cytochrome P450 specificities of alkoxyresorufin o-dealkylation in human and rat liver. *Biochemical Pharmacology.* 48:923–936.

Cascorbi, I., J. Brockmoller, and I. Roots. 1996. A C4887A polymorphism in exon 7 of human CYP1A1: population frequency, mutation linkages, and impact on lung cancer susceptibility. *Cancer Research.* 56:4965–9.

Chevalier, D., D. Allorge, J.M. Lo-Guidice, C. Cauffiez, M. Lhermitte, J.J. Lafitte, and F. Broly. 2001. Detection of known and two novel (M331I and R464S) missense mutations in the human CYP1A1 gene in a French Caucasian population. *Hum Mutat.* 17:355.

Dewailly, É., P. Ayotte, S. Bruneau, C. Laliberté, D.C.G. Muir, and R.J. Norstrom. 1993. Inuit exposure to organochlorines through the aquatic food chain in Arctic Québec. *Environmental Health Perspectives.* 101:618–620.

Garte, S., L. Gaspari, A.K. Alexandrie, C. Ambrosone, H. Autrup, J.L. Autrup, H. Baranova, L. Bathum, S. Benhamou, P. Boffetta, C. Bouchardy, K. Breskvar, J. Brockmoller, I. Cascorbi, M.L. Clapper, C. Coutelle, A. Daly, M. Dell'Omo, V. Dolzan, C.M. Dresler, A. Fryer, A. Haugen, D.W. Hein, A. Hildesheim, A. Hirvonen, L.L. Hsieh, M. Ingelman-Sundberg, I. Kalina, D. Kang, M. Kihara, C. Kiyohara, P. Kremers, P. Lazarus, L. Le Marchand, M.C. Lechner, E.M. van Lieshout, S. London, J.J. Manni, C.M. Maugard, S. Morita, V. Nazar-Stewart, K. Noda, Y. Oda, F.F. Parl, R. Pastorelli, I. Persson, W.H. Peters, A. Rannug, T. Rebbeck, A. Risch, L. Roelandt, M. Romkes, D. Ryberg, J. Salagovic, B. Schoket, J. Seidegard, P.G. Shields, E. Sim, D. Sinnet, R.C. Strange, I. Stucker, H. Sugimura, J. To-Figueras, P. Vineis, M.C. Yu, and E. Taioli. 2001. Metabolic gene polymorphism frequencies in control populations. *Cancer Epidemiol Biomarkers Prev.* 10:1239–48.

Gladen, B.C., N.B. Ragan, and W.J. Rogan. 2000. Pubertal growth and development and prenatal and lactational exposure to polychlorinated biphenyls and dichlorodiphenyl dichloroethene. *Journal of Pediatrics.* 136:490–6.

Hakkola, J., M. Pasanen, J. Hukkanen, O. Pelkonen, J. Maenpaa, R.J. Edwards, A.R. Boobis, and H. Raunio, 1996. Expression of xenobiotic-metabolizing cytochrome P450 forms in human full-term placenta. *Biochemical Pharmacology.* 51:403–11.

Hakkola, J., O. Pelkonen, M. Pasanen, and H. Raunio. 1998. Xenobiotic-metabolizing cytochrome P450 enzymes in the human feto-placental unit: role in intrauterine toxicity. *Critical Reviews in Toxicology.* 28: 35–72.

Hayashi, S., J. Watanabe, K. Nakachi, and K. Kawajiri. 1991a. Genetic linkage of lung cancer-associated MspI polymorphisms with amino acid replacement in the heme binding region of the human cytochrome P450IA1 gene. *Journal of Biochemistry* (Tokyo). 110: 407–11.

Hayashi, S.I., J. Watanabe, K. Nakachi, and K. Kawajiri. 1991b. PCR detection of an A/G polymorphism within exon 7 of the CYP1A1 gene. *Nucleic Acids Research.* 19:4797.

Kawajiri, K., K. Nakachi, K. Imai, J. Watanabe, and S. Hayashi. 1993. The CYP1A1 gene and cancer susceptibility. *Critical Reviews in Oncology/Hematology.* 14: 77–87.

Lagueux, J., E.B. Affar, D. Nadeau, P. Ayotte, É. Dewailly, and G.G. Poirier. 1997. A microassay for the detection of low levels of cytochrome P450 O-deethylation activities with alkoxyresorufin substrates. *Molecular and Cellular Biochemistry.* 175:125–129.

Lagueux, J., D. Pereg, P. Ayotte, É. Dewailly, and G. Poirier. 1999. Cytochrome p450 CYP1A1 enzyme activity and DNA adducts in placenta of women environmentally exposed to organochlorines. *Environmental Research.* 80:369–82.

Lucier, G.W., K.G. Nelson, R.B. Everson, T.K. Wong, R.M. Philpot, T. Tiernan, M. Taylor, and G.I. Sunahara. 1987. Placental markers of humans exposure to polychlorinated biphenyls and polychlorinated dibenzofurans. *Environmental Health Perspectives.* 76: 79–87.

Moran, P., D.A. Dightman, and L.K. Park. 1998. Non-electrophoretic genotyping using allele-specific PCR and a dsDNA-specific dye. *Biotechniques.* 24:206–8, 210, 212.

Moysich, K.B., C.B. Ambrosone, J.E. Vena, P.G. Shields, P. Mendola, P. Kostyniak, H. Greizerstein, S. Graham, J.R. Marshall, E.F. Schisterman, and J.L. Freudenheim. 1998. Environmental organochlorine exposure and postmenopausal breast cancer risk. *Cancer Epidemiology, Biomarkers and Prevention.* 7:181–88.

Muckle, G., P. Ayotte, É. Dewailly, S.W. Jacobson, and J. L. Jacobson. 2001a. Determinants of polychlorinated biphenyls and methylmercury exposure in Inuit women of childbearing age. *Environmental Health Perspectives.* 9:957–963.

Muckle, G., P. Ayotte, É. Dewailly, S.W. Jacobson, and J.L. Jacobson. 2001b. Prenatal Exposure of the Northern Quebec Inuit Infants to environmental contaminants. *Environmental Health Perspectives.* 12: 1291–1299.

Muckle, G. 2003. Transplacental exposure to PCBs and infant development/human exposure assessment. *Synopsis of Research.* Ottawa, Northern Contaminants Program, Indian and Northern Affairs Canada: in press.

Okey, A.B. 1990. Enzyme induction in the cytochrome P-450 system. *Pharmacology and Therapeutics.* 45:241–98.

Ostrea, E.M., D.K. Knapp, A. Romero, M. Montes, and A.R. Ostrea. 1994. Meconium analysis to assess fetal exposure to nicotine by active and passive maternal smoking. *Journal of Pediatrics.* 124:471–476.

Patandin, S., C. Koopman-Esseboom, M.A. de Ridder, N. Weisglas-Kuperus, and P.J. Sauer. 1998. Effects of environmental exposure to polychlorinated biphenyls and dioxins on birth size and growth in Dutch children. *Pediatric Research.* 44:538–45.

Peacock, J.L., D.G. Cook, I.M. Carey, M.J. Jarvis, A.E. Bryant, H.R. Anderson, and J.M. Bland. 1998. Maternal cotinine level during pregnancy and birthweight for gestational age. *International Journal of Epidemiology.* 27: 647–56.

Pelkonen, O., N.T. Kärki, M. Koivisto, R. Tuimala, and A. Kauppila. 1979. Maternal cigarette smoking, placental aryl hydrocarbon hydroxylase and neonatal size. *Toxicology Letters.* 3:331–335.

Pereg, D., J. Lagueux, É. Dewailly, G.G. Poirier, and P. Ayotte. 2001. Cigarette smoking during pregnancy: comparison of biomarkers for inclusion in epidemiological studies. *Biomarkers.* 6:161–173.

Pereg, D., É. Dewailly, G.G. Poirier, and P. Ayotte. 2002. Placental CYP1A1 activity in Inuit women environmentally exposed to polychlorinated biphenyls. *Environmental Health Perspectives.* 110:607–612.

Taylor, P.R., J.M. Stelma, and C.E. Lawrence. 1989. The relation of polychlorinated biphenyls to birth weight and gestational age in the offspring of occupationally exposed mothers. *American Journal of Epidemiology.* 129:395–406.

Wang, X., B. Zuckerman, C. Pearson, G. Kaufman, C. Chen, G. Wang, T. Niu, P.H. Wise, H. Bauchner, and X. Xu. 2002. Maternal cigarette smoking, metabolic gene polymorphism, and infant birth weight. *Jama.* 287:195–202.

Wong, T.K., R.B. Everson, and S.T. Hsu. 1985. Potent induction of human placental mono-oxygenase activity by previous dietary exposure to polychlorinated biphenyls and their thermal degradation products. *Lancet.* 1:721–724.

Zelko, I. and M. Negishi. 2000. Phenobarbital-elicited activation of nuclear receptor CAR in induction of cytochrome P450 genes. *Biochemical and Biophysical Research Communications.* 277:1–6.

Monitoring the Health of Arctic Peoples and Ecosystems and the Effectiveness of International Controls

Part A: Abiotic Monitoring and Modelling

Northern Contaminants Air Monitoring and Interpretation 2001–2002

Project leader

Pierrette Blanchard, Meteorological Service of Canada (MSC), 4905 Dufferin Street, Toronto, ON M3H 5T4; phone: (416) 739-5701; fax: (416) 793-5708; e-mail: pierrette.blanchard@ec.gc.ca

Project team

Hayley Hung and Terry Bidleman, MSC, Toronto, ON; Phillip Fellin and Henrik Li, AirZone, Mississauga, ON; Gary Stern, Brian Billeck, and Bruno Rosenberg, Freshwater Institute, Winnipeg, MB.

Abstract

Atmospheric measurements of persistent organic pollutants, including herbicides, pesticides, synthetic industrial compounds and PAHs, have been made on a weekly basis in the Canadian (Alert, Tagish, Kinngait [Cape Dorset]) and Russian Arctic (Dunai, Amderma) since January 1992. Long-term atmospheric trends were derived for PCBs and organochlorine pesticides (OCs) at Alert using a digital filtration method as reported in the previous Synopsis of Research. An update of these trends is given here with one additional year of data from 1998. Different PCB congeners manifested different rates of decline in air at Alert. To investigate the relationship between the physical chemical properties of the congeners and their rates of decline observed at Alert, as well as those found at five sites in the Great Lakes region, GloboPOP, a global distribution model of POPs, was used to identify the dominant removal processes involved. Preliminary results are reported. The results of a special study measuring particle-bound PCDD/F concentrations in air at Alert in the winter of 2000–2001 will also be summarised. An outline of a plan to update the spatial analysis of PCB, OC and PAH concentrations in Arctic air is also described.

Key Project Messages

1. Rates of decline of PCBs and OCs in arctic air became slightly slower, reflected by the slightly longer first order halflives, when 1998 data were added to the time series since 1993.
2. Air concentrations of lighter PCB congeners and heptachlorinated PCB 180 showed slow rates of decline while those of intermediate congeners stayed relatively constant. This may be attributed to the difference in their physical chemical properties which are responsible for their fate in the environment.
3. GloboPOP, a zonally averaged global distribution model for POPs, elucidated the atmospheric decline rates of PCB congeners at Alert, and at five Great Lakes sites as well. This model will be used to identify the dominant removal processes that drive the difference in atmospheric rates of decline of PCBs congeners.
4. Particle-bound PCDD/F concentrations observed at Alert were lower than those found at other locations worldwide and episodic high concentrations in winter was influenced by airmass originating from Eurasia occurring within 5 days.

5. An updated spatial analysis of POPs in Arctic air will be conducted to investigate the difference in PCB and OC profiles observed at Arctic sites located in Canada and Russia.

Objectives

1. To measure and understand the occurrence and trends of selected organochlorines (OCs) and polycyclic aromatic hydrocarbons (PAHs) in the Arctic atmosphere and to determine whether concentrations are changing in response to national and international initiatives.
2. To provide insight into contaminant pathways (sources, transport, transformation and removal processes) to the Arctic environment.
3. To enable validation of models of toxic chemicals in the Arctic environment with atmospheric observations.
4. To operate a major long-term trends measurement station at Alert, Nunavut (in operation since 1992) in parallel with other Arctic sites (e.g. Kinngait [eastern Arctic] and western Russian Arctic station [Amderma]) to advise Canadian negotiators in preparing contaminant control strategies.

Activities

In 2001–2002

1. Regular weekly atmospheric measurements of OCs and PAHs continued at Alert and Kinngait. This involved the collection, extraction and analysis of air samples.
2. An exploratory visit near Whitehorse, Yukon has identified Little Fox Lake as a new sampling site for operation in 2002–2003. This new site will allow further examination of incidences of trans-pacific transport as was observed at Tagish in 1993–1995.
3. Data analysis has been progressing well with the recent publication of two articles describing OC pesticide trends at Alert (Hung et al., 2002a) and PCDD/F atmospheric concentrations at Alert (Hung et al., 2002b). A new collaboration was initiated with Dr. Frank Wania of the University of Toronto to investigate removal pathways of PCB in the environment using a global model and data from the NCP and IADN programs. Arctic air data have now been compiled to undertake an updated spatial analysis.

Results and Discussion

Update of PCB and OC trends at Alert

The seasonal cycles and trends (1993–1997) of selected PCBs and OC pesticides were derived by the digital filtration technique (DF) and reported in the Synopsis of Research in 2001. Since then, an additional year of data from 1998 has become available and can now be included in the trend analysis. An example of the trend and seasonal cycles derived for endosulfan I is shown in Figure 1. The gas phase air

Figure 1. Increasing trend of Endosulfan I (1993–1998)

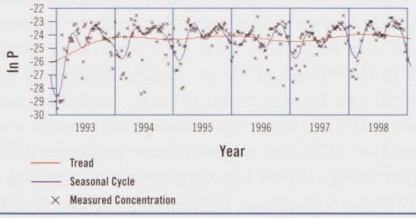


Table 1. Comparison of halflives of OCs and PCBs for periods of 1993–1998 and 1993–1997

	1993–1998		1993–1997			1993–1998		1993–1997	
OCs	$t_{1/2}$ (yr)	r^2	$t_{1/2}$ (yr)	r^2	PCBs	$t_{1/2}$ (yr)	r^2	$t_{1/2}$ (yr)	r^2
α-HCH	14	0.85	17	0.79	28	21	0.29	12	0.58
γ-HCH	6.5	0.81	4.9	0.88	31	8.6	0.78	6.4	0.87
t-chlordane	8.7	0.57	8.3	0.48	52	4.1	0.85	3.5	0.86
c-chlordane	5.8	0.63	4.1	0.71	101	17	0.52	11	0.73
t-nonachlor	8.3	0.68	6.2	0.71	105	450	< 0.10	INC	< 0.10
c-nonachlor	10	0.37	7.9	0.29	118	INC	< 0.10	INC	< 0.10
heptachlor epoxide	8.0	0.72	6.3	0.72	138	INC	0.41	INC	< 0.10
dieldrin	INC	< 0.10	INC	< 0.10	153	INC	< 0.10	17	0.18
endosulfan	−5.5	0.33	−5.2	0.25	180	5.8	0.73	4.4	0.78

concentration is expressed as the natural log of partial pressure (P). Table 1 shows the estimated apparent first order halflives ($t_{½}$) determined from the regression slope (m) of the DF trend lines as follows:

$$t_{½} = \frac{1n\ 2}{m}$$

The halflife of a compound is the time required for the concentration of the compound to decrease to half its original value. With the addition of one more year of data, it can be seen that the halflives of most of the PCBs and OCs increased slightly over previous estimates.

PCDD/F in Arctic air

Very little information is available on the atmospheric concentrations of polychlorinated dibenzo-*p*-dioxin and dibenzofurans (PCDD/F) in the Arctic environment. The only study was conducted by Schlabach et al. (1996) who had taken two composite samples (amounting to 10000 to 11000 m^3 of air in each sample) during the spring and summer of 1995 at Ny-Ålesund, Spitsbergen (78°55'N, 11°56'E). For a special study, weekly filter samples, representing airborne particles, at Alert, Nunavut, (82°30'N, 62°20'W) collected during the winter of 2000–2001 have been analyzed for polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (Hung et al., 2002b). The filters collected from week 46 of 2000 to week 7 of 2001 (sampling dates are listed in Figure 2) were cut into approximately half for the purpose of this special study. One half was used for extraction and analysis of PCDD/Fs and the other was used for the routine PCB/OC and PAH analysis. The sampling period coincided with the occurrence of Arctic Haze (December to April) when airborne particulate concentrations are generally high at Alert.

The concentrations of both ΣPCDDs and ΣPCDFs observed were lower than those found at Ny-Ålesund (78°55'N, 11°56'E) and other locations worldwide. This is attributable to the remoteness of the site and the absence of anthropogenic activities nearby. An apparent peak in concentrations occurred during the third week of 2001 (15–22/1/2001) (Figure 2). Weekly averaged five-day Lagrangian back trajectories have shown that Alert was mainly affected by air originated from the North Atlantic and North America during the first week of 2001. The origin of the airmass shifted eastwards further into Russia and Eurasia during the second and third weeks when the air concentrations of PCDD/Fs peaked at Alert. During the fourth and fifth weeks, the influence from Eurasia decreased while the North Atlantic sector regained dominance and PCDD/F concentrations tapered off.

In spite of the remoteness of Alert, congener profiles in most samples were enriched with PCDFs, corresponding to "source" profiles as suggested by Wagrowski and Hites (2000). Similar profiles were observed in air and tree bark at other Arctic locations. These profiles were probably the result of PCDD/F physical-chemical properties, which influence their transport behaviour between sources and receptors, as well as the unique Arctic environmental conditions. Therefore, the "source" and "sink" homologue profiles generally applicable to samples collected at temperate sites cannot be applied to those collected in the high Arctic.

Use of a global distribution model to explain PCB trends in the Arctic and the Great Lakes region

As can be seen in Table 1, the lighter PCB congeners and PCB-180 showed slow rates of decline, whereas the air concentrations of intermediate congeners stayed relatively constant. If remote air concentrations reflect the rate of overall global loss, this suggests that different removal processes control the loss of different PCB congeners on a global scale. PCB congeners also manifested different atmospheric rates of decline in the Great Lakes region under the Integrated Atmospheric Deposition Network (IADN) (Simcik et al., 1999). The relative rates of decline between light and heavy congeners differ from site to site. GloboPOP, a zonally averaged global distribution model for persistent organic pollutants (Wania and Mackay, 2000), will be employed to assess the relative importance of PCB removal processes on a global scale. The purpose is to identify the dominant removal process for different PCB congeners, especially (1) atmospheric reaction with OH radicals, (2) transfer to deep sea, (3) fresh water sediment burial, and (4) microbial and (5) all other degradation. Congener-specific rates of decline from various locations are used to explore whether certain combination of model input parameters can reproduce and explain the observed decline patterns at different sites. The most updated emission inventory data composed by Breivik et al. (2002a, b) will be used as input to the model.

Halflives of different PCB congeners are estimated from trends determined by the DF method at five sites located in the Great Lakes region, namely Point Petre (1992–1998, Lake Ontario), Burnt Island (1993–1998, Lake Huron), Eagle Harbour (1991–1998, Lake Superior), Sleeping Bear Dune (1992–1998, Lake Michigan) and Sturgeon Point (1992–1998, Lake Erie). Although data are available up to the end of 2000 for the three latter sites, trends were only derived up to the end of 1998 for the purpose of comparison with the other sites as well as Alert. The GloboPOP model was then applied to identify the

Figure 2a. Particle-Phase Concentrations of PCDDs observed at Alert

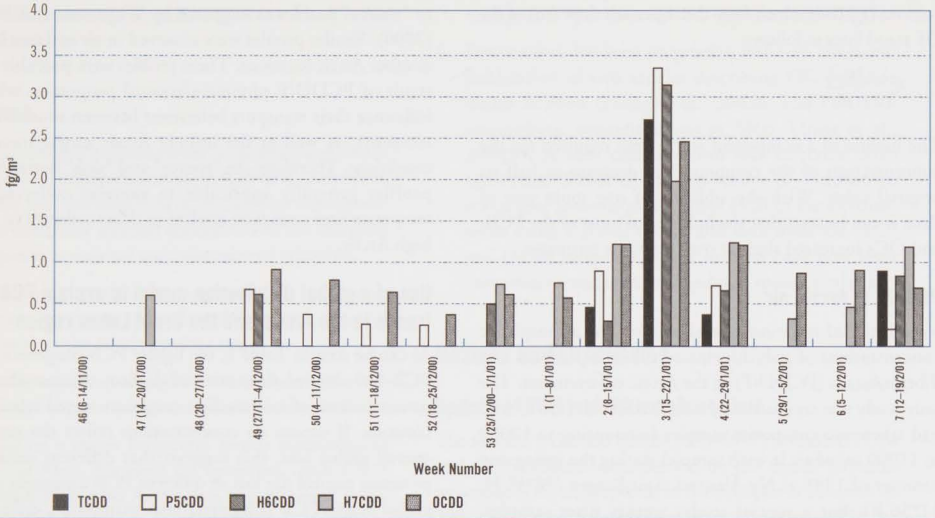
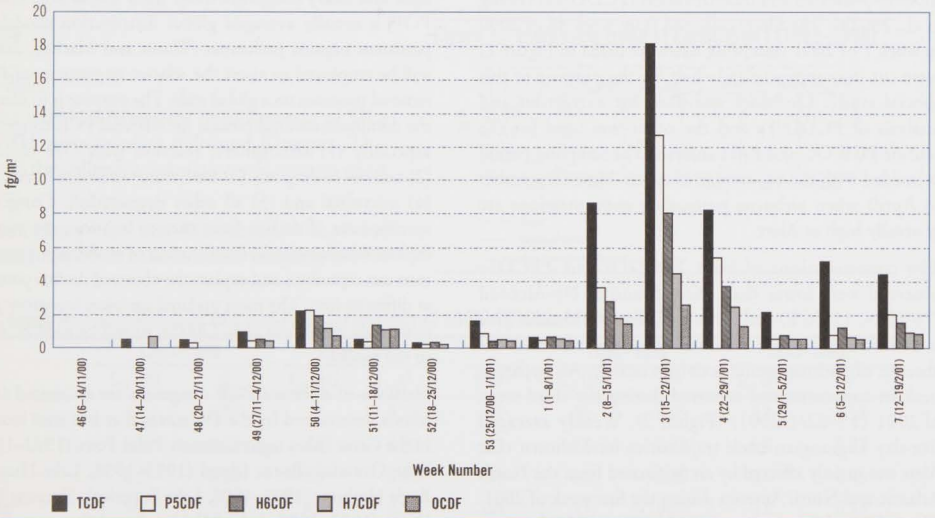


Figure 2b. Particle-Phase Concentrations of PCDFs observed at Alert



dominant removal processes for 8 PCB congeners at three different latitudes in the northern hemisphere, namely polar, boreal and temperate. The model was first applied with all five aforementioned removal processes in effect, then with only one of them in force while the other ones were nullified. The modelling results were also trended and halflives determined using the DF technique.

Preliminary results have shown that the model with all the removal processes in effect elucidated the relative rates of decline of different congeners in very remote locations, such as Alert and Eagle Harbour (Lake Superior), fairly well. All the modelled $t_{½}$ were within a factor of 3 of those derived from the measured results (Hung et al., in preparation). However, it should be noted that PCB trends are strongly site-dependent. Further study is required to explain the different patterns of trends observed at the other sites. Preliminary results of this study were presented at the 45th Annual Conference of the International Association for Great Lakes Research (IAGLR) in Winnipeg in June 2002.

Spatial and temporal comparisons of Arctic air data from Alert, Dunai, Amderma and Kinngait

Spatial comparisons of PCB, OC and PAH concentrations in Arctic air monitored under NCP have been reported by Stern et al. (1997), Halsall et al. (1998) and Halsall et al. (1997), respectively. These three articles provided a comprehensive overview of data obtained between 1992 and 1994 for the stations of Alert on Ellesmere Island, Tagish in the western Yukon and Dunai in eastern Siberia, Russia. Over time, more data has become available from various sites operated by NCP allowing the analysis of spatial trends to be updated.

Multiple sites were operating simultaneously during two sampling periods, namely from March 1994 to March 1995 and from October 2000 to March 2001. In 1994–1995, Kinngait on Baffin Island, Alert, Tagish and Dunai were running simultaneously. In 2000–2001, concurrent sites include Amderma in Russia, Kinngait and Alert. This updated spatial analysis of POPs in Arctic air will provide a different perspective to the previous studies. It will cover sites in Arctic regions where data so far have been lacking but are essential in documenting the effectiveness of international controls. These sites include Amderma, which is in close proximity to industrial activity in Eastern Europe and the European region of the Russian Federation, and Kinngait, which is located on the eastern side of the Canadian Arctic. This spatial comparison study is in progress and only preliminary results are summarized here.

For Amderma, a selected set of 25 vapour phase samples collected between 1999 and 2000 showed that the DDT group presented a different pattern than at the other sites. Technical DDT is made up of 80% p,p'-DDT and 20% o,p'-DDT (Ramesh et al., 1989). Once in the environment, the parent DDT compounds are metabolized (e.g. in soil) to p,p'-DDE and o,p'-DDE. At Alert, summertime DDT/DDE ratios of the order of 1–1.5 have been observed indicating long-range transport sources with high proportions of metabolite DDEs. At Amderma, however, the DDT/DDE ratios were about 3. A larger DDT/DDE ratio has also been observed at Tagish in Western Canada and is linked to rapid trans-Pacific transport from Asia which occurred within five days (Bailey et al., 2000). Bailey et al. have used back-trajectories analyses to establish these links. Similar analyses will be performed for Amderma to try segregating potential sources of elevated DDT concentrations at this site.

At all arctic stations, tri-substituted PCBs dominated the PCB air concentration profiles. Homologues at Amderma were more evenly distributed than for sites such as Alert and Tagish. There were similarities between Amderma and Dunai which are both Russian sites. The importance of penta-substituted PCBs for airmasses of Eurasian origin (Stern et al.,1997) was not observed with the current Amderma dataset. Although the absolute concentrations of PCBs at Amderma appeared to be similar to other Arctic sites, there were some differences in the homologue profiles. Further analysis of the data will focus on potential explanations for these differences.

References

Bailey, R., L.A. Barrie, C.J. Halsall, P. Fellin and D.C.G. Muir. 2000. Atmospheric organochlorine pesticides in the western Canadian Arctic: Evidence of transpacific transport. *J Geophy Res.* 105(D9):11805–11811.

Breivik, K., A. Sweetman, J.M. Pacyna and K.C. Jones. 2002a. Towards a global historical emission inventory for selected PCB congeners — a mass balance approach. 1. Global production and consumption. *Sci Tot Environ.* 290:181–198.

Breivik, K., A. Sweetman, J.M. Pacyna and K.C. Jones. 2002b. Towards a global historical emission inventory for selected PCB congeners — a mass balance approach. 2. Emissions. *Sci Tot Environ.* 290:199–224.

Halsall, C.J., R. Bailey, G.A. Stern, L.A. Barrie, P. Fellin, D.C.G. Muir, B. Rosenberg, F. Ya. Rovinsky, E. Ya. Kononov, B. Pastukhov. 1998. *Environ Pollut.* 102: 51–62.

Halsall, C.J., L.A. Barrie, P. Fellin, D.C.G. Muir, B.N. Billeck, L. Lockjart, F. Ya. Rovinsky, E. Ya. Kononov,

and B. Pastukhov. 1997. Spatial and temporal variation of polychyclic aromatic hydrocarbons in the arctic atmosphere. *Environ Sci Technol.* 31:3593–3599.

Hung, H., C.J. Halsall, P. Blanchard, H.H. Li, P. Fellin, G. Stern and B. Rosenberg. 2002a. Temporal trends of organochlorine pesticides in the Canadian Arctic atmosphere. *Environ Sci Technol.* 36:862–868.

Hung, H., P. Blanchard, G. Poole, B. Thibert and C.H. Chiu. 2002b. Measurement of Particle-Bound PCDD/PCDFs in Arctic Air at Alert, Canada. *Atmos Environ.* 36:1041–1050.

Hung, H., F. Wania, P. Blanchard, G.L. Daly, K. Brice and R. Hites. (in preparation) Long Term Trends of Air Concentrations of Polychlorinated Biphenyls (PCBs) in the Northern Hemisphere.

Li, Y.F., T.F. Bidleman, L.A. Barrie, and L.L. McConnell. 1998. Global hexachlorocyclohexane use trends and their impact on the arctic atmospheric environment. *Geophys Res Lett.* 25:39–41.

Li, Y.F. 1999. Global technical hexachlorocyclohexane usage and its contamination consequences in the environment: from 1948 to 1997. *Sci Tot Environ.* 232:121–158.

Ramesh, A., S. Tanabe, R. Tatsukawa, A.N. Subramanian, S. Palanichamy, D. Mohan and V.K. Venugopalan. 1989. Seasonal variations of organochlorine insecticide residues in air from Porto Novo, South India. *Environ Pollut.* 62:213–222.

Wania, F. and D. Mackay. 2000. *The Global Distribution Model. A Non-Steady State Multi-Compartmental Mass Balance Model of the Fate of Persistent Organic Pollutants in the Global Environment.* Technical Report and Computer Program on CD-ROM: 21 pp.

Schlabach, M., A. Biseth, H. Gundersen. 1996. Sampling and Measurement of PCDD/PCDF and non-ortho PCB in Arctic Air at Ny-Ålesund, Spitsbergen. *Organohalogen Compounds.* 28:325–329.

Simcik, M.F., I. Basu, C.W. Sweet and R.A. Hites. 1999. Temperature Dependence and Temporal Trends of Polychlorinated Biphenyl Congeners in the Great Lakes Atmosphere. *Environ Sci Technol.* 33:1991–1995.

Stern, G.A., C.J. Halsall, L.A. Barrie, D.C.G. Muir, P. Fellin, B. Rosenberg, F. Ya. Rovinsky, E. Ya. Kononov, and B. Pastuhov. 1997. Polychlorinated biphenyls in arctic air. 1. Temporal and spatial trends: 1992–1994. *Environ Sci Technol.* 31:3619–3628.

Wagrowski, D.M., R.A. Hites. 2000. Insights into the Global Distribution of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans. *Environ Sci Technol.* 34: 2952–2958.

Northern Contaminants Air Monitoring and Interpretation 2002–2003

Project leader

Hayley Hung, Meteorological Service of Canada (MSC), 4905 Dufferin Street, Toronto, ON M3H 5T4; phone: (416) 739-5944; fax: (416) 793-5708; e-mail: hayley.hung@ec.gc.ca

Project team

Pierrette Blanchard and Terry Bidleman, MSC, Toronto, ON; Phillip Fellin and Henrik Li, AirZone, Mississauga, ON; Gary Stern, Brian Billeck, and Bruno Rosenberg, Freshwater Institute, Winnipeg, MB.

Abstract

An updated spatial analysis of persistent organic pollutants (POPs) in Arctic air, including data from sites at Alert on Ellesmere Island, Kinngait on Baffin Island, Tagish in Yukon and Dunai in Russia between March 1994 and April 1995, are presented. Atmospheric concentrations of most organochlorine pesticides (OCs) were found to be highest in spring at Alert and Dunai. This may be attributed to chemicals deposited on the snowpack over winter and revolatilized during snowmelt in spring. Comparisons of air concentration ratios at Kinngait between 2000–2001 and 1994–1995 with those estimated for Alert show that OC air concentrations seem to decline faster at Kinngait, probably due to its proximity to temperate regions where removal rates are faster.

Statistically significant Spearman correlations found between indices representing atmospheric low-frequency fluctuations, such as the North Atlantic Oscillation (NAO) and the El Niño-Southern Oscillation (ENSO), and OC air concentrations observed at Alert and five Great Lake sites suggest interactions between climate variations and the global distribution of POPs.

Key Project Messages

1. Air concentrations of different organochlorine pesticides (OCs) observed at the four stations of Kinngait, Alert, Tagish and Dunai during the same period in 1994–1995 differ among seasons. Spring average concentrations of most OCs were similar at Kinngait, Alert and Dunai with slightly higher concentrations at Dunai for some compounds and lowest concentrations at Tagish. For both fall and winter, OC air concentrations were highest at Kinngait which may be attributable to the proximity of this site to eastern North American sources.
2. Higher air concentrations of OCs in spring were observed at Alert and Dunai which may be due to chemicals deposited on the snowpack over winter and revolatilized during snowmelt in spring.
3. Strong association found between atmospheric low-frequency fluctuations, e.g. North Atlantic Oscillation (NAO) and the El Niño-Southern Oscillation (ENSO), and OC air concentrations observed at Alert and five Great Lakes sites suggests the influence of climate variation patterns on the distribution of these chemicals in air.

4. Strong link between γ-HCH air concentrations at Alert and the Pacific North American pattern (PNA) in spring may suggest enhanced volatilization of Lindane (99% + γ-HCH), used in large amounts on the Canadian Prairies, according to increased surface air temperatures associated with PNA followed by transport to the Arctic.

Objectives

1. To measure and understand the occurrence and trends of selected OCs and polycyclic aromatic hydrocarbons (PAHs) in the Arctic atmosphere to determine whether concentrations are changing in response to national and international initiatives.
2. To provide insight into contaminant pathways (sources, transport, transformation and removal processes) to the Arctic environment.
3. To enable validation of models of toxic chemicals in the Arctic environment with atmospheric observations.
4. To operate a major long-term trends measurement station at Alert, Nunavut (in operation since 1992), to contribute to the next assessments by the Northern Contaminants Program and the Arctic Monitoring and Assessment Programme, and to advise Canadian negotiators in preparing contaminant control strategies.

Introduction

Atmospheric measurements of POPs, including herbicides, pesticides, synthetic industrial compounds and PAHs, have been made on a weekly basis in the Canadian (Alert, Tagish, Little Fox Lake, Kinngait [Cape Dorset]) and Russian Arctic (Dunai, Amderma) since January 1992. Kinngait and Alert in Nunavut, Tagish in Yukon and Dunai Island in Russia were operating simultaneously from March 1994 to April 1995. An update on the spatial comparisons of OC air concentrations and profiles from this concurrent sampling period are presented. Air samples were also collected at Kinngait and analyzed for POPs between October 2000 to April 2001. A discussion of how the air concentrations of these compounds have changed between 1994–1995 and 2000–2001 as compared to Alert air concentrations will be given.

A preliminary investigation on the influence of climate variation patterns, such as the El Niño-Southern Oscillation (ENSO), on POPs air concentrations observed at Alert and five IADN sites has been conducted. Results are summarized below.

Activities

In 2002–2003

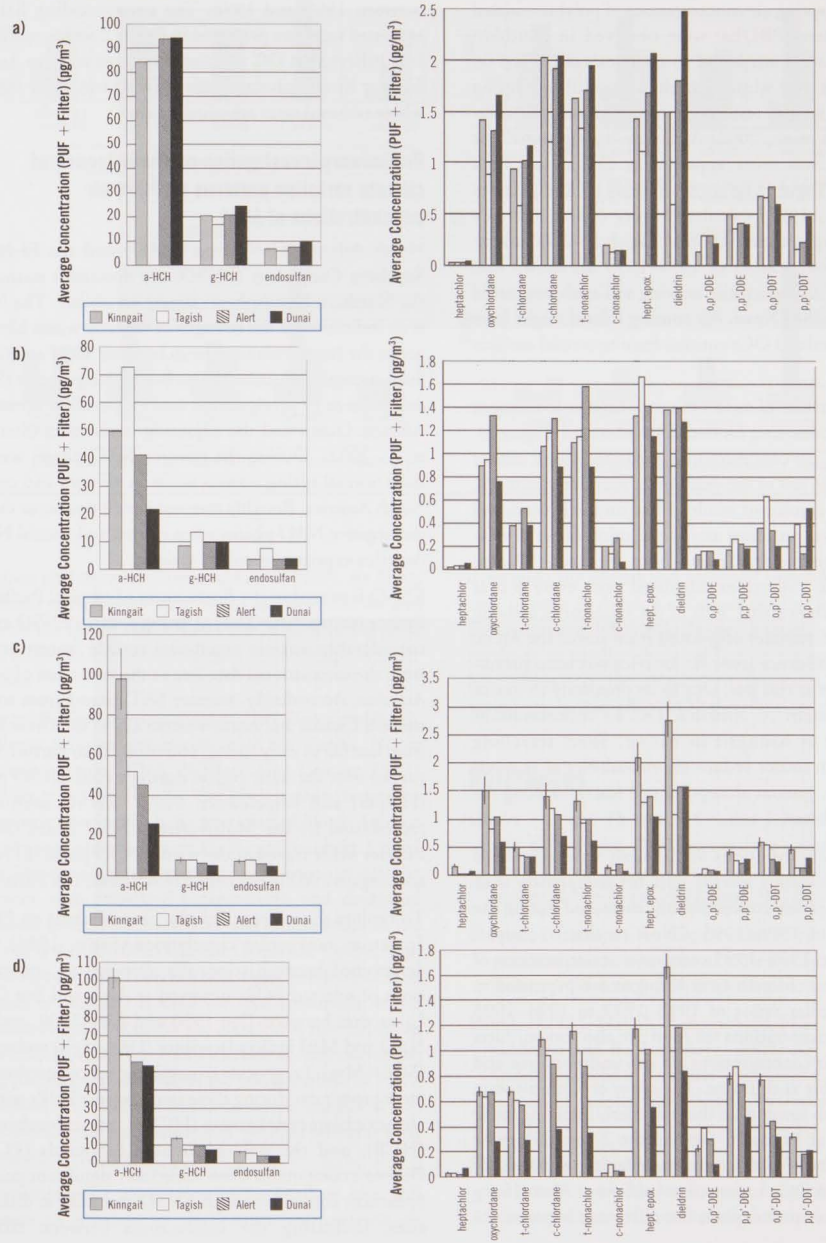
- Regular weekly atmospheric measurements of OCs and PAHs continued at Alert. This involved the collection, extraction and analysis of air samples.
- The site of Little Fox Lake in Yukon was activated in July 2002, to quantify the change in the western Canadian Arctic by comparison with observations made earlier at Tagish (December 1992 – March 1995), will be decommissioned in July 2003.
- Measurements at Kinngait, in the eastern Canadian Arctic, have been completed with the last samples collected in December 2002.
- Data analysis has been progressing well. In collaboration with Drs. Y.F. Li, J.M. Ma, S. Venkatesh and R.W. Macdonald, an article describing a mass balance model to estimate the historical budget of α-hexachlorocyclohexane (α-HCH) in the Arctic Ocean has been submitted to *Science of Total Environment* for consideration for publication. Two manuscripts are currently in preparation which describe: (1) the forecasting of PCB atmospheric trends in the Northern Hemisphere using the GloboPOP model, a zonally-averaged global transport model for POPs, the global PCB emission inventory and atmospheric PCB time trends at Alert and five Great Lakes sites (collaboration with Dr. Frank Wania of the University of Toronto at Scarborough); (2) an investigation on the influence of climate variation patterns, e.g. North Atlantic Oscillation (NAO) and the El Niño-Southern Oscillation (ENSO), on POP air concentrations measured under NCP and IADN (collaboration with Dr. Jianmin Ma at MSC). Part of the results from this study is presented below.

Results and Discussion

Spatial comparisons of OC concentrations at Kinngait, Alert, Tagish and Dunai

The average total concentrations (gas + particle phase) of selected OCs observed at the four stations, Kinngait, Alert, Tagish and Dunai Island, during the 1994–1995 concurrent sampling period are presented in Figure 1. The relative concentrations of different OCs differ among seasons (Figure 1). The spring average concentrations of most OCs were similar at Kinngait, Alert and Dunai, with slightly higher concentrations at Dunai for some, such as

Figure 1. OC seasonal average concentrations (a) spring (week 13–21 of 94), (b) summer (week 22–30 of 94), (c) fall (week 31–42 of 94), and (d) winter (week 43 of 94 – week 16 of 95). (Error bars for Kinngait in 1c and 1d represent errors involved in calculating seasonal averages from monthly composites rather than weekly samples at Kinngait.)



oxychlordane, t-nonachlor, heptachlor epoxide and dieldrin, and the lowest concentrations were observed at Tagish. Among all four seasons, the atmospheric concentrations of most OCs were highest in spring at Alert and Dunai. High spring air concentrations of polybrominated diphenyl ethers (PBDEs) were observed in Southern Ontario and were attributed to chemicals deposited on the snowpack over winter and then revolatilized during snowmelt in spring, resulting in elevated air concentrations. (Gouin et al., 2002) A similar "spring pulse" for several OCs was most apparent at Dunai and least significant at Tagish. Lagrangian five-day back trajectories (Olson et al., 1978) calculated every 6 h at 700 hPa (corresponding to the elevation of Tagish at ~2200 m) for each of the four seasons of 1994–1995 has shown that 88 to 96% of all trajectories arriving at Tagish originated across the Pacific Ocean. Air coming inland might have diluted revolatilized OCs emitted from terrestrial surfaces at this site.

The concentrations of most OCs were highest at Kinngait compared to other sites for both fall and winter (Figure 1). However, OC air concentrations at Kinngait were similar throughout the rest of the year with a summer minimum, probably the combined result of fast summer biotic and abiotic removal processes and the dilution effect of relatively clean air moving inland from the Arctic Ocean. Five-day back trajectories calculated once every 6 h at 925 hPa has shown that 53% of the trajectories arriving at Kinngait in summer originated from across the Arctic Ocean. Yet, influence from N. America was most prominent in winter at this site. Due to its proximity to source regions in eastern N. America, OC air concentrations were highest at Kinngait in winter. Short travelling distances from source reduce the probability of removal by deposition, gaseous absorption and reactions along the transport pathway.

Composite concentrations at Kinngait were calculated from the 2000–2001 weekly data for comparison with monthly composite concentrations measured during the same weeks in 1994–1995. "Now to then" ratios of 2000–2001 to 1994–1995 composite concentrations of the HCHs and chlordanes at Kinngait are presented in Figure 2. Similar ratios of 1998–1999 to 1994–1995 composite concentrations for Alert are also shown. Alert 2000–2001 air concentrations are still under analysis and are not available at this time. The ratios at Kinngait were generally much lower than those at Alert, implying faster OC removal at Kinngait. Despite the 2-year difference between the "now" data for the two sites, the atmospheric decline rates of OCs, expressed as halflives at Alert (Hung et al., 2001), cannot explain the difference between the "now to then" ratios of the two locations. To confirm this, air concentrations at Alert in 1998–1999 and 2000–2001 were estimated using measured concentrations in 1994–1995 and halflives determined from OC trends at Alert between 1993 and 1998. The corresponding halflife-estimated ratios are presented in Figure 2 for comparisons. It is believe that OC air concentrations seem to decline faster at Kinngait because it is closer to temperate regions, where removal rates are usually faster.

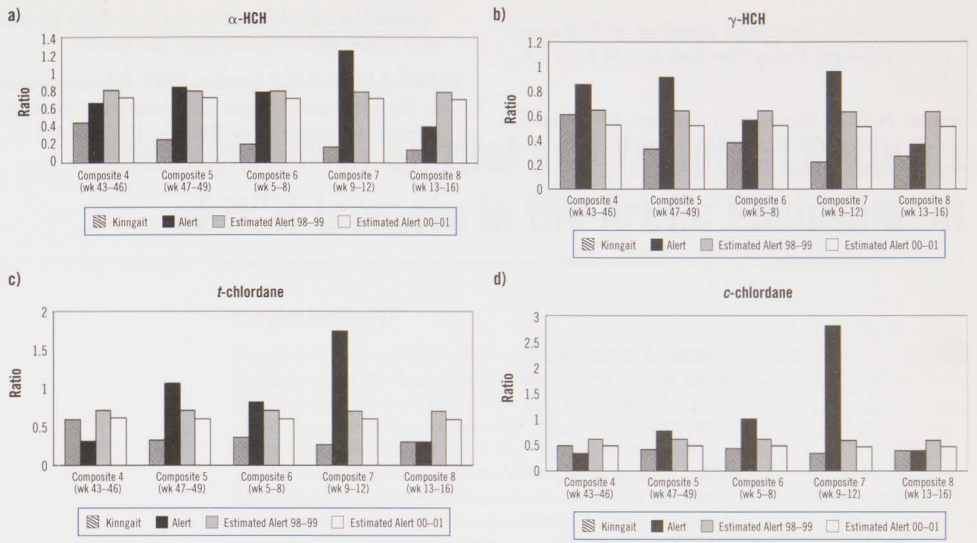
Preliminary investigation on the influence of climate variation patterns on POPs air concentrations at Alert

North Atlantic Oscillation (NAO) and the El Niño-Southern Oscillation (ENSO) are dominant sources of the Northern Hemisphere climate variability. The NAO is an indication of the strength of westerly winds blowing across the North Atlantic Ocean between 40°N and 60°N. Such strength influences the surface air temperature (SAT) and balance of precipitation and evaporation across the Atlantic Ocean and the adjoining landmasses (Stenseth et al., 2002). During the positive NAO phase, warmer than normal spring seasons occur in western and central North America. Roughly reversed conditions occur during the negative NAO phases when eastern and central North America experiences colder springs.

ENSO is related to the fluctuations of tropical Pacific sea surface temperature (SST). During a warm ENSO event, considerably warmer equatorial surface waters extend from the international date line to the west coast of South America. Accordingly, warmer SAT extend from south-western Canada and north-western US to the Great Lakes from late fall to early spring, and cooler than normal SATs prevail over the same region during a cold ENSO phase (Halpert and Ropelewski, 1992). ENSO events are represented by the Multivariate ENSO Index (MEI). Positive MEIs represent the warm ENSO phase (El Niño) and negative MEIs the cold ENSO phase (La Niña).

To explore the influence of climate variations on POPs, Spearman rank-order correlations (Sachs, 1984) were determined between seasonally averaged air concentrations of selected POPs observed at Alert and five Great Lakes sites between Dec 1990 and May 2000, and the NAO and MEI indices in winter (Dec – Feb) and spring (Mar – May). Large-scale atmospheric teleconnections are most prominent during these two seasons. POPs selected are hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB), and the polychlorinated biphenyls (PCBs). Different compounds show statistically significant positive Spearman correlations with ENSO and MEI at different sites, indicating the interactions between climate

Figure 2. "Now to then" ratios for (a) α-HCH, (b) γ-HCH, (c) *t*-chlordane and (d) *c*-chlordane



variations and the environmental fate of POPs. At Alert, significant correlations were found for PCB 31, 44 and 138 with the spring NAO, and PCB 28 with spring MEI which might be a reflection of their relationships at lower latitudes.

Spring γ-HCH air concentrations at Alert show a statistically significant positive correlation with the Pacific North American pattern (PNA, Wallace and Gutzler 1981) (r_s = 0.86, p = 0.01, N = 7). The PNA is characterized by atmospheric flow in which the west coast of North America is out of phase with the Eastern Pacific and Southeast United States. During its positive phase, wavy flow occurs over the continent with increased temperatures and decreased storminess in the Northwest and cold temperatures in the Southeast (NOAA-CIRES Climate Diagnostic Centre, http://www.cdc.noaa.gov/Teleconnections/pna.html). Since large amounts of Lindane is used for seed treatment in the Canadian Prairies (Waite et al., 2001), it is not surprising that γ-HCH air concentrations increase at Alert during the spring planting season towards the positive phase of PNA. Anomalous SAT increase in northwestern Canada at this time enhances the volatilization of γ-HCH which is then transported to the Arctic.

In the coming year, air monitoring for POPs at Alert will continue to provide us with more information to determine the spatial and temporal variabilities of these com pounds in Arctic air. Longer time series of POP air concentrations will enable the development of forecasting methods to predict chemical fate in the long term and how changes in the physical environment, e.g. climate variations, would affect POP distribution.

References

Gouin, T., G.O. Thomas, I. Cousins, J. Barber, D. Mackay and K.C. Jones. 2002. Air-surface exchange of polybrominated diphenyl ethers and polychlorinated biphenyls. *Environ Sci Technol.* 36:1426–1434.

Halpert, M.S. and C.F. Ropelewski. 1992. Surface temperature patterns associated with the Southern Oscillation. *J Climate.* 5:577–593.

Hung, H., C.J. Halsall, P. Blanchard, H.H. Li, P. Fellin, G. Stern and B. Rosenberg. 2001. Are PCBs in the Canadian arctic atmosphere declining? Evidence from 5-years of monitoring. *Environ Sci Technol.* 35:1303–1311.

Olson, M.P., K.K. Oikawa and A.W. MacAfee. 1978. A trajectory model applied to the long-range transport of air pollutants: a technical description and some

model intercomparisons. Environment Canada/AES, Toronto, Canada, Internal report LRTAP 78–4.

Sachs, L. *Applied Statistics. A Handbook of Techniques.* p. 395 (Springer-Verlag New York Inc., N.Y., U.S.A., 1984).

Stenseth, N.C., A. Mysterud, G. Ottersen, J.W. Hurrell, K.-S. Chan and M. Lima. 2002. Ecological effects of climate fluctuations. *Science.* 297:1292–1296.

Waite, D.T., N.P. Gurprasad, J.F. Sproull, D.V. Quiring and M.W. Kotylak. 2001. Atmospheric movements of lindane (γ-hexachlorocyclohexane) from canola fields planted with treated seed. *J Environ Qual.* 30:768–775.

Wallace, J.M., and D.S. Gutzler. 1981. Teleconnections in the geopotential height field during the Northern Hemisphere winter. *Mon Wea Rev.* 109:784–812.

Assessment of Spatial and Temporal Patterns of HCH Isomers in the Arctic Environment

Project leader(s)

Birgit Braune, National Wildlife Research Centre (NWRC), Canadian Wildlife Service (CWS), Environment Canada, Hull, PQ K1A 0H3; phone: (819) 953-5959; fax: (819) 953-6612; e-mail: birgit.braune@ec.gc.ca; Terry Bidleman, Meteorological Service of Canada (MSC), Downsview, ON M3H 5T4; phone (416) 739-5730; fax: (416) 739-5708; e-mail: terry.bidleman@ec.gc.ca; Aaron Fisk, National Water Research Institute (NWRI), Burlington, ON L7R 4A6; Current address: Warnell School of Forest Resources, University of Georgia, Athens, GA 30602, USA; phone: (706) 542-1477; e-mail: afisk@forestry.uga.edu; Derek Muir, National Water Research Institute (NWRI), Burlington, ON L7R 4A6; phone: (905) 319-6921; fax: (905) 336-6430; e-mail: derek.muir@cciw.ca

Project team

Bill Strachan (NWRI), Burlington, ON; Jason Duffe and Ross Norstrom (NWRC), Hull, PQ; Richard Addison and Robie Macdonald (IOS) Sidney, BC; Barry Hargrave, (BIO) Dartmouth, NS; Liisa Jantunen, Paul Helm, Liz Sahsuvar, and Yi-Fan Li (MSC) Toronto, ON; Henrik Kylin, Swedish University of Agricultural Sciences, Uppsala, Sweden.

Abstract

The objectives of this study are to compare the spatial and temporal trends of HCH isomers in biotic and abiotic samples. During the first year of this project, trends of HCH data in arctic biota (thick-billed murre [*Uria lomvia*] and ringed seals [*Phoca hispida*]) were examined; HCH concentrations, including β-HCH, were determined in water from the eastern Archipelago of the Canadian Arctic; and Henry's law constants (HLC) were determined for α-, γ- and β-HCH. The variability in spatial and temporal trends between HCH isomers in biota suggests that reporting only the ΣHCH is not appropriate for assessing these chemicals in the Arctic. Concentrations of α- and γ-HCH in eastern Archipelago ocean water are lower than those in the Beaufort Sea and comparable to levels in the Northern Canada Basin and Bering-Chukchi seas. β-HCH concentrations in the eastern Archipelago are 25 times lower than α-HCH and 4 times lower than γ-HCH. Concentrations of α- and γ-HCH in air samples collected during the Tundra Northwest 1999 expedition and at Resolute Bay in summer 1999 were similar to those reported for Alert in 1997. The Henry's law constant (HLC) determined for β-HCH is 20 times lower than for α-HCH. This lower HLC may lead to preferential rain scavenging of β-HCH from the atmosphere during its transport across the North Pacific and subsequent delivery to the high Arctic by ocean currents rather than direct atmospheric deposition. This would delay the transport of β-HCH to the Arctic and may in part

explain the delay in its decline. A re-evaluation of gas exchange in the western Arctic Ocean was done using the most recently determined HLCs. This assessment showed that α-HCH was significantly oversaturated in the south Bering Sea and Beaufort Sea but not different from air–water equilibrium in the northern Canada Basin and Chukchi Sea, whereas γ-HCH was undersaturated in all four regions. β-HCH was not distinguishable from equilibrium in the northern Canada Basin and Chukchi Sea, but showed oversaturation in the south Bering Sea and undersaturation in the Beaufort Sea.

Key Project Messages

- β-HCH concentrations in surface water of the eastern Archipelago, sampled in 1999, are 25 times lower than α-HCH and 4 times lower than γ-HCH.
- The Henry's law constant (HLC) for β-HCH (0.0030 Pa m^3/mol at 0°C) measured in fresh water is approximately 20 and 10 times lower than the HLCs of α- and γ-HCH.
- Because of its lower HLC, β-HCH may be preferentially scavenged by rain during air transport across the North Pacific, with the result that its delivery to the western Arctic Ocean may be via ocean currents rather than direct atmospheric deposition.
- An assessment of gas exchange in the western Arctic Ocean, using the HLCs determined in this work, shows significant oversaturation (net volatilization) for α-HCH in the south Bering and Beaufort seas, but near air-water equilibrium in the Chukchi Sea and the northern Canada Basin. γ-HCH is undersaturated (net deposition) in all four regions. β-HCH is oversaturated in the south Bering Sea, undersaturated in the Beaufort Sea, and near equilibrium in the other two regions.

Objectives

To assess the spatial and temporal patterns and trends of the α-, β- and γ-isomers of HCH in the arctic biotic and abiotic environment. Specifically:

- Compare concentrations and ratios of HCH isomers over time in air, water, seals and seabirds to determine any shifts in isomeric ratios and how those shifts interrelate among the various media.
- Compare concentrations and ratios of HCH isomers spatially in the abiotic and biotic media and explore reasons for any patterns.

Introduction

Hexachlorocyclohexanes (HCH) are pesticides that have been manufactured as two predominant products: technical HCH (60–70% α-HCH, 10–15% γ-HCH, 5–12% β-HCH) and lindane (γ-HCH). Only γ-HCH displays significant insecticidal properties although β-HCH and α-HCH have been shown to disrupt endocrine processes (Kendall et al., 1998; Willett et al., 1998). The key physical properties that control the ultimate fate of HCH in the environment are high volatility, low Henry's law constant (HLC), low affinity for particles and resistance to degradation in cold water (Ngabe et al., 1993). These physical-chemical properties result in the evaporation of HCH from temperate and tropical regions (Takeoka et al., 1991), dispersion through the atmosphere and deposition into the Arctic. Partitioning of HCHs from air to water is favoured at lower temperatures (Kucklick et al., 1991; Li et al., 2002; Sahsuvar et al., 2002) with the result that concentrations of HCHs in the Arctic Ocean are typically an order of magnitude or higher than those in tropical waters, although the distribution of HCHs in the Arctic Ocean is far from uniform. HCHs are the most abundant organochlorines in the Arctic Ocean, but few measurements have been made for β-HCH.

Two significant drops in global technical HCH usage have been identified. In 1983, China banned the use of technical HCH and in 1990 India and the former Soviet Union have reduced or banned the use of technical HCH (Li et al., 1998a, b). Significant drops in atmospheric α-HCH in the Arctic were observed between 1982 and 1983 and again between 1990 and 1992 (Li et al., 1998a). No temporal data for β-HCH are currently available. Concentrations of HCHs in arctic waters have a different trend from those in air. The strong partitioning of HCH from air to water means that water phases ultimately become more important reservoirs than the atmosphere, containing over 90% of the inventory. The result of the dramatic decrease in atmospheric HCH concentration is that the surface water in some oceanic regions became undersaturated and therefore started to outgas (Jantunen and Bidleman, 1995, 1996). In other words, the concentration of α-HCH (and probably β-HCH) in arctic waters increased until around 1990–1992 and γ-HCH reached an equilibrium stage around 1993. Since contamination of the marine environment by HCH depends mainly on the concentration of HCH in water, concentrations of both α-HCH and β-HCH in arctic marine biota should show a decrease after 1992.

When this project began, little was known about β-HCH in the Arctic or how its HLC varied with temperature. β-HCH is present at low levels in arctic air (Halsall et al.,

1998; Hung et al., 2002) and sea water (Li et al., 2002) but is found in increasing concentrations at higher trophic levels although the percentage of β-HCH in ΣHCH does not increase smoothly with trophic level (Muir et al., 1988).

Activities

In 2001–2002

An initial report of β-HCH in high volume (HV) water samples (100 L) from the TNW-99 expedition in the eastern Archipelago was presented last year (Braune et al., 2001). These results are now finalized and reported along with levels of α- and γ-HCH in the HV samples. The Henry's law constant (HLC) of β-HCH as a function of temperature was reported last year (Braune et al., 2001). During this year, a reassessment of gas exchange for the three HCH isomers in the western Arctic Ocean and marginal seas was done using these HLCs (Sahsuvar et al., 2002). The spatial distribution of β-HCH in the western Arctic Ocean is quite different from α-HCH, and a hypothesis to explain the differences was constructed based on differential rain scavenging of the HCH isomers during atmospheric transport (Li et al., 2002).

Results

New measurements of HCH isomers in Arctic marine waters

HCH isomers were determined in 6 HV (100 L) water samples collected in the eastern Archipelago on the Swedish Tundra Northwest-99 (TNW-99) expedition in July 1999. Preliminary results for β-HCH in the HV samples were given in Braune et al. (2001); these are finalized here for all the HCH isomers and compared to previously reported results for α- and γ-HCH in low-volume (LV) samples (Braune et al., 2001) in Table 1. Average concentrations (ng/L) for all high-volume samples collected in the region were 2.2 ± 0.2 ng/L α-HCH, 0.086 ± 0.020 ng/L β-HCH and 0.35 ± 0.07 ng/L γ-HCH.

Measurements of HCHs in air on TNW-99 and at Resolute Bay

High volume air samples were collected during the TNW-99 expedition (10 samples, July 1999) and also at Resolute Bay (20 samples, June – August 1999) using a glass fiber filter-polyurethane foam (PUF) sampler. Only the gas phase (PUF) was analysed, since very little HCH is typically found on aerosols. Air volumes were ~500 m^3 on TNW-99 and ~1300 m^3 at Resolute Bay.

Concentrations of α- and γ-HCHs in these samples are listed in Table 2. These were close to annual mean values measured at Alert during 1997 (Hung et al., 2002). β-HCH was below the detection limit in the samples, with limits of < 0.1 pg/m^3 at Resolute Bay and < 0.25 pg/m^3 on TNW-99 (differences are due to the larger air volumes sampled at Resolute Bay). Concentrations below the detection limit are consistent with a reported mean of only 0.089 pg/m^3 at Alert in 1997, with somewhat higher values in 1994–96 (0.13–0.36 pg/m^3, Hung et al., 2002). β-HCH was measureable at Alert because of the larger air volumes sampled in the routine monitoring program.

Table 1. HCHs in high-volume (HV) and low-volume (LV) surface water samples from TNW-99, ng/L

Location	HV Samples	α-HCH HV	α-HCH LV[a]	β-HCH HV	γ-HCH HV	γ-HCH LV
Hudson Strait[b]	2	2.4–2.5	2.8 ± 1.0	0.062–0.072	0.32–0.39	0.28 ± 0.09
Foxe Channel[b]	2	2.0–2.1	2.3 ± 0.4	0.079–0.083	0.28–0.29	0.21 ± 0.03
Foxe Basin	1	2.2	2.7 ± 0.5	0.11	0.34	0.21 ± 0.01
Gulf of Boothia	1	2.0	2.9 ± 0.7	0.11	0.48	0.31 ± 0.06

[a] Braune et al., 2001, 33 total samples

[b] Duplicate samples

Table 2. HCHs in air samples from TNW-99 and Resolute Bay, pg/m^3

Compound	TNW–99	Resolute Bay	Alert, 1997[a]
α-HCH	42.4 ± 9.9	43.9 ± 11.2	47
β-HCH	< 0.25	< 0.1	0.089
γ-HCH	10.4 ± 2.0	7.4 ± 2.9	6.4

Annual mean, Hung et al. (2002)

Re-evaluation of α- and γ-HCH gas exchange in the western Arctic Ocean and estimation of β-HCH exchange

Gas exchange of α- and γ-HCH was previously estimated for the Bering-Chukchi seas in 1993 (Jantunen and Bidleman, 1995) and the northern Canada Basin in 1994 (Jantunen and Bidleman, 1996) from paired air and water concentration measurements. Maps showing the locations of the measurements are shown in these publications. The exchange was estimated using the HLCs of Kucklick et al. (1991) and indicated oversaturation of α-HCH and near-equilibrium conditions for γ-HCH. A new set of HLCs was determined in this work (Braune et al., 2001; Sahsuvar et al., 2002) which includes all three HCH isomers. The new HLCs (Sahsuvar et al., 2002) of α- and γ-HCH at 20°C are 30–40% lower than Kucklick's values but agree with those reported by Jantunen and Bidleman (2000).

The new HLCs were applied to re-evaluate the gas exchange in the south Bering Sea and the Chukchi Sea (stations 1–15 and 43–61, in Jantunen and Bidleman, 1995), the northern Canada Basin (stations 7–35, Jantunen and Bidleman, 1996) and the Beaufort Sea. In the case of β-HCH, this is the first estimate of air-water gas exchange. Calculations were made using regionally averaged concentrations of α- and γ-HCH in air and surface water in the south Bering and Chukchi seas and northern Canada Basin (Jantunen and Bidleman, 1995, 1996; Kalhok et al., 2002; Li et al., 2002). Concentrations of α- and γ-HCH in air over the Beaufort Sea were assumed to be the same as for the northern Canada Basin. β-HCH was not measured in air on any of the expeditions, so the June – September mean concentrations from air monitoring stations at Alert and Tagish (Hung et al., 2002 and personal communication) were averaged and used for gas exchange calculations in all regions. Concentration and temperature data for these estimates are summarized in Table 3, from Sahsuvar et al. (2002).

Fugacities (partial pressures, Pa) of the HCHs in air (f_a) and water (f_w) were calculated according to published relationships (Jantunen and Bidleman,1995, 1996). The water/air fugacity ratio (FR) is:

$$FR = f_w/f_a = C_w H/C_a RT_a$$

where C_a and C_w are concentrations of the HCHs in air and surface water ($mol \cdot m^{-3}$), T_a (K) is the air temperature, H is the HLC ($Pa\ m^3 \cdot mol^{-1}$) at the surface water temperature (K) and R = 8.31 $Pa\ m^3 \cdot mol^{-1}\ K$. Values of FR > 1.0, FR < 1.0 and FR = 1.0 correspond to oversaturation (net volatilization), undersaturation (net deposition) and air-water equilibrium, respectively. The calculations were made for late summer conditions (July – September), corresponding to the months of the expeditions in 1993–94, and the air and surface water temperatures were taken from those publications (Jantunen and Bidleman, 1995, 1996). Temperature conditions for the Beaufort Sea were assumed to be the same as in the northern Canada Basin. Uncertainties in the FRs were estimated as described by Sahsuvar et al. (2002).

No adjustments were made for the effect of salinity. Generally, HLCs are higher in seawater due to the salting-out effect (DeWulf et al., 1995; Rice et al., 1997). Kucklick et al. (1991) found that HLCs for α- and γ-HCH were ~60–220% higher in artificial seawater of 35 parts-per-thousand salinity than in deionized water at 35°–45°C, 5–7% higher at 23°C, but not significantly different at 10°C nor 0.5°C. Atlas et al. (1982) reported an HLC for α-HCH in seawater at 23° that is about half the distilled water value.

Table 3 (Sahsuvar et al., 2002) gives mean FRs for the HCHs in the four northern regions and the propagated standard deviations. Significance of differences from equilibrium (FR = 1.0) were assessed for the mean FRs using a t-test at p = 0.05. In most cases the numbers (n) of water and air samples used to calculate mean FRs in each region differed; e.g. 19 water samples and 7 air samples in the Chukchi Sea. The n-value used in the t-tests corresponded to the lowest for the water-air pair; e.g. 7 for the Chukchi Sea.

Differences in the net gas exchange direction of α-HCH and γ-HCH were predicted using the HLCs determined in this work (Sahsuvar et al., 2002) and those of Kucklick et al. (1991), which were employed in previous gas exchange estimates (Jantunen and Bidleman, 1995, 1996). Using the results determined here, α-HCH was significantly oversaturated (FR > 1.0) in the south Bering Sea and Beaufort Sea but not different from air-water equilibrium in the other two regions; γ-HCH was undersaturated (FR < 1.0) in all four seas. Oversaturation or equilibrium conditions for α-HCH are consistent with observed enantiomer fractions (EF) in air similar to those in surface water, demonstrating transfer of water-derived α-HCH from sea to the air boundary layer (Jantunen and Bidleman, 1996; Ridal et al., 1997). Employing the HLCs of Kucklick et al. (1991), α-HCH was significantly oversaturated in all four regions and γ-HCH was near air-water equilibrium. This exercise demonstrates that differences of 2–3 fold in the HLC can have profound effects on gas exchange predictions when the system is close to equilibrium.

The FR of β-HCH was not distinguishable from equilibrium in the northern Canada Basin and Chukchi Sea, but showed oversaturation in the south Bering Sea and undersaturation

Table 3. Water/air fugacity ratios (FR) of HCHs in northern regions, 1993–94

	T_a, K	T_w, K	α-HCH C_w, ng/m³	α-HCH C_a, ng/m³	FR This work[a]	FR Kucklick[a]	β-HCH C_w, ng/m³	β-HCH C_a, ng/m³	FR This work[a]	γ-HCH C_w, ng/m³	γ-HCH C_a, ng/m³	FR This work[a]	FR Kucklick[b]
South Bering Sea													
Mean	283	283	1990	0.100	**1.34**	**2.14**	160	0.00034	**1.84**	450	0.024	**0.52**	1.03
s.d.			390	0.023	0.48	0.77	48	0.00033	1.90	120	0.010	0.28	0.59
Samples			14	14			26[b]	57[c]		14	14		
Chukchi Sea													
Mean	276	276	2120	0.072	0.99	**1.64**	246	0.00034	1.33	440	0.020	**0.31**	0.73
s.d.			550	0.008	0.35	0.57	42	0.00033	1.33	88	0.010	0.18	0.43
Samples			19	7			2	57[c]		19	7		
Northern Canada Basin													
Mean	273	272	2430	0.064	0.89	**1.49**	176	0.00034	0.63	480	0.015	**0.30**	0.75
s.d.			220	0.017	0.31	0.52	55	0.00033	0.66	110	0.009	0.21	0.52
Samples			12	14			7	57[c]		12	14		
Beaufort Sea													
Mean	273	272	4930	0.064	**1.81**	**3.04**	140	0.00034	**0.50**	600	0.015	**0.38**	0.94
s.d.			990	0.017	0.70	1.18	42	0.00033	0.52	138	0.009	0.26	0.65
Samples			> 50[b]	14			8[b]	57[c]		> 50[b]	14		

[a] Using the HLCs determined in this work (Braune et al., 2001; Sahsuvar et al., 2002) or by Kucklick et al. (1991). Bolded values are significantly different ($p < 0.05$) from FR = 1.0

[b] Weekly air samples at Alert and Tagish, June – September 1993–94

[c] Compilations by Kalhok et al., 2002 and Li et al., 2002 for the Beaufort Sea and western Canadian Archipelago, standard deviations estimated (Sahsuvar et al., 2002)

in the Beaufort Sea (Table 3). The uncertainty in the β-HCH FRs was larger due to the small number of water samples (especially for the Chukchi, where n = 2) and the larger standard deviation of air concentrations.

Transport of β-HCH to the Arctic Ocean: a contrast to α-HCH

The spatial distributions of α-HCH and β-HCH in northern waters are quite different. Concentrations of α-HCH in surface water increase from the Bering Sea into the Canada Basin and are highest in the Beaufort Sea, whereas β-HCH concentrations peak in the Chukchi Sea and fall off at more northern latitudes (Li et al., 2002). New insight to pathways by which the two HCHs reach the western Arctic Ocean is provided by examining the influence of their different HLCs on atmospheric transport and deposition. The HLC of β-HCH is about 20 times lower than for α-HCH; in other words, gaseous β-HCH is 20 times more soluble in water. A simple mechanism is suggested to explain the apparent large difference in distribution between α-HCH and β-HCH in the upper ocean of the North Pacific and the Canada Basin.

Emitted into the atmosphere from Asian source regions during the 1970s and 80s, both HCHs became separated during their journey northward. α-HCH was transported by both air and ocean currents; the air component arrived quickly in the Arctic where the α-HCH dissolved into the cold surface water. Being more soluble than α-HCH, β-HCH was preferentially deposited into the North Pacific by rain and exchange with ocean surface water before it had a chance to reach the high Arctic, and ocean currents then finished the job of delivering it to the Canada Basin. Evidence for removal of β-HCH en route is also given by its depletion in high arctic air relative to α-HCH (Halsall et al., 1998; Hung et al., 2002).

Because of this difference, delivery of β-HCH to the Canada Basin lagged α-HCH by perhaps a decade or longer and the highest concentrations during the late 1980s and mid-1990s were observed in marginal seas rather than in the high Arctic. β-HCH is highly persistent in seawater and its deposition into the North Pacific does not ultimately protect the Arctic Ocean but only delays the input and alters its spatial distribution.

A scenario constructed along this hypothesis (Li et al., 2002) suggests that loading pathways of HCHs to the Canada Basin have changed over time. In 1980, direct atmospheric deposition and advection by ocean currents through the Bering Strait contributed about equal proportions of α-HCH to the Canada Basin (49% and 51%, respectively). By 1995, atmospheric deposition of α-HCH dwindled due to declining air concentrations caused by elimination of technical HCH usage in China, and flow through the Strait took over as the major supply route, delivering 90% of α-HCH input. Direct atmospheric deposition was always a minor pathway for β-HCH loadings to the Canada Basin, delivering only 20% of the total input in 1980 and 2% in 1995. For this isomer, the dominant pathway was always flow through the Bering Strait.

Discussion and Conclusions

A review and evaluation of the existing abiotic and biotic data for HCH isomers was presented in Braune et al. (2001). This project has shown that the spatial and temporal trends of concentrations and relative proportions vary among HCH isomers, among species and among populations of seabirds and marine mammals. Future work on HCH should consider all isomers and not just ΣHCH. The results also support the continued monitoring of organochlorine contaminants in a number of species and at a number of locations. β-HCH concentrations are much lower than α- and γ-HCH in Canadian Arctic waters. The low water concentrations support conclusions that higher levels of β-HCH in organisms are due to the recalcitrant nature of this isomer. The HLC of β-HCH is an order of magnitude lower than α- and γ-HCH. Because of its higher affinity for water, transport of β-HCH to the western Arctic Ocean may have taken place primarily via ocean currents rather than direct atmospheric deposition. Thus, migration of β-HCH to the Arctic and outgassing from Arctic Ocean waters will be slower than for the other HCH isomers. This will likely result in delays in the decline of β-HCH in the Arctic environment, and advocates more attention to this isomer in future studies in the Arctic. Identification of a predominantly oceanic pathway for β-HCH suggests that ocean transport may be important for other chemicals which share similar physicochemical properties of fairly high water solubility and long persistence in the aquatic environment.

References

Atlas, E., R. Foster, and C.S. Giam. 1982. Air-sea gas exchange of high molecular weight organic pollutants: laboratory studies. *Environ Sci Technol.* 16:283–286.

Braune, B., T. Bidleman, A. Fisk, and D. Muir. 2001. Assessment of spatial and temporal patterns of HCH isomers in the arctic environment. pp. 152–159. In: Kalhok, S. (ed.), *Synopsis of Research Conducted Under the 2000–2001 Northern Contaminants Program.* Dept. of Indian Affairs and Northern Development.

DeWulf, J., D. Drijvers, and H. Van Langenhove. 1995. Measurement of Henry's law constant as function of temperature and salinity for the low temperature range. *Atmos Environ.* 29:323–331.

Halsall, C.T., R. Bailey, G.A. Stern, L.A. Barrie, P. Fellin, D.C.G. Muir, B. Rosenberg, F. Ya Rovinski, E. Ya Konovov, and B. Pastukhov. 1998. Multiyear observations of organohalogen pesticides in the Arctic atmosphere. *Environ Pollut.* 102:51–62.

Hung, H., C.J. Halsall, P. Blanchard, H.H. Li, P. Fellin, G. Stern, and B. Rosenberg. 2002. Temporal trends of organochlorine pesticides in the Canadian Arctic atmosphere. *Environ Sci Technol.* 36:862–868.

Jantunen, L.M. and T.F. Bidleman. 1995. Reversal of the air-water gas exchange direction of hexachlorocyclohexanes in the Bering and Chukchi Seas: 1993 vs. 1998. *Environ Sci Technol.* 29:1081–1089.

Jantunen, L.M. and T.F. Bidleman. 1996. Air-water gas exchange of HCHs and the enantiomers of α-HCH in arctic waters. *J Geophys Res.* 101:28837–28846; corrections Ibid. 102:19279–19292.

Jantunen, L.M. and T.F. Bidleman. 2000. Temperature-dependent Henry's law constant for technical toxaphene. *Chemosphere — Global Change Science* 2: 225–231.

Kalhok, S. et al., 2002. *Canadian Arctic Contaminants Assessment Report, Phase 2.* Vol 2, Abiotic Pathways. Indian and Northern Affairs Canada, Ottawa, Ontario, in preparation.

Kendall, R.J., A. Brouwer, and J.P. Giesy. 1998. A risk-based field and laboratory approach to assess endocrine disruption in wildlife. In: R.J. Kendall, R. Dickerson, J. Giesy and W. Suk (eds.), *Principles and Processes for Evaluating Endocrine Disruption in Wildlife*, Pensacola FL: SETAC, pp 1–15.

Kucklick, J.R., D.A. Hinckley, and T.F. Bidleman. 1991. Determination of Henry's law constant for hexachlorocyclohexanes as a function of temperature in distilled water and seawater. *Mar Chem.* 34:197–209.

Li, Y.-F., L.A. Barrie, T.F. Bidleman, and L.L. McConnell. 1998a. Global HCH use trends and their impact on the arctic atmospheric environment. *Geophys Res Lett.* 25:39–41.

Li, Y.-F., D.J. Cai, and A. Singh. 1998b. Technical HCH use trends in China and their impact on the environment. *Arch Environ Contam Toxicol.* 35:688–697.

Li, Y.-F., R.W. Macdonald, L.M. Jantunen, T. Harner, T.F. Bidleman, and W.M.J. Strachan. 2002. The transport of β-hexachlorocyclohexane to the western Arctic Ocean: a contrast to α-HCH. *Sci Total Environ.* 291: 229–246.

Muir, D.C.G., R.J. Norstrom, and M. Simon. 1988. Organochlorine contaminants in arctic marine food chains: Accumulation of specific PCB and chlordane-related compounds. *Environ Sci Technol.* 22:1071–1079.

Ngabe, B., T.F. Bidleman, and R.L. Falconer. 1993. Base hydrolysis of α- and γ-hexachlorocyclohexane. *Environ Sci Technol.* 27:1930–1933.

Rice, C.P., S.M. Chernyak, and L.L. McConnell. 1997. Henry's law constants for pesticides measured as a function of temperature and salinity. *J Agric Food Chem.* 45:2291–2298.

Ridal, J.J., T.F. Bidleman, B.R. Kerman, M.E. Fox, and W.M.J. Strachan. 1997. Enantiomers of α-hexachlorocyclohexane as tracers of air-water gas exchange in Lake Ontario. *Environ Sci Technol.* 31:1940–1945.

Sahsuvar, L., P.A. Helm, L.M. Jantunen, and T.F. Bidleman. 2002. Henry's law constants for α-, β-, and γ-hexachlorocyclohexanes (HCHs) as a function of temperature and gas exchange in arctic regions. *Atmos Environ.*, submitted.

Takeoka, H., A. Ramesh, H. Iwata, S. Tanabe, A.J. Subramanian, D. Mohan, A. Magendran, and R. Tatsukawa. 1991. Fate of HCHs in the tropical coastal area. *Mar Pollut Bull.* 22:290–297.

Willett, K.L., E.M. Ulrich, and R.A. Hites. 1998. Differential toxicity and environmental fates of HCH isomers. *Environ Sci Technol.* 32:2197–2207.

Global Organochlorine Pesticide Emission Inventories

Project leader

Yi-Fan Li, Air Quality Research Branch, Meteorological Service of Canada, Environment Canada, 4905 Dufferin Street, Downsview, ON, M3H 5T4; phone: (416) 739-4892; fax: (416)739-4288; e-mail: yi-fan.li@ec.gc.ca

Abstract

Global emission inventories for DDT, toxaphene and endosulfan have been created, and the linkages between the trends of global emissions for these organochlorine pesticides (OCPs) and their concentrations in the Arctic atmosphere have been studied. The total production of DDT was estimated to be about 5,000 kt between the 1940s and 2000. The usage, residue, and emission of DDT in 2000 were 0.1, 132, and 4 kt, respectively. The total application of toxaphene was about 1,330 kt between 1947 and 2000. The usage, residue, and emission of toxaphene in 2000 were 0.09, 100, and 1.2 kt, respectively. The total global use of endosulfan was around 338 kt between 1954 and 2000. The usage, residue, and emission reached to about 12.5, 0.08, and 5.7 kt in 2000, respectively. Global endosulfan emissions and the air concentrations of α-endosulfan in the Arctic were strongly correlated between 1987 and 1997 with correlation coefficient $r^2 = 0.75$, giving the evidence that the atmospheric long-range transport is a major pathway to bring α-endosulfan from the source regions to the Arctic air. It has also been found that the air concentrations of ΣDDT and Σtoxaphene in the Arctic were also strongly linked to their global emissions respectively, indicating that most DDTs (DDT and its metabolites) and most toxaphene congeners in Arctic air were directly transported from source regions through atmospheric long-range transport, which, however, may not be true for each DDT metabolite or each toxaphene congener.

Key Project Messages

1. The total production of DDT was estimated to be about 5,000 kt between the 1940s and 2000. Total usage in agriculture was estimated to be around 2,400 kt, and around another 2,000 kt used for public health purpose.
2. The total application of toxaphene was estimated to be about 1,330 kt between 1947 and 2000.
3. The total global use of endosulfan for crops was estimated to be 338 kt between 1954 and 2000.
4. Global endosulfan emissions and the air concentrations of α-endosulfan in the Arctic were strongly correlated between 1987 and 1997. The air concentrations of ΣDDT and Σtoxaphene in the Arctic were also strongly linked to their global emissions.

Objectives

1. To create global gridded inventories for DDT, toxaphene, and endosulfan.
2. To study the link between global emissions for these OCPs and the concentrations of these OCPs in the Arctic atmosphere.

Introduction

During the last decade, a number of studies have been devoted to quantifying the sources and emissions of Persistent Organic Pollutants (POPs) at regional and global scales. Organochlorine pesticides (OCPs) in which carbon and chlorine are combined, make up a major portion of POPs. There is considerable evidence that OCPs circulate globally and accumulate in remote areas like the Arctic, and have attracted international concern (Macdonald et al., 2000).

Due to their long-range transport potential and harmful effects on man and wildlife, international agreements are now coming into effect to reduce future environmental burdens of POPs. One such agreement is the 1998 Aarhus Protocol on POPs under the 1979 Geneva Convention on Long-range Transboundary Air Pollution (UNECE, 1998). The overall and long-term goal of the Aarhus Protocol on POPs is to eliminate any discharges, emissions and losses of POPs to the environment. At present, the Protocol focuses on a list of 16 substances, 11 of which are OCPs, which are aldrine, dieldrine, endrine, chlordane, DDT, heptachlore, hexachlorobenzene (HCB), mirex, chlordecone, lindane, and toxaphene.

The other recent international agreement is the Stockholm Convention on POPs, which will eliminate or at least control 12 POPs, 9 of which are OCPs, which are aldrine, dieldrine, endrine, chlordane, DDT, heptachlore, hexachlorobenzene (HCB), mirex, and toxaphene (UNEP, 2003). Within these conventions, the establishment of emission inventories for POPs are mandatory and provide the basis for further emission reductions among Parties (e.g. UNEP, 2001). Furthermore, emission data and release estimates are also used by modellers, who aim to understand and predict source-receptor relationships for POPs at regional (e.g. Van Jaarsveld et al., 1997; Cohen et al., 2002) and global scales (e.g. Wania et al., 1999; Wania and Daly, 2002).

Knowledge about sources and releases (emissions) of POPs into the environment are therefore essential if environmental burdens are to be minimized in a cost-efficient manner, and if quantitative source-receptor relationships at regional and global scales are to be established.

The objective of this project is to create global emission inventories for DDT, toxaphene, and endosulfan, and to find out the sources and pathways of these OCPs entered into the Canadian Arctic system.

Activities

In 2001–2003

In order to develop DDT, toxaphene, and endosulfan emission inventories, a large amount of data, such as production, usage, registration status, and use modes, have been searched and collected. The Simplified Gridded Pesticide Emission and Residue Model (SGPERM, Li et al., 2003) has been applied to created emission inventories for these pesticides. The links between global emissions and the air concentrations in the Arctic for these OCPs are also studied.

Results

DDT

The organochlorine pesticide DDT was one of the first synthetic chemicals to be produced in large quantities, and one of the most widely used chemicals for controlling insects on agricultural crops and controlling insects that carry such diseases as malaria and typhus. DDT is also one of a few organochlorine pesticides that are still allowed to be used in many countries to control malaria and typhus.

As of 1995, DDT has been banned in 59 countries, severely restricted in 20 countries, never registered in 2 countries, unregistered and voluntarily withdrawn by manufacturer in 1 country, and not banned in 13 countries. The total production of DDT was estimated to be about 5,000 kt between 1940s and 2000. Total usage in agriculture was estimated to be around 2,400 kt, and around another other 2,000 kt for public health purpose. The remaining 600 kt was used on livestock and forests. The top 7 countries with the highest DDT use between 1948 and 2000 are listed in Table 1. The total usage in these 7 countries was around 2,400 kt, almost half of the total global production.

DDT is one of the most persistent organochlorine pesticides. The half-life of DDT in soil is 2 to 15 years in the USA (US EPA, 1986; Augustijn-Beckers, et al., 1994) and ranges from 18 to 20 years in Canada's southern mainland (Spears, 2001). Concentrations of DDTs ranged from 0.6 to 15.8 ng/L in the water column off the Palos Verdes Peninsula, CA, USA in 1997, the source of which is sediments contaminated by DDT more than 20 years ago (Zeng et al., 1999).

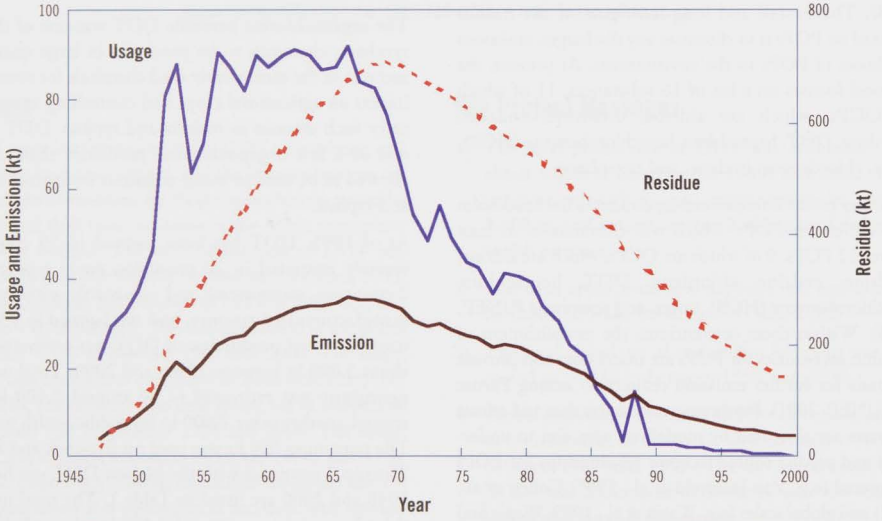
Figure 1 depicts temporal trends of DDT in usage, emissions, and residues due to agricultural applications from 1945 to 2000. It shows that the total global use, emissions,

Table 1. Top 7 countries with highest DDT use (kt) in between the 1940s and 2000

Country	Agriculture	Public health	Total	Year of ban in agriculture
United States	590		590	1972
India	75	340	415	N.A.
Former Soviet Union	320		320	1971
Indonesia	0.7	290	290	
China	260	20	280[a]	1983
Mexico	180	100	280	N.A.
Brazil	106	100	206	1998
Total			2380	

[a] Total production between 1952 and 1983 was 270 kt

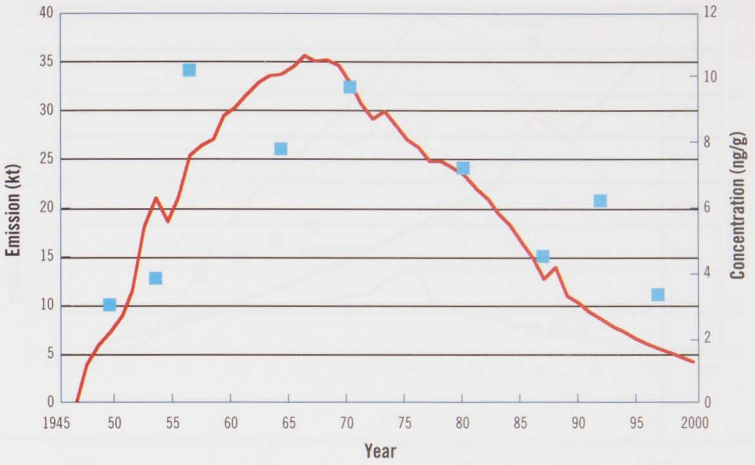
Figure 1. Temporal trends of DDT usage, emissions, and residues due to agricultural applications from 1947 to 2000



and residues of DDT have decreased continuously since the end of the 1960s and the beginning of the 1970s. During this period, total usage in agriculture and emissions were around 2380 kt and 1090 kt respectively. The sharp global decrease in use started in 1966 and was driven by decreases in use and/or bans on DDT in the USA and other western countries. The emissions reached a peak point of 35.7 kt in 1966, then decrease continuously, to around 4 kt in 2000. Residue peaked at 710 kt in 1969, then decreased continuously, to around 132 kt in 2000.

Widespread use and atmospheric transport of DDT account for its ubiquitous global distribution. Due to DDT's high vapour pressure it may evaporate from plants and soils following application. Subsequently, it attaches itself to suspended particular matter that can be transported great distances (thousands of kilometers) and is ultimately deposited by precipitation and dustfall. DDT has been detected in virtually all environmental media and in human tissues throughout the world, including remote regions such as the Arctic. Figure 2 shows trends of global DDT emissions due to the use in agriculture between 1945 and 2000 and down-core profiles of DDT in slices of a laminated sediment core from Devon Island, Nunavut (Lockhart et al., 2000). The correlation coefficient between the emissions and the down-core profiles

Figure 2. Trends of global DDT emissions due to the use in agriculture between 1945 and 2000 and down-core profiles of DDT in slices of a laminated sediment core from a lake located in Devon Island (75°34' N and 89°19' W), Nunavut (Lockhart et al., 2000)



is $r^2 = 0.63$. This indicates that atmospheric long-range transport is responsible for DDT contamination of the lakes in Canadian Arctic. The increasing concentration observed in the core during the 1990s may be attributed in part to heavy use of DDT for vector control in Mexico during 1990s.

Figure 3 depicts temporal trends in concentrations of DDT in the Canadian Arctic air (the squares) and the calculated global emissions of DDT (the curve) from 1985 to 2000. It turns out that the correlation between Arctic air concentration and the global emissions of DDT is quite strong ($r^2 = 0.80$), indicating that atmospheric long-range transport has played a very significant role in bringing DDT from source regions to Arctic air.

Toxaphene

Toxaphene is a complex mixture of polychlorinated bornanes (CHBs) and camphenes. It is also referred to as camphechlor or polychlorinated camphenes (PCCs), although CHBs is preferred as a generic designation (Muir et al., 1993). The theoretical number of different chlorinated compounds is ~16,000 (Vetter, 1995), but only a few hundred have environmental significance.

As of 1995, toxaphene has been banned in 55 countries, severely restricted in 20 countries, never registered in 2 countries, never used in 1 country, unregistered and voluntarily withdrawn by manufacturer in 4 countries, and not banned in 21 countries. This information should be used only as a general indication of status in the country. In cases where the product has not been specifically noted as banned or prohibited, it has been assumed that the product is in use. According to the survey done by UNEP for the POPs convention negotiations, toxaphene manufacture has ceased in recent years.

Toxaphene had been used as a pesticide since 1947, and was one of the most heavily used pesticides on a global basis, with an estimated cumulative usage of (1.33 million t (Voldner and Li, 1995). Table 2 lists the top 10 countries with the highest toxaphene use between 1947 and 2000. The United States consumed the highest amount of toxaphene in the world (440 kt), followed by the former Soviet Union (254 kt).

Figure 4 shows temporal trends of toxaphene usage, emissions, and residues from 1945 to 2000. During this period of time, total usage in agriculture and emissions were around 1330 kt and 400 kt respectively. The sharp decrease of usage started in 1976 (from 66 kt in 1975 to 38 kt in 1976) and was due to the decrease of toxaphene use in USA (from 37 kt in 1975 to 13 kt in 1976 [Li, 2002]) and other western countries. The usage in 2000 was around 0.09 kt. Residue reached a peak of 390 kt in 1975, then decreased continuously, to around 100 kt in 2000. The emissions reached a peak of 19.5 kt in 1974, then decreased continuously, to around 1.2 kt in 2000.

Figure 3. Temporal trends in concentrations of DDT in the Canadian Arctic air (the squares) and the calculated global emissions of DDT (the curve) from 1985 to 2000 (sources of air concentration data: data for 1988, Patton et al. [1991]; data for 1993 and 1994, Halsall et al. [1998]; data for 1995–1997, Hung et al. [2002])

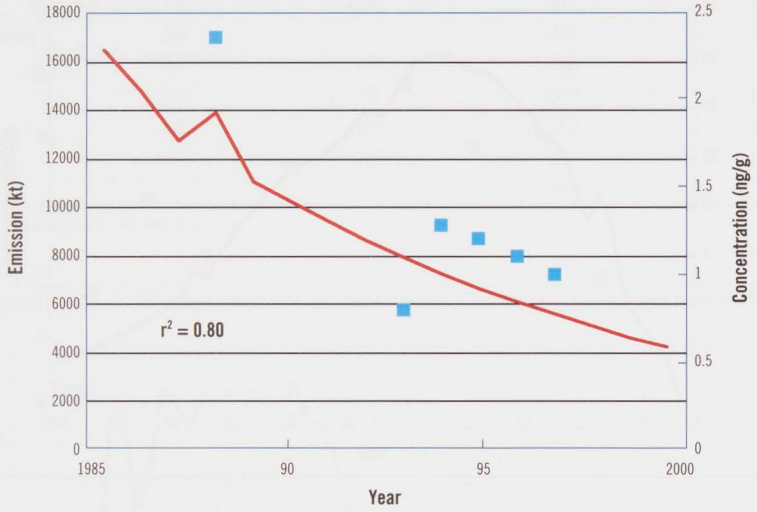


Table 2. Top 10 countries with highest toxaphene use between 1947 and 2000

Country	Usage (kt)
United States	440
Former Soviet Union	254
Mexico	71
Egypt	55
Brazil	50
Nicaragua	48
Syria	33
France	26
Columbia	23
Germany	22

Figure 5 shows temporal trends in concentrations of toxaphene in the Canadian Arctic air (the bars) and the estimated global emissions of toxaphene (the curve) from 1985 to 1995. The estimated emissions of toxaphene are generally consistent with the concentrations of toxaphene in Canadian Arctic air in the summer. The correlation between Arctic air concentrations in summer and global emissions of toxaphene between 1986 and 1993 ($r^2 = 0.82$) is stronger than that between Arctic air concentrations in summer and emissions from toxaphene residues in US soil ($r^2 = 0.76$) (Li et al., 2002), indicating the existence of other sources from regions outside the USA.

Endofulfan

Endosulfan was first introduced in the 1950s as a pesticide for use on a wide variety of agricultural crops (Joint Canada-Philippines Planning Committee, 1995; Sang and Sanya, 1999). Cumulative global use of endosulfan for crops is estimated to be 338 kt from 1954 to 2002. The average annual endosulfan consumption in the world is estimated to be 10 kt from 1980 to 1989 and 13 kt from 1990 to 1999. This data corresponds to WHO's report of worldwide production at 10 kt in the 1980s (WHO, 1984) and also agrees with the reported 12 to 13 kt production in the 1990s (Joint Canada-Philippines Planning Committee, 1995). The top 10 countries with highest usage are listed in Table 3. India is the largest consumer of endosulfan in the world followed by the United States. The total use is estimated to be 113 kt in India from 1958 to 2002, and 26 kt in the United States from 1954 to 2002. Large quantities of endosulfan, approximately 0.9 kt, are used in Australia each year (NRA, 1998).

Figure 4. Temporal trends of toxaphene usage, emissions, and residues from 1945 to 2000

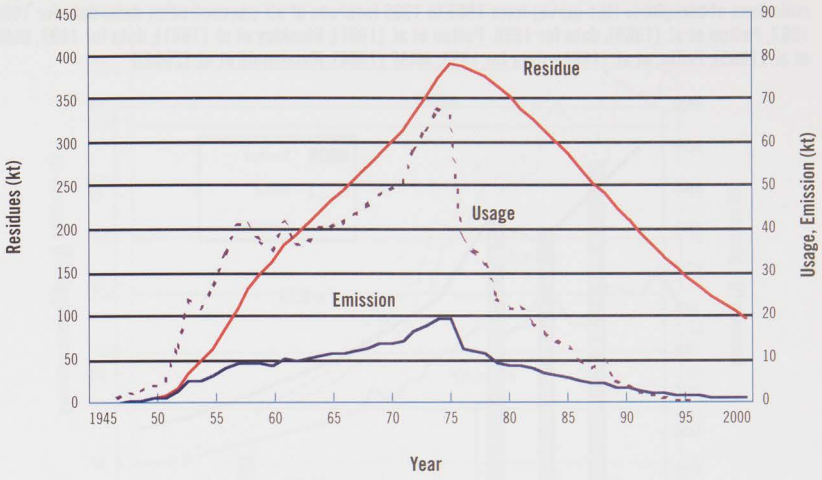


Figure 6 depicts temporal trends of endosulfan usage, emissions, and residues from 1954 to 2000. During this period of time, total usage and emissions were around 338 kt and 145 kt respectively. Usage, emission, and residue reached to around 12.5, 5.7, and 0.08 kt in 2000, respectively.

Endosulfan enters the air, water and soil when it is manufactured or used as a pesticide. Endosulfan has been detected in all environmental compartments including humans and in remote areas such as the Arctic. Figure 7 shows temporal trends in concentrations of endosulfan I (α-endosulfan) in Canadian Arctic air (the shadowed bars) and the calculated global emissions of endosulfan (the curve) from 1985 to 2000. The correlation between Arctic air concentrations of endosulfan I and global emissions of total endosulfan is quite strong ($r^2 = 0.75$), indicating the major pathway for endosulfan I entering Arctic air is atmospheric long-range transport.

Discussion and Conclusions

A large amount of data, such as production, usage, registration status, and use modes, have been searched and collected. The Simplified Gridded Pesticide Emission and Residue Model (SGPERM) has been applied to emissions and residue inventories for DDT, toxaphene, and endosulfan. The total global usage of DDT between the 1940s and 2000 was estimated to be around 5,000 kt, and around 1,090 kt were emitted to the atmosphere due to agricultural application. The usage, residue, and emission of DDT in 2000 were 0.1, 132, and 4 kt respectively. The total global usage of toxaphene between 1947 and 2000 was estimated to be around 1,330 kt, and around 400 kt were emitted to the atmosphere due to agricultural application. The usage, residue, and emission of toxaphene in 2000 were 0.09, 100, and 1.2 kt respectively. The total usage of endosulfan between 1954 and 2002 was estimated to be around 338 kt, and around 145 kt were emitted to the atmosphere. The usage, residue, and emission of endosulfan reached around 12.5, 0.08, and 5.7 kt in 2000, respectively. Although the usage and emissions of DDT and toxaphene have decreased since 1960s and 1970s, the trends of the usage and emissions for endosulfan are increasing.

Global endosulfan emissions and air concentrations of α-endosulfan in the Arctic were strongly correlated between 1987 and 1997 with correlation coefficient $r^2 = 0.75$, providing evidence that atmospheric long-range transport is a major pathway delivering α-endosulfan from source regions to the Arctic. It has also been found that air concentrations of ΣDDT and Σtoxaphene in the Arctic were also strongly linked to their global emissions respectively, indicating that most DDTs (DDT and its metabolites) and most toxaphene congeners in the Arctic air were directly transported from source regions through atmospheric long-range transport, which, however, may not be true for each DDT metabolite or each toxaphene congener.

Figure 5. Temporal trends in concentrations of toxaphene in the Canadian Arctic air (the shadowed bars for the air concentration in summer, and the blank bars for the air concentration in winter) and the calculated global emissions of toxaphene (the curve) from 1985 to 1995 (sources of air concentration data: data for 1986 and 1987, Patton et al. [1989]; data for 1988, Patton et al. [1991], Hinckley et al. [1991]; data for 1992, Bidleman et al. [1995], Fellin, et al. [1996]; data for 1993, AMAP [1998], Macdonald et al. [2000])

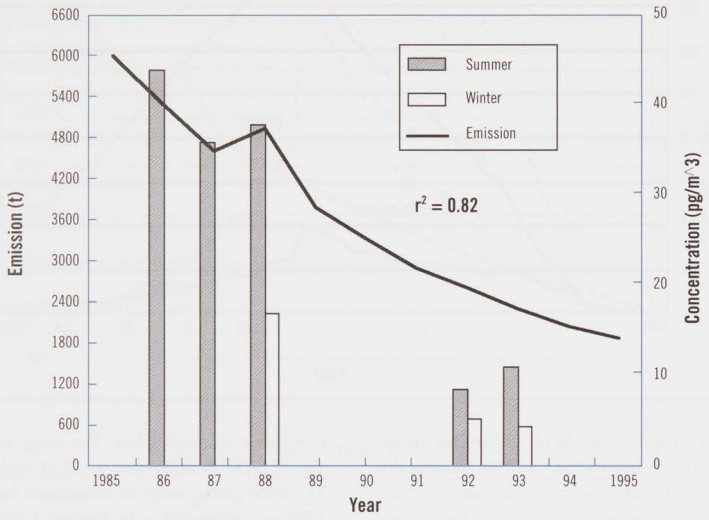


Table 3. Top 10 countries with highest endosulfan use between 1954 to 2002

Country	Volume (kt)	Registration status
India	113	Registered for use
United States	26	Registered for use
Brazil	23	Authorized for agriculture
Australia	21	Registered for use
Sudan	19	N.A.
Former Soviet Union	13	Approved insecticide until 1991
Argentina	10	Restricted
Thailand	9	Ban in rice
Bangladesh	8	Ban in rice
Mexico	7	N.A.

Li and his co-workers (Li et al., 2002) identified a dominant oceanic pathway for β-HCH in contrast with the atmospheric pathway for α-HCH. A smaller data base for β-HCH suggests that it did not exhibit an even stronger predisposition to accumulate under the pack ice of the Arctic Ocean as might be inferred from an emission history similar to that of α-HCH and a Henry's law constant 20 times lower. In contrast, β-HCH appears have been less subject to direct atmospheric loadings into the high Arctic. Rather, it was rained out or partitioned into North Pacific surface water and subsequently entered the Arctic in ocean currents passing through Bering Strait. Identification of a dominant oceanic pathway for β-HCH has influenced the Arctic science research directions in several ways: (1) The role of ocean currents in transport is probably more important for contaminant level in the Arctic than was previously thought, and thus needs to be considered more seriously; (2) Clearly, the use of ∑HCH as a trend parameter would make little

Figure 6. Temporal trends of endosulfan usage, emissions, and residues from 1954 to 2000

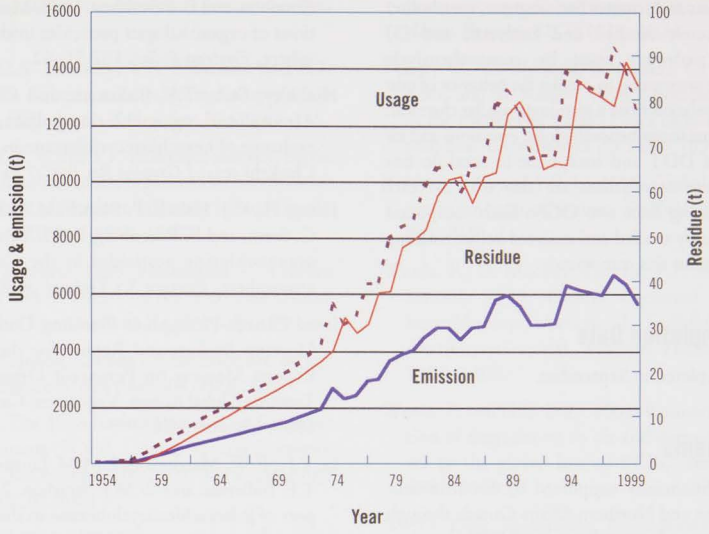
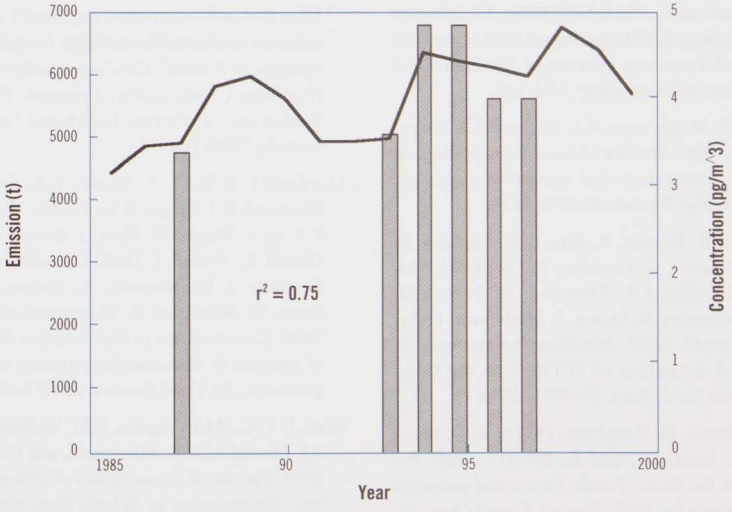


Figure 7. Temporal trends in concentrations of endosulfan I (α-endosulfan) in the Canadian Arctic air (the shadowed bars) and the calculated global emissions of endosulfan I (the curve) from 1985 to 2000 (sources of air concentration data: data for 1987, Patton et al. [1989]; data for 1993 and 1994, Halsall et al. [1998]; data for 1995–1997, Hung et al. [2000])



sense in the western Arctic, and it is likely that other such combining of related compounds may lead to misleading inferences, and thus each isomer (or congener, metabolite) should be separately studied and analyzed; and (3) Environmental pathways must be comprehensively understood before attempting to predict the behavior of one chemical by extrapolation from a seemingly similar chemical. Therefore, the correlations between global emissions and air concentrations of DDT and toxaphene in total do not indicate that these correlations are also true for each compound containing these two OCPs. Each compound should be individually studied and analyzed before reaching any conclusions about this compound.

Expected Completion Date

Data will be completed in September.

Acknowledgments

This work was financially supported by Environment Canada and Indian and Northern Affairs Canada through the Northern Contamination Program (NCP).

References

AMAP, 1998. AMAP Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway. xii+ 859 pp.

Augustijn-Beckers, et al. 1994. SCS/ARS/CES Pesticide Properties Database for Environmental Decisionmaking II. Additional Properties Reviews of Environmental Contamination and Toxicology, Vol. 137.

Bidleman, T.F., L.M. Jantunen, R.L. Falconer, L.A. Barrie, and P. Fellin. 1995. Decline of hexachlorocyclohexane in the Arctic atmosphere and reversal of air-sea gas exchange. *Geophys Res Lett.* 22:219–222.

Cohen, M.D., R.R. Draxler, R. Artz, B. Commoner, P. Bartlett, P. Cooney, K. Couchot, A. Dickar, H. Eisl, C. Hill, J. Quigley, J.R. Rosenthal, D. Niemi, D. Ratté, M. Deslauriers, R. Laurin, L. Mathewson-Brake, and J. McDonald. 2002. Modeling the atmospheric transport and deposition of PCDD/F to the Great Lakes. *Environ Sci Technol.* 36:4831–4845.

Fellin, P., L.A. Barrie, D. Dougherty, D. Toom, D. Muir, N. Grift, L. Lockhart, and B. Billeck. 1996. Air monitoring in the Arctic: Results for selected persistent organic pollutants for 1992. *Environ Toxicol Chem.* 15: 253–261.

Halsall, C.J., R. Bailey, G.A. Stern, L.A. Barrie, P. Fellin, D.C.G. Muir, B. Rosenberg, F. Ya Rovinsky, E. Ya Kononov, and B. Pastukhov. 1998. Multi-year observations of organohalogen pesticides in the Arctic atmosphere, *Environ Pollut.* 102:51–62.

Hinckley, D.A., T.F. Bidleman, and C.P. Rice. 1991. Atmospheric organochlorine pollutants and air-sea exchange of hexachlorocyclohexane in the Bering and Chukchi seas. *J Geophys Res.* 96C:7201–7213.

Hung, H., C.J. Halsall, P. Blanchard, H.H. Li, P. Fellin, G. Stern, and B. Rosenberg. 2002. Temporal trends of organochlorine pesticides in the Canadian Arctic atmosphere. *Environ Sci Technol.* 36:862–868.

Joint Canada-Philippines Planning Committee. 1995. Meeting Background Report for the International Experts Meeting on Persistent Organic Pollutants: Towards Global Action, Vancouver, Canada, June 4–8, 1995, Chapter AII4.

Li, Y.F., R.W. Macdonald, L.M.M. Jantunen, T. Harner, T.F. Bidleman and W.M.J. Strachan. 2002. The transport of β-hexachlorocyclohexane to the western Arctic Ocean: a contrast to α-HCH. *Sci Total Environ.* 291: 1–3, 229–246.

Li, Y.F., S. Venkatesh, and D.C. Li. 2003. Modeling global emissions and residues of pesticides. *Environ Sci Technol.* Submitted.

Lockhart, L., G. Stern, P. Outridge, P. Wilkinson, B. Danell, G. Boila, J. DeLaronde, and B. Rosenberg. Mercury and other contaminants in a laminated sediment core from Devon Island. In: Kalhok, S., editor. Synopsis of Research Conducted under the 1999/2000 Northern Contaminants Program, Environmental Studies no. 76. Ottawa, Indian and Northern Affairs Canada, 2000:104–112.

Macdonald, R.W., L.A. Barrie, T.F. Bidleman, M.L. Diamond, D.J. Gregor, R.G. Semkin, W.M.J. Strachan, Y.F. Li, F. Wania, M. Alaee, S. Backus, M. Bewers, C. Gobeil, C. Halsall, J. Hoff, L. Lockhart, D. Mackay, D. Muir, J. Pudykiewicz, K. Reimer, J. Smith, G. Stern, W. Schroeder, R. Wagemann, and M. Yunker. 2000. Contaminants in the Canadian Arctic: five years of progress in understanding sources, occurrence and pathways. *Sci Total Environ.* 254:93–234.

Muir, D.C.G., M.D. Segstro, P.M. Welibourn, D. Toom, S.J. Eisenrelch, C.R. Macdonald, and D.M. Whelpdale. 1993. Patterns of accumulation of airborne organochlorine contaminants in lichens from the Upper Great Lakes region of Ontario. *Environ Sci Technol.* 27: 1201–1210.

NRA (National Registration Authority for Agricultural and Veterinary Chemicals, Australia). 1998. The NRA review of endosulfan. (http://www.nra.gov.au/chemrev/prsendo11.pdf).

Patton, G.W., D.A. Hinckley, T.F. Bidleman, and B.T. Hargrave. 1989. Airborne organochlorine compounds in the Canadian High Arctic. Tellus, Ser. B, 41:243–255.

Patton, G.W., M.D. Walla, T.F. Bidleman, and L.A. Barrie. 1991. Polycyclic aromatic and organochlorine compounds in the atmosphere of Northern Ellesmere Island, Canada. *J Geophys Res.* 96(D6), 10:867–10:877.

Sang, S. and S. Petrovic. 1999. Endosulfan — A review of its toxicity and its effects on the endocrine system. World Wildlife Fund Canada Report, July, 1999.

Spears. 2001. Mapping Canada's toxic hotspots. http://www.mapcruzin.com/news/news041800b.htm

UNECE. 1998. The 1998 Aarhus Protocol on Persistent Organic Pollutants (POPs). United Nations Economic Commission for Europe. (Internet: www.unece.org/env/lrtap/pops_h1.htm)

UNEP. 2001. The Stockholm Convention on Persistent Organic Pollutants. United Nations Environmental Programme. (Internet: www.chem.unep.ch/sc/default.htm)

UNEP. 2003. List of signatories and ratifications to the Stockholm Convention on POPs. (Internet: www.pops.int/documents/signature/signstatus.htm)

U.S. Environmental Protection Agency (EPA). 1986. Information on Lead, Mercury, PCBs, BaP, DDT, Dieldrin/Aldrin, Toxaphene, Mirex, TCDD, TCDF, Federal Register.

Van Jaarsveld, J.A., W.A.J. Van Pul, and F.A.A.M. De Leeuw. 1997. Modelling transport and deposition of persistent organic pollutants in the European region. *Atmos Environ.* 31(7):1011–1024.

Vetter, W., C. Natzeck, B. Luckas, G. Heidemann, B. Kiabi, and M. Karami. 1995. Chorinated hydrocarbons in the blubber of a seal (*Phoca caspica*) from the Caspian Sea. *Chemosphere.* 30:1685–1696.

Voldner, E.C. and Y.F. Li. 1995. Global usage of selected persistent organochlorines. *Sci Total Environ.* 160/161: 201–210.

Wania, F., D. Mackay, Y.F. Li, T.F. Bidleman, and A. Strand. 1999. Global chemical fate of alpha-hexachlorocyclohexane. 1. Evaluation of a global distribution model. *Environ Toxicol Chem.* 18(7): 1390–1399.

Wania, F. and G.L. Daly. 2002. Estimating the contribution of degradation in air and deposition to the deep sea to the global loss of PCBs. *Atmos Environ.* 36: 5581–5593.

WHO. 1984. Endosulfan. International programme on chemical safety. Environmental Health Criteria 40. Geneva, Switzerland: World Health Organization. Cite: Sang, S. and S. Petrovic. 1999. Endosulfan — A review of its toxicity and its effects on the endocrine system. World Wildlife Fund Canada Report, July, 1999.

Zeng, E.Y., C.C. Yu, and K. Tran. 1999. In situ measurements of chlorinated hydrocarbons in the water column off the Palos Verdes Peninsula, California. *Environ Sci Technol.* 33:392–398.

Contributing to the Scientific Justification for POPs, Mercury and LRTAP Control Initiatives Globally and in North America

Project leader

Donald Mackay, Canadian Environmental Modelling Centre,
Trent University, 1600 West Bank Drive, Peterborough, Ontario K9J 7B8;
phone: 705-748-1011 ext. 1489; fax: (705) 748-1080;
e-mail: dmackay@trentu.ca

Project team

Todd Gouin, David Woodfine, Liisa Toose, Matthew MacLeod, Karen Foster, and Eva Webster, Canadian Environmental Modelling Centre, Trent University, 1600 West Bank Drive, Peterborough, Ontario K9J 7B8.

Abstract

This report describes the progress made in 2001–2003 on evaluating and modeling the fate of persistent organic pollutants and mercury on a global scale with the view to contributing scientific justification for Canadian initiatives related to the control of these substances internationally.

Part I of this report describes the development, testing and verification of a geographically explicit (BETR-World) model of chemical fate on a global scale designed to demonstrate and quantify transport of organic contaminants to the Arctic. The model is tested on α-hexachlorocyclohexane and yields results that are consistent with monitoring data and with those of the Wania-Mackay meridional model (1999). A transfer matrix approach has been developed by which chemical use in one region of the planet can be related, using the model, to deposition in another region. This characterization of the efficiency of chemical transport to the Arctic on a global scale will, we believe, be useful in international negotiations.

Part II describes a novel computational strategy by which this, and other models can be applied to treat mercury as a multi-species substance. Data have been gathered to parameterize the model and information obtained on related mercury modeling by other groups.

Part III reports on studies of long range transport of organic substances with particular reference to transport to the Arctic and the phenomenon of "grass-hopping". These studies enable a comparison to be made of the potential for transport to the Arctic of a variety of existing, new and potential persistent organic pollutants.

Key Project Messages

1. The capability now exists, as a result of this and other studies, to calculate, using computer models, how organic contaminants become dispersed globally, how long they survive in the environment and how far they can travel.
2. This capability can now be extended to mercury.
3. We are now able to compare chemicals for their relative likelihood of transport to the Arctic, thus identifying those existing and "new" substances of greatest concern which merit international regulation.

Objectives

The long term and general objective is to place in the hands of Canadian representatives at the various international fora such as UNEP, scientifically sound and peer reviewed documentation demonstrating that certain POPs and heavy metals, notably mercury, are deposited in the circumpolar ecosystem as a result of use in temperate and tropical regions. Three sub-projects are designed to provide the substantiation needed at the international negotiating table to achieve appropriate restrictions on release of these contaminants.

1. First is finalizing the geographically explicit global model (now the BETR-World model) which will predict the extent to which a defined organic chemical or POP used in a defined region will be transported to the Arctic, how long this will take and the likely duration of the resulting toxic burden in the Arctic.
2. Development of a novel method by which the BETR-World model can be modified to treat mercury, with validation and demonstration to assist in the UNEP Global Mercury Assessment.
3. Finalize simpler "evaluative" methods of ranking numerous chemicals for their long range transport potential especially as they migrate northwards into colder climates, thus assisting the identification of new POPs based on their properties.

Part I — The BETR-World Model

Introduction

In a related project funded by the Toxic Substances Research Initiative of Environment Canada and Health Canada we developed the BETR (Berkeley-Trent) model which describes the fate of chemicals in 24 regions of the North American continent. The rest of the world is treated as a 25th region. This model has been successfully applied to several chemicals including toxaphene which have been used in one region of the continent and have been observed to travel to other regions such as the Great Lakes Basin and the arctic (MacLeod et al., 2002) . In this project, we have used the mathematical skeleton of this model, modified and re-parameterized it to apply to the entire global or world environment of continents, sub-continents, oceans and polar regions. The model has been referred to as a "Geographically Explicit" model to distinguish it from the Wania-Mackay (1999) meridionally segmented model and is now named the "BETR-World" model. Whereas in the meridional model, distant regions such as the Mediterranean, the Great Lakes Basin and the Korean Peninsula are combined because they are on the same latitude, these are now treated as separate regions. This is useful because chemical usage and concentrations differ in these regions, as do the rates of transfer to specific receptor regions such as the Canadian Arctic. This capability of assigning source-receptor relationships on a geographically specific basis is regarded as being particularly important in international negotiations since it avoids "lumping" disparate source regions. It is essential to provide convincing evidence that quantities of a chemical used by one nation have the potential to reach the Arctic. The only feasible strategy for reducing future contamination of the Arctic is to document the various sources and convince appropriate agencies in these national source regions to reduce emissions as part of international agreements. A geographically explicit model can demonstrate such relationships.

In this report we describe the model briefly, full details being given in a companion paper which is being submitted for publication (Toose et al., 2003). Its application to α-hexachlorocyclohexane (α-HCH) is then described and discussed. The results are compared with monitoring data and with those of the Wania-Mackay meridional model (Wania et al., 1999).

Segmentation

The global environment has been divided into 25 regions depicted in Figure 1. Each region represents an area which is mostly land or ocean. All regions may contain the following compartments: upper and lower atmospheres, soil, vegetation, freshwater, freshwater sediment and coastal or open ocean as illustrated in Figure 2. The regions range in area from 5 million km^2 to nearly 50 million km^2. Because there is relatively slow transport across the equator, there is a north/south hemispheric segmentation.

Parameterization

Considerable effort was devoted to obtaining data on properties of each region including areas and effective volumes of land and water, flows of air and water to and from adjacent regions, temperature variations seasonally, vegetation cover, soil organic matter contents, deposition rates of particulate matter in water, precipitation rates, mass transfer coefficients and other parameters controlling intermedia transport of contaminants. Where possible, reputable GIS sources were used to obtain parameters.

Emissions

The initial substance treated was α-HCH. Usage estimates of technical-HCH have been compiled by Li (1999) on national and gridded scales from 1948 to 1997. This with

Figure 1. The BETR-World region segmentation

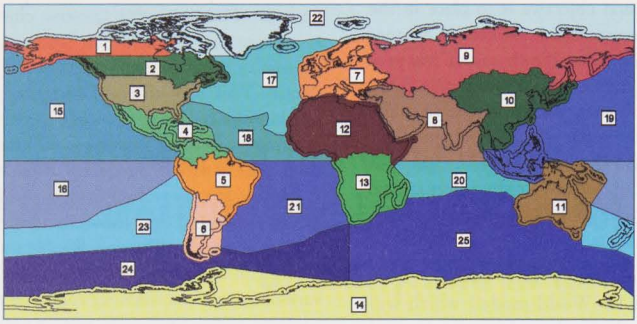
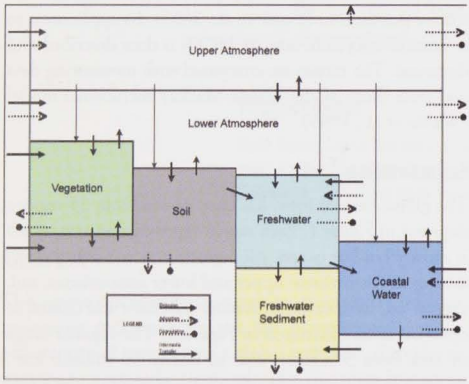


Figure 2. Compartments potentially contained within each region



the Wania-Mackay (1999) meridonal emissions curves provided the basis for α-HCH usage from 1948 to 1997 used in this model. An emission estimate was made for each region in the form of a non-symmetrical logistic function illustrated in Figure 3, which describes the increase then decrease of emission over the period 1948 to 1997.

Mass Balance Equations

For each of the 7 compartments in the 25 regions a first order differential equation was written of the conventional form

$$d(VZf)/dt = E + \Sigma fD_{IN} - f\Sigma D_{OUT}$$

where V is the compartment volume (m^3), Z is the bulk fugacity capacity or ratio of concentration (mol/m^3) to fugacity (f, Pa), t is time (h), E is emission rate (mol/h) to the compartment and the two remaining terms represent the total transport into and out of the compartment, including degradation reactions. A steady-state algebraic solution is possible if the left side of the equation is zero. The set of 175 differential equations is solved numerically using an initial condition and all emissions specified over the time period of interest. This yields data on the time course of all fugacities from which concentrations, masses and fluxes can be calculated. The entire history of global contamination is then documented and modest extrapolation into the future is possible.

Results

Figure 4 gives illustrative dynamic or unsteady-state showing that the calculated concentrations are in satisfactory agreement with monitoring data. Concentrations are generally within a factor of five of measured values which is regarded as accurate as is feasible given the many assumptions inherent in the model. The global rise and fall in concentrations is reproduced. Several features and capabilities of the model and its results are worthy of note.

The model can be run in dynamic form yielding results of the type shown in Figure 4. It is, however, difficult to interpret these results. The individual source-receptor relationships are not apparent, e.g. how much of the substance observed in the Arctic was derived from usage in India. Nor does it indicate the transport time, i.e. how long it takes for chemical emitted at a specific point in time to reach the Arctic. Further, it is important to evaluate the potential recovery time, especially in the Arctic. These aspects are believed to be particularly relevant in international negotiations. Insights into these aspects of global contamination can be obtained by

Figure 3. Time-variable global emission curves by climatic band, 1948–1997

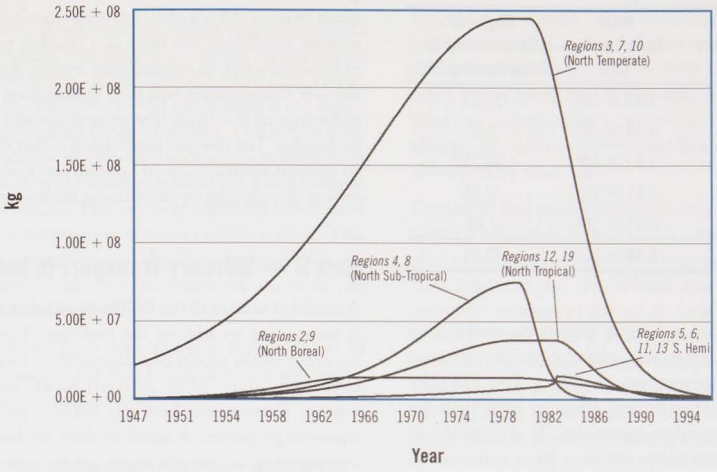
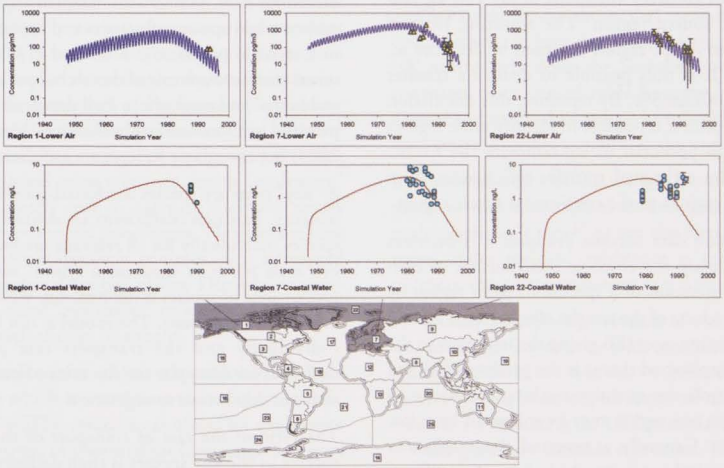


Figure 4. Average annual predicted vs. measured concentrations in air, freshwater and coastal water compartments in the Canadian Arctic (Region 1), Europe (Region 7) and the Arctic (Region 22)



running the model in both unsteady-state form yielding results such as Figure 4 or in steady-state form in which the constant concentrations resulting from prolonged constant emissions are deduced.

The model clearly demonstrates that a persistent contaminant emitted in one region of the globe has the potential to reach all other regions, albeit in some cases in small quantities. The potential for transport to the Arctic differs considerably from region to region and presumably from chemical to chemical. Transport occurs both in the oceans and the atmosphere, the relative proportions being determined largely by the air-water partition coefficient and the degradation half-lives in both phases.

Since the model is linear in character, doubling the emission rate will double all concentrations resulting from that emission. The implication is that accurate emission

Table 1. Estimated transfer efficiencies and contribution to total loading for select regions

Region (i)	Transfer Efficiency (TE_i)	Total Emission, kg (E_i)	Regional Contribution to Total Loading (%)
7	15.33	5.01×10^8	21.31
8	2.76	5.39×10^8	4.13
9	12.47	3.82×10^8	13.22
10	3.36	3.51×10^9	32.69
12	4.04	6.48×10^8	7.26
Total		**5.58×10^9**	**78.61**

data are essential when seeking to validate the model using monitoring data. Regrettably, global emission estimates are available for relatively few substances. This difficulty can be circumvented to a limited extent by using fictitious or hypothetical emission quantities. It is possible to examine the concentrations resulting from emissions in each region individually, then in total. This enables concentration observed in specific receptor region such as the Arctic to be apportioned to various source regions. This is most readily accomplished by running the steady-state model with constant emissions of say 100 kg/year into a specific source region. The resulting flow of chemical into an Arctic region can then be deduced as, say, 3 kg/year. It is thus possible to deduce a transfer efficiency, in this case 3%. By repeating this calculation for all source regions it is possible to identify those regions that have a high potential to contaminate the Arctic. Table 1 lists the estimated transfer efficiencies from selected source regions to the continental Arctic region.

As better emission data become available it is becomes possible to calculate the absolute contribution of each region to contamination of a specific receptor region by summing the products of the transfer efficiencies (TEi) and the regional emission rates (Ei) giving the total flow to the receptor. It is emphasized that it is the product of Ei and TEi which controls the quantity reaching the Arctic. A substantial use in one region may be mitigated by a low transfer efficiency. Generally, as expected, those regions in the northern hemisphere from which there is significant atmospheric flows to the Arctic tend to be those with the greatest impact. It is possible that this approach may be adequate to demonstrate the need for regulatory action without having actual emission data. It may also be adequate for evaluating contaminants of emerging concern for which emissions may increase in the future.

To obtain time-of-response data requires running the unsteady-state model for emissions during a one year period then observing the propagation of the chemical globally in succeeding years. Likewise, assessing recovery times requires the use of an unsteady-state model in which present conditions are used as a starting point and the gradual reduction in contaminant levels is deduced. Given the low temperatures and long degradation times in the polar regions it is likely that these times will be measured in decades. The obvious implication is that there is a need to prevent future entry of contaminant into the Arctic region by reducing or eliminating emissions.

Part II — Mercury Transport to the Arctic

A modified version of the BETR-World described in Part I is being used to address the mercury. This adaptation requires that the model treat at least three mercury species, elemental, ionic (often referred to as "reactive") and organic. These species have very different partitioning and transport properties. A novel method has been devised to treat mercury as a pseudo single species substance in order that the model will apply, but such that it retains mercury's multi-species character when describing partitioning, transport and transformation processes. The new method is regarded as an improvement of that developed by Diamond et al. (1992) who adapted fugacity models to address multi-species substances and applied it successfully in a series of papers, e.g. Diamond (1999). It should be noted that development of this technique required considerable trial and error effort. Full details of the method are provided in a forthcoming publication (Mackay and Toose, 2003) but the salient features are as follows.

A "key" mercury species is selected, preferably elemental mercury. Partition coefficients are defined for all mercury species individually for all relevant media combinations. For each phase or medium a typical monitored set of proportions of species is defined, e.g. 90%, 9%, 1% on a mass of mercury basis. The model is run for each species individually and the transport rate parameters are deduced, for example, for the rates of evaporation from water or deposition to vegetation.

The ratio of the rate of transport of the two non-key species to the key species is then deduced as a function of the proportions present in the source medium and the various rate parameters. These ratios are then used to determine an overall "multiplier" by which the total rate of transport of all three species exceeds that of the key species. For every transport process a unique multiplier is deduced. This enables the BETR-World model to be easily modified. All that is required is insertion of a set of single number multipliers at appropriate points in the computer code. The model is then run and the

results interpreted in terms of both total mercury and individual species.

This novel method has been successfully applied to simple multimedia models and a paper describing the principles has been written for publication (Mackay and Toose, 2003). An issue which the model can address is the depletion of mercury during the polar sunrise. This results from enhanced oxidation of elemental mercury to reactive ionic mercury caused by the combination of oxidizing halogen species and sunlight. This involves adjusting the ratio of elemental to ionic mercury at times of polar sunrise. This drives faster deposition and depletes the total mercury concentration in air, but increases amounts in the terrestrial and oceanic phases.

In conclusion, we have demonstrated the feasibility of including mercury in the BETR-World model and implementation is currently proceeding.

Part III — Long Range Transport Potential of Existing and Emerging POPs to the Arctic

Monitoring programs have convincingly demonstrated that certain POPs have been transported from temperate regions of use to the Arctic. They have also shown, by comparing relative quantities in source and receptor regions, that the potential for transport differs from substance to substance. Accordingly, there is an incentive to understand the properties of a substance which cause this potential and use this as a basis for assigning a relative transport potential for existing and emerging POPs. This can be accomplished using relatively simple "evaluative" models which merely seek to compare chemicals under standard and hypothetical conditions. They do not seek to calculate absolute distances or times, as is attempted in the global models described earlier. Obviously consistency between these "evaluative" models and the global simulation models should be sought.

Our original work on this subject was published by Beyer et al. (2000) in which it was shown that a "characteristic travel distance" (CTD) could be calculated for a substance and used as a metric of potential for long range transport (LRT). In a subsequent study we have evaluated the effect of temperature on CTD and shown that a drop in temperature can cause increases or decreases in CTD depending on the temperature coefficients of the substances partitioning and degradation process rates (Beyer et al., 2003). Some substances, on a journey northwards, are retarded by the lower temperatures, but others proceed faster. It is now clear that vegetation and snow play important roles in determining LRT potential. The Canadian Environmental Modelling Centre has placed this "Transport and Persistence Level III" or TAPL3 model on its website (www.trentu.ca/cemc). This model has been thoroughly tested, is now widely used and is one of the models being tested in 2003 by an OECD sponsored expert group on LRT models. A related activity has been participation in a review of how global climate change may affect contaminant behaviour in the Arctic (MacDonald et al., 2003).

Central to this issue is the phenomenon of "hopping" in which a substance deposits on a terrestrial surface, then after some delay, evaporates, is transported some distance then deposits again. These hops may be diurnal, weekly, monthly, seasonal or annual in nature. The importance of this process is that if a substance repeatedly hops it can continue a multi-year journey northwards, possibly "overwintering" in soils then evaporating in the spring and summer. This can introduce a delay in transport with the result that the benefits of source reduction are delayed.

A review and analysis of this issue has been prepared and is being submitted for publication (Gouin et al., 2003). Briefly, it sets out the mathematical basis of hopping and shows that the average number of hops and the distribution in this number can be determined from the results of multimedia models. It also shows that measurements of POP concentrations in long distance transects such as from the UK northwards along the Scandinavian Peninsula are consistent with considerable hopping. Observation of diurnal and seasonal variations in atmospheric concentrations provide further support for this contention.

In a parallel study we are using a version of the BETR model in which the regions are arranged in the form of a multi-segment "tunnel" to test the distance and time of travel under realistic conditions as may apply in the northern temperate, Subarctic and Arctic regions.

In summary, by exploring a number of evaluative approaches and testing for consistency with monitoring data and the results of simulation models, we believe that modelling instruments can be developed, improved and rendered more credible, for evaluating the LRT potential of large numbers of existing and new chemical substances. This approach can, we believe, contribute significantly to the scientific justification for regulating POPs internationally.

References

Beyer, A., D. Mackay, M. Matthies, F. Wania and E. Webster. 2000. Assessing long-range transport potential of persistent organic pollutants. *Environ Sci Technol.* 34: 699–703.

Beyer A., F. Wania, T. Gouin, D. Mackay and M. Matthies. 2003. Temperature dependance of the characteristic travel distance. *Environ Sci Technol.* 37(4): 766–771.

Diamond, M.L., D. Mackay, and P. Welbourn. 1992. Models of multi-media partitioning of multi-species chemicals: the fugacity/aquivalence approach. *Chemosphere.* 25:1907–1921.

Diamond, M.L. 1999. Development of a fugacity/aquivalence model of mercury dynamics in lakes. *Water, Air and Soil Pollution.* 111:337–357.

Gouin, T., D. Mackay, K.C. Jones, T. Harner, and S. Meijer. 2003. Evidence for hopping of organic contaminants during long range atmospheric transport. (in prep).

Li, Y.F. 1999. Global technical hexachlorocyclohexane usage and its contamination consequences in the environment: from 1948 to 1997. *Sci Total Environ.* 232:121–158.

MacDonald, R.W., D. Mackay, Y.-F. Li, and B. Hickie. 2003. How will global climate change affect risks from long-range transport of persistent organic pollutants. *Hum Ecol Risk Ass.* 9(3):643–660.

Mackay, D. and L. Toose. 2003. Adaptation of fugacity models to treat speciating chemicals with constant species concentration ratios. (in prep.)

MacLeod, M., D. Woodfine, J.R. Brimacombe, L. Toose, and D. Mackay. 2002. A dynamic mass budget for toxaphene in North America. *Environ Toxicol Chem.* 21:1628–1637.

Toose, L., D.G. Woodfine, M. MacLeod, D. Mackay, and J. Gouin. 2003. A spatially explicit global model of chemical fate: application to assess contaminant transport from source to sink. *Environ Pollution.* (submitted).

Wania, F. and D. Mackay. 1999. Global chemical fate of α-hexachlorocyclohexane. 2. Use of a global distribution model for mass balancing, source apportionment, and trend prediction. *Environ Toxicol Chem.* 18:1400–1407.

Spatial Trends in Loadings and Historical Inputs of Mercury Inferred from Arctic Lake Sediment Cores

Project leaders

Derek Muir, National Water Research Institute, Burlington, ON; phone: (905) 319-6921; fax: (905) 336-6430; Togwell Jackson, National Water Research Institute, Burlington, ON; phone: (905) 336-4795; Doug Halliwell, Atmospheric & Hydrologic Sciences Division, Meteorological Service of Canada, Environment Canada, Yellowknife NT; phone: (867) 669-4741.
Note: Until his untimely death in June 2002 this project was led by Ven Cheam, National Water Research Institute, Burlington, ON.

Project team

Environment Canada: Nien Nguyen, Gino Sardella, Fan Yang and Xiaowa Wang, National Water Research Institute, Burlington, ON; Geoff Howell, Environment Canada, Dartmouth, NS.
University: John Smol (Queens University); Marianne Douglas (University of Toronto); Reinhard Pienitz and Warwick Vincent (Université Laval); Alex Wolfe (University of Alberta); and Günter Köck (University of Innsbruck, Austria).

Abstract

In this study 15 cores from Arctic lakes were analyzed for mercury and lead as well as extractable iron and manganese. Fourteen of the sediment cores were dated and historical deposition profiles and fluxes (concentration × sedimentation rate) of mercury and lead were examined over a broad geographic area from southwestern NWT to northern Ellesmere Island. Higher deposition of anthropogenic (man-made) sources of mercury and lead were found in the Subarctic lakes of Labrador and northern Quebec compared to other areas. Mercury deposition appeared to have peaked in the 1980s and was on the decline in the 1990s in about half of the cores analyzed and in all cores with high temporal resolution. The results of this study suggest that "reactive" Fe and Mn may influence Hg concentrations in lakes with very low sedimentation rates i.e. < 50 g m^{-2} yr^{-1}. Stable isotopes of mercury were determined in cores from two high Arctic lakes. The mercury isotope ratios (expressed as per mil deviations with respect to a standard) are independent of total mercury concentration but vary systematically with the age and chemical composition of the sediment, suggesting that isotope fractionation of Hg is occurring within the lakes and is controlled by environmental factors and related microbial activities. The study has added significantly to the existing data available on deposition of mercury and lead in Arctic Canada and provided the first information on mercury isotope ratios in Arctic lake sediments.

Key Project Messages

1. Mercury deposition to Arctic lake sediments has declined in the 1990s in Subarctic and Arctic areas of Canada as has been observed in northern Europe and in mid-latitude North America.
2. Combined with results from Subarctic lakes of Labrador and northern Quebec the results demonstrate that there are higher rates of man-made mercury and lead deposition to lakes in the eastern Arctic.

Objectives

1. To determine the depth profiles of mercury (Hg) and lead (Pb) as well as manganese (Mn) and iron (Fe) in 15 dated Arctic sediment cores collected over a three year period.
2. To quantify geographic trends in fluxes of Hg and its enrichment factors in Nunavut, NWT, and compare with results from Nunavik, and Labrador.
3. To link findings for Hg with those of paleolimnological indicators, persistent organic pollutants, as well as indicators of biogeochemical processes of Mn and Fe, all of which are obtained from the same cores, or cores from the same sites whenever possible.
4. To complement existing data on Hg in Arctic sediment cores with data generated over a much wider latitudinal and longitudinal range than previous work in order to provide a better understanding of Hg in the Canadian North.
5. To examine fractionation of Hg isotopes by natural processes in Arctic lake sediments.

Introduction

Mercury has emerged as a priority contaminant in the Arctic and inland lakes of central and eastern Canada with evidence of increasing Hg levels in biota (Braune 1999; Muir et al. 1999; Fisk et al. 2003) and in lake sediments (Macdonald et al. 2000; Landers et al. 1998; Lockhart et al. 1998). There have been major advances in knowledge of levels and temporal trends in Hg in the Canadian Arctic in the last five years (Fisk et al. 2003; Blanchard et al. 2003). Information on sources has improved as a result of continuous atmospheric Hg measurements in the high Arctic (Schroeder 2001) and Subarctic (Poissant 2001) and the identification of Hg depletion events (MDEs) during polar sunrise (Schroeder et al. 1998). Inputs of Hg^{2+} to lake surfaces and catchments may occur as a result of annual spring time MDEs. Information on temporal trends of Hg in biota has also improved with studies of Hg in Arctic seabirds (Braune 1999), in marine mammals (Muir et al. 2003a) and in fish in Great Slave Lake and other lakes (Evans and Muir 2001; Fisk et al. 2003).

What was lacking prior to the development of this project was time trends of Hg and other metals in freshwater environments over a very wide spatial scale. This kind of information is best obtained using sediment, peat or ice cores. Lake sediments have advantages over peat and ice cores in the Canadian Arctic because there are thousands of undisturbed lakes which theoretically permits wide geographical coverage. Lake sediments are available for sampling where ice cores may not be readily available owing to low altitude or where peat bogs are uncommon due to historically low plant growth rates (Muir and Rose 2003).

Landers et al. (1998) compiled results from studies of Hg in dated sediment cores from Alaska, northern Canada, Scandinavia, and Russia. This work was based in part on studies by Lockhart et al. (1995; 1998) who analysed cores from about 13 lakes in Nunavut, NWT and Yukon. Landers et al. (1998) concluded that there is an especially big gap in results for Hg deposition in the eastern Arctic and northern Quebec/Labrador, where no cores had been analysed for Hg except in central Quebec (Lucotte et al. 1995). A recent study by Lockhart et al. (2000a) examined Hg, Pb and other metals in a single laminated sediment core from Lake DV09 on Devon Island and provided a high-resolution picture of inputs to the mid-1990s. Graf-Pannatier (1997) determined Hg in several lakes in the Mackenzie Delta and showed that these western Arctic lakes have less pronounced enrichment factors for Hg than those from sites elsewhere in the Canadian Arctic. Hermanson (1998) reported elevated enrichment of Hg in dated sediment cores from two lakes near Sanikiluaq.

In the case of lead, several authors have shown, by studying the ice cores, that the element has been easily long-range transported from the other parts of the hemisphere to the Arctic (Boutron et al. 1991; Cheam et al. 1998). Outridge et al. (2002), using cores first reported on by Lockhart et al. (1995; 1998) and Hermanson (1998), showed that two lakes situated in the western and southeastern Hudson Bay lowlands had significant anthropogenic Pb sources which accounted for 70–90% of acid-leachable Pb by the 1980s or 1990s. By contrast, lakes in the western Canadian Arctic had low anthropogenic Pb signals. Isotopic trends through time indicated that Eurasian sources contributed most of the anthropogenic Pb to northwest Hudson Bay, with possibly a minor Canadian contribution at the southeastern Hudson Bay site.

This project, which began in April 2000 complements previous studies on deposition of Hg and other heavy metals in the Canadian Arctic and Subarctic by investigating lake sediment cores in more high Arctic locations as well as in southwestern NWT. It was combined with a parallel Northern Ecosystem Initiative study of Hg in dated sediment cores collected from the Hudson Bay lowlands of Manitoba and Ontario as well as northern Quebec and Labrador (Muir et al. 2003b) to obtain a Pan-Northern perspective on deposition of Hg and other metals.

Activities

In 2001–02 and 2002–03

The lake sediment cores were collected from 11 lakes in NWT and Nunavut (Figure 1) and analyzed during 2001–2003, adding to the four NWT/Nunavut lakes reported on previously (Cheam et al. 2001). All sites were from undisturbed, pristine locations with the exception of Resolute Lake near the village of Qausuittuq (Resolute). Some of the sites were located in or near EMAN (Ecological Monitoring and Assessment Network) sites (e.g. near Resolute and Daring Lake) and National parks/EMAN sites (e.g. Nahanni NPR; Tuktut Nogait NP; Aulavik NP; Quttinirpaaq NP).

Sediment collection

Cores were obtained with a KB or Glew corer (Glew 1998) from a small boat or from a float-equipped Cessna 206 or other aircraft. Collections were made by our University based partners (Douglas, Smol, Vincent, Pienitz, Wolfe and Köck and their co-workers) and by Environment Canada personnel working out of Yellowknife. Cores were extruded on site and slices placed in polyethylene (WhirlPak®) bags or glass ointment jars with screw capped lids. Slice thickness varied depending on the sampling team and their equipment. In low sedimentation systems, 0.5 cm slices were obtained for the top 5 cm to achieve maximum temporal resolution while obtaining sufficient mass for ^{210}Pb dating and contaminant analysis. At locations with higher sedimentation rates, slice thickness was generally 1 cm.

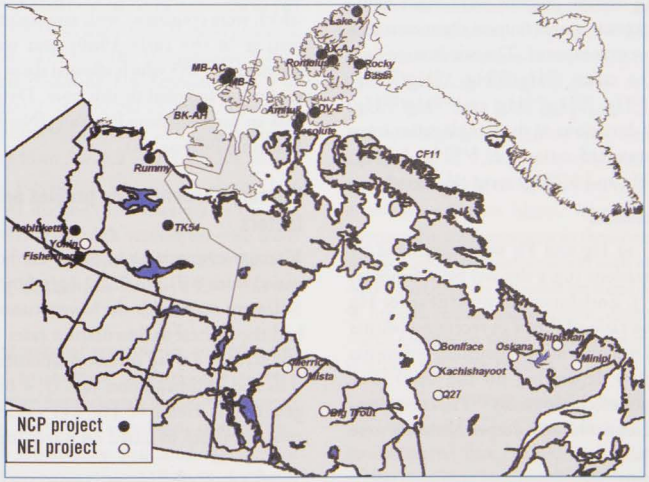
Sediment dating

The cores were first dated using ^{210}Pb and ^{137}Cs (Robbins 1978). Homogeneous portions of samples from each core were treated using a variation on the Eakins and Morrison (1978) polonium distillation procedure. Sediment cores were dated using ^{210}Pb and/or ^{137}Cs, sedimentation rates and dates of each slice were estimated using the Constant Initial Concentration (CIC) and the Constant Rate of Supply (CRS) models (Oldfield and Appleby 1984; Turner and Delorme 1996).

Sediment analyses

Subsamples from the 11 cores were analysed for Hg, Pb, Mn, and Fe. The analyses were performed on extracts prepared by subjecting subsamples of the sediments to acid digestion in a high-pressure microwave oven. Hg was

Figure 1. Location of lake sediment cores collected under the NCP and NEI projects



determined by cold vapour atomic absorption spectrophotometry (CVAAS), and Pb by inductively coupled plasma mass spectrometry (ICP-MS) (PQ-2, VG Elemental), whereas Mn and Fe were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). "Reactive" Fe and Mn were extracted with 1 M HCl (Leventhal and Taylor 1990; Gobeil et al. 1999), and the extracts were analysed by ICP-AES. Separate sets of subsamples were analysed for organic C, inorganic C, and organic N using a CHN analyser. All analyses were performed by the National Laboratory for Environmental Testing (NLET) at NWRI, Burlington.

Mercury stable isotope analyses

Core sections from Romulus Lake and Amituk Lake were analysed for Hg isotopes. Freeze-dried subsamples were digested with HNO_3/HCl (*aqua regia*) at 120°C, and HNO_3, HCl, and $KMnO_4$ were added to the extracts. The stable isotope composition of the extracted Hg was then determined with an automated, computerized ThermoFinnigan Neptune multicollector-ICP-MS unit (Activation Laboratories Ltd., Ancaster, ON) employing argon as the carrier gas following online reduction of dissolved Hg(II) to Hg(0) gas. A standard solution of Hg in 3.5% HNO_3 (lot S-HGO2027, Inorganic Ventures Inc.) was analysed before and after every batch of five sample extracts, and, on completion of the run, extracts of three reference materials were analysed: forest soil from Quebec, Canada (sample SO-2 from the Canada Centre for Mineral and Energy Technology) and soil and coppermill heads from Utah, U.S.A. (GXR-2 and GXR-4, respectively, from the U.S. Geological Survey). For each sample, standard, or reference solution, 25 replicate measurements of Hg isotope content were made automatically in rapid succession, whereupon the means and standard deviations were computed. The raw isotope data were expressed as the ratios $^{196}Hg/^{202}Hg$, $^{198}Hg/^{202}Hg$, $^{199}Hg/^{202}Hg$, $^{200}Hg/^{202}Hg$, $^{201}Hg/^{202}Hg$, and $^{204}Hg/^{202}Hg$, and the per mil (‰) deviations of the sample ratios from the corresponding standard ratios (i.e. $\delta^{196}Hg$, $\delta^{198}Hg$, $\delta^{199}Hg$, $\delta^{200}Hg$, $\delta^{201}Hg$ and $\delta^{204}Hg$) were calculated.

Flux and enrichment calculations

Fluxes (ug $m^{-2}yr^{-1}$) of Hg and Pb were calculated by multiplying concentrations (ug/g dry wt) by sedimentation rates (g $m^{-2}yr^{-1}$). Enrichment factors (EFs) for Hg were calculated as the ratio of fluxes in recent sediments (dated to the 1990s) to fluxes in pre-industrial sediments (generally 1840–1900 depending on the core). For Lake A, which had undetectable excess ^{210}Pb, concentration data for surface horizons and deeper horizons were used to compute EFs.

Quality assurance

Certified sediment reference materials and spike recoveries were used to ensure accuracy. NLET is a certified analytical laboratory which participates regularly and performs consistently very well in NCP interlaboratory studies (Stokker 2003) as well as in international intercomparison exercises.

Results and Discussion

Collection and dating

The name, location and year of collection of 15 sediment cores collected for this project are shown in Table 1 along with sedimentation rates and concentrations of Hg and Pb in the top slices. Dating reports were prepared on all the cores listed in Table 1. In general, cores were dateable by use of the ^{210}Pb technique as indicated by exponential decline of unsupported (or excess) ^{210}Pb with depth and with cumulative dry weight of sediment. However, excess ^{210}Pb activity was low in high Arctic cores. ^{210}Pb deposition declines exponentially with latitude, and, in North America, is about 5-fold lower at 60°N than at 30°N because of lower precipitation at higher latitudes (Preiss et al. 1996). In the high Arctic permafrost may reduce radon gas (the parent of ^{210}Pb) emissions from soil and extended periods of ice cover may prevent atmospheric ^{210}Pb from reaching lake sediments (Hermanson 1990). The core from Lake A was also undateable (it has been submitted for ^{137}Cs dating), however, the top 6 slices were varied sediments. The core from Resolute Lake also had non-detectable excess ^{210}Pb activity, however, gamma counting of ^{137}Cs showed significant subsurface peaks which were consistent with atmospheric nuclear weapons testing in the early 1960s and with the Chernobyl accident of 1985 which allowed dates and a sedimentation rate to be assigned to this core. Dating reports on each core are available from Fan Yang (National Water Research Institute, Burlington).

Mercury concentration profiles and enrichment factors

Mercury concentrations in surface horizons of each core varied from 0.017 to 0.251 ug/g (dry wt) in the 15 lakes. Sediment cores with the lowest concentrations generally had the highest sedimentation rates (Table 1) and there was actually a weak inverse relationship of Hg concentration and sedimentation rate ($r^2 = 0.16$; $P = 0.15$). No geographic trend of Hg was evident based on these concentrations or based on fluxes (ug m^{-2} yr^{-1}).

Table 1. Concentrations of mercury and lead in surface slices of 15 dated sediment cores[1] collected under this NCP funded project

Location	Lake	Year collected	Latitude	Longitude	Sedimentation rate g m^{-2} yr^{-1}	Mercury μg/g dw	Lead μg/g dw
Fort Liard, NT	Fisherman	2001	60° 21'N	123° 48'W	250	0.050	11.8
Nahanni NPR, NT	Rabbitkettle	2000	61° 58'N	127° 13'W	177	0.131	2.8
Central NT	TK-54	1998	64° 31'N	112° 42'W	97	0.073	6.0
Tuktut Nogait NP, NT	Rummy	1999	69° 04'N	123° 38'W	79	0.096	19.4
Northeast Baffin Is	CF11	2002	70° 29'N	68° 40'W	70	0.029	13.5
Northern Banks Is.	BK-AH	2000	73° 36'N	119° 35'W	46	0.095	15.5
Cornwallis Is.	Resolute	1999	74° 41'N	94° 55'W	750	0.019	9.0
Devon Is.	DVE	2000	75° 15'N	89° 30'W	120	0.018	8.1
Cornwallis Is.	Amituk	2001	75° 03'N	93° 46'W	210	0.050	11.1
Prince Patrick Is.	MB-AC	1999	76° 15'N	119° 18'W	380	0.028	4.5
Prince Patrick Is.	MB-S	1999	76° 13'N	119° 19'W	220	0.017	2.9
Southeast Ellesmere Is.	Rocky Basin	1998	78° 30'N	76° 47'W	10	0.251	5.8
Southwest Ellesmere Is.	Romulus	2000	79° 54'N	85° 06'W	780	0.052	13.7
Axel Heiberg	AX-AJ	1998	80° 00'N	87° 00'W	110	0.283	19.0
Northern Ellesmere Is.	Lake A	2001	83° 00'N	70° 30'W	—[1]	0.097	12.4

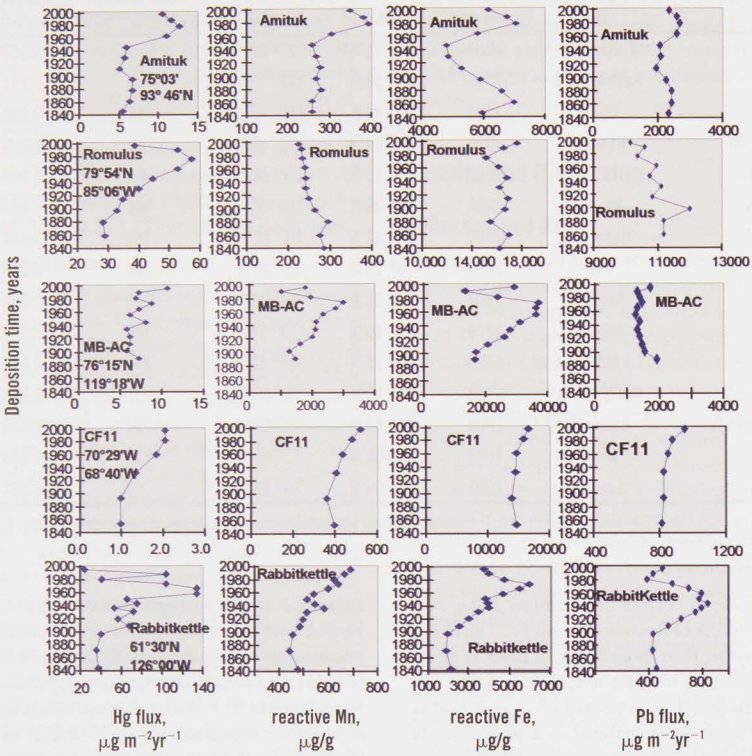
[1] Two cores, Resolute Lake and Lake A were undateable with ^{210}Pb. The Resolute Lake core was dateable with ^{137}Cs while varved sediments discernable in the top 6 cm of the Lake A permitted an assessment of the age

Figure 2 shows depth profiles of Hg fluxes along with concentration profiles of reactive Mn and Fe. The recent Hg fluxes are greater than those of earlier dates as determined by ^{210}Pb dating in these five cores and this was generally the case in all 15 cores as well as in 10 other cores from Subarctic lakes analyzed in a parallel study (Muir et al. 2003b). An interesting feature of the historical profiles, which was not observed in cores collected in the late 1980s and early 1990s in the Arctic (Graf-Pannatier 1997; Lockhart et al. 1995;1998; Hermanson 1990; 1998), was the recent declining Hg deposition in 3 of 5 lakes shown in Figure 2. In 7 of the 15 cores there were subsurface maxima indicating a decline in inputs in recent years (Table 2). Cores from Amituk and Romulus, which have good temporal resolution (Figure 2), show clear indications of a recent decline from maxima in the late 1970s and early 1980s. The high resolution core from Devon Island analysed by Lockhart et al. (2000) showed a leveling off of Hg deposition in the 1990s but no significant decline.

The concentration profiles of reactive Fe and Mn also showed a tendency to increase towards the surface although generally not in parallel with Hg concentrations (Figure 2). However, there were significant positive correlations between % reactive Fe and total Hg in 4 of 14 cores (Table 2). Two cores (Lake MB-S; Rocky Basin Lake) had significant negative correlations of % reactive Fe and total Hg. There were also statistically significant relationships of Hg concentrations with % Mn. One core (BK-AH) had positive correlations of Hg concentration and % reactive Mn ($P < 0.05$) while two others had marginally significant correlations ($P = 0.05–0.06$). In three cores (Rocky Basin, Resolute and Romulus) there were significant negative correlations. The significant or marginally significant positive correlations of Hg and % Mn were in lakes with very low sedimentation rates (< 50 g m^{-2} yr^{-1}) in this study and in Subarctic lake cores (Muir et al. 2003). However, Rocky Basin Lake is an exception. Resolute and Romulus had very high sedimentation rates compared to the others. Lockhart et al. (2000) also observed significant negative correlations of Hg concentrations with % Mn and % Fe in a core from Devon Island. Whether the Mn and Fe are affecting Hg concentrations in these cores is difficult to assess without additional information such as the oxygen regime. Additional data are available on some of the cores including % organic carbon and nitrogen, diatom counts, as well as water chemistry taken during coring, which may help interpret the metal profiles.

Landers et al. (1998) equated the Hg enrichment factor (EF) to the ratio of its recent flux (~1970 – present) to its pre-industrial flux (~1860 and older). We have used a similar definition but confined the "modern" concentrations

Figure 2. Profiles of mercury and lead fluxes, and concentrations of reactive manganese and reactive iron in 5 dated sediment cores



to the 1990s in most cores and the 1970s–90s in low sedimentation cores where the upper slices represented longer time periods. For Lake A, which was undateable, but varved, we used an EF based on the ratio of Hg concentrations in the top and bottom slices. To assess EFs over as wide an area as possible we combined the results for the 15 cores with 10 Subarctic cores reported by Muir et al. (2003b). Highest Hg EFs were found in cores from lakes in Labrador while lowest EFs were generally in the cores from western NWT. This is illustrated in Figure 3 which shows the Hg EFs versus longitude and latitude. There was a weak but statistically significant negative relationship between Hg EF and longitude ($r^2 = 0.18$) indicating higher anthropogenic enrichment in cores from eastern Canada and the high Arctic compared to NWT. The relationship with latitude was more complex. There was a declining trend of Hg EFs for cores from 50–65°N and an increasing trend for cores from 70 to 83°N. The apparent latitudinal decline is due to the fact that the western NWT cores are at 60–65°N while those in Hudson Bay lowlands, Quebec and Labrador are at 53–60°N; thus it is reflecting the higher anthropogenic Hg in eastern cores. In the case of the cores from 65–83°N, there was a marginally significant increase in Hg EF with latitude ($r^2 = 0.33$; $P = 0.03$; $N = 13$).

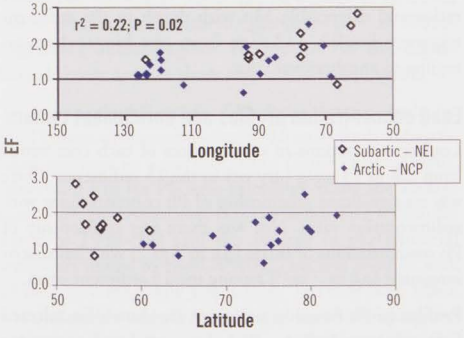
The Hg EFs observed in this study were within the range found by Lockhart et al. (1998) for the central and western Canadian Arctic and higher than reported by Landers et al. (1998) for Alaska. The EFs were generally lower than those reported for Sweden, Finland, South Florida, mid-continental U.S.A. and Adirondack Lakes (Engstrom and Swain 1997; Lorey and Driscoll 1999) as well as in mid-latitude glaciers (Schuster et al. 2002).

Table 2. Evidence for recent declining deposition of mercury in Arctic lake sediment from the presence of sub-surface maximum concentrations

Lake	Subsurface max?	Depth horizon (cm)	Median year[1]	Hg, µg/g
A	Surface	0–1.0	–	0.10
Amituk	Sub-surface	1.0–1.5	1979	0.06
AX-AJ	Surface	0–0.5	1995	0.28
Rocky Basin	Sub-surface	0.5–1	1989	0.25
BK-AH	Surface	0–0.5	1991	0.10
CF11	Surface	0–0.5	1998	0.03
DV-E	Surface	0–0.5	1989	0.02
Fisherman	Surface	0–0.5	1987	0.05
MB-AC	Surface	0–0.5	1997	0.03
MB-S	Sub-surface	0.5–1	1989	0.02
Rabbitkettle	Sub-surface	2.0–2.5	1967	0.76
Resolute	Sub-surface	1.5–2.0	1988	0.03
Romulus	Sub-surface	2.0–3.0	1976	0.08
Rummy	Surface	0–1.0	1996	0.10
TK-54	Sub-surface	4.0–5.0	1941	0.11

[1] Median age of the sediment section based on CRS dating of ^{210}Pb except for Resolute Lake (^{137}Cs) and Lake A which was undateable with ^{210}Pb

Figure 3. Enrichment factors (EF) for mercury versus longitude and latitude in 25 Arctic and Subarctic sediment cores



Variations in the stable isotope ratios of mercury

The δ^{198}Hg, δ^{199}Hg, δ^{200}Hg, δ^{201}Hg and δ^{204}Hg values varied in a distinctly nonrandom fashion in the core profile of Romulus Lake (Figure 4), but their profiles were entirely different from that of total Hg, suggesting that they resulted from fractionation of isotopes by environmental processes rather than preservation of original isotope signatures that might help to identify the sources of pollution. The profiles of the δ-values are characterized by complex but systematic variations with depth (i.e. with increasing age). The following regularities are immediately apparent: (1) Throughout the stratigraphic section, which spans the years 1899–1999, the Hg is enriched in ^{198}Hg, ^{199}Hg, ^{200}Hg, and ^{201}Hg but correspondingly depleted in ^{204}Hg; (2) The degree of enrichment is an inverse function of atomic mass (decreasing in the order of $\delta^{198}Hg > \delta^{199}Hg > \delta^{200}Hg > \delta^{201}Hg$, with δ^{204}Hg showing negative enrichment, i.e. depletion); (3) The δ-values alternately rise and fall smoothly and regularly with depth, the lowest (pre-1930) core sections consistently showing the greatest enrichment in δ^{198}Hg, δ^{199}Hg, δ^{200}Hg, and δ^{201}Hg and depletion in δ^{204}Hg. The profiles of δ^{198}Hg, δ^{199}Hg, δ^{200}Hg, and δ^{201}Hg all have essentially the same shape and the profile of δ^{204}Hg is a mirror image of them. Similar profiles of these isotopes ratios were found in the Amituk Lake core. The precision of the analysis was very high with standard deviations averaging 0.039% for the standard Hg solution run during the analysis and 0.003% for replicate analyses of the same sample.

The δ-values for Hg were found to correlate with $NH_2OH{\cdot}HCl/HNO_3$ extractable Mn, but not Fe, in the Romulus Lake core (Jackson et al. 2003). This correlation was negative in the oldest core sections (the 5 lowest core sections) but positive in the youngest ones (the top 6 sections), and there was no significant correlation in the intermediate horizons. These findings suggest fractionation of Hg isotopes in the lake through the agency

Figure 4. Variations in the total Hg concentrations and $\delta^{198}Hg$, $\delta^{199}Hg$, $\delta^{200}Hg$, $\delta^{201}Hg$, and $\delta^{204}Hg$ with depth in the Romulus Lake sediment core. The radiometric dates of the core sections are listed on the right

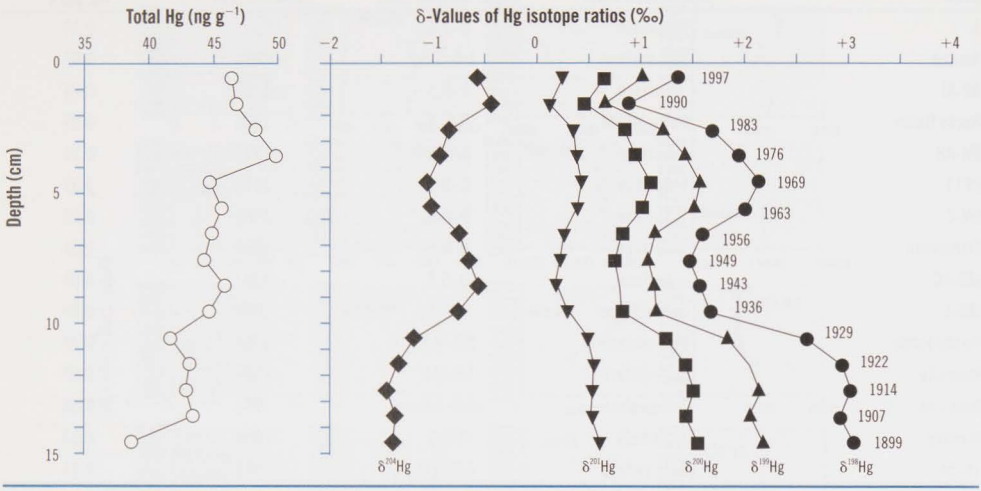
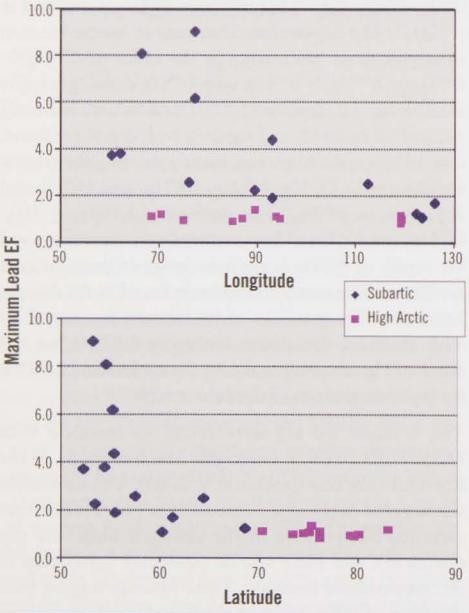


Figure 5. Geographic trends in maximum Enrichment Factors (EFs) for lead in dated sediment cores from this study (N = 24). Subarctic = lakes south of 70°N; High Arctic = lakes north of 70°N



of microbial activities linked to oxidation-reduction reactions but provide no evidence for preservation of source-related isotopic signatures. Furthermore, the systematic change in the relations between Hg isotope ratios and extractable Mn with depth in the sediment sequence implies a change from one biogeochemical regime to another over time.

Lead concentration profiles and enrichment factors

Lead concentrations in surface slices of each core varied from 2.8 to 19 μg/g (dry wt) in the 15 sediments. There was no significant relationship of Pb concentrations with sedimentation rates. Nor was there any relationship of Pb concentrations or fluxes (μg m^{-2} yr^{-1}) with latitude or longitude (μg m^{-2} yr^{-1}) among the 15 sediment cores.

Profiles of Pb fluxes in sediment are shown for selected Subarctic cores in Figure 2. A distinct subsurface maxima was found for Rabbitkettle Lake. This lake is located in northwestern Nahanni National Park Reserve within the Taiga Cordillera Ecozone and the Mackenzie Mountains. Just upstream of Nahanni NPR, but downstream of Rabbitkettle Lake, lie two past-producing metal mines, the Canada Tungsten (tungsten-copper) Mine and the Cadillac/Prairie Creek (silver-lead-zinc) Mine. More importantly, a 1993 Geological Survey of Canada Memoir by Gordey and Anderson inventories and describes at least 31 as yet undeveloped metal deposits upstream of Rabbitkettle Lake and Nahanni NPR (Ballantyne 1991).

Table 3. Correlations of mercury concentrations with % reactive iron (Fe) and manganese (Mn) in 14 Arctic lake sediment cores. Significant correlations and Bonferroni probabilities are bolded[1]

		Correlation Coefficients			Probabilities		
Lake	N[2]	Hg vs Fe	Hg vs Mn	Fe vs Mn	Hg vs Fe	Hg vs Mn	Fe vs Mn
Amituk	14	0.564	0.179	0.089	NS	NS	NS
AX-AJ	19	0.190	−0.135	0.633	NS	NS	0.050
Rocky Basin	6	**−0.961**	**−0.841**	**0.918**	**0.007**	NS	**0.030**
BK-AH	13	**0.803**	**0.959**	**0.839**	**0.003**	**< 0.001**	**0.001**
CF11	10	−0.333	0.374	0.716	NS	NS	0.059
DV-E	12	0.552	0.597	0.565	NS	NS	NS
Fisherman	9	0.441	0.711	0.477	NS	0.096	NS
MB-AC	12	0.291	0.195	**0.940**	NS	NS	**< 0.001**
MB-S	11	**−0.756**	−0.697	**0.913**	**0.021**	0.052	**< 0.001**
Rabbitkettle	17	**0.709**	0.390	**0.803**	**0.004**	0.364	**< 0.001**
Resolute	15	0.535	**−0.606**	−0.464	NS	**0.050**	NS
Romulus	15	−0.253	**−0.773**	0.344	NS	**0.002**	NS
Rummy	12	−0.355	0.663	−0.390	NS	0.057	NS
TK-54	15	−0.151	−0.269	**0.908**	NS	0.995	**< 0.001**

[1] NS = not significant = $P > 0.10$; marginally significant probabilities, $P < 0.1$ and > 0.05 are shown

[2] Number of slices analysed per core

Despite the importance of local geological sources of Pb, Rabbitkettle shows a distinct subsurface maxima similar to cores in lakes near Sankiluaq (Outridge et al. 2002) and in Labrador and northern Quebec (Muir et al. 2003b) suggesting anthropogenic Pb inputs. All the higher latitude cores did not show increased Pb deposition.

To examine the full extent of Pb deposition the results for the 15 cores were combined with 10 cores from Subarctic lakes analysed in a parallel study (Muir et al. 2003b). Maximum EFs for Pb were calculated using the average maximum concentrations (usually subsurface sediments dated to 1950–70) and the average in preindustrial sediments (dated to 1840–1900). This was possible with 24 cores, omitting only Yohin Lake. The core from Yohin was undateable with ^{210}Pb, possibly due to slumping and or beaver activity (Ruhland and Smol 2003), and therefore the preindustrial layer could not be identified. EFs for Pb ranged from 0.84 to 9.1 with the highest values observed in northern Quebec and Labrador sediments. Distinct geographical trends in Pb EFs are apparent when results are plotted against longitude and latitude (Figure 5). Pb EFs in Subarctic cores were significantly negatively correlated with longitude ($r^2 = 0.40$; $P < 0.01$). The EFs in cores from high Arctic lakes were not significantly correlated with longitude. The lack of significant anthropogenic enrichment of Pb in high Arctic lake sediments is clearer when EFs are plotted against latitude (Figure 4, bottom panel). Pb EFs declined exponentially with latitude (in EF vs latitude, $r^2 = 0.67$; $P < 0.001$) with an apparent half-distance (i.e. 50% decline in EFs) of 1400 km.

It is somewhat surprising that low Pb EFs were found in all cores from the high Arctic. Cheam et al. (1998) observed Pb pollution peaks in a snow pit during the period from 1986 to 1993 at Agassiz Ice Cap, Nunavut, and other researchers observed the rise and fall of Pb concentrations in Greenland ice (Candelone et al. 1995). Analyses of several sediment samples were also made for Pb isotopes 206, 207, 208 and 204 (using ICP with low resolution MS), however, no definite pattern was apparent and no specific information could be derived from the data at this time. Other studies have found a range of Pb EFs in the North American Arctic. In southwestern Greenland, Pb concentrations in dated lake sediment cores showed that significant concentration increases occurred during the 18th and 19th centuries, with a maximum in the 20th century around 1970 (Bindler et al. 2001) and EFs averaging 2.5. Outridge et al. (2002) examined Pb fluxes and isotope ratios in dated sediment cores from six lakes in the Canadian Arctic including three in the eastern high Arctic, Yaya Lake in the Mackenzie Delta area, as well as two lakes near Hudson Bay. They found no anthropogenic Pb signal in high Arctic sites similar to what we have observed. They

concluded that reduced atmospheric Pb deposition at higher latitudes was associated with lower precipitation rates, while over Hudson Bay the polar front, an area of meteorological disturbance, may play a role in increasing both precipitation and Pb deposition.

Conclusions

This study has added significantly to the existing data available on deposition of Hg and Pb in Subarctic and Arctic Canada, more than doubling the number of results available from dated sediment cores in Nunavut and Northwest Territories.

Combined with the parallel NEI study of Subarctic lakes, the results demonstrate that there is higher anthropogenic Hg and Pb in eastern Subarctic lakes of Labrador and northern Quebec. This is consistent with the greater density of Hg sources in eastern North America such as coal burning power plants and, in the case of Pb, with proximity to former emission areas for alkyl lead. The EFs for Pb are particularly elevated in Labrador and northern Quebec and, unlike Hg, decline exponentially with latitude consistent with a relatively short travel distance in the atmosphere.

The results also demonstrate that Hg deposition was on the decline in the 1990s in Subarctic and Arctic areas of Canada as has been observed in some lakes near sources in mid-latitude North America (Lockhart et al. 1998; Engstrom and Swain 1997; Lorey and Driscoll 1999) as well as in mid-latitude glaciers (Schuster et al. 2002). However, the decline is most readily observed in cores with high temporal resolution cores.

The results of this study suggest that "reactive" Fe and Mn may influence Hg concentrations in lakes with very low sedimentation rates i.e. < 50 g m^{-2} yr^{-2}. This needs to be further investigated perhaps using other extraction techniques for the reactive phases of Mn and Fe oxyhydroxides. If confirmed, the results may help to explain increasing Hg in very low sedimentation rate high Arctic sediment cores.

Stable isotope ratios of mercury in the Romulus Lake core were independent of total Hg concentration but did show highly significant relationships with extractable Mn content, suggesting that fractionation of Hg isotopes is occurring within the lakes as a direct or indirect result of microbial activities linked to MnOOH precipitation. Further research on a wide variety of lakes is needed to determine whether the stable isotope composition of Hg can, under suitable circumstances, be linked to sources of Hg contamination, as has been done with Pb.

Acknowledgements

We thank the following post-doctoral fellows and graduate students for their help in sediment core collection and water chemistry data on individual lakes. Dermot Antoniades (PhD) U of T, Claude Belzile (PhD) U. Laval, Marie-Andree Fallu (PhD) U Laval, John Gibson (Post-doc) U Laval, Doerte Koester (PhD) U Laval, Tamsin Laing (Post-doc) U Laval, Darlene Lim (PhD) U of T, Derek Meuller (Post-doc) U Laval, Neal Mitchelutti (PhD) Queens, Patrick Van Hove (MSc) U Laval. We thank Mike Mawhinney (NWRI, Research Support Services) for sediment core collections in Labrador, Big Trout Lake and northern Manitoba.

References

Ballantyne, S.B. 1991. Stream Geochemistry in the Canadian Cordillera: Conventional and Future Applications in Exploration. In Geological Survey of Canada Open File 2390. Exploration Geochemistry Workshop, Energy Mines and Resources Canada, March 1991. Pp. 6–1 to 6–74, Table 3 (p. 6–20).

Bindler, R., I. Renberg, P.G. Appleby, N.J. Anderson, and N.L. Rose. 2001. Mercury accumulation rates and spatial patterns in lake sediments from west Greenland: A coast to ice margin transect. *Environ Sci Technol.* 35: 1736–1741.

Blanchard, P., H. Hung, C. Halsall, T. Bidleman, G. Stern, P. Fellin, D. Muir, L. Barrie, L. Jantunen, P. Helm, and A. Konoplev. 2003. Occurrence and Trends. In: Sources, Occurrence, Trends and Pathways in the Physical environment. Canadian Arctic Contaminants Assessment Report II. Indian and Northern Affairs Canada. 77–184.

Boutron, C.F., U. Gorlach, J.P. Candelone, M.A. Bolshov, and R. Delmas. 1991. Decrease in anthropogenic lead, cadmium and zinc in Greenland snows since the late 1960s. *Nature.* 353;153–156.

Braune, B.M. 1999. Contaminants in Arctic seabirds eggs. Synopsis of Research Conducted under the 1998–99 Northern Contaminants Program. 77–80.

Cheam, V., G. Lawson, J. Lechner, and R. Derosiers. 1998. Recent metal pollution in Agassiz Ice Cap. *Environ Sci Technol.* 32:3974–3979.

Candelone, J.P., S. Hong, C. Pellone, and C.F. Boutron. 1995. Post-industrial revolution changes in large-scale atmospheric pollution of the northern hemisphere by heavy metals as documented in central Greenland snow and ice. *J Geophys Res.* 100(D8):16605–16616.

Eakins, J.D. and R.T. Morrison. 1978. A new procedure for determination of lead-210 in lake and marine sediments. *Int'l J Appl Rad Isotopes.* 29:531–536.

Engstrom, D.R. and E.B. Swain. 1997. Recent declines in atmospheric mercury deposition in the Upper Midwest. *Environ Sci Technol.* 31:960–967.

Evans, M. and D. Muir. 2001. Spatial and long-term trends in organic contaminants and metals in fish species important to the commercial, sports and domestic fisheries of Great Slave Lake and the Slave River ecosystem. In: S. Kalhok (ed.), Synopsis of Research Conducted Under the 2000–2001 Northern Contaminants Program, pp. 185–193. Indian and Northern Affairs Canada, Ottawa, ON.

Fisk, A.T., K.E. Hobbs, and D.C.G. Muir. (eds) 2003. Contaminant Levels and Trends in the Biological Environment, Canadian Arctic Contaminants Assessment Report II. Indian and Northern Affairs Canada. 202 pp.

Glew, J.R. 1988. A portable extruding device for close interval sectioning of unconsolidated core samples. *J Paleolimnol.* 1:235–239.

Gobeil, C., R.W. MacDonald, and J.N. Smith. 1999. Mercury profiles in sediments of the Arctic Ocean Basins. *Environ Sci Technol.* 33:4194–4198.

Graf Pannatier, E. 1997. Sediment Accumulation and Historical Deposition of Trace Metals and Trace Organic Compounds in the Mackenzie Delta (Northwest Territories, Canada). Terre et Environnement, Volume 10, Institut Forel, Section des Sciences et de la Terre, Université de Genève Thèse 2952.

Hermanson M.H. 1998. Anthropogenic mercury deposition to Arctic lake sediments. *Water Air Soil Pollut.* 101:309–321.

Hermanson M.H. 1990. ^{210}Pb and ^{137}Cs chronology of sediments from small shallow Arctic lakes. *Geochem Cosmochim Acta.* 54:1443–1451.

Jackson, T.A., D.C.G. Muir, and W.F. Vincent. 2003. Historical variations in the stable isotope composition of mercury in Arctic lake sediments. *Environ Sci Technol.* Submitted.

Landers, D.J., C. Gubala, M. Verta, M. Lucotte, K. Johansson, T. Vlasova, and W.L. Lockhart. 1998. Using lake sediment mercury flux ratios to evaluate the regional and continental dimensions of mercury deposition in Arctic and boreal ecosystems. *Atmos Environ.* 31:919–928.

Leventhal, J., and C. Taylor. 1990. Comparison of methods to determine degree of pyritization. *Geochim Cosmochim Acta.* 54:2621–2625.

Lockhart, W.L., P. Wilkinson, B.N. Billeck, R.A. Danell, R.V. Hunt, G.J. Brunskill, J. Delaronde, and V. St. Louis. 1998. Fluxes of mercury to lake sediments in central and northern Canada inferred from dated sediment cores. *Biogeochem.* 40:163–173.

Lockhart, W.L., P. Wilkinson, B.N. Billeck, G.J. Brunskill, R.V. Hunt, and R. Wagemann. 1995. Polycyclic aromatic hydrocarbons and mercury in sediments from two isolated lakes in central and northern Canada. *Water Sci Technol.* 28:43–52.

Lockhart, W.L., G.A. Stern, and P. Outridge. 2000. Mercury and other contaminants in a laminated sediment core from Devon Island. In: S. Kalhok (ed.), Synopsis of Research Conducted Under the 2000–2001 Northern Contaminants Program, pp. 104–112. Indian and Northern Affairs Canada, Ottawa, ON.

Lorey, P. and C.T. Driscoll. 1999. Historical trends of mercury deposition in Adirondack lakes. *Environ Sci Technol.* 33:718–722.

Lucotte, M., A. Mucci, C. Hillaire-Marcel, P. Pichet, and A. Grondin. 1995. Anthropogenic Mercury Enrichment in Remote Lakes of Northern Quebec (Canada). *Water Air Soil Polut.* 80:467–476.

Macdonald, R., L. Barrie, T. Bidleman, M. Diamond, D. Gregor, R. Semkin, W. Strachan, M. Alaee, S. Backus, M. Bewers, C. Gobeil, C. Halsall, J. Hoff, A. Li, L. Lockhart, D. Mackay, D. Muir, J. Pudykiewicz, K. Reimer, J. Smith, G. Stern, W. Schroeder, R. Wagemann, F. Wania, and M. Yunker. 2000. Sources, occurence and pathways of contaminants in the Arctic. *Sci Total Environ.* 254:93–234.

Muir, D., B. Braune, B. DeMarch, R. Norstrom, R. Wagemann, L. Lockhart, B. Hargrave, D. Bright, R. Addison, J. Payne, and K. Reimer. 1999. Spatial and temporal trends and effects of contaminants in the Canadian Arctic marine ecosystem: A review. *Sci Total Environ.* 230:83–144.

Muir, D.C.G. and N.L. Rose. 2003. Lake sediments as records of Arctic and Antarctic pollution by heavy metals, persistent organics, and anthropogenic particles. In: R. Pienitz, M.S.V. Douglas, and J.P. Smol, (eds), Developments in Paleoenvironmental Research, Volume 8: Long-term Environmental Change in Arctic and Antarctic Lakes. Kluwer Academic Publishers.

Muir, D., A. Fisk and M. Kwan. 2003a. Temporal trends of persistent organic pollutants and metals in ringed seals from the Canadian Arctic. In. S. Smith (ed). Synopsis of research conducted under the 2001–2002 and 2002–2003 Northern Contaminants Program. In press.

Muir, D., D. Halliwell, and V. Cheam. 2003b. Spatial Trends in Loadings and Historical Inputs of Mercury Inferred from Pan-Northern Lake Sediment Cores. Report to the Northern Ecosystem Initiative, NEI Secretariat, Environment Canada, Yellowknife, NT. 17 pp.

Oldfield, F. and P.G. Appleby. 1984. Empirical testing of ^{210}Pb dating models for lake sediments in Lake Sediments and Environmental History (Eds. E.Y. Harworth and J.W.G. Lund). University of Minnesota Press, Minneapolis. 93–124.

Outridge, P.M., M.H. Hermanson, and W.L. Lockhart. 2002. Regional variations in atmospheric deposition and sources of anthropogenic lead in lake sediments across the Canadian Arctic. *Geochim Cosmochim Acta.* 66:3521–3531.

Poissant, L. 2001. Atmospheric mercury transport, oxidation and fallout in Northern Quebec (Nunavik) an important potential route of contamination. In: S. Kalhok (ed.), Synopsis of Research Conducted Under the 2000/2001 Northern Contaminants Program, pp. 125–129. Indian and Northern Affairs Canada, Ottawa, ON.

Preiss, N., M.-A. Méliées, and M. Pourchet. 1996. A compilation of data on lead-210 concentration in surface air and fluxes at the air-surface water and water-sediment interfaces. *J Geophys Res.* 1001:28847–28862.

Robbins, J.A. 1978. In: Biogeochemistry of lead in the environment, Nriagu, J.O., Ed., Elsevier, Amsterdam. 285–293.

Ruhland, K. and J. Smol. 2003. *A diatom-based palaeolimnological assessment of environmental changes in Yohin Pond, Nahanni National Park Reserve, NWT.* Final Report Prepared for Douglas Halliwell, Environment Canada, Yellowknife. Prepared by Queen's University Biology Department, Palaeoecological Environmental Assessment and Research Laboratory (PEARL), March 2003. 21 pp.

Schroeder, W.H. 2001. Mercury measurements at Alert. In: S. Kalhok (ed.), Synopsis of Research Conducted Under the 2000/2001 Northern Contaminants Program, pp. 130–135. Indian and Northern Affairs Canada, Ottawa, ON.

Schroeder, W.H., K.G. Anlauf, L.A. Barrie, J.Y. Lu, A. Steffen, D.R. Schneeberger, and T. Berg. 1998. Arctic springtime depletion of mercury. *Nature.* 394:331–332.

Schuster, P.F., D.P. Krabbenhoft, D.L. Naftz, L.D. Cecil, M.L. Olson, J.F. Dewild, D.D. Susong, J.R. Green, and M.L. Abbott. 2002. Atmospheric mercury deposition during the last 270 years: a glacial ice core record of natural and anthropogenic sources. *Environ Sci Technol.* 36:2303–2310.

Stokker, Y. 2003. Interlaboratory Quality Assurance for the Northern Contaminants Program. In: Part II. Contaminant Levels and Trends in the Biological Environment, Canadian Arctic Contaminants Assessment Report II. Indian and Northern Affairs Canada. 111–127.

Turner, L.J. and L.D. Delorme 1996. Assessment of ^{210}Pb data for Canadian Lakes using the CIC and CRS models. *Environ Geol.* 28:78–87.

Atmospheric Mercury Transport, Oxidation and Fallout in Northern Quebec: An Important Potential Route of Contamination

Project leader

Dr. Laurier Poissant, Meteorological Service of Canada, Atmospheric Toxic Processes Section, Environment Canada, 105 McGill, 7th floor (Youville), Montréal, QC H2Y 2E7; phone: (514) 283-1140; fax: (514) 283-8869; e-mail: laurier.poissant@ec.gc.ca

Project team

Dr. Gerd Hoenniger, University of Heidelberg, Germany; Dr. Marc Amyot, INRS-EAU, Sainte-Foy, QC; Dr. Yves Bégin, Centre d'étude nordique, Université Laval, Sainte Foy, QC.

Abstract

Recent observations of mercury and ozone concentrations along Hudson Bay in Kuujjuarapik/Whapmagoostui, Quebec, (Lat. 55°N) showed that mercury and ozone depletion events, originally observed in the high Arctic, also occur at latitudes as low as 55°N. During mercury depletion events (MDE), total gaseous mercury (TGM, mainly elemental mercury) is converted in reactive gaseous mercury (RGM) and total particulate mercury (TPM). Moreover, mercury and ozone depletions events were correlated to high amounts of bromine monoxide (BrO) in air masses originating from the north and which were in contact with the Hudson Bay sea ice for several days. Bromine monoxide (BrO) is correlated to RGM and both species exhibit maximum concentrations at low temperatures (< 10°C). In the Kuujjuarapik/Whapmagoostui region the ration TPM/RGM appears to fluctuate between one and nine whereas the concentration of TGM appears to be decreasing. If this observation is real (i.e., not an artefact), it means that total atmospheric mercury is being made up of more TPM than before. Mercury fluxes are different over various landscapes. Mossy vegetation seemed to pump mercury from the atmosphere whereas small lakes seemed to be supersaturated and pumped mercury to the atmosphere.

Key Project Messages

1. Total Gaseous Mercury concentrations in Kuujjuarapik/Whapmagoostui region are decreasing.
2. Total Particulate Mercury appears to be increasing. The Ratio TPM/RGM is fluctuates over time.
3. Mercury concentrations in snow are low except during Mercury Depletion Events.

Objectives

1. To measure total gaseous mercury concentrations in air at Kuujjuarapik/Whapmagoostui (Hudson Bay, 77° 75'W 55° 28'N) and make comparisons with other locations in Canada (e.g., Canadian Atmospheric Mercury Network (CAMNet));

2. To study mercury oxidation processes by measuring ozone in air;
3. To measure total mercury concentrations in precipitation (as well as major ions, such as Cl- and Br-) at Kuujjuarapik/Whapmagoostui and to study their relationships with long-range transport and mercury fallout;
4. To measure mercury surface-air fluxes, especially during springtime;
5. To measure mercury concentrations in various abiotic components (soil, water, snow, etc.), over spaces and time in Nunavik and to study their potential connection with atmospheric mercury fallout.

Introduction

Mercury is one of the most toxic contaminants in the environment and is of particular concern in the northern environment because it is subject to long-range transport (Poissant, 1999; 2000; Cheng and Schroeder, 2000) Moreover, mercury can be chemically transformed to the organic, bioavailable form methylmercury, which bioaccumulates in the Arctic food web (Macdonald et al., 2000; Schroeder et al., 1998). Atmospheric mercury and ozone depletion events have been observed in the high Arctic region (eg., Alert, Canada) during polar sunrise. Although the mechanisms are still not fully understood, bromine (Br) radicals have been identified in the literature as a potential oxidation species. Besides their significant contribution to the destruction of ozone in the polar stratosphere, reactive bromine species also play a key role in boundary layer ozone depletion and can be an effective oxidant for mercury.

This study presents data that offer a unique opportunity to study the temporal evolution of ozone and mercury depletion events in the low Arctic and contributes significantly to the discussion of atmospheric mercury transport and fate in the northern environment. An understanding of mercury depletion events is critical to assessing the mechanistic route of mercury contamination in the northern region and its further transfer to the biosphere.

Activities

In 2001–2002

Various activities were done in the third year of this NCP research project. The site is located in Kuujjuarapik/Whapmagoostui region in northern Quebec, at the Centre d'Étude Nordique (CEN) (Université Laval). Meteorological data are available from the CEN and Navigation Canada. Instruments for the measurement of total gaseous mercury (TGM) and ozone were installed by mid-August 1999 and ozone and Hg data (TGM: 15 min intervals; O_3: 5 min intervals) were collected daily through telemetry (Poissant et al., 1996). TGM measurements were audited (quality controlled) at the site during a national audit realised by the Canadian Atmospheric Mercury Measurements Network (CAMNet) in mid-November 2000. Internal audits were done every 4 months following the same protocol (Poissant and Casimir, 1998). TGM data were quality controlled through the RDMQ mercury package (Natchem, ARQM, MSC, Downsview).

A cost effective and high quality monthly sampling protocol for Hg and major ions was elaborated and applied. Precipitation samples were collected since September 1999. Precipitation samples were analyzed at INRS-Eau (Dr. M. Amyot) for mercury, bromide and chloride (not presented here). Three intensive field campaigns were completed in spring 2000, 2001 and 2002. Hg snow surveys were carried out in the vicinity of Kuujjuarapik/Whapmagoostui. Also, snow-air Hg gas exchange flux experiments were conducted. These were the first Hg flux measurements conducted in the Arctic. Mercury air-surface gas exchanges were measured in August 2001 over various landscapes (snow, sand, bedrock, moss and a small lake). Measurements of mercury speciation (Reactive Gaseous Mercury (RGM) and Total Particulate Mercury (TPM)), TGM, ozone, TGM flux and Hg in snow were carried out simultaneously during Mercury Depletion Events.

In spring 2001, a European research team did parallel chemistry measurements using a Differential Optical Absorption Spectroscopy-Method (DOAS). *In situ* measurement of BrO has revealed mixing ratio of up to 30 ppt (*G. Hoenninger, Ph.D. Thesis*).

Results and Discussion

TGM and ozone results

Table 1 presents a statistical summary of daily TGM and ozone measurements at Kuujjuarapik/Whapmagoostui from August 1999 to April 2002. The daily median value was 1.72 ng m^{-3}. Minimal values of TGM and ozone were low (0.28 ng m^{-3} and 1.23 ppbv, respectively).

Figure 1 gives the daily median time series of TGM and ozone at Kuujjuarapik/Whapmagoostui. This historical time series shows specific low Hg and ozone concentrations from February to April. Three springtime periods have been measured to date and showed distinct climatology. The largest daily depletion event was recorded on February 21,

Table 1. Statistical summary of daily TGM and ozone in Kuujjuarapik/Whapmagoostui (Aug. 1999 to April 2002)

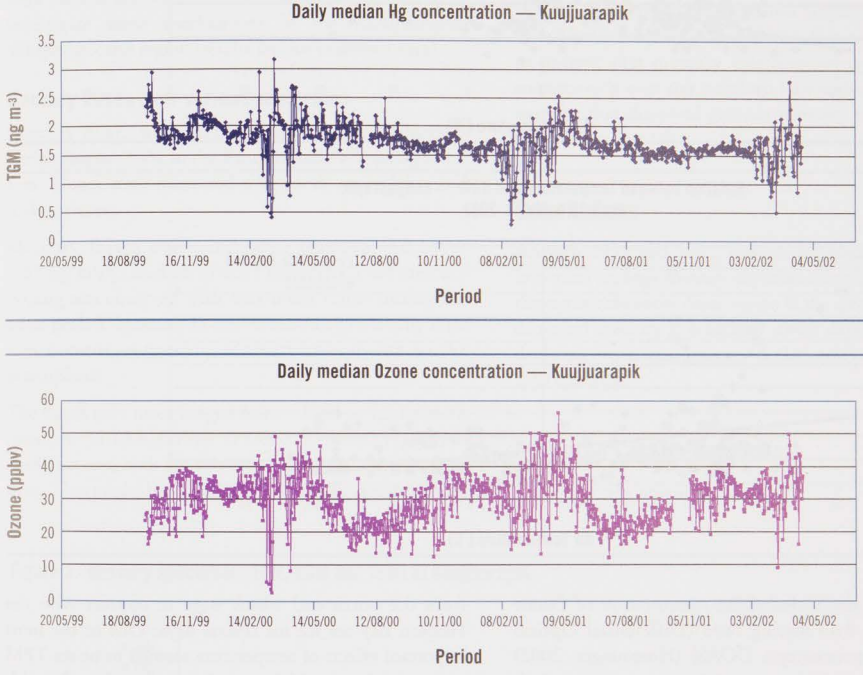
	TGM (ng/m³)	Ozone (ppbv)
median	1,717	29,225
min	0,286	12,775
max	3,172	56,325
n	1098	1100

Table 2. Annual Average of TGM at Kuujjuarapik/ Whapmagoostui

Kuujjuarapik/ Whapmagoostui (TGM ng m^{-3})	1999*	2000	2001
Annual Average (s.d.)	2.24 (0.72)	1.84 (0.38)	1.62 (0.33)

* August to December

Figure 1. Time series of TGM and Ozone at Kuujjuarapik/Whapmagoostui (Quebec)



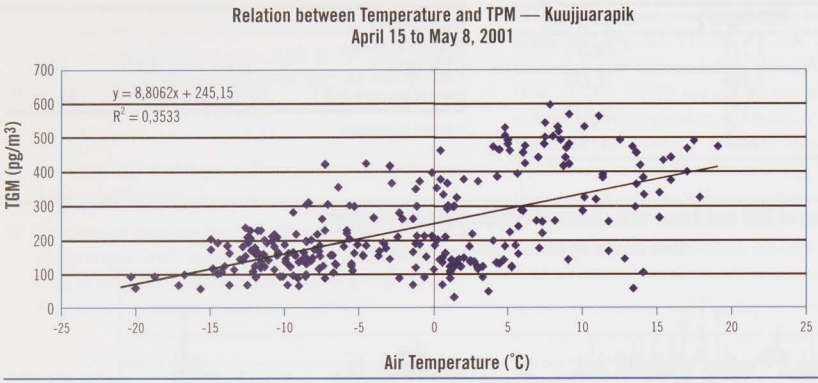
2001. These results demonstrate that the implications of polar mercury events extend beyond the high Arctic environment and are important in the low Arctic as well.

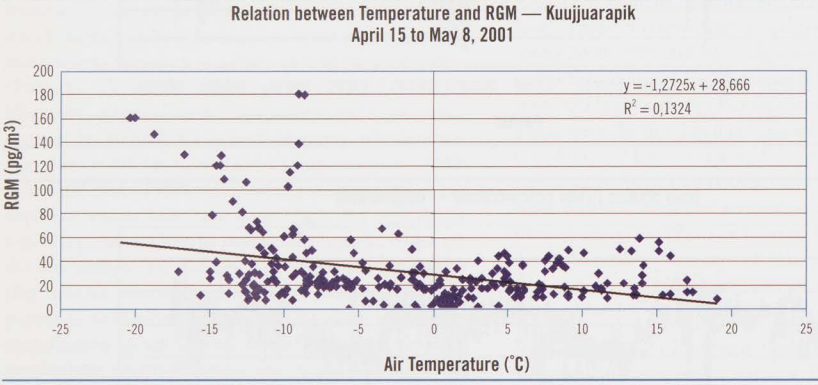
Annual average concentrations of TGM at Kuujjuarapik/ Whapmagoostui showed a significant decreasing trend (Table 2). Average TGM concentrations dropped from 2.24 to 1.62 ng.m^{-3} within three years. This might be explained by the reduction of anthropogenic mercury emission in the Kuujjuarapik/Whapmagoostui vicinity, however, TPM observed during spring seasons in 2001 and 2002 showed a significant shift upwards (from 100 pg/m^3 to 600 pg/m^3). If these trends are real (i.e., not an instrumental artefact) they suggest that in this location the proportion of TPM in total atmospheric mercury is increasing whereas the proportion of TGM is decreasing.

Mercury speciation during mercury depletion events

From April 15 to May 8, 2001, an investigation of Mercury Depletion Events (MDE) in low Arctic regions as carried out at Kuujjuarapik/Whapmagoostui as part of an international intensive field campaign to study this phenomena (Hoenniger, 2002; Poissant et al., 2002). Mercury concentrations (Total Gaseous Mercury (TGM), Total Particulate Mercury (TPM) and Reactive Gaseous Mercury (RGM)) were determined using new mercury speciation units, namely the Tekran 1130 and 1135. The

Figure 2. Air temperature regression with TPM and RGM in Kuujjuarapik (April 15 to May 8, 2001)





investigation also included the measurement of Ozone (Teco 49C), BrO mixing ratio (Differential Optical Absorption Spectroscopy, DOAS) (Hoenninger, 2002) and meteorological parameters (eg. temperature, wind, etc.). Results generated during the period of study provided the following median concentrations: TGM (1.93 ng/m^3); TPM (183 pg/m^3); RGM (22 pg/m^3); O_3 (36.5 ppb) and BrO (0.35 ppt). The median ratio of TPM/RGM was 9.2. Furthermore, BrO mixing ratio was anti-correlated with TGM (*TGM = − 0.05 BrO + 1.99*: R^2 = 0.35) and O_3 (*O_3 = − 1.0 BrO + 38.9*: R^2 = 0.33) whereas it was correlated with RGM (*RGM = 4.6 BrO + 21.3*: R^2 = 0.54). Interestingly, larger BrO mixing ratios (> 5 ppt) and RGM concentrations (> 60 pg/m^3) appeared only at cold temperature (~ < minus 8°C) (Poissant et al., 2002).

Mercury and ozone depletions were correlated with high amounts of BrO associated with air masses originating from the north and which were in contact with the Hudson Bay sea ice for several days. One of the most important effects of temperature seemed to be on TPM concentrations, which correlated significantly with temperature (*TPM = 8.8 T(°C) + 245*: R^2 = 0.35). Temperature did not correlate significantly with other species (Figure 2).

These latter results did not agree with those from a pre-intensive period from March 8 to April 15, 2001 (without DOAS measurements) where TPM, RGM correlated together but anti-correlated with TGM and O_3 (Figure 3). For this period TPM/RGM Ratio was close to one.

Mercury in snow

Mercury snow surveys done before and after depletion events confirmed an increase of mercury concentrations in snow (Figure 4) (Poissant et al., 2001; Amyot et al.,

2001). Mercury in the snow surface, however, can be re-volatilised back to the atmosphere when the air temperature is below 0°C and under sunlight.

Mercury can be also removed from the snow pack through melt water. Results suggested that Hg could be removed from snow surface with melting water when the air temperature is above 0°C. Hence, competitive processes will work to remove reactive mercury from the snow, namely photo-reduction and melt water. The former is not active under dark conditions. In spring 2002, specific experiments were carried out with Dr. C. Ferrari (U. Grenoble) to investigate these mechanisms in the Kuujjuarapik/Whapmagoostui region (results are not presented here).

Mercury fluxes over various substrates

Mercury fluxes were measured over various substrates during August 2001 in the Kuujjuarapik/Whapmagoostui area. Fluxes were measured over sand, moss, lake, and rock surfaces.

Mercury fluxes over sand were between −0.14 to 1.67 ng/m²/h (median of 0.35 ng/m²/h). Diel mercury cycling was observed with maximum values during the noon period. Mercury fluxes increased significantly after a rain event, suggesting mercury re-emission to the atmosphere.

The fluxes over moss ranged from −0.58 to 1.3 ng/m²/h (median −0.18 ng/m²/h). It seems that moss vegetation could act as a sink for mercury, especially during night time. This might have an impact on the bioaccumulation of mercury in the food web especially if mercury methylation is possible.

Mercury fluxes over typical bedrock (granite type) in the vicinity of Kuujjuarapik/Whapmagoostui were very low, varying between −0.2 to 0.56 ng/m²/h (median −0.03 ng/m²/h). This suggests that bedrock is not a significant emitter of volatile mercury in the Kuujjuarapik/Whapmagoostui region.

Finally, water-air mercury gas exchange measured over a small lake in summertime in Kuujjuarapik/Whapmagoostui showed emissions ranging from 0.59 to 4.5 ng/m²/h (median 1.5 ng/m²/h). It is very interesting to observe that mercury volatilisation is taking place continuously over this northern lake surface. This result suggests that dissolved gaseous mercury may be super-saturated in this lake.

Conclusions

Between 1999 and 2002, this project resulted in several important findings: mercury depletion events are experienced throughout the entire Arctic region in the springtime; freshly deposited mercury is volatilised in the days following the depleting event; and, mercury depletion is connected with BrO episodes.

Expected Completion Date

This project is ongoing.

Figure 3. Mercury speciation (TGM, RGM and TPM) at Kuujjuarapik

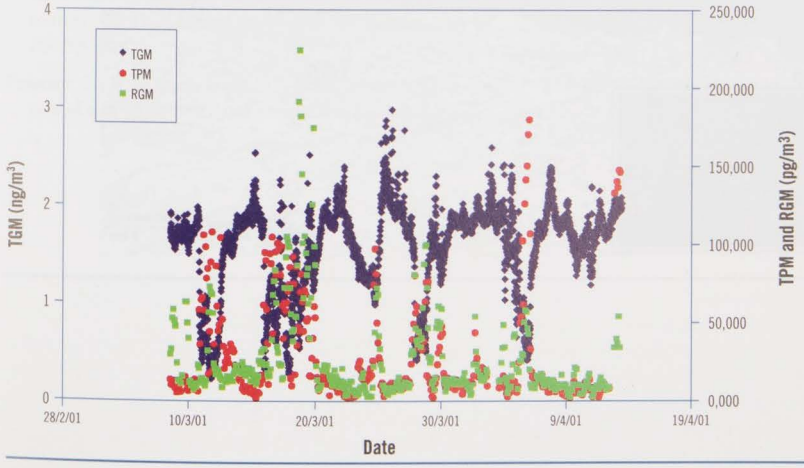
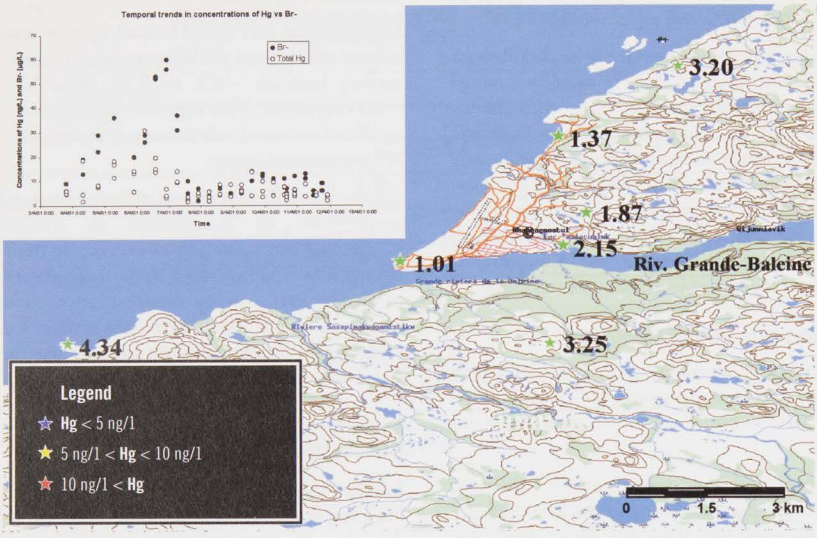
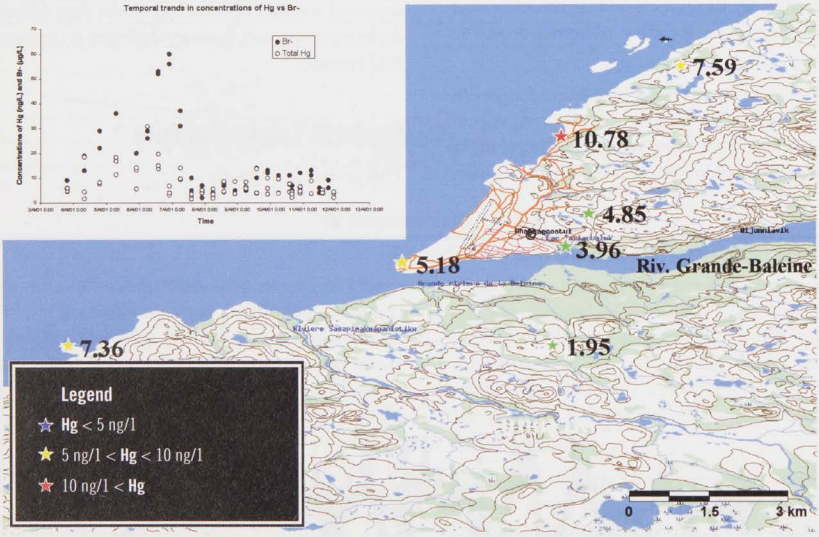


Figure 4. Temporal and spatial snow survey (Top is April 3–4, 2001; bottom is April 10, 2001)





Acknowledgements

L. Poissant would like to thank Martin Pilote, Meteorological Service of Canada, for his technical support (laboratory, field, instrumentation, etc.); Claude Tremblay (CEN) for his wonderful contribution in field support and for his hospitality. Special thanks to the Municipality of Kuujjuarapik for field support and community information about our work and NCP for funding this project.

References

Amyot, M., J.D. Lalonde and L. Poissant. 2001. Temporal Changes in Hg and Major Ion Concentrations in Surface Snow Following a Hg Depletion Event in Northern Quebec. The 6th International Conference on Mercury as a Global Pollutant (ICMGP), held in Minamata, Kumamoto Prefecture, Japan, from October 15 to 19, 2001.

Cheng, M.-D. and W.H. Schroeder. 2000. Potential atmospheric transport pathways for mercury measured in the Canadian high arctic, *J Atmos Chem.* 35:101–107.

Hönninger, G. 2002. Hologene Oxide Studies in the Boundery Layer by Multi Axis Differential Optical Absorption Spectroscopy and Active Longpath-DOAS. Dissertation submitted to the Combined Faculties for the Natural Sciences and for Mathematics of the Ruperto Carola University of Heidelberg, Germany for the degree of Doctor of Natural Sciences, February 14, 2002. p 262.

Macdonald, R.W., et al. 2000. Contaminant in the Canadian Arctic: 5 year of progress in understanding sources, occurrence and pathways. *Sci Tot Environ.* 254:93–234.

Poissant, L., B. Harvey, and A. Casimir. 1996. Application of a new telemetry and remote monitoring design for an automatic atmospheric vapour phase mercury analyser: Preliminary results. *Environ Technol.* 17: 891–896.

Poissant, L. and A. Casimir. Audit Protocol for Total Gaseous Mercury Measurement. Canadian Atmospheric Mercury Network (CAMNet). 22 pp.

Poissant, L. 1999. Potential sources of atmospheric total gaseous mercury in the St. Lawrence River valley. *Atmos Environ.* 33:2537–2547.

Poissant, L. 2000. Total gaseous mercury in Quebec (Canada) in 1998. *Sci Tot Environ.* 259:191–201.

Poissant, L., M. Amyot, M. Pilote, and D. Lean. Mercury water-air exchange over the upper St. Lawrence River and Lake Ontario. *Environ Sci Technol.* 34:3069–3078.

Poissant, L., M. Pilote, M. Amyot, and J.D. Lalonde. 2001. Atmospheric mercury depletion events, fallout and snow-air gas exchanges in northern environment. *Geophys Res Lett.* (Submitted).

Poissant, L. and M. Pilote. 2001. Atmospheric mercury and ozone depletion events observed at low latitudes along the Hudson Bay in Northern Quebec (Kuujjuarapik: 55°N), Presentation AT-23 at the 6th International Conference of Hg as a Global Pollutant. Oct 15–19, 2001, Minamata, Japan.

Poissant, L., G. Hoenninger, M. Pilote, H. Leser, O. Sebastian, and U. Platt. 2002. Atmospheric Mercury Speciation and Ozone Depletion Events Observed at Low Latitude on the Shore of the Hudson Bay in Northern Quebec (Kuujjuarapik: 55°N) (DOAS) Measurements. EGS Conference, Nice, France, April 2002.

Schroeder, W.H., K.G. Anlauf, L.A. Barrie, J.Y. Lu, A. Steffen, D.R. Schneeberger, and T. Berg. 1998. Arctic springtime depletion of mercury. *Nature.* 394:331–332.

Deposition of Mercury in Snow and Glacial Runoff of Mercury on Ellesmere Island in the High Arctic

Program leader

Vincent L. St. Louis, Department of Biological Sciences, University of Alberta, Edmonton, Alberta T6G 2E9; phone: (780) 492-9386; fax: (780) 492-9234; e-mail: vince.stlouis@ualberta.ca

Project team members

Dr. Martin Sharp and Joel Barker, Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta; Alexandra Steffen, Meteorological Service of Canada, Environment Canada, Toronto, Ontario.

Abstract

Recently it was observed that gaseous elemental mercury in the atmosphere, the form that allows mercury (Hg) to circulate around the globe, is "oxidized" in the Arctic to reactive gaseous mercury at polar sunrise, which then falls out of the atmosphere onto snowpacks. Arctic snowpacks were thought to be important reservoirs of mercury because of these springtime atmospheric "*mercury depletion events*." However, in a sampling program we conducted in the Arctic in spring 2001, we found extremely low concentrations of mercury in snow at 23 different sites over land and glaciers on Ellesmere and Devon Islands, Nunavut. Concentrations of mercury in glacial meltwater were also very low. Our results have led us to now hypothesize that either there is very little mercury deposition in areas remote from sea ice due to lack of the marine halogens bromine and chloride thought to catalyse mercury depletion events, or once atmospheric mercury is oxidized and deposited onto the snowpack, it is then rapidly "photoreduced" back to gaseous elemental mercury and emitted to the atmosphere.

Key Project Messages

1. Mercury is stripped from the Arctic atmosphere during "photochemically induced" springtime mercury depletion events.
2. The mercury is thought to be deposited on the Arctic snowpack.
3. We found little mercury in the snowpack on Ellesmere and Devon Islands, suggesting either that this region in the Arctic has few mercury depletion events, or that mercury is "photoreduced" and emitted back to the atmosphere soon after deposition.

Objectives

The objectives of our study were to conduct an initial characterization of:

1. Hg deposition in the high Arctic prior to and following polar sunrise over a range of elevations along an east-west transect from Baffin Bay and at Alert; and

2. Hg in glacial melt proceeding from initial snowmelt through to melt of glacier ice that is probably hundreds of years old.

In particular, we examined seasonal and spatial changes in atmospheric deposition of Hg in the Arctic along with seasonal changes in the flux of Hg from the atmosphere to the ocean via glacial runoff.

Introduction

There is increasing evidence of contamination by persistent, toxic pollutants including the metal mercury (Hg) in the Arctic (Schroeder et al. 1998). Hg is considered a global pollutant because it can undergo long-range atmospheric transport to areas far from point source emissions such as coal-combustion facilities (Schroeder and Munthe 1998). This behaviour is due to the fact that, in the atmosphere, Hg exists primarily as elemental Hg(0), a relatively inert gas (Schroeder et al. 1998). Over time, however, Hg(0) may become oxidized to inorganic, divalent Hg (Hg(II)). Although Hg(II) comprises a smaller proportion of the total Hg pool, it is the predominant species which leaves the atmosphere and is deposited to remote areas such as the Arctic.

The degree of Hg(II) deposition in the Arctic varies more seasonally than in most other regions of the globe with a pulse of deposition occuring annually after polar sunrise. In a study conducted in Alert, Nunavut, Schroeder et al. (1998) found that Hg(0) levels in the troposphere ranged between 1–2 ng/m^3 prior to polar sunrise. However, for three months after polar sunrise and until temperatures reach ~0°C, atmospheric Hg(0) levels frequently drop below 1 ng/m^3 (Schroeder et al. 1998). Where did the Hg go? It is thought that photochemical oxidation of gaseous Hg(0), in conjuction with tropospheric ozone depletion chemistry and marine halogens such as bromine or chloride, yields either reactive gaseous Hg (RGHg) and/or particulate-phase Hg (Lu et al. 2001; Lindberg et al. 2002; Berg et al. 2001; Lindberg et al. 2001), both of which have dry-deposition velocities greater than gaseous Hg(0) and fall out onto the snowpack. In fact, elevated concentrations of Hg(II) (sometimes exceding 100 ng/L) have been found in surface snow following these atmospheric Hg depletion events (Lu et al. 2001; Scott 2001). Since the initial discovery by Schroeder et al. (1998) at Alert, springtime Hg depletion events have been shown to be widespread in both the Arctic and Antarctic (e.g., Lindberg et al. 2002; Ebinghaus et al. 2002).

The form of Hg that is of most concern to humans is methyl Hg. MeHg is a strong vertebrate neurotoxin with the ability to bioaccumulate through aquatic food webs to levels in fish and marine mammals that may be toxic to consumers (Wolfe et al. 1998). Bacteria active in anaerobic environments including aquatic sediments, wetlands, and under glaciers can methylate deposited Hg(II) into the MeHg form (Berman et al. 1990).

We examined *net* springtime deposition of Hg(II) and MeHg to Arctic snowpacks on Ellesmere and Devon Islands. We also quantified runoff of Hg in glacial melt that could potentially contribute to the elevated concentrations of Hg currently found in certain Arctic freshwater fishes and marine mammals used for food by northern Aboriginal peoples (e.g., Canadian Arctic Contaminants Assessment Report 1997).

Activities

In 2001–2002

Sites

We conducted our research at three sites on Ellesmere and Devon Islands in the Canadian high Arctic. In May 2001, we collected snow samples from the Prince of Wales Icefield in eastern Ellesmere Island. Samples were collected every 200 metre increase/decrease in elevation along an east to west transect from Baffin Bay across the northern part of the icefield that also ranges over an elevation gradient of approximately 2,000 metres. We sampled both the upper snow deposited in the springtime 2001, and the deeper, older winter snowpack deposited in the fall of 2000. The snow survey was meant to ascertain whether (a) deposition was indeed maximised by polar sunrise-induced fallout of Hg from the atmosphere, and (b) whether proximity to Baffin Bay was important to atmospheric Hg fallout, as would be expected if halogens derived from the sea ice surface are important factors in Hg depletion reactions. We also collected upper and deep snow from four sites on Devon Ice Cap on Devon Island, and, in collaboration with Dr. William Schroeder, from five sites at Alert on the northern tip of Ellesmere Island. These samples allowed us to determine spatial variability in rates of deposition of Hg in the high Arctic.

A third site on Ellesmere Island (John Evans Glacier) allowed us to examine Hg runoff in glacial melt. Initial runoff from the glacier consisted of snowmelt from its surface, but as the melt season progressed the contribution from several hundred year old glacier ice laid down prior to industrialization and anthropogenic releases of Hg increased. A significant fraction of runoff at this site is routed under the glacier where active microbial communities including organisms known to methylate Hg, such as sulfate-reducing bacteria, exist

(Skidmore et al. 2000). Sampling subglacial runoff allowed us to determine if the microbial communities found there actually methylated Hg.

Field sampling

All sampling of snow and glacial runoff were conducted by two people using the well-established double-bagged "clean hands, dirty hands" ultraclean sampling protocol (St.Louis et al. 1996). Snow was collected in 2 litre acid-cleaned teflon jars as described by St. Louis et al. (1995). Snow samples were kept frozen and in the dark until they were returned to the University of Alberta clean room for analyses of total Hg (THg; all forms of Hg), MeHg, and bioavailable Hg (see below). Runoff samples were collected in the same manner using 250 ml acid-cleaned teflon bottles. Four runoff samples were collected during each sampling event (for duplicate analysis of unfiltered and filtered MeHg and THg). Both unfiltered and filtered (through 0.45 um filters [to remove large particulates] following standard Hg filtering protocol) THg and MeHg runoff samples were preserved with appropriate additions of trace metal grade hydrochloric acid at the time of sampling, and stored in clean coolers. Runoff was collected as melt proceeded from early June to early August, with additional samples taken during exceptionally high or exceptionally low discharge flows from the glacier. The latter will typically result in release of water that has spent a long time exposed to the subglacial microbial communities where Hg methylation could occur. This was also true of the very first runoff from the subglacial environment. We also sampled locations where surface water sunk into the glacier to determine changes in Hg speciation (i.e., inorganic versus MeHg) as it passed through the glacier.

Analyses

THg and MeHg analyses were completed in the University of Alberta Hg cleanroom. Samples were analysed for THg using now standard techniques described by Bloom and Crecelius (1983) and for MeHg using the highly sensitive and selective ethylation, chromatography and cold vapor atomic flourescence spectroscopy technique, recently developed by Bloom (1989) and Horvat et al. (1993). Using these approaches, the detection limits for THg and MeHg, respectively, are approximately 0.2 ng/L and 0.02 ng/L. QA/QC were maintained through random THg and MeHg interlaboratory comparison with numerous Hg analytical laboratories throughout Canada and the United States.

Because not all inorganic Hg is available for methylation or uptake by organisms (because it readily binds with, for example, organic matter), a number of the snow samples were also analysed for bioavailable Hg using a newly developed analytical technique known as the *mer-lux* bioreporter (Barkay et al. 1997). *Mer-lux* bioreporters are genetically engineered bacteria which produce light in proportion to the amount of Hg(II) that enters their cells. Traditional chemical analyses cannot distinguish between Hg(II) that can enter a bacterial cell and Hg(II) that can not. The importance of this analytical tool lies in the fact that microorganisms play a critical role in the transformation of Hg in aquatic and terrestrial environments including the conversion of Hg(II) to the highly toxic MeHg. The *mer-lux* bioreporter assay was conducted at the Freshwater Institute in Winnipeg. Glacial runoff was not analysed for bioavailable Hg because water samples currently cannot be preserved for this type of analysis.

Results

Our intensive snow survey of 23 sites on Ellesmere and Devon Islands, Nunavut, yielded extremely low concentrations of THg even at Alert where springtime Hg depletion events are known to occur (Table 1). At each site we subsampled snow from the lower depth hoar component of the snow pack deposited in the fall of 2000 (on average 0.65 ng THg/L) and from the upper part of the snow pack deposited in spring 2001 that *excluded* the very surface of the snow pack and the most recent deposition events (0.41 ng THg/L). These results counter those of other studies where high concentrations of THg were measured in the very surface snow only (Lu et al. 2001; Scott 2001). Our two fresh snow samples collected at Alert had on average only 5.34 ng THg/L (Table 1). Snow samples have yet to be analysed for concentrations of MeHg,

Table 1. Concentrations of total Hg (THg) in snow collected from various sites on Ellesmere and Devon Islands in the Canadain high Arctic

Location	Sample Dates	Fresh Snow (ng/L)	Top Spring Layer (ng/L)	Bottom Fall Layer (ng/L)
Alert	4–12 April 2001	5.34 ± 1.32 (2)	1.30 ± 1.42 (4)	0.59 ± 0.23 (3)
Devon Island Icecap	19–22 April 2001		0.27 ± 0.13 (3)	0.42 ± 0.15 (3)
Prince of Wales Icefield	5–19 May 2001		0.38 ± 0.21 (16)	0.23 ± 0.13 (13)

but we expect them to be low because THg concentrations were low.

Bioavailable Hg, or the amount of Hg that can pass into a bacterial cell and be potentially methylated to MeHg [7], was only detected in 40% of our samples analysed, most of them being from the upper snow pack layer. On average, 75 ± 56% of the measured THg was bioavailable in these samples.

Using the depth of the layered snow pack, water equivalent of the snow, and measured THg concentrations, we calculated an annual deposition rate for 2000–2001 of ~0.04 ± 0.02 μg THg/m^2 (Table 2), much lower than that observed in other regions of Canada (e.g., 7 μg THg/m^2 in the Boreal ecoregion [13]) and throughout the U.S. (3–20 μg THg/m^2; [14]).

Table 2. Annual net deposition of total Hg on Ellesmere and Devon Islands in the Canadian high Arctic

Location	Annual Net Deposition of THg (ug/m^2)
Alert	0.19 ± 0.25 (4)
Prince of Wales Icefield	0.04 ± 0.02 (16)
Devon Island Icecap	0.07 (1)

We also examined Hg in limited snow and glacial melt samples collected on John Evans Glacier, Ellesmere Island in 2001. Concentrations of THg in snowmelt were on average lower than what we observed in the snow pack (~0.2 ng THg/L). Concentrations in meltwater that drained from under the glacier were ~3 ng THg/L, but most Hg was on particulates because filtered water only contained ~0.2 ng THg/L.

Discussion and Conclusions

Hg(II) and MeHg can also be reduced photochemically to Hg(0) and lost back to the atmosphere (Sellers et al. 1996; Amyot et al. 1997). Large and rapid losses of new Hg deposited in lakes and snow have been observed due to photoreduction. The amount of "re-emission" of Hg to the atmosphere influences the residence time of Hg in biosphere pools, and hence the amount of Hg subsequently available for methylation and bioaccumulation.

Because we found extremely low concentrations of THg in our snow samples, *we now hypothesize that following Hg depletion events, deposited Hg is quickly photoreduced to Hg(0) and re-emitted back to the atmosphere.* We hypothesize that this is because the infrequency and low magnitude of snowfall in the high Arctic keeps Hg in surface snow exposed to solar radiation and susceptible

Table 3. Concentrations of total Hg (THg) in glacial surface pools and glacial runoff on John Evans Glacier, Ellesmere Island

		THg (ng/L)	
Location	Date	Unfiltered	Filtered
Surface pools on glacier			
Nunatak Lake	23 June 2001	0.52	0.30
Ridge Lake Moulin	28 July 2001	0.80	0.29
Pond Surface	18 July 2001	0.22	0.15
Pond Bottom	18 July 2001	0.23	0.16
Surface streams on glacier			
Supraglacial Stream	20 June 2001	1.76	1.32
Supraglacial Stream	13 July 2001	0.22	0.15
Supraglacial Stream	30 July 2001	0.17	0.14
Water bursting out from under glacier			
Subglacial Outburst	30 June 2001	2.07	0.24
Subglacial Outburst	30 June 2001	1.39	0.17
Stream running under glacier			
Subglacial Stream	15 July 2001	3.03	0.13
Subglacial Stream	29 July 2001	4.06	0.39

to photoreduction. During the extended period of depletion events in the polar springtime, the reduction of oxidized Hg keeps the majority of the depleted Hg in the very surface layer of the snow pack (Steffen et al. 2002; Lalonde et al. 2002). *As a result, we also hypothesize that little depleted Hg enters Arctic ecosystems in snowmelt despite large springtime deposition events.*

An alternative hypothesis is that *proximity to sea ice is important if bromine or chloride halogens derived from the sea ice surface are important factors in atmospheric Hg depleting reactions.* Preliminary statistical analyses show that THg concentrations in the upper snow layer decrease westwards away from Baffin Bay, and that chloride shows similar trends with distance from Baffin Bay. Future sampling efforts should include sites on the sea ice to test this hypothesis.

Expected Completion Date

December 2002.

Acknowledgements

We wish to thanks those who helped collect snow samples in Alert (Aaron Lawrence, Simon Llewellyn, and William Schroeder, Meteorological Service of Canada), Prince of Wales Icefield (Shawn Marshal, University of Calgary) and Devon Island Ice Cap (Doug Mair and Dave Burgess, University of Alberta). Sarah Boon and Dave Lewis (University of Alberta) helped collect snow melt and glacial runnoff samples on John Evans Glacier. Karen Scott, University of Manitoba, analysed snow samples for bioavailable Hg. Dave Kelly and Jane Kirk analysed all samples for concentrations of THg.

References

Amyot, M., D. Lean, and G. Mierle. 1997. Photochemical formation of volatile mercury in high Arctic lakes. *Environ Toxicol Chem.* 16:2054–2063.

Barkay, T., M. Gillman and R.R. Turner. 1997. Effects of dissolved organic carbon and salinity on bioavailability of mercury. *Appl Environ Microbiol.* 63:4267–4271.

Berg, T., J. Bartnicki, J. Munthe, H. Lattila, J. Hrehoruk, and A. Mazur. 2001. Atmospheric mercury species in the European Arctic: measurements and modeling. *Atmos Environ.* 35:2569–2582.

Berman, M., T. Chase, and R. Bartha. 1990. Carbon flow in mercury biomethylation by Desulfovibrio desulfuricans. *Appl Environ Microbiol.* 56:298–300.

Bloom, N.S. 1989. Determination of picogram levels of methylmercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapour atomic fluorescence detection. *Can J Fish Aquat Sci.* 46:1131–1140.

Bloom, N.S. and E.A. Crecelius. 1983. Determination of mercury in seawater at subnanogram per liter levels. *Mar Chem.* 14:49–59.

Canadian Arctic Contaminants Assessment Report. 1997. Indian and Northern Affairs Canada, Ottawa.

Ebinghaus, R., H.H. Kock, C. Temme, J.W. Einax, A.G. Lowe, A. Richter, J.P. Burrows, and W.H. Schroeder. Antarctic springtime depletion of atmospheric mercury. *Environ Sci Technol.* 36:1245–1256.

Horvat, M., N.S. Bloom, and L. Liang. 1993. Comparison of distillation with other current isolation methods for determinion of methyl mercury compounds in low level environmental samples. *Anal Chim Acta.* 281: 135–152.

Lalonde, J.D., A. Poulain, and M. Amyot. 2001. Photooxidation of Hg(0) in artificial and natural waters. *Environ Sci Technol.* 35:1367–1372.

Lindberg, S.E., M. Landis, R. Stevens, and S.B. Brooks. 2001. Comments on "Atmopsheric mercury species in the European Arctic: measurements and modeling" by Berg et al. Atmospheric Environment 14. 2000. 2569–2582. *Atmos Environ.* 35:5377–5378.

Lindberg, S.E., S. Brooks, C.-J. Lin, K. Scott, T. Meyers, L. Chambers, M. Landis, and R. Stevens. 2001. Formation of reactive gaseous mercury in the Arctic: evidence of oxidation of Hg0 to gas-phase Hg-II compounds after arctic sunrise. *Water Air Soil Pollut.* (In press).

Lindberg, S.E., S.B. Brooks, C.-J. Lin, K.J. Scott, M.S. Landis, R.K. Stevens, M. Goodsite, and A. Richter. 2002. Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise. *Environ Sci Technol.* 36:1245–1256.

Lu, J.Y., W.H. Schroeder, L.E. Barrie, A. Steffen, H.E. Welch, K. Martin, L. Lockhart, R.V. Hunt, G. Boila, and A. Richter. 2001. Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry. *Geophys Res Lett.* 28:3219–3222.

Scott, K.J. 2001. Bioavailable mercury in Arctic snow determined by a light-emitting mer-lux bioreporter. *Arctic.* 54:92–101.

Schroeder, W.H. and J. Munthe. 1998. Atmopheric mercury — an overview. *Atmos Environ.* 32:809–822.

Schroeder, W.H., K.G. Anlauf, L.A. Barrie, J.Y. Lu, A. Steffen, D.R. Schneeberger, and T. Berg. Arctic springtime depletion of mercury. 1998. *Nature.* 394:331–332.

Seller, P., C.A. Kelly, J.W.M. Rudd, and A.R. MacHutchon. 1996. Photodegradation of methylmercury in lakes. *Nature.* 380:694–697.

Skidmore, M.L., J.M. Foght, and M.J. Sharp. 2000. Microbial life beneath a high Arctic glacier. *Appl Environ Microbiol.* 66:3214–3220.

Steffen, A., W. Schroeder, J. Bottenheim, J. Narayan, and J.D. Fuentes. 2001. Atmospheric mercury concentrations: measurements and profiles near snow and ice surfaces in the Canadian Arctic during Alert 2000. *Atmos Environ.* 36: 2653–2661.

St. Louis, V.L., J.W.M. Rudd, C.A. Kelly, K.G. Beaty, R.J. Flett and N.T. Roulet. 1996. Production and loss of methylmercury and loss of total mercury from boreal forest catchments containing different types of wetlands. *Environ Sci Technol.* 30:2719–2729.

St. Louis, V.L., J.W.M. Rudd, C.A. Kelly and L.A. Barrie. 1995. Wet deposition of methyl mercury in northwestern Ontario compared to other geographical locations. *Water Air Soil Pollut.* 80:405–414.

Wolfe, M., S. Schwarzbach, and R. Sulaiman. 1998. Effects of mercury on wildlife: a comprehensive review. *Environ Toxicol Chem.* 17:146–160.

Mercury Measurements at Amderma, Russia

Project leader

Bill Schroeder, Meteorological Service of Canada, 4905 Dufferin St., Toronto, Ontario M3H 5T4; phone (416) 739-4839; fax (416) 739-4318; e-mail bill.schroeder@ec.gc.ca

Project team

Alexandra Steffen, Meteorological Service of Canada, Toronto, Ontario; Phil Fellin, AirZOne Inc., Mississauga, Ontario; Alexei Konoplev, SPA Typhoon, Obninsk, Russia.

Abstract

The investigation of atmospheric mercury in Arctic environments has gained considerable attention since the discovery of springtime mercury depletion episodes at Alert, Nunavut, and the possible impact this mechanism has on the Arctic environment. For several years, a number of Arctic countries have been routinely measuring mercury and have been studying its interesting behaviour throughout the polar sunrise period. However, there has been a gap in data from the sizable Russian Arctic. To address this gap in information, atmospheric mercury measurements began in June 2001 at Amderma, Russia. This study, in conjunction with 3 other polar countries (Denmark, Norway and the US), is intended to assess the not yet completely understood behaviour of mercury in Arctic regions and whether mercury concentration levels are increasing or decreasing. The preliminary data collected between June 2001 and April 2002 show mercury concentrations similar to those found at other Arctic sites and the occurrence of mercury depletion events.

Key Messages

1. Gaseous Elemental Mercury (GEM) is being measured at Amderma, Russia.
2. Mercury depletion events were found to occur at this location.
3. There are several sites in the Arctic investigating GEM and the addition of this Russian site will help complete a circumpolar network to measure mercury in the Arctic environment.

Objectives

1. Measure continuous GEM concentrations at Amderma, Russia.
2. Investigate and establish temporal (annual, seasonal) variability in GEM concentrations.
3. Study the circumpolar behaviour of GEM by comparing data between high Arctic sites.
4. Use the data to develop representative models of atmospheric pathways and processes of mercury and potential sources.

Introduction

The atmosphere is the first medium in which to observe the trends and behaviour of pollutants such as mercury as well as the effects of various national and international control efforts. Atmospheric mercury has been measured in various Arctic locations since 1995. Significant advances in the understanding of the behaviour of atmospheric mercury in the Arctic environment have been made since

the inception of our research at Alert, Nunavut. The discovery of the "Arctic springtime depletion of mercury" (Schroeder et al., 1998) laid the foundation for subsequent significant discoveries regarding the transformation and deposition of mercury in the Arctic. It has been found that the annual accumulation rate of Hg in the snow is enhanced in the springtime (Lu et al., 2001). These discoveries can have profound effects on the Arctic environment and have sparked international interest and scientific investigations into this phenomenon in the Arctic and the Antarctic by various international agencies (Ebinghaus et al., 2002; Lindberg et al., 2002).

In support of international environmental commitments (e.g. the AMAP program), Gaseous Elemental Mercury (GEM) is currently being measured at a site in northern Russia (Amderma, 69°N, 61°E) (see Figure 1). This is a collaborative research effort between Canadian and Russian scientists, with supplementary financial support provided by Denmark. Other Arctic measurement sites that investigate atmospheric mercury are also shown in Figure 1 including Alert, Canada; Pt. Barrow, USA; Svalbard/Spitsbergen, Norway; Station Nord and Nuuk, Greenland/Denmark and Thorshaven, Denmark. This investigation enhances the current understanding of this toxic metal by providing new information on the spatial extent and temporal transport trends of mercury from this region in the Russian Arctic. It will fill in gaps of knowledge regarding the distribution of mercury to the Arctic environment as a whole and provide important information for the development of long-term international strategies for the sustainable development and protection of polar regions. The addition of this site to the circumpolar network will help close the gaps in knowledge about key atmospheric transport, transformation and deposition processes of this priority pollutant that can lead to contamination of Arctic ecosystem and traditional food supplies for aboriginal people in Russia and all circumpolar countries. As well, the data generated from this network will help ascertain whether atmospheric mercury concentrations are increasing or decreasing in the Arctic environment.

Activities

In 2001–2002

The instrument was installed at the measurement site in Amderma in June 2001 and data collection commenced

Figure 1. Current polar sites for continuous GEM measurements

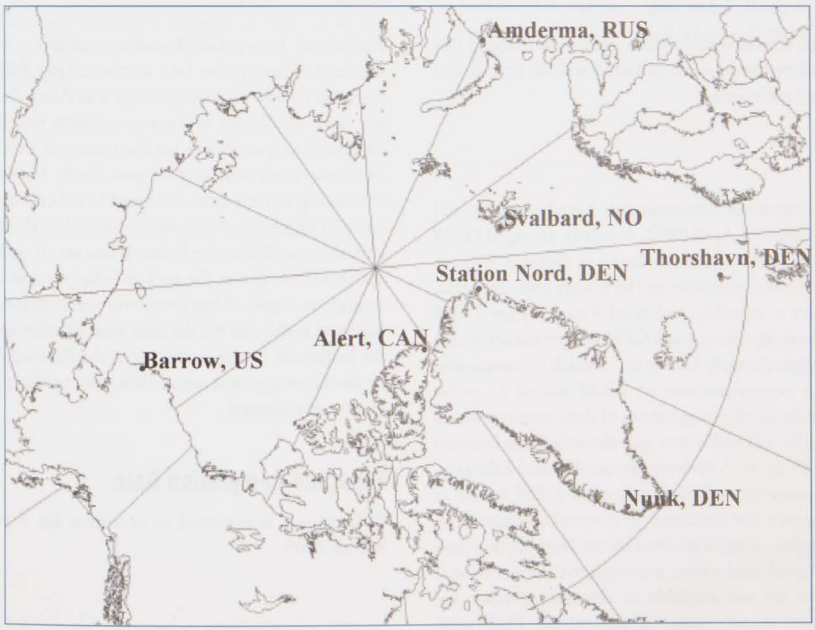
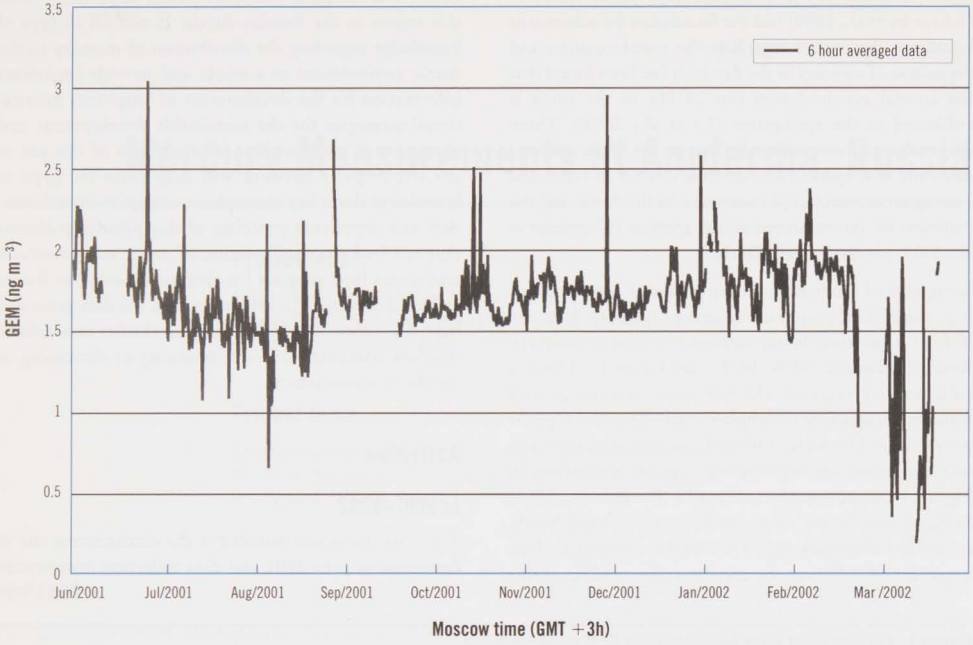


Figure 2. 6-hourly averaged GEM concentration measurements from June 2001 to April 2002



at this time. Several quarterly site visits were made to this location where the data was collected and the instrument verified and calibrated.

Results

GEM concentration measurements have been collected from June 2001 to April 2002. 6-hourly averaged GEM data from this time period are shown in Figure 2. Table 1 shows a statistical summary of the hourly averaged data, thus far, on a monthly and total basis. Figure 2 and Table 1 reveal that the average GEM concentration in this region is approximately 1.7 ng m^{-3}, which is comparable to average concentrations of GEM found in polar regions. From this first time-series of data, concentrations of GEM in the fall and winter are relatively stable between 1.5 and 1.83 ng m^{-3}, between September and February. This is consistent with the pattern of GEM found at Alert. However, the frequency of elevated concentration events is higher at this location than at Alert. At this time meteorological and other atmospheric observational information are not available so the source/reason for these elevated events cannot be ascertained. There were also some lower GEM concentrations observed at Amderma during the late summer/early fall which is uncharacteristic of a location such as Alert. Since we do not have a full year of data to confirm this interesting observation, speculation on the source of these outlying concentrations will not be put forth. However, it is interesting to note that, as found in other polar regions, mercury depletion events were observed in the springtime at Amderma. From the limited data set, it was observed that MDEs began at the end of February and continued though to April. Measurements are continuing to be collected at this site for the next year. Further insight into the behaviour of this pollutant in the Russian Arctic will be forthcoming once more data and ancillary measurements are collected.

Expected Completion Date

This project is expected to continue for 5 years until March 2005.

Table 1. Statistical summary of 1-hour (integrated sampling) GEM measurement data from Amderma (note April data is up to April 12, 2002)

Month	Mean (ng m^{-3})	Std Dev (ng m^{-3})	Median (ng m^{-3})	Min (ng m^{-3})	Max (ng m^{-3})	Count
July	1.87	0.22	1.81	1.50	3.52	523
August	1.56	0.19	1.56	0.30	4.10	711
September	1.55	0.30	1.51	0.01	3.36	587
October	1.64	0.07	1.64	1.41	1.91	505
November	1.70	0.22	1.66	1.32	5.26	689
December	1.73	0.16	1.72	1.48	4.26	699
January	1.83	0.18	1.79	1.48	2.65	1195
February	1.80	0.18	1.82	0.91	2.32	651
March	1.66	0.44	1.85	0.27	2.54	515
April	1.02	0.56	0.85	0.18	2.02	152
Total	1.70	0.29	1.70	0.01	5.26	6227

References

Ebinghaus, R., H.H. Kock, C. Temme, J.W. Einex, A.G. Lowe, A. Richter, J.P. Burrows, and W.H. Schroeder. 2002. Antarctic springtime depletion of atmospheric mercury. *Environ Sci Technol.* 36:1238–1244.

Lindberg, S.E., S.B. Brooks, C.J. Lin, K.J. Scott, M.S. Landis, R.K. Stevens, M. Goodsite, and A. Richter. 2002. Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise. *Environ Sci Technol.* 36:1245–1256.

Lu, J.Y., W.H. Schroeder, L.A. Barrie, A. Steffen, H.E. Welch, K. Martin, W.L. Lockhart, R.V. Hunt, G. Boila, and A. Richter. 2001. Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry. *Geophys Res Lett.* 28:3219–3222.

Schroeder, W.H., K.G. Anlauf, L.A. Barrie, J.Y. Lu, A. Steffen, D.R. Schneeberger, and T. Berg. 1998. Arctic Springtime Depletion of Mercury. *Nature.* 394:331–332.

Mercury Measurements at Alert

Project leader(s)

Alexandra Steffen and Bill Schroeder, Meteorological Service of Canada (MSC), 4905 Dufferin St, Toronto, Ontario M3H 5T4; phone: (416) 738-4116; fax (416) 739-4318; e-mail: Alexandra.Steffen@ec.gc.ca

Project team

Cathy Banic, Meteorological Service of Canada (MSC), 4905 Dufferin St, Toronto, Ontario; Greg Lawson and Bill Strachan, National Water Research Institute, 867 Lakeshore Dr., Burlington, Ontario.

Abstract

Mercury is a toxic pollutant of great concern to the Arctic environment. Since 1995, atmospheric mercury concentration measurements have been made at Alert, Nunavut. Continuous measurements of gaseous elemental mercury (GEM) have shown a distinct repeatable seasonal/annual pattern. Atmospheric mercury depletion and subsequent deposition events have been identified to occur in the springtime and ongoing studies have found that GEM is chemically converted to more reactive species such as reactive gaseous mercury (RGM) and particle-associated mercury (PM) which can be deposited to the snow and ice surfaces. Currently, it is still unclear what species of mercury are being measured during these depletion events. To address this issue a study was undertaken in the spring of 2002 at Alert to investigate different measurement techniques of such mercury species. This research focuses on understanding the cycling of atmospheric mercury in the Arctic environment to understand the impact of the large annual pulse of this toxic material to this ecosystem.

Key Project Messages

1. Atmospheric mercury measurements have been made at Alert, Nunavut, from 1995–2003.
2. Continued studies of mercury depletion/deposition episodes and their impact on the Arctic environment were undertaken.
3. Research into the measurement, formation and the fate of the various reactive mercury species has continued.
4. Further insight into the cycling of mercury in the Arctic has been gained but a complete understanding of the cause, effects and implications of the depletion/deposition events are still pending.

Objectives

The objectives of this project are to establish baseline atmospheric mercury concentrations and to study the behaviour of mercury in the Canadian high Arctic. By collecting information on ambient air concentrations of gaseous elemental mercury (GEM), temporal variability and long-term trends can be established. This information will be crucial in the development of Canadian strategies for national and international pollution control objectives. The behaviour of atmospheric mercury in the high Arctic in the springtime is unique and this project aims to further elucidate the chemical and physical aspects of atmospheric mercury depletion and deposition events after polar sunrise and the resulting link to enhanced Hg concentrations in the Arctic environment.

Introduction

Mercury is a toxic metal that has been identified as a priority pollutant by various national and international organisations. Although levels of mercury in many aquatic wildlife in the Arctic are elevated there are no large local anthropogenic sources of mercury (Steffen et al., 2003a). Gaseous elemental mercury (GEM) has a long atmospheric residence time, which allows it to be transported from emission sources to remote regions such as the Arctic. GEM measurements have been ongoing in the Canadian Arctic at Alert, Nunavut, since 1995. Since this time, significant advances in our knowledge of atmospheric mercury cycling in this environment have been made. It was discovered that a substantial amount of reactive mercury is present in the air and on particles during the springtime, when levels of GEM in the air are very low (Schroeder et al., 1998). Further research has found there are a series of photo-chemically driven reactions that lead to the oxidation of GEM from its stable form to a more reactive, but less volatile, species. A portion of these reactive mercury species remain in the air while a large amount is deposited onto the snow and ice surfaces. It is very likely that this conversion of mercury (and subsequent deposition) after polar sunrise may provide a pathway by which these more reactive (potentially bioavailable) mercury species are introduced into the Arctic environment and thus may be impacting large areas of the Northern Hemisphere (Lu et al., 2001). This project, within the Northern Contaminants Program, provides long term data on the spatial variability and temporal trends of mercury in the Arctic environment as well as information concerning the behaviour of mercury that may have a significant impact on the Arctic environment. Results from this project have created international interest and have resulted in similar measurements being made in countries throughout the circumpolar area and in the Antarctic (Schroeder et al., 2003). These data (Canadian and other) will provide important information on the atmospheric transport, transformation and deposition processes of this priority pollutant throughout the polar regions.

Activities

In 2002–2003

Ground-based continuous atmospheric GEM measurements continued at Alert as well as special measurements of several mercury species. For 5 weeks in the spring of 2002, an intensive field campaign was undertaken to investigate mercury speciation measurement techniques and to further understand the behaviour of mercury during the Arctic spring. This project investigated different sample collection techniques including manual and automated RGM and PM collection, TAM (total atmospheric mercury) and comparison of RGM and PM concentrations at different locations.

Results

Ground-level measurements were continued for GEM in ambient air at Alert. The data to the end of 2002 have been quality assured. There are currently 8 years of GEM concentration data from this site but more data are required to establish whether or not there is a statistically significant trend of annually increasing or decreasing concentrations. Distinct seasonal trends are observed each year where concentrations are higher than the annual mean in the summer, lower in the springtime and around the mean in the fall and winter.

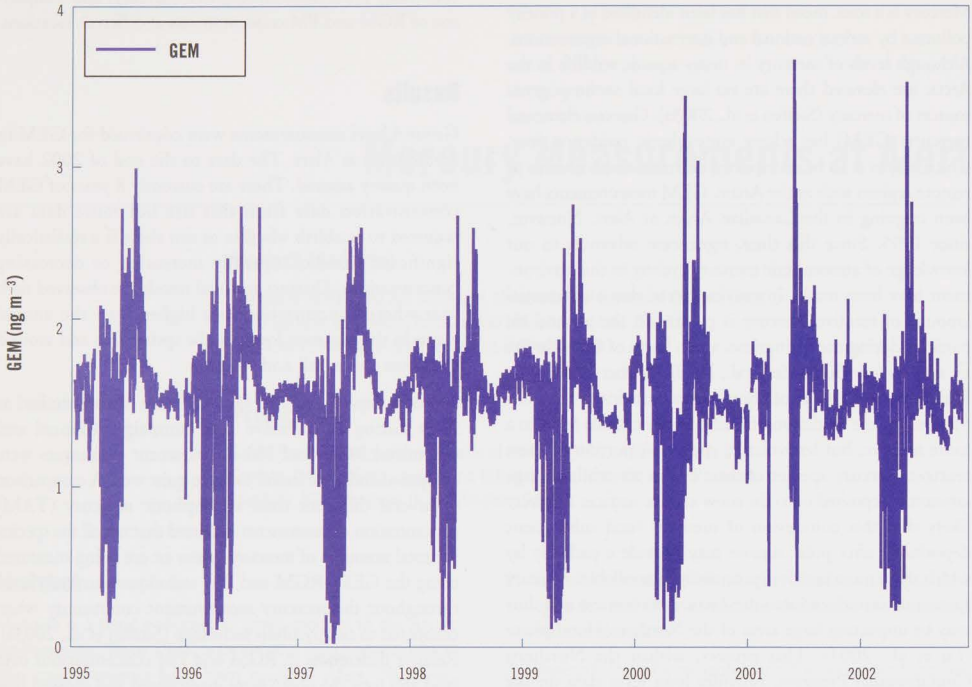
Mercury depletion events (MDEs) were further studied at Alert during an intensive field campaign. Manual and automated RGM and PM measurement techniques were compared and were found to agree quite well. A comparison of several different total atmospheric mercury (TAM) concentration measurements indicated that not all the species (or total amount) of mercury in the air are being measured using the GEM, RGM and PM techniques currently used throughout the mercury measurement community when compared to our pyrolysis technique (Steffen et al., 2003a). Relative differences in RGM and PM concentrations over land and over the ocean were investigated and showed that PM concentrations are consistently higher than RGM at Alert and that this relative abundance is similar at both sample sites.

Discussion and Conclusions

GEM concentration data collection continued during 2002–2003. GEM annual concentrations from 1995 to 2002, inclusive, are shown in Figure 1. This annually recurring pattern clearly signals that there are distinct seasonal variations in GEM concentrations. The data collected in 2002 fit well within the pattern of previous years.

An intensive field project was undertaken in April 2002 at Alert to compare manual and automated techniques for measuring RGM and PM under Arctic conditions. As well, this study aimed to establish whether measuring and calculating TAM by measuring GEM, RGM and PM with these techniques gives the same response as measuring total atmospheric mercury (TAM) using the cold regions pyrolysis unit (CRPU). Additionally, the relative distribution of PM and RGM at different sites was investigated.

Figure 1. Annual time series of GEM measurements at Alert from 1995 to 2002



Automated and manually collected samples of RGM and PM were compared during 3-hour and overnight sampling periods (~12 hours). In general, the 2 methods compared well (Steffen et al., 2003b) and are shown in Table 1. Overall, the manual 3-hour samples yielded slightly higher average concentrations of RGM and higher PM than the automated unit. However, when samples were left to run overnight on the manual system, the PM concentrations were considerably lower than those measured with the automated system (overnight automated samples are 3-hour data averaged over the collection time period of the manual sample). The same was not found for the RGM samples where overnight concentrations between the 2 methods were similar. Heating the housing box for the manual samplers proved to be a difficult task under harsh Arctic conditions and improvements to the manual sample method should be investigated.

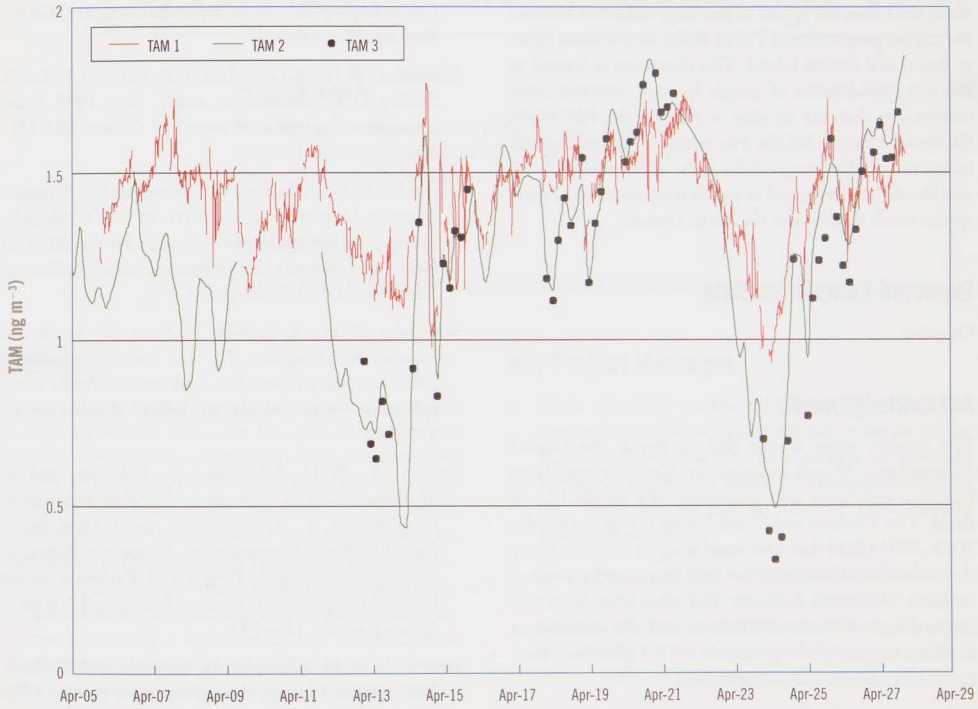
TAM is the total amount of measured mercury in the air during MDEs. It is currently presumed that TAM comprises of the sum of GEM, RGM and PM during a given time period. In this study, TAM was measured in 3 different ways (TAM 1, 2 and 3). TAM 1 was measured using the CRPU (Steffen et al., 2003b) where all incoming air is collected. TAM 2 was measured using an automated system (Tekran 1130/1135/2537A) combining GEM collected on a Tekran 2537A with RGM collected on a denuder and PM collected on a filter (2.5-μm cut off). TAM 3 was measured by collecting RGM and PM measured manually with denuders and filters (2.5-μm cut off), respectively and adding to GEM concentration collected with the Tekran 2537A. Results from these measurements are shown in Figure 2. The results from this experiment show that during non-MDEs TAM 1, 2 and 3 agree reasonably well with each other. However, during a MDE (GEM < 1.0 ng m^{-3}) concentrations were found to differ considerably between TAM 2, 3 and TAM 1. The set-up of the TAM 1 system is such that all the incoming air is pyrolysed in the system whereas TAM 2 and 3 measure air with particles < 2.5 μm. Therefore, perhaps a notable fraction of the PM concentration is found on particles > 2.5 μm and simply not collected by the other systems. As well, it is not clear what the coated denuders (supposedly collecting RGM) are in fact collecting (Schroeder et al., 2003). It is

Table 1. Results from Alert 2002 field campaign comparison of manual and automated sampling methods for RGM and PM (data reported in pg m^{-3})

	Manual Sample		Automated Sample	
Experiment	RGM	PM	RGM	PM
3-Hour Sample	59.3 *(44.2–75.4)*	216 *(103–314)*	49.3 *(21.9–93.8)*	144 *(35.5–191)*
Overnight Sample	36.3 *(15.8–54.7)*	29.2 *(5.3–54.9)*	25.0 *(10.3–42.7)*	93.2 *(2.9–220)*

(range of data)

Figure 2. Comparison of total atmospheric mercury (TAM) measurements Alert 2002 using 3 different sample collection methods



known that these denuders collect $HgCl_2$ (Landis et al., 2002) but it is uncertain if they are as efficient at collecting other Hg-halogen or non halogen reactive species that may be present in the air during depletion events. The results from this study indicate that not all the mercury species in the air during MDEs are being collected using techniques currently used by the scientific community. It demonstrates that further investigations are warranted into these so-called RGM and PM species for understanding what species of mercury are present and what are being measured during MDEs in the Arctic springtime.

Finally, past studies have found that the relative concentration of PM and RGM differ during MDEs between Alert, Canada and Barrow, Alaska, two high Arctic monitoring sites (Lindberg et al., 2002). At Alert, PM concentrations are found to be higher than RGM and the opposite is seen in Barrow (reported PM:RGM ratio of 0.1 to 0.2 [Lindberg et al., 2002]). It is thought that these conflicting PM:RGM ratios may be a result of age of the air mass measured as well as location of the sampling site. It is speculated that RGM is formed over or close to the ocean and is then either sorbed onto particles, is dry deposited or remains in the air while

the air mass moves to a sampling site, thereby making the sample collection location important. To address this issue at Alert, RGM and PM samples were simultaneously collected at 2 sites: over ice and over land. The ICE site was located about 1 km from the shore (over frozen ocean) where samples are more readily exposed to incoming air masses from over the ocean. The land site was located 8-km inland. Results show that, in general, the PM:RGM ratio is similar at both locations and that PM concentrations appear to dominate during MDEs. The PM:RGM ratio was close to 1 during non-MDEs. However, during well defined MDEs the PM:RGM ratio was on average 4 and 6 inland and ICE, respectively. Overall, this experiment demonstrates that at Alert, there does not appear to be a large difference between the relative proportions of PM to RGM on the ocean (close to shore) and further inland. This discussion is limited to this one consideration of sample location, however other factors are thought to play a role in the PM/RGM distribution during MDEs. For example, the amount and nature of available host particles at the different high Arctic sites should be investigated as well as concentrations of these species much further over the Arctic Ocean.

Expected Completion Date

Ongoing

Acknowledgements

The project team would like to thank the Global Atmospheric Watch program at Alert for supplying facilities, assistance and personnel. We would like to thank Tim Christie and Vivek Voora for collecting the 2002–2003 GEM data and snow samples at Alert. Many thanks to DRDC Atlantic for their continued assistance in Alert. Also, the facilities and assistance from the Department of National Defence and the continuous excellent support of the personnel at CFS Alert have been invaluable and are truly appreciated.

References

Landis, M.S., R.K. Stevens, F. Schaedlich, and E.M. Prestbo. 2002. Development and characterization of an annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air. *Environ Sci Technol.* 36:3000–3009.

Lindberg, S.E., S.B. Brooks, C.J. Lin, K.J. Scott, M.S. Landis, R.K. Stevens, M. Goodsite, and A. Richter. 2002. Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise. *Environ Sci Technol.* 36:1245–1256.

Lu, J.Y., W.H. Schroeder, L.A. Barrie, A. Steffen, H.E. Welch, K. Martin, W.L. Lockhart, R.V. Hunt, G. Boila, and A. Richter. 2001. Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry. *Geophys Res Lett.* 28:3219–3222.

Schroeder, W.H., K.G. Anlauf, L.A. Barrie, J.Y. Lu, A. Steffen, D.R. Schneeberger, and T. Berg. 1998. Arctic springtime depletion of mercury. *Nature.* 394:331–332.

Schroeder, W.H., A. Steffen, G. Lawson, and W. Strachan. Mercury Measurements at Alert. In S. Kalhok (ed.), Synopsis of Research Conducted under the 2000–01 Northern Contaminants Program. Ottawa: Indian and Northern Affairs Canada. 130–135.

Schroeder, W.H., A. Steffen, K. Scott, T. Bender, E. Prestbo, R. Ebinghaus, J.Y. Lu, and S.E. Lindberg. 2003. Summary report: first international Arctic atmospheric mercury research workshop. *Atmos Environ.* 37(18).

Steffen, A., W.H. Schroeder, L. Poissant, and R. MacDonald. 2003a. Mercury in the Arctic atmosphere. In: Bidleman, T., R. Macdonald, and J. Stow. (eds.), Canadian Arctic Contaminants Assessment Report II: Sources, Occurrence, Trends and Pathways in the Physical Environment. Ottawa: Indian and Northern Affairs Canada. 124–142.

Steffen, A., W.H. Schroeder, G. Edwards, and C. Banic. 2002. 2003b. Mercury throughout polar sunrise. *J Phys IV France.* 107:1257–1270.

A Comprehensive Theoretical Investigation of Organic Contaminant Behaviour as Influenced by Falling Snow and a Seasonal Snow Cover

Project leader

Frank Wania, University of Toronto at Scarborough, Toronto, Ontario M1C 1A4; phone: (416) 287-7225; fax: (416) 287-7279; e-mail: frank.wania@utoronto.ca

Project team

Ying D. Lei and Gillian L. Daly, University of Toronto, Toronto, Ontario.

Abstract

Theoretical investigations sought to quantify and compare the capacity of rain and snow to scavenge gaseous and particle-bound organic contaminants from the atmosphere at different temperatures. Whether snow or rain is more efficient in scavenging organic contaminants depends on the characteristics of the chemical (size and polarity), the characteristics of the snow (esp. specific snow surface area) and atmospheric temperature. At the freezing point, rain is expected to better scavenge small organic molecules, whereas snow with a high surface area will be a more effective scavenger for large non-polar chemicals. Whether such chemicals are scavenged as vapours or while sorbed to particles, depends largely on the snow characteristics. A seasonal snow pack was included in a multimedia fate and transport model, and was found to greatly influence the overall environmental fate of organic contaminants. Contaminant volatilisation during snow melt can result in a spring-time peak in the atmospheric concentrations of relatively volatile organic contaminants. The process descriptions developed in this project should be instrumental in achieving a quantitative understanding of the delivery of organic contaminants to, and their environmental behaviour, in the Canadian Arctic.

Key Project Messages

1. To be effectively scavenged by snow, chemicals either need to have an adsorption coefficient at the ice surface K_{IA} of more than 0.1 m or a particle-air partition coefficient K_{PA} of more than10^{11} at temperatures below 0°C. Many organic contaminants of Arctic concern have such properties.
2. As temperature decreases, more and more of a chemical partitions from the vapour phase to liquid water droplets, atmospheric particles and the snow surface. This temperature effect is one of the reasons that snow scavenging ratios are often higher than rain scavenging ratio.
3. At 0°C rain is typically more effective in scavenging the vapours of small organic molecules than snow, because the capacity of the ice surface to sorb such chemicals is smaller than that of liquid water droplets. Snow with a high specific surface area ($> 0.1\ m^2/g$) may, however, be more efficient in scavenging the vapours of larger, non-polar organic compounds, such as the PCBs, which are only sparingly water soluble.
4. The mode of scavenging (vapour vs. particles) and the total scavenging efficiency for such substances will be highly variable and dependent on the snow characteristics

(particle scavenging ratio, the specific snow surface area and temperature).

5. How a contaminant is delivered and lost from a seasonal snow pack is highly dependent on the chemical's physical-chemical properties. Water soluble and highly particle-sorbed substances are most likely to be delivered to the ecosystem during snow melt, either by dissolution in melt water or with the flush of particles during the end of snow melt.
6. Volatile chemicals can be lost to a significant extent to the atmosphere prior to snow disappearance, resulting in a peak in air concentrations during snow melt.

Objectives

The main objective of the project was to increase the quantitative understanding of organic chemical fate as influenced by falling snow and seasonal snow packs. Specifically, we performed two comprehensive theoretical studies on how temperature influences precipitation scavenging of organic chemicals in the atmosphere, and how a seasonal snow pack influences the overall fate of organic chemicals. This investigation yielded quantitative knowledge of:

1. Which chemicals are efficiently deposited by precipitation scavenging at low temperatures, and which are most strongly affected by the occurrence of a seasonal snow cover;
2. How and to what extent (i) organic chemicals are scavenged by precipitation at low temperatures, and (ii) organic chemical fate is affected by a seasonal snow cover;
3. What factors contribute most to the uncertainty in estimating (i) precipitation scavenging, and thus atmospheric deposition rates, at low temperatures, and (ii) the effect of a seasonal snow cover on the overall fate of organic chemicals.

Introduction

In order to understand the delivery of organic contaminants to the Arctic ecosystem, it is of considerable interest to be able to describe quantitatively their atmospheric deposition. In the Arctic such deposition is greatly influenced by low temperatures and in particular the phase transition of water at 0°C. Precipitation occurs in the form of snow rather than rain, and the ground is covered by a seasonal or permanent cover of ice and snow. Earlier work conducted under NCP had suggested that snow may be very efficient as a scavenger of organic vapours (Wania et al., 1999a) due to its high specific surface area (Hoff et al., 1995, 1998). A simple model of chemical fate in an ageing snow pack (Wania, 1997) had been developed and used to describe the measured run-off concentration in a creek in the Amituk Lake area of Cornwallis Island during snow melt (Wania et al., 1999b). At the time, further progress on both these issues was hampered by a lack of a quantitative understanding of the specific surface area of snow and of the sorption of organic chemicals onto the air-ice interface (Goss, 1993). During the past few years considerable progress in these two fields has been made, suggesting that further progress in quantifying organic chemical fate as influenced by snow and ice is possible. Specifically, F. Dominé and co-workers at the Laboratoire Glaciologie et Géophysique de l'Environnement in Grenoble, France, have conducted extensive investigations into the specific surface area of snow and the factors that control its variability (Hanot and Dominé, 1999; Dominé et al., 2000, 2001; Leganeux et al., 2002). They have performed the first measurements on the physical properties of Arctic snow, reporting specific surface areas of freshly fallen and aged snow from Alert, Nunavut (Dominé et al., 2002; Cabanes et al., 2002, 2003). As a result of their work, we are beginning to gain a quantitative understanding of the range of specific surface area encountered in snow from various regions, and even how the surface area changes as a function of time and ambient temperature. Substantial progress has also been made with respect to quantifying the sorption of organic substances at the air-water and air-ice interface (Donaldson and Anderson, 1999; Mmereki et al., 2000; Sokolov and Abbatt, 2002). Of particular practical value are the predictive relationships for the sorption coefficient and its temperature dependence by Goss (1997), Goss and Schwarzenbach (1999) and Roth et al. (2002). This project set out to use this new information to gain insight into how temperature influences the extent of precipitation scavenging of organic chemicals in the atmosphere, and how a seasonal snow cover influences the overall chemical fate of organic chemicals.

Activities

In 2002–2003

A comprehensive study was conducted of how temperature influences the extent of precipitation scavenging of organic chemicals in the atmosphere. A seasonal snow cover was incorporated in a dynamic multimedia contaminant fate and transport model. We explored how this impacts the simulated environmental fate of a variety of organic contaminants. Two draft manuscripts have been prepared.

Results and Discussion

Influence of temperature on precipitation scavenging of organic chemicals

Phase distribution in a cloud

We first estimated the phase partitioning of organic chemicals in a warm and a cold cloud, because the distribution between atmospheric phases determines how efficient a chemical will be scavenged by precipitation. We assumed that the chemical may either be in the vapour phase, sorbed to atmospheric particles, dissolved in liquid water droplets (at temperatures above 0°C) or adsorbed to the surface of frozen aqueous hydrometeors (at temperatures below 0°C) (Fig. 1). The equilibrium distribution between these phases is controlled by the dimensionless equilibrium partitioning coefficients between air and water (K_{AW}) and between atmospheric particles and air (K_{PA}), and the adsorption coefficient at the ice-air interface (K_{IA} in units of meter). Instead of calculating this phase distribution for individual chemicals, we chose to map it as a function of these partition coefficients, thus allowing the instant graphical estimation of the phase distribution of any organic chemical for which these partitioning properties are known. Specifically, the phase distribution in a warm cloud is mapped as a function of K_{AW} and K_{PA} (Fig. 2), whereas the phase distribution in a cold cloud is plotted as a function of K_{IA} and K_{PA} (Fig. 3).

In these maps, the pink areas in the upper left corner indicate substances that partition predominantly (> 90%) in the atmospheric vapour phase, the yellow areas to the upper right highlight substances that are found mostly sorbed onto the atmospheric particles, whereas the blue areas to the lower left correspond to substances that are strongly associated with liquid or frozen hydrometeors in the atmosphere. The region in-between these areas indicates substances that are found in more than one phase of the cloud in appreciable fractions (> 10%). The exact boundaries of these areas are dependent on the assumption concerning the amount of particles and water in the cloud and the specific surface area of the frozen hydrometeors. In the construction of the maps in Figs. 2 and 3, volume fractions of 10^{-12} and $3{\cdot}10^{-7}$ were used for particles and liquid water, respectively, and a specific surface area of 0.1 m^2/g, typical for snowflakes, was assumed to apply. If the particle content is higher, the boundaries between the dominant partitioning areas shift to the left in Figs. 2 and 3; if the liquid water content in the cloud decreases, these boundaries in Fig. 2 shift downward. Finally, the boundaries in Fig. 3 shift downward if the specific ice surface area is lower.

Figs. 2 and 3 suggest that in the atmosphere the transition from vapour phase to particle phase occurs at a log KPA between 11 and 13. In the warm cloud, the transition from vapour to dissolved phase occurs at a log KAW of −5.5 to 7.5. The diagonal transition area between dissolved and particle sorbed phase in the lower right corresponds to particle-water partition coefficients log KPW between 5 and 7. At temperatures below 0°C the transition from vapour phase to ice sorption corresponds to a log (K_{IA}/m)

Figure 1. Conceptual model of the equilibrium phase distribution of an organic chemical in a warm and a cold cloud. K_{PA}: particle-air partition coefficient, K_{AW}: air-water partition coefficient, K_{IA}, interfacial sorption coefficient on the ice surface

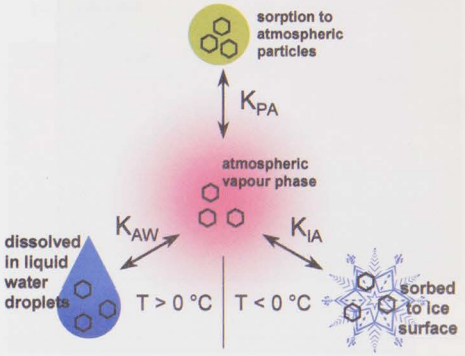


Figure 2. Equilibrium phase distribution of an organic chemical in a warm cloud as a function of its particle-air partition coefficient K_{PA} and its air-water partition coefficient K_{AW}. Pink areas show regions of dominant vapour phase distribution, yellow areas dominance of particle sorption and blue areas preference for the liquid water phase. The volume fraction of particles is assumed to be 10^{-12}, that of liquid water $3{\cdot}10^{-7}$. The lines indicate the partitioning properties of selected polychlorinated biphenyls (PCBs, green), polycyclic aromatic hydrocarbons (PAHs, red) and chlorinated phenols (CPs, blue) in the temperature range +25 to 0°C

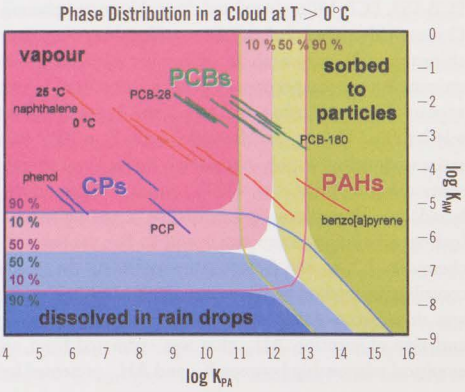
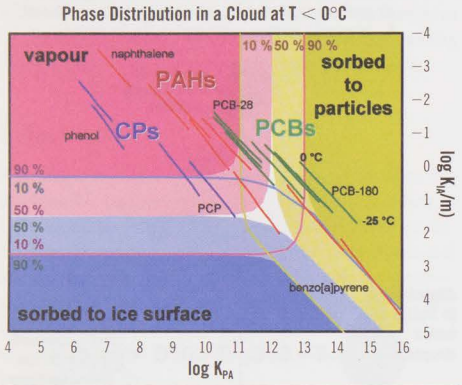


Figure 3. Equilibrium phase distribution of an organic chemical in a cold cloud as a function of its particle-air partition coefficient K_{PA} and its interfacial sorption coefficient on the ice surface K_{IA} in m. Pink areas show regions of dominant vapour phase distribution, yellow areas dominance of particle sorption and blue areas preference for the frozen water surface. The volume fraction of particles is assumed to be 10^{-12}, that of water $3 \cdot 10^{-7}$. A specific ice surface area of 0.1 m^2/g was assumed to apply. The lines indicate the partitioning properties of selected polychlorinated biphenyls (PCBs, green), polycyclic aromatic hydrocarbons (PAHs, red) and chlorinated phenols (CPs, blue) in the temperature range 0 to −25°C



between 0.5 and 2.5, whereas that between absorption to particles and adsorption to the ice surface at a log (K_{IP}/m) of −9 to −11.

The partitioning properties of several organic contaminants were plotted into the maps of Figs. 2 and 3. Specifically, we derived the K_{PA}, K_{AW}, and K_{IA} for eight polycyclic aromatic hydrocarbons (naphthalene, acenaphthene, fluorene, anthracene, phenanthrene, pyrene, chrysene, benzo[a]pyrene), eight polychlorinated biphenyls (PCB-28, PCB-31, PCB-52, PCB-101, PCB-105, PCB-138, PCB-153, PCB-180), phenol and three chlorinated phenols (2-monochlorophenol, 2,3,4,6-tetrachlorophenol, pentachlorophenol) as functions of temperature. K_{PA} was estimated from temperature-dependent subcooled liquid vapour pressures using the empirical Junge-Pankow relationship. The K_{IA} for the water surface at 20°C was estimated using a poly-parameter linear free energy relationship by Roth et al. (2002), which is based on the hexadecane-air partitioning coefficient L^{16}, and Abraham's hydrogen bonding parameters α and β. For the example chemicals, L^{16}, α, and β were estimated using the group contribution method by Platts et al. (1999, 2000). The K_{IA} was then extrapolated to other temperatures using an enthalpy of sorption ΔH_{IA} that was estimated from an empirical relationship between K_{IA} and ΔH_{IA} presented by Goss and Schwarzenbach (1999). This extrapolation implies the assumption that the sorption to the ice surface is similar to that on the liquid water surface.

Because the three partitioning coefficients are functions of temperature, each chemical corresponds to a short line rather than a point in the partitioning space. At higher temperatures, the vapour phase is favoured, and K_{PA} and K_{IA} decrease, whereas K_{AW} increases. In Figure 2, the phase distribution of the chemicals is shown between 25°C (upper left) and 0°C (lower right), in Figure 3 the temperature range is 0°C (upper left) and −25°C (lower right). A comparison of the location of the lines corresponding to individual chemicals and the areas of dominant phase distribution, suggests that the lighter PAHs, PCBs and chlorophenols are predominantly in the gas phase within warm clouds (Fig. 2). The heavier PCBs, and especially the PAHs with more than 4 rings, tend to sorb appreciably to atmospheric particles, especially at temperatures close to the freezing point, whereas more than 10% of PCP partitions into cloud droplets at lower temperatures. In the cold cloud (Figure 3), the lightest PAHs and phenols remain in the vapour phase, whereas even the light and intermediate PCBs start to sorb to particles to a significant extent. A significant fraction of the highly chlorinated phenols and the heavy PAHs also sorb to the ice surface.

Dominant atmospheric deposition processes

The phase distribution within the atmosphere determines the dominant atmospheric deposition mechanism of an organic contaminant, as a chemical can only be scavenged by precipitation if it either sorbs to particles or associates directly with the liquid and frozen hydrometeors. Again, maps were employed to delineate dominant deposition processes as a function of the distribution coefficients above (Fig. 4) and below (Fig. 5) the freezing point. Once more, three areas dominated by one type of deposition mechanism are indicated. These deposition mechanisms correspond to the main phases identified in Figure 1: dry gaseous deposition of chemicals in the vapour phase (pink in upper left), dry and wet deposition of chemical sorbed to atmospheric particles (yellow in upper right), and the deposition with liquid and frozen hydrometeors (blue in lower left). In addition to the distribution coefficients, the deposition rates obviously depend on a number of kinetic parameters. In the construction of Figures 4 and 5 we assumed a particle scavenging ratio of 10^5, a precipitation rate of 1 m/a, a dry particle deposition velocity of 1 m/h and a dry vapour deposition velocity of 2 m/h. The boundaries between the regions of dominant deposition mechanism are dependent on these values. Factors that increase particle-associated deposition (such as higher precipitation

Figure 4. Dominant atmospheric deposition processes of an organic chemical at temperatures above freezing as a function of its particle-air partition coefficient K_{PA} and its air-water partition coefficient K_{AW}. Pink areas show regions of dominant dry gaseous deposition, yellow areas dominance of wet and dry particle deposition and blue areas preference for vapour scavenging. The volume fraction of particles is assumed to be 10^{-12}, that of liquid water $3 \cdot 10^{-7}$. A particle scavenging ratio of 10^5, a precipitation rate of 1 m/a, a dry particle deposition velocity of 1 m/h and a dry vapour deposition velocity of 2 m/h were assumed to apply. The lines indicate the partitioning properties of selected polychlorinated biphenyls (PCBs, green), polycyclic aromatic hydrocarbons (PAHs, red) and chlorinated phenols (CPs, blue) in the temperature range +25 to 0°C

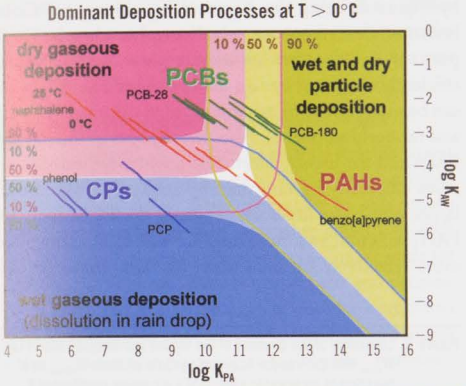
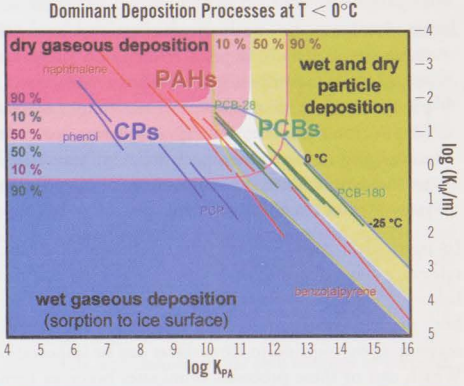


Figure 5. Dominant atmospheric deposition processes of an organic chemical at temperatures below freezing as a function of its particle-air partition coefficient K_{PA} and its interfacial sorption coefficient on the ice surface K_{IA} in m. Pink areas show regions of dominant dry gaseous deposition, yellow areas dominance of wet and dry particle deposition and blue areas preference for vapour scavenging. The volume fraction of particles is assumed to be 10^{-12}, that of water $3 \cdot 10^{-7}$. A specific ice surface area of 0.1 m^2/g, a particle scavenging ratio of 10^5, a precipitation rate of 1 m/a, a dry particle deposition velocity of 1 m/h and a dry vapour deposition velocity of 2 m/h were assumed to apply. The lines indicate the partitioning properties of selected polychlorinated biphenyls (PCBs, green), polycyclic aromatic hydrocarbons (PAHs, red) and chlorinated phenols (CPs, blue) in the temperature range 0 to −25°C



rate, higher particle scavenging ratio, higher dry particle deposition, higher particle content in the atmosphere) shift the boundaries to the left, whereas factors that increase wet gaseous deposition (higher precipitation rate, higher specific ice surface area) will shift them upwards. Finally a higher gaseous deposition velocity (as would be observed over some surfaces or at higher wind speeds) will shift them to the lower right.

A comparison of Figures 2 and 4 and Figures 3 and 5 shows that the areas and boundaries of dominant phase distribution and dominant deposition mechanism do not coincide exactly. In particular, the boundaries in Figures 4 and 5 lie at lower K_{PA}, lower K_{IA} and higher K_{AW} than in Figures 2 and 3. Wet gaseous deposition already becomes an important deposition mechanism at log K_{AW} below −3, even though clearly less than 10% of the chemical partitions into the liquid cloud droplets (Fig. 4). Similarly, particle associated processes start to become important at log K_{PA} values of 10 (Figs. 4 and 5), which is one order of magnitude lower than the threshold for significant partitioning (> 10%) into atmospheric particles (Figs. 2 and 3). Deposition with frozen hydrometeors of 0.1 m^2/g surface area already becomes important at a log (K_{IA}/m) of −2 (K_{IA} = 1 cm) (Fig. 5). The reason for the different thresholds is the fact that particles and hydrometeors have faster deposition rates and shorter atmospheric residence times than vapours, and thus even very small fractions partitioning into particles and hydrometeors (< 10%) can result in significant rates of deposition.

Superimposing the partitioning properties of selected contaminant chemicals on Figs. 4 and 5, we can state what the dominant atmospheric deposition processes are likely to be at various temperatures. Only the deposition of the most volatile PAHs (naphthalene) and PCBs will be dominated by dry gaseous deposition. Intermediate PAHs such as pyrene and chrysene have partitioning properties that make them susceptible to all three types of deposition mechanisms at temperatures above 0°C. Five-ring PAH, such as benzo[a]pyrene, will be deposited mostly by particle deposition. At temperatures above freezing most PCBs will be deposited by a combination of dry gaseous and wet and dry particle deposition processes, whereas their solubility in water is too low to result in significant wet vapour scavenging. At temperatures below 0°C the lighter and intermediate PCBs and PAHs

have partitioning properties that make them susceptible to all three types of deposition, whereas the heavy PCBs and PAHs are deposited with both particles and frozen hydrometeors. The phenolic compounds, especially PCP, will be deposited with falling hydrometeors at temperatures above and below 0°C.

Most of the selected example chemicals fall in the transition regions, implying that they are subject to more than one atmospheric deposition mechanism. This implies that:

1. the identification of the dominant deposition mechanism for these chemicals requires precise knowledge of their distribution properties as a function of temperature.
2. the dominant deposition mechanism and rates for these chemicals will depend strongly on the exact values of phase composition (specific ice surface area, particle content in atmosphere), kinetic parameters (deposition velocities, precipitation rate, particle scavenging ratio) and temperatures. As these values are highly variable in the environment, the deposition rates of these chemicals will also vary.

In particular, many organic contaminants of Arctic relevance have distribution properties at temperatures below 0°C that place them in the transition area, where both particle-associated deposition processes and vapour scavenging by sorption to ice surfaces can be important. Which one of these processes dominates becomes then dependent on the highly variable parameters specific ice surface area and particle scavenging ratio.

Is precipitation scavenging more efficient above or below 0°C?

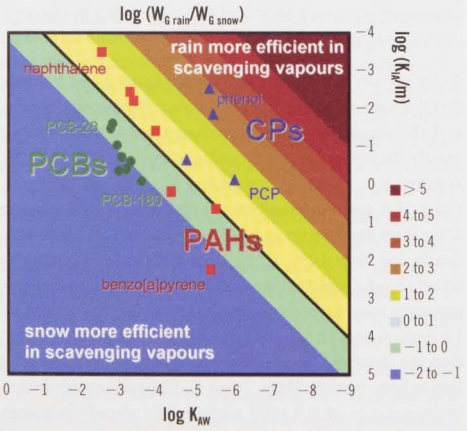
Although the above analysis informs us about the dominant deposition mechanism, it does not allow statements about atmospheric deposition efficiency. In particular, we have yet to answer whether rain or snow is more efficient in scavenging organic contaminants. We will try to approach this question in steps, by first evaluating the relative efficiency of snow and rain to scavenge vapours and particle-associated chemicals, and then to additionally take into account the issue of gas-particle partitioning as a function of temperature.

Is precipitation scavenging of organic vapours more efficient above or below 0°C?

K_{IA} and K_{AW} control the efficiency of vapour scavenging (Figure 1). We thus plotted the logarithm of the ratio of the gas scavenging ratios for rain and snow as a function of these two distribution coefficients in Figure 6. For the chemicals in the upper right of that plot (small K_{IA} and small K_{AW}), rain is more efficient than snow in scavenging vapours, for those in the lower left the opposite is true. The latter chemicals have a low solubility in water, but have high affinity for the ice surface. There is a limit to the extent to which snow is more efficient than rain in scavenging vapours, because for very highly surface active chemicals sorption to the liquid water droplet surface becomes an important mechanism of wet gaseous deposition. The exact location of the boundary in Figure 6 is dependent on the assumption concerning the specific surface area of the snow and the radius of the liquid water droplet (0.1 m^2/g and 1 mm, respectively in Figure 6). For smaller specific ice surface areas the boundary moves further to the lower left.

We placed the 20 example chemicals in the space defined by Figure 6, using the K_{AW} and K_{IA} values at 0°C. It becomes clear that most small organic chemicals, in particular if they are somewhat polar, will be more efficiently scavenged by rain than by snow. The difference can be many orders of magnitude, as in the case of phenol and monochlorophenol. Also, the vapours of the smaller PAHs and the highly chlorinated phenols are washed out more efficiently by rain than by snow. The vapours of larger non-polar molecules such as the PCBs and the PAHs with four and more rings are washed out somewhat more effectively by snow than by rain, although this

Figure 6. Logarithm of the quotient of the vapour scavenging ratio of rain $W_{G\text{-}rain}$ and the vapour scavenging ratio of snow $W_{G\text{-}snow}$ as a function of an organic chemical's air-water coefficient K_{WA} and its interfacial sorption coefficient on the ice surface K_{IA} in m. The markers indicate the partitioning properties of selected polychlorinated biphenyls (PCBs, green), polycyclic aromatic hydrocarbons (PAHs, red) and chlorinated phenols (CPs, blue) at 0 °C. A specific snow surface area of 0.1 m^2/g and a rain drop radius of 1 mm was assumed to apply. For substances above the black diagonal line, rain is more efficient in scavenging vapours than snow. Below the line, vice versa



depends on the specific surface area of the snow. At a specific ice surface area of 0.01 m^2/g, snow and rain are about equally effective in scavenging vapour of these larger apolar substances.

Is precipitation scavenging of particle bound organic substances more efficient above or below 0°C?

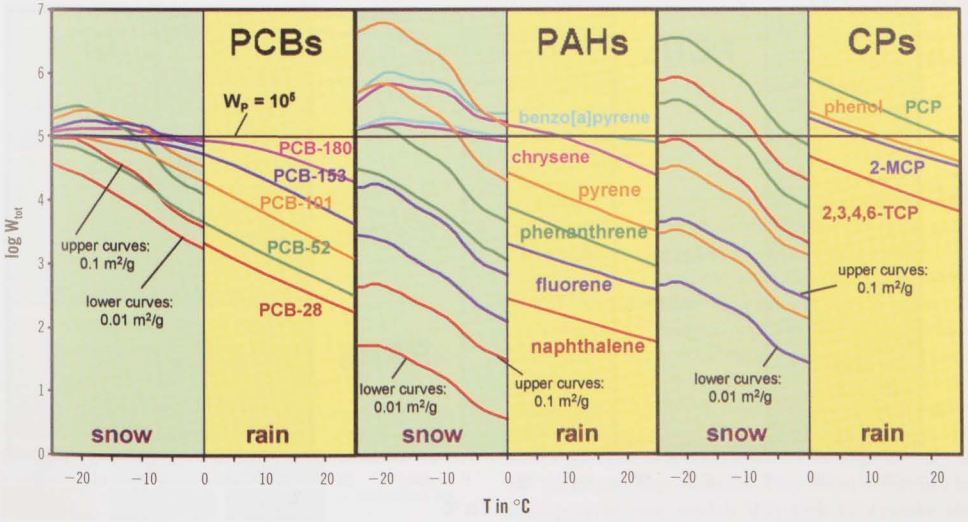
Particle scavenging ratios are highly variable and uncertain, presumably being dependent on both particle properties (size, hygroscopic properties, concentration) and characteristics of the hydrometeors (type, size). Considering such variability, it is not possible to make general statements as to whether rain or snow is more efficient in scavenging particle-associated organic substances (Wania et al., 1998). There are some indications that snow may sometimes be more efficient in scavenging particles than rain (Franz and Eisenreich, 1998).

Is precipitation scavenging more efficient above or below 0°C?

For organic chemicals that are sufficiently volatile to not sorb to particles, rain will typically be a more efficient scavenger than snow. The difference in scavenging efficiency will be larger with increasing polarity of such substances, and can reach several orders of magnitude for small polar substances. With increasing size and decreasing polarity the ice surface of frozen hydrometeors becomes as efficient in accommodating organic vapours as the liquid water phase of rain droplets. However, increasing size also increases the likelihood of particle sorption of an organic chemical, especially at low temperatures. Such larger substances, which include many organic contaminants of Arctic relevance, will either sorb to particles or adsorb to the ice surface, depending on the specific ice surface area and particle concentration. The dominant deposition mechanism will be highly variable, further being dependent on such parameters as particle scavenging ratio, dry particle deposition velocity and precipitation rate, preventing the possibility to state in general terms whether snow or rain will be a more efficient scavenger.

The results of calculations of the total scavenging ratio W_{tot} for the example chemicals in the temperature range −25 to 25°C are shown in Figure 7. In these calculations, a particle scavenging ratio W_p of 10^5 was assumed to apply to both rain and snow. The specific surface area of the snow was assumed to be either 0.1 m^2/g or 0.01 m^2/g. The scavenging ratios range over six orders of magnitude. In general, W_{tot} increases as temperature decreases, because more and more of the chemical partitions from the vapour phase to liquid water droplets, atmospheric particles and the snow surface. This temperature effect is one of the reasons that snow scavenging ratios are often higher than rain scavenging ratios. At temperatures above freezing, chemicals with a low K_{AW}, such as the phenolic compounds, and chemicals that sorb strongly to particles,

Figure 7. Total scavenging ratios W_{tot} of selected polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and chlorinated phenols (CPs) in the temperature range −25 to +25°C. Specific snow surface area was assumed to be either 0.1 or 0.01 m^2/g. The particle scavenging ratio for both snow and rain is assumed to be 10^5, rain drop radius is 1 mm



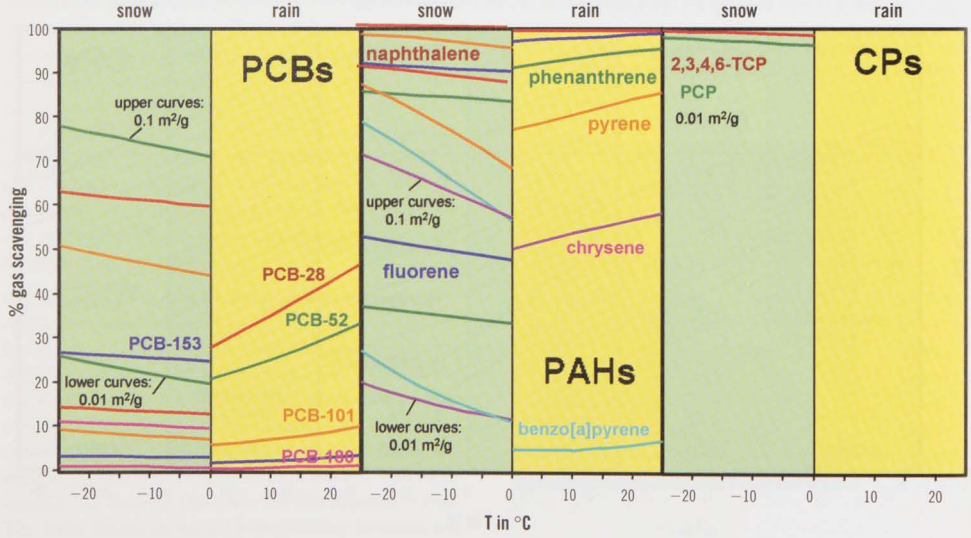
such as benzo-a-pyrene and PCB-180, have the highest W_{tot}. The latter compound's W_{tot} obviously is strongly dependent on the value for W_p. Gas phase chemicals with a high K_{AW}, such as naphthalene and PCB-28, have the lowest W_{tot}. At temperature below freezing, chemicals with a high K_{IA}, such as pyrene and pentachlorophenol, have the highest W_{tot}, which then is highly dependent on the specific snow surface area. Such chemicals may even achieve W_{tot} which exceed those of W_p, and thus the W_{tot} of chemicals that are mostly particle sorbed at low temperatures.

The discontinuity of W_{tot} at 0°C (Fig. 7) indicates whether snow or rain is a better overall scavenger at the same temperature. Depending on the specific snow surface area, snow is generally as efficient (low surface area) or more efficient (high surface area) than rain in scavenging PCBs and heavy PAHs. On the other hand, snow is much less efficient in scavenging the phenolic compounds and the lighter PAHs than is rain of the same temperature. The specific snow surface area is a highly sensitive parameter in the estimation of the W_{tot} of the PAHs and the CPs, but apparently much less so for the PCBs (Fig. 7). The reason for this lies in the fact that the gas scavenging ratio $W_{G\text{-}snow}$ estimated for PCBs is on the same order of magnitude as the assumed W_p. If the surface area for snow is higher, the contribution of gas scavenging to the overall scavenging of PCBs increases substantially (Figure 8), but the overall W_{tot} is little affected because vapour and particle phase PCBs are scavenged to the same extent. If W_p is different from $W_{G\text{-}snow}$, a change in snow surface area will not only affect the relative importance of vapour scavenging but also the absolute value of W_{tot} for the PCBs.

Influence of a seasonal snow cover on the overall chemical fate of organic chemicals

Earlier snow pack model (Wania, 1997; Wania et al., 1999b) only investigated the fate of a contaminant in a snow pack, but did not evaluate the effect of the snow pack on overall chemical fate in the environment. As part of this project, we therefore incorporated a seasonal snow pack compartment into an existing non-steady state multimedia model and used it to investigate the effect of that change to the model on the overall calculated fate of organic chemicals in a hypothetical environment. Specifically, we used the CoZMo-POP model (Wania et al., 2000) for that study. In the model it is assumed that the snow pack compartment gradually grows during the winter season as snow keeps falling. It then melts over a short snow melt period in spring and is non-existent for the remainder of the year. Atmosphere-snow exchange of organic chemicals takes place by diffusive gas exchange, particle deposition and snow scavenging. Exchange of chemical between snow

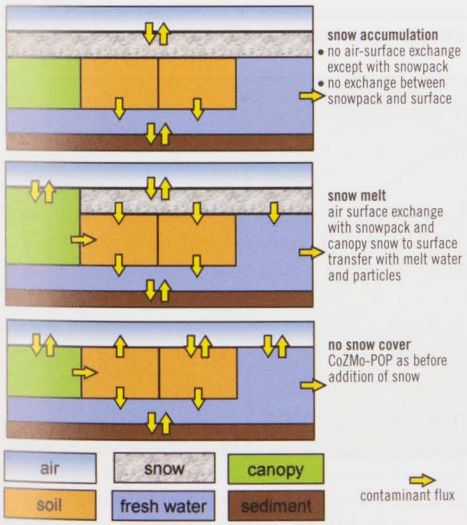
Figure 8. Percentage contribution of vapour scavenging to the total precipitation scavenging of selected polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and chlorinated phenols (CPs) in the temperature range −25 to +25°C. Chlorinated phenols are always scavenged as vapours. The contribution of gas scavenging for PCBs and PAHs is very dependent on the assumption concerning specific snow surface area (either 0.1 or 0.01 m²/g). The particle scavenging ratio for both snow and rain is assumed to be 10^5, rain drop radius is 1 mm



and other surface media (soils and water) occurs by advective transfer of melt-water and particles. The effect of the snow cover on the exchange between air and other surface media is also accounted for (Figure 9). The model includes a non-steady state water balance that describes dynamically the changes in snow pack height, water run-off, water volume and soil moisture.

Using the modified CoZMo-POP model we performed hypothetical scenario simulations with and without a seasonal snow cover, to find out how the snow cover affects the pathways, major reservoirs and seasonal variability of contaminants in the environment. Only a very limited illustration of selected results can be provided in the context of this report. It is, for example, possible to evaluate the simulated cumulative origin and fate of contaminants in a snow pack. Such an analysis reveals the widely divergent behaviour of different organic chemicals (Fig. 10). Volatile chemicals, such a phenanthrene, are taken up by, and lost from, the snow pack mostly through diffusive vapour exchange, suggesting that the scavenging during the actual snowfall event has little impact on contaminant delivery to the ecosystem. Highly particle sorbed substances, such as benzo[a]pyrene, are delivered to the snow pack by particle scavenging and are eventually transferred to the underlying surface when the snow melts completely and the particles are all that remains. Pyrene's snow pack fate is somewhere in-between that of phenanthrene and benzo[a]pyrene, but it is lost from the snow pack to a greater extent than either of these by dissolution in the snowmelt water. More water soluble chemicals, such as α-HCH, are brought to the snowpack predominantly by vapour scavenging and are lost with the draining melt-water.

Figure 9. **Contaminant transport processes between the major compartments of the CoZMo-POP fate model during the three snow seasons. During the existence of a seasonal snow cover, exchange between the atmosphere and other surface compartments ceases. Only during the snow melt is chemical transport from the snow to the underlying surface assumed to occur**



The model confirmed that snow-melt can result in temporary peaks in air concentration. Figure 11 displays the seasonal variability in the simulated concentration of PCB-52 in relationship to the development of a seasonal snow cover. During the snow melting season, air concentrations increase rapidly in response to increasing temperatures and the disappearance of the snow pack. Toward the end of the snow-melt, the snow pack rapidly loses its capacity to retain chemicals such as PCB-52, which are then forced to revolatilise back into the atmosphere. During summer, the air concentrations peak a second time in response to high summertime temperatures (Fig. 10). Intriguingly, a comparable two-peak seasonal pattern was produced when accounting for the seasonal variability in forest canopy development in the CoZMo-POP model (Wania and McLachlan, 2001). Hornbuckle et al. (1994) has observed similar seasonal concentration trends, with an early concentration maximum during spring. In the boreal region, characterized by extensive forest cover and seasonal snow packs, the two effects may reinforce each other and result in very pronounced springtime peak concentrations of PCB-like contaminants. The model simulations thus provide a mechanistic explanation for the phenomenon of a spring pulse as observed for polybrominated diphenylethers in southern Ontario by Gouin et al. (2002).

Conclusions

With the tools developed in this project, it is now feasible to quantitatively describe the influence of falling snow and a seasonal snow cover on the environmental fate of many organic contaminants. Model simulations reveal that the impact of snow on the fate of contaminants can be very large in magnitude, and is very varied in its nature depending on the specific characteristics of the chemical and the snow. The new models and process descriptions should be instrumental in achieving a quantitative understanding of the delivery of organic contaminants to, and their environmental behaviour in, cold regions, such as the Arctic and high altitudes. They should therefore be incorporated into models that seek to describe the

Figure 10. Cumulative origin and fate of α-hexachlorocyclohexane, phenanthrene, pyrene and benzo[a]pyrene during an entire snow season (autumn to snow melt), as calculated by the CoZMo-POP model. The four organic contaminants differ widely in how they enter and leave the snow pack

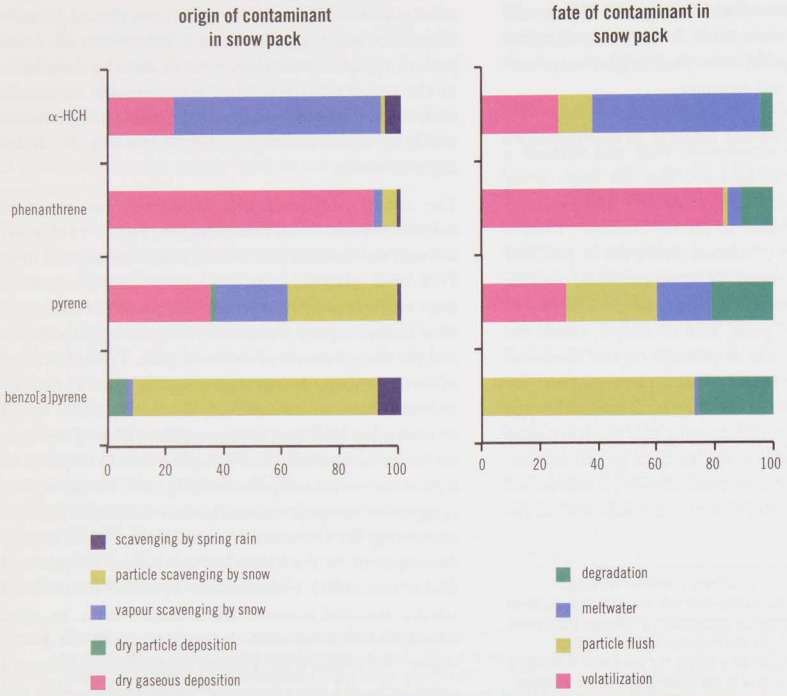
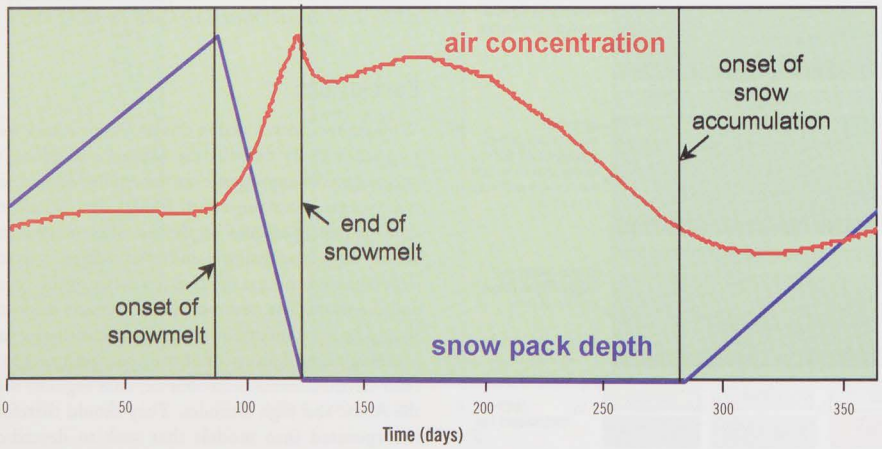


Figure 11. Simulated seasonal variability of the snow depth and the air concentration of polychlorinated biphenyl 52. A peak in air concentration coincides with the end of the snow melt period



atmospheric transport of organic contaminants to the Canadian Arctic.

Expected Completion Date

Two manuscripts on the project results are currently being finalised and are expected to be submitted by fall 2003. The project will be completed with the publication of two peer-reviewed papers. This is expected to occur by early 2004.

Acknowledgments

G. Daly's contribution to this project was financed through a NSERC postgraduate scholarship.

References

Cabanes, A., L. Legagneux, and F. Dominé. 2002. Evolution of the specific surface area and of crystal morphology of Arctic fresh snow during the ALERT 2000 campaign. *Atmos Environ.* 36:2767–2777.

Cabanes, A., L. Legagneux, and F. Dominé. 2003. Rate of evolution of the specific surface area of surface snow layers. *Environ Sci Technol.* 37:661–666.

Dominé, F., L. Chaix, and L. Hanot. 2000. Reanalysis and new measurements of N_2 and CH_4 adsorption on ice and snow. *J Colloid Interf Sci.* 227:104–110.

Dominé, F., A. Cabanes, A.S. Taillandier, and L. Legagneux. 2001. Specific surface area of snow samples determined by CH_4 adsorption at 77 K and estimated by optical, microscopy and scanning electron microscopy. *Environ Sci Technol.* 35:771–780.

Dominé, F., A. Cabanes, and L. Legagneux. 2002. Structure, microphysics, and surface area of the Arctic snow pack near Alert during ALERT 2000. *Atmos Environ.* 36:2753–2765

Donaldson, D.J. and D. Anderson. 1999. Adsorption of atmospheric gases at the air-water interface. 2. C1-C4 alcohols, acids, and acetone. *J Phys Chem. A* 103: 871–876.

Franz, T.P. and S.J. Eisenreich. 1998. Snow scavenging of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in Minnesota. *Environ Sci Technol.* 32: 1771–1778.

Gouin, T., G.O. Thomas, I. Cousins, J. Barber, D. Mackay, K.C. Jones. 2002. Air-surface exchange of polybrominated biphenyl ethers and polychlorinated biphenyls. *Environ Sci Technol.* 36:1426–1434.

Goss, K.-U. 1993. Adsorption of organic vapors on ice and quartz sand at temperature below 0°C. *Environ Sci Technol.* 27:2826–2830.

Goss, K.-U. 1997. Conceptual model for the adsorption of organic compounds from the gas phase to liquid and solid surfaces. *Environ Sci Technol.* 31:3600–3605.

Goss, K.-U. and R.P. Schwarzenbach. 1999. Empirical prediction of heats of vaporization and heats of adsorption of organic compounds. *Environ Sci Technol.* 33: 3390–3393.

Hanot, L. and F. Dominé. 1999. Evolution of the surface area of a snow layer. *Environ Sci Technol.* 33:4250–4255.

Hoff, J.T., D.J. Gregor, D. Mackay, F. Wania, and C.Q. Jia. 1998. Measurement of the specific surface area of snow with the nitrogen adsorption technique. *Environ Sci Technol.* 32:58–62.

Hoff, J.T., F. Wania, D. Mackay, and R. Gilham. 1995. Sorption of non-polar organic vapors by ice and snow. *Environ Sci Technol.* 29:1982–1989.

Hornbuckle, K.C., J.D. Jeremiason, C.W. Sweet and S.J. Eisenreich. 1994. Seasonal variation in air-water exchange of polychlorinated biphenyls in Lake Superior. *Environ Sci Technol.* 28:1491–1501.

Legagneux L., A. Cabanes, and F. Dominé. 2002. Measurement of the specific surface area of 176 snow samples using methane adsorption at 77 K. *J Geophys Res.* 107 (D17): art. no. 4335.

Mmereki, B.T., J.M. Hicks, and J.D. Donaldson 2000. Adsorption of atmospheric gases at the air-water interface. 3. Methylamines. *J Phys Chem. A* 104:10789–10793.

Roth C.M., K.-U. Goss, and R.P. Schwarzenbach. 2002. Adsorption of a diverse set of organic vapors on the bulk water surface. *J Colloid Interf Sci.* 252:21–30.

Platts, J.A., D. Butina, M.H. Abraham, and A. Hersey. 1999. Estimation of molecular linear free energy relation descriptors using a group contribution approach. *J Chem Inf Comput Sci.* 39:835–845.

Platts, J.A., M.H. Abraham, D. Butina, and A. Hersey. 2000. Estimation of molecular linear free energy relationship descriptors by a group contribution approach. 2. Prediction of partition coefficients. *J Chem Inf Comput Sci.* 40:71–80.

Sokolov, O., and J.P.D. Abbatt. 2002. Adsorption to ice of n-alcohols (ethanol to 1-hexanol), acetic acid and hexanal. *J Phys Chem. A* 106:775–782.

Wania, F. 1997. Modelling the behaviour of non-polar organic chemicals in an ageing snow pack. *Chemosphere.* 35:2345–2363.

Wania, F., J.T. Hoff, C.Q. Jia, and D. Mackay. 1998. The effects of snow and ice on the environmental behaviour of hydrophobic organic chemicals. *Environ Pollut.* 102: 25–41.

Wania, F., D. Mackay, and J.T. Hoff. 1999a. The importance of snow scavenging of polychlorinated biphenyl and polycyclic aromatic hydrocarbon vapors. *Environ Sci Technol.* 33:195–197.

Wania, F., R. Semkin, J.T. Hoff, and D. Mackay. 1999b. Modelling the fate of non-polar organic chemicals during the melting of an Arctic snowpack. *Hydrol Proces.* 13:2245–2256.

Wania, F., J. Persson, A. Di Guardo, and M.S. McLachlan. 2000. *CoZMo-POP. A fugacity-based multi-compartmental mass balance model of the fate of persistent organic pollutants in the coastal zone.* WECC-Report 1/2000, 27 pp.

Wania, F., and M.S. McLachlan. 2001. Estimating the influence of forests on the overall fate of semivolatile organic compounds using a multimedia fate model. *Environ Sci Technol.* 35:582–590.

Quantifying and Reducing Uncertainty in Model Calculations of Global Pollutant Fate

Project leader

Frank Wania, WECC Wania Environmental Chemists Corp., 27 Wells Street, Toronto, Ontario M5R 1P1; phone: (416) 516-6542; fax: (416) 516-7355; e-mail: frank.wania@utoronto.ca

Project team

Ying Duan Lei, WECC Wania Environmental Chemists Corp., Toronto;
Martin Scheringer, Federal Technical University (ETH) Zürich, Switzerland.

Abstract

The amplification of organic contaminants in the Arctic environment can be described quantitatively with zonally averaged global transport models. Such enrichment can be caused by temperature dependent physical-chemical processes or by differential persistence. A high potential for relative Arctic enrichment occurs for chemicals that are sufficiently mobile to reach the Arctic (either by atmospheric or oceanic convection), and at the same time have an intermediate climate-dependent degradability, that leads to rates of concentration decline that are faster in source regions than in the Arctic. Evidence of such enrichment are elevated concentration levels in Arctic media, e.g. α-HCH levels in Arctic Ocean water, and shifts in the relative composition of contaminant mixtures, such as the PCBs. Arctic amplification neither implies nor requires a redistribution of the bulk of the emitted global amount of a chemical to Northern latitudes. The model calculations reveal that even relatively small fractions of an organic chemical's inventory being transferred northward can results in inverted concentration profiles (levels that increase with distance from source) and fractionation patterns (shifts in relative composition with distance from source). It is possible to assess and predict the Arctic amplification potential of an organic chemical from a knowledge of its temperature dependent partitioning properties and climate dependent degradation rates.

Key Project Messages

1. Zonally averaged global box models have been used to describe the transport and fate of selected polychlorinated biphenyl (PCBs) congeners over the entire time period of their release to the environment. These simulations reveal the origin of elevated levels of these substances in the Arctic environment, pinpoint the major loss processes on a global scale, and identify the importance of various transport pathways.
2. Atmospheric degradation and transfer to the deep sea have been identified as the major global loss processes for the PCBs, the relative importance of these processes being very dependent on the degree of chlorination. As new emissions of PCBs decline, soils become the dominant environmental storage medium, controlling the overall global loss rate.
3. Global model calculations reproduce observed shifts in the relative composition of PCBs, that are consistent with the "global fractionation" hypothesis. They further show that these patterns can been established with only minor fractions of the global inventory of PCBs being transferred northward.
4. Global models have been used to identify the chemical characteristics that make a chemical susceptible to enrichment in Arctic ecosystems. A high potential for

Arctic amplification is predicted for very hydrophobic, semi-volatile organic substances, if emitted into the atmosphere. Water-soluble, highly persistent substances can experience delayed Arctic amplification as a result of slow oceanic transport to the North.

Objectives

The main objective of the project was to describe quantitatively with model calculations the global distribution behaviour of persistent organic contaminants, and to establish credibility in the results of these simulations. Specifically, we propose to accomplish the following tasks within project year 2001–2002:

1. Disseminate the results of the previous project years in several peer-reviewed journal publications. This includes the simulation of the global fate of the PCBs, including an uncertainty analysis, and the use of the global model in an evaluative fashion to investigate the global distribution behaviour of organic chemicals.
2. Contribute to the writing of the POPs-related chapters of the CACAR-2 and 2nd AMAP Arctic Assessment Report.
3. Continue the comparison of the zonally averaged global distribution model with those obtained by other global modelling studies for POPs.

Introduction

In this project, we use model calculations to describe and understand the global fate and transport of persistent organic pollutants on a global scale, with a focus on the transport and accumulation behaviour in the Arctic. Globo-POP, a zonally averaged global transport model, forms the basis of most of these calculations (Wania and Mackay, 2000). This model is used either in an evaluative mode, i.e. hypothetical situations are simulated in an effort to understand important principles of global POP fate, or in a realistic mode, i.e. an attempt is made to reproduce quantitatively the real historical fate of a particular global contaminant. Combinations of both modes are possible, namely when the simulation conditions for a particular contaminant are deliberately simplified or varied in order to explore the effect on the calculated fate outcome.

The application of the realistic mode is limited by the availability of suitable emission estimates, and has so far only been used for α-hexachlorocyclohexanes and the polychlorinated biphenyls (PCBs). The use of the model in the evaluative mode has focussed on understanding the conditions that favour accumulation of a contaminant in Arctic regions.

Activities

In 2001–2002

This constituted the last year of this project. The activities thus were related to finalizing the model calculations, interpreting the results and writing of publications.

Writing of sections for the 2nd Canadian Arctic Contaminants Assessment Report

Two sections were written for the 2nd Canadian Arctic Contaminants Assessment Report (CACAR2), namely:

1. Air/Snow Exchange of Persistent Organic Pollutants
2. Global Modelling in Support of International Negotiations

The section on "Air/Snow Exchange of Persistent Organic Pollutants" includes new calculations of the scavenging efficiency of precipitation for persistent organic pollutants as a function of temperature and precipitation type (rain vs. snow). These two sections were also used for Canada's contribution to the AMAP Report.

Further, a report on "The Significance of Long Range Transport of Persistent Organic Pollutants by Migratory Animals" has been made available for potential inclusion in CACAR2. Finally, we contributed to the CACAR2 section on "Physical-Chemical Properties of POPs" authored primarily by Dr. Tom Harner of the Meteorological Service of Canada (MSC).

New transport process of importance to global fate

In a collaboration with Dr. Michael McLachlan from the Institute for Baltic Sea Research in Germany, we discovered a major shortcoming of existing regional and global scale fate and transport model. In particular, we could show that for chemicals with POP-like partitioning properties, the extent of air-soil exchange is greatly underestimated if the slow transport of contaminants with the solid soil phase is not taken into account. Such transport occurs as a result of bioturbation by worms and moles. We found that the impact on the modelled soil and air concentrations is substantial. The results of this investigation were summarised in a recently submitted manuscript (McLachlan, Czub and Wania, submitted 2002).

In response to these findings, we decided to revise the description of air-soil exchange in the Globo-POP model to include solid phase transport in the soil. This in turn

necessitated the replication of all simulations for the PCBs and the Arctic Amplification Potential (see below). This massive effort somewhat delayed the finalization and submission of several of the planned manuscripts on global modelling.

Estimation of the potential of organic chemicals for accumulation in the Arctic

As described in the synopsis report 2000/2001 (Wania et al., 2001), we are using the Globo-POP model in connection with generic emission estimates to assess what combination of properties makes a chemical prone to be transported to and accumulate in Arctic latitudes. In this connection we introduced the quantitative measure of an Arctic Amplification Potential (AAP), distinguishing between the immediate AAP_1, and the delayed $AAP1_{+9}$, the latter indicating the potential for enrichment well after emissions have ceased. Part of this AAP analysis is an extensive assessment of the sensitivity of various model input parameter on the results. In response to the change in the description of air-soil exchange in Globo-POP (see above) we had to repeat more than 1000 AAP calculations, specifically:

1. AAP_1 and $AAP1_{+9}$ as a function of physical chemical partitioning properties in the space $3 < \log K_{OA} < 12$ and $-4 < \log K_{AW} < 3$, assuming emissions to occur either into air, water or soil (80 × 3 combinations = 240 simulations).
2. Testing of the influence of the zone of emission on the AAP_1 and AAP_{1+9} of five selected physical-chemical property combinations (10 zones × 5 chemicals × 3 mode of emissions = 150 simulations)
3. Testing of the influence of the environmental input parameters on the AAP_1 and AAP_{1+9} of five selected physical-chemical property combinations (45 environmental parameters × 5 chemicals × 3 mode of emissions = 675 simulations)

The replication of these calculations is complete and a paper discussing and interpreting these results is very close to submission (Wania, in preparation).

Simulations of the global fate of the polychlorinated biphenyls

Early in 2002, all the required elements for the simulation of the global fate of the PCBs were finally in place:

1. The recent global emission estimates by Breivik et al. (2002a and b) had become available, and we transformed them into the format required by the Globo-POP model.
2. A very thorough compilation and evaluation of the physical-chemical properties of various PCB congeners had been completed (Li and Wania, in prep.).
3. The Globo-POP model had been revised to include solid phase transport in the description of air-soil exchange (See above).

Using these elements, the global fate of eleven individual PCB congeners (PCB-8, 28, 31, 52, 101, 105, 118, 138, 153, 180 and 194) was simulated and the results interpreted. In a first step, we interpreted the model results in terms of the relative importance of various processes for the loss of PCBs from the global environment. Building upon and extending the synopsis report from 1999/2000 (Wania et al., 2000), this study includes the semi-empirical estimations of OH reaction loss and deep sea transfer, and compares them with the results of the global PCB model simulations. It also includes the evaluation of the simulated air and sea water concentrations through comparison with measured data. A paper on this part of the global PCB calculations is close to submission (Wania, in preparation).

We are also in the process of investigating the global fractionation of PCBs as calculated by Globo-POP. We try to understand the calculated and observed shifts in the congeneric composition of PCBs in various media, zones and times. This is to our knowledge the first effort to model the compositional patterns of complex POP mixtures. Of particular value are hypothetical calculations, which help us to tease out what processes are responsible for particular fractionation patterns. Specifically, we calculated the following scenarios:

1. All PCB congeners have identical partitioning properties and emission trends, yet differ in their persistence.
2. All PCB congeners have identical partitioning properties and persistence, yet differ in their emission trends.
3. All PCB congeners have identical persistence and emission trends, yet differ in their partitioning properties.

This way we can distinguish to what extent the oberserved fractionation patterns are a result of the variable persistence, variable partitioning properties, and variable emission trends. We aim to submit a paper on this part of the global PCB fate calculations by the end of summer 2002 (Wania and Su, in preparation).

Scientific collaborations on the global fate of POPs

In addition to conducting our own work on the global modelling of POPs we are collaborating with several scientists within Canada and Europe on related topics, often involving the use of the Globo-POP model.

Review paper on global modelling of POPs

Together with Martin Scheringer from the Federal Technical University in Zürich, Switzerland, we have written an extensive review paper on the global modelling of persistent organic pollutants (Scheringer and Wania).

This paper will be published later this year in a special volume of the *Handbook of Environmental Chemistry on Persistent Organic Pollutants.*

Influence of particle settling in the oceans on the long range transport behaviour of POPs

In another collaboration with M. Scheringer, we have compared results from various long range transport assessment models. Discrepancies between models for highly hydrophobic substances could be explained by the variable treatment of the process of particle settling in the water compartments of the models. It transpired that models that do not include this fate process (e.g. ChemRange), greatly overestimate the LRT potential of hydrophobic chemicals. M. Scheringer adjusted his ChemRange model accordingly and we are currently writing a paper on the significant impact of this particular fate process on global transport (Scheringer and Wania).

Comparison of measured and simulated global distribution of HCHs

Sönke Lakaschus from the Alfred-Wegener-Insitute in Bremerhaven, Germany has generated a unique historical data set of HCHs air and surface water concentrations in the Atlantic Ocean between Svalbard and Antarctica. We compared this data set with results obtained with the Globo-POP global distribution model and found very encouraging agreement with respect to both latitudinal profiles and time trends. This comparison was presented by S. Lakaschus at the SETAC meeting in Baltimore in November of 2001 and also included in a publication of these data in *Environ Sci Technol.* (Lakaschus, Weber, Wania, Bruhn and Schrems, 2002).

Modelling of long range transport potential of organic chemicals

We have continued collaborating with Andreas Beyer and Michael Matthies from the University of Osnabrück in Germany and with Donald Mackay and Todd Gouin from Trent University on simple methods of assessing the potential of chemicals for long range atmospheric transport. Two joint publication have resulted from that collaboration. The first publication provides the required chemical input parameters for the second paper, which investigates the influence of temperature on the long range transport behaviour of organic chemicals (Beyer, Wania, Gouin, Mackay and Matthies, 2002a) (Beyer, Wania, Gouin, Mackay and Matthies, 2002b).

Rates of PCB concentration decline in the atmosphere

In a collaboration with Hayley Hung from the Meteorological Service of Canada, we are using the Globo-POP model to understand rates of PCB concentration decline in the atmosphere. Specifically, we are trying to understand differences in concentration decline observed for different PCBs congeners and for different locations (Arctic vs. Great Lakes region). Early models results indicate that the rates of air concentration decline are strongly influenced by the rates of decline of the primary emissions, especially in temperate latitudes. Differences between PCB congeners, in particular, may be related to differences in the relative importance of the two major global loss processes atmospheric degradation and transfer to deep sea. Intermediate PCB congeners appear to have somewhat slower rates of concentration decline than the light and heavy congeners, because neither of these two processes is particularly effective for congeners of intermediate degree of chlorination.

Results and Discussion

Only a very small selection of the results of above investigations can be presented in the framework of this summary report. We restrict ourselves to presenting figures that illustrate the type of information that could be gained from the model calculations.

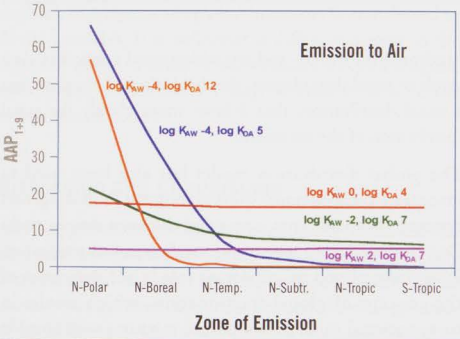
AAP Calculations

Figure 1 shows the result of calculations exploring the effect of the emission location on the potential of five completely persistent organic chemicals of variable partitioning properties to accumulate in the Arctic. Specifically, it plots the calculated AAP_{1+9}, i.e. the delayed Arctic accumulation potential, versus the zone of emission (in contrast to the generic emission scenario used in the normal AAP calculations, it is assumed that all the emissions occur into one climate zone only) if emission occurs into the atmosphere only. The results suggest that it depends very much on the type of chemical, whether the zone of emission influences the potential for Arctic enrichment. Namely, the AAP_{1+9} of the volatile substances ($\log K_{AW}$ 0, $\log K_{OA}$ 4 and $\log K_{AW}$ 2, $\log K_{OA}$ 7) is virtually independent from where the chemical had been released into the environment, whereas the AAP_{1+9} of a very involatile chemical ($\log K_{AW}$ −4, $\log K_{OA}$ 12) and a highly water soluble substance ($\log K_{AW}$ −4, $\log K_{OA}$ 5) is much higher if the emission occurred further North. For chemicals with the partitioning properties of relatively volatile POPs ($\log K_{AW}$ −2, $\log K_{OA}$ 7), the AAP_{1+9} is

notably higher if emission occurs into the two northernmost zones, but remains high even if emission occurs fairly far from the Arctic.

Table 1 lists the results of the study investigating the sensitivity of the AAP calculations on the selection of environmental input parameters for the same five substances. The sensitivities are very different for different chemicals, i.e. their global transport behaviour is controlled by a different set of processes. E.g. the global transport behaviour of a chemical with log K_{AW} 2, log K_{OA} 7 is entirely controlled by the rate of air-soil exchange, whereas the global fate of the volatile, but less hydrophobic chemical with log K_{AW} 0, log K_{OA} 4 is determined much more by the uptake and transport in the oceans. The highly sorptive chemical with log K_{AW} –4, log K_{OA} 12 can only reach the Arctic upon initial emission into air, and the AAP_{1+9} thus becomes dependent on parameters that influence the extent of atmospheric deposition. Not surprisingly, the Arctic accumulation behaviour of the multimedia chemical with log K_{AW} –2, log K_{OA} 7 is sensitive to the largest number of parameters, because its fate is influenced by a large number of diverse processes. It should be noted that the sensitivity changes if we analyse AAP_1 rather than AAP_{1+9}, or if the mode of emission changes from emission to air to emission to water or soil.

Figure 1. Effect of the climate zone of emission on the delayed Arctic Amplification Potential (AAP_{1+9}) of five perfectly persistent chemicals with different partitioning properties, if emission occurs into the atmosphere



Global Fate Calculation for the Polychlorinated Biphenyls

The Globo-POP model was used to examine the relative contribution of major loss processes to the total loss of selected PCB congeners from the global environment. Figure 2 compares the relative contribution of sediment burial, deep sea transfer, degradation in air and degradation in media other than air to the cumulative loss of the seven PCB congeners. Atmospheric degradation is more important for the lighter congeners while deep sea transfer contributes more significantly to the loss of the heavier congeners. For the lighter PCBs, reaction rates with the OH radical are high and sorption to oceanic particles is low. For the heavier congeners, deep sea transfer dominates because of a large K_{OW} and a slower rate of atmospheric degradation. The model suggests that degradation in media other than air (mostly in soil) contributed about 20% of the cumulative loss of all congeners. Sediment burial appears to be of very limited importance for all congeners. A temporal analysis reveals that the relative importance of the various loss processes has undergone significant shifts in time. For all but the two most volatile congeners, degradation in media other than air has been increasing steadily since 1980. This is caused by a shift in the relative distribution of the PCBs between environmental media. As emissions decreased, air

Table 1. Parameters with notable impact on the AAP_{1+9} of five perfectly persistent chemicals with different partitioning properties emitted into air, listed in sequence of impact

log K_{AW} 0, log K_{OA} 4 ("volatile")	Depth of surface ocean > air-water MTC (water side) > extent of sea ice cover > temperature > eddy diffusion coefficients in oceans
log K_{AW} 2, log K_{OA} 7 ("volatile/hydrophobic")	Soil depth > soil moisture content > solid phase diffusion in soils > temperature > organic carbon content in soil > soil-air MTC (air side)
log K_{AW} –4, log K_{OA} 12 ("involatile/sorbing")	Extent of sea ice cover > dry particle deposition velocities > particle scavenging ratio > precipitation rate > depth of surface ocean > particle concentration in air > organic carbon content in air particles > soil-air MTC (air side) > particle settling rate in oceans
log K_{AW} –4, log K_{OA} 5 ("water soluble")	Eddy diffusion coefficients in oceans > size of fresh water compartment > precipitation rate > air-water MTC (air side) > temperature > extent of sea ice cover > water run-off rate
log K_{AW} –2, log K_{OA} 7 ("multimedia")	Extent of sea ice cover > air-water MTC (air side) > depth of surface ocean > temperature > eddy diffusivity in ocean > precipitation rate > organic carbon content in soil > particle settling rate in ocean > water content in fresh water sediments > size of fresh water compartment > water exchange with deep ocean

Figure 2. Relative importance of four processes for the loss of 7 PCB congeners from the global environment as a function of time

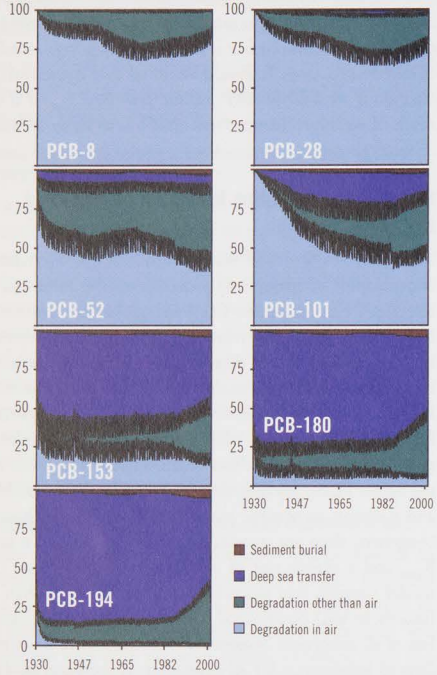
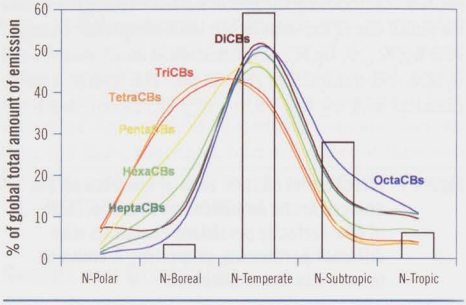


Figure 3. Simulated zonal distribution of the total global amount of various PCB homologue in 2000. The zonal distribution of the cumulative emissions from 1930 until 2000 are depicted as bars. The bulk of the distribution of the lighter PCBs, in particular those with three and four chlorines, is shifted towards the higher latitudes, whereas the distribution of the octachlorobiphenyl is similar to that of the emissions. The highly reactive dichlorobiphenyls also is restricted largely to the zones of emission

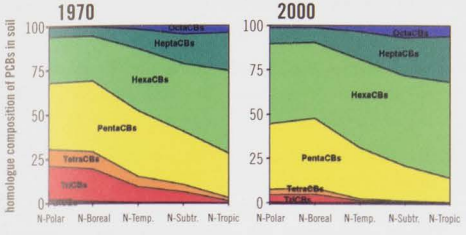


and water concentrations responded relatively rapidly, whereas soils respond much slower. As the rates of atmospheric degradation and oceanic settling decreased in concert with falling air and water concentrations, the loss by degradation in soils remained relatively high, because the concentrations in soil decrease much more slowly. This means that future rates of decrease for many PCB congeners will be tied to their rate of clearance in soils.

Another focus of the PCB calculations has been on the extent of global redistribution. The general dispersion and northbound migration of several PCB congeners is revealed by plotting the relative distribution among the five climate zones of the Northern hemisphere (Figure 3). The congeners with five and more chlorines retain the maximum of their distribution within the temperate zone, which received the bulk of the cumulative emissions. This is a reflection of both the long-lasting and ongoing release of PCBs into that zone, and the large sorptive capacity of the soils for these heavy PCBs. As the degree of chlorination decreases, the extent of the northward shift in distribution increases, reaching a maximum for the tri- and tetrachlorinated congeners. As a result of rapid degradation, the dichlorinated congener has a zonal distribution, that follows more closely the zonal distribution of the emissions.

The global distribution model has also been used to investigate compositional shifts among the PCB congeners between compartments, zones and different time periods. Due to their wide range of physical-chemical properties, PCBs have played an important role in the derivation of the concept of global fractionation, which results in compositional shifts of compound mixtures with latitude (Wania and Mackay, 1993, 1996). The model succeeded in reproducing shifts towards lighter PCB congeners with increasing latitude, as have been observed in various measurement campaigns (Muir et al., 1996; Ockenden et al., 1998). The model suggests that these shifts are rather complex, namely differ between various environmental media, have sometimes surprising anomalies, and change in time. This is illustrated in Figure 4, which shows how the simulated homologue composition of PCBs in soil shifts to increasingly more volatile homologues with increasing latitude. In the time period between 1970 and 2000, the less volatile congeners increased in relative importance as the lighter ones are degraded more readily. It should be stressed that these global fractionation patterns have been established with only relatively minor fractions of the global inventory of PCBs being transferred

Figure 4. Simulated homologue composition of PCBs in soil in 1970 and 2000. The composition shifts to increasingly more volatile homologues with increasing latitude. In the past thirty years of steadily declining emissions, the less volatile congeners increased in relative importance as the lighter ones are degraded more readily



northward (Figure 3). Compositional shifts consistent with the global fractionation hypothesis, as well as inverted concentration profiles with higher concentrations in the Arctic than at lower latitudes, do not require that the bulk of a chemical's global inventory is transferred to Arctic latitudes. It is sufficient if differences exist in the extent of re-distribution of the various PCB homologues, even if that re-distribution may be small relative to the total global amount.

Discussion and Conclusions

Arctic amplification of organic contaminants occurs and can be quantitatively reproduced and explained with zonally averaged global transport models. Such enrichment can be caused by temperature dependent physical-chemical processes or by differential persistence. Often it is a combination of both. The highest potential for relative Arctic enrichment is predicted for chemicals that are sufficiently mobile to reach the Arctic (either by atmospheric or oceanic convection), and at the same time have an intermediate climate-dependent degradability, that leads to rates of concentration decline that are faster in source regions than in the Arctic. Evidence of such enrichment are elevated concentration levels in Arctic media ("cold condensation") and shifts in the relative composition of contaminant mixtures ("global fractionation"). Both phenomena are reproduced by the models.

Importantly, Arctic amplification neither implies nor requires a redistribution of the bulk of the emitted global amount of a chemical to Northern latitudes. The model calculations reveal that even relatively small fractions of an organic chemical's inventory being transferred northward can results in inverted concentration profiles (levels that increase with distance from source) and fractionation patterns (shifts in relative composition with distance from source). Relatively small amounts can result in high concentrations in the Arctic because of the relatively small size of the Arctic as a whole and of the environmental phases with high capacity for hydrophobic organic chemicals (organic soils, vegetation, organic sediments) within the Arctic. Speaking in fugacity terms, the Arctic environment has a relatively small fugacity capacity or Z-value for hydrophobic organic chemicals because of the sparsity of organic matter in the terrestrial and marine environment. Because of this limited "dilution potential" relatively small amounts of such chemicals can result in high fugacities and concentrations.

It is possible to assess and predict the Arctic amplification potential of an organic chemical from a knowledge of its temperature dependent partitioning properties and climate dependent degradation rates.

Expected Completion Date

The bulk of the research project has been completed. The last of the publications will likely be submitted by the end of the year 2002.

References

Beyer, A., F. Wania, T. Gouin, D. Mackay, and M. Matthies. 2002a. Adjusting physical-chemical properties to internal constraints. *Environ Toxicol Chem.* 21:941–953.

Beyer, A., F. Wania, T. Gouin, D. Mackay, and M. Matthies. 2002b. Temperature dependence of the characteristic travel distance. *Environ Sci Technol.* Submitted.

Breivik, K., A. Sweetman, J.M. Pacyna, and K.C. Jones. 2002a. Towards a global historical emission inventory for selected PCB congeners — a mass balance approach. 1. Global production and consumption. *Sci Total Environ.* 290:181–198.

Breivik, K., A. Sweetman, J.M. Pacyna, and K.C. Jones. 2002b. Towards a global historical emission inventory for selected PCB congeners — a mass balance approach. 2. Emissions. *Sci Total Environ.* 290:199–224.

Lakaschus, S., K. Weber, F. Wania, R. Bruhn, and O. Schrems. 2002. The air-sea equilibrium and time trend of hexachlorocyclohexanes in the Atlantic Ocean between the Arctic and Antarctica. *Environ Sci Technol.* 36:138–145.

Li, N. and F. Wania. A comprehensive and critical compilation, evaluation and selection of physical chemical property data for selected polychlorinated biphenyls. *J Phys Chem Ref Data.* In preparation.

McLachlan, M.S., G. Czub, and F. Wania. 2002. The influence of vertical sorbed phase transport on the fate of organic chemicals in surface soils. *Environ Sci Technol.* Submitted.

Muir, D.C.G., A. Omelchenko, N.P. Grift, D.A. Savoie, W.L. Lockhart, P. Wilkinson, and G.J. Brunskill. 1996. Spatial trends and historical deposition of polychlorinated biphenyls in Canadian midlatitude and Arctic lake sediments. *Environ Sci Technol.* 30:3609–3617.

Ockenden, W.A., A.J. Sweetman, H.F. Prest, E. Steinnes, and K.C. Jones. 1998. Toward an understanding of the global atmospheric distribution of persistent organic pollutants: The use of semipermeable membrane devices as time-integrated passive samplers. *Environ Sci Technol.* 32:2795–2803.

Scheringer, M., and F. Wania. Multimedia models of global transport and fate of persistent organic pollutants. In: Fiedler, H. (Ed.) Handbook of Environmental Chemistry, Springer-Verlag, Berlin.

Scheringer, M., and F. Wania. Influence of particle settling to the deep sea on the LRT potential of hydrophobic organic contaminants. *Environ Sci Pollut Res.* In preparation.

Wania, F. Assessing the potential of organic chemicals for long-range transport and accumulation in polar regions. *Environ Sci Technol.* In preparation.

Wania, F., and G. Daly. Estimating the global loss of PCBs. *Atmos Environ.* In preparation.

Wania, F. and D. Mackay. 1993. Global fractionation and cold condensation of low volatility organo-chlorine compounds in polar regions. *Ambio.* 22:10–18.

Wania, F. and D. Mackay. 1996. Tracking the distribution of persistent organic pollutants. *Environ Sci Technol.* 30:390A–396A.

Wania, F. and D. Mackay. 2000. *The global distribution model. A non-steady state multi-compartmental mass balance model of the fate of persistent organic pollutants in the global environment.* Technical Report and Computer Program, 21 pages (www.utsc.utoronto.ca/~wania).

Wania, F., Y.D. Lei, and A. Wong. 2001. Quantifying and reducing uncertainty in model calculations of global pollutant fate. In: Kalhok, S. (Ed.) *Synopsis of research conducted under the 2000–2001 Northern Contaminants Program.* Department of Indian Affairs and Northern Development, Ottawa, Canada, 138.

Wania, F., and Y. Su. Quantifying cold condensation and global fractionation of the polychlorinated biphenyls. *Ambio.* In preparation.

Monitoring the Health of Arctic Peoples and Ecosystems and the Effectiveness of International Controls

Part B: Biotic Monitoring

Assessment of Persistent Organochlorine Contaminant and Essential/ Non-Essential Element Concentrations in Canadian Arctic Fox and Wolverines

Project leader(s)

Birgit Braune, National Wildlife Research Centre, Canadian Wildlife Service, Environment Canada, Carleton University (Raven Road), Ottawa, ON K1A 0H3; phone: (613) 998-6694; fax: (613) 998-0458; e-mail: birgit.braune@ec.gc.ca
Paul Hoekstra, University of Guelph, Department of Environmental Biology, Guelph, ON N1G 2W1; phone: (905) 336-4746; fax: (905) 336-6430; e-mail: paul.hoekstra@ec.gc.ca
Brett Elkin, Wildlife & Fisheries Division, GNWT Department of Resources, Wildlife & Economic Development, Yellowknife, NT X1A 2L8; phone: (867) 873-7761; fax: (867) 873-0293; e-mail: brett_elkin@gov.nt.ca
Derek Muir, National Water Research Institute, Environment Canada, Burlington, ON L7R 4A6; phone: (905) 319-6921; fax: (905) 336-6430; e-mail: derek.muir@ec.gc.ca

Project team

Robert Mulders, GNWT Wildlife & Fisheries Division; Brent Patterson, Nunavut Dept. Sustainable Development, Kugluktuk, NU; Mitch Campbell, Nunavut Dept. Sustainable Development, Arviat, NU; Olokhaktomiut HTC, Holman, NT; Arviat HTO, Arviat, NU; Local Hunters and Wildlife Officers; Matson's Laboratory, Milltown, MT, USA; Joachim Obst, Yellowknife, NT; Dept. of Soil Science, Univ. Saskatchewan, Saskatoon, SK; Bryan Wakeford, DOE, CWS, NWRC, Ottawa, ON.

Abstract

The arctic fox and wolverines are a circumpolar species found across the Canadian and Alaskan arctic environment. The feeding selection of the arctic fox differs between summer and winter, and inland versus coastal/ island environments due to seasonal distribution and abundance of available prey. The omnivorous diet of wolverines, on the other hand, is generally regarded as terrestrial-based. Stable isotope analyses of arctic fox from Barrow, AK, Holman (Ulukhaqtuuq), NT, and Arviat, NU show that trophic position (as inferred from $\delta^{15}N$) was correlated with increasing stable carbon isotope values ($\delta^{13}C$), suggesting that trophic level increases as these populations shift their terrestrial/freshwater-based feeding selection to the marine environment. However,

comparison of stable isotope data with persistent organochlorine (OCs) concentrations indicates that trophic position may not influence concentrations for all major OC groups. Contaminant profiles suggest that arctic fox and wolverines have similar ability to biotransform OCs, and that marine mammals may represent a significant contribution to the overall exposure of persistent organochlorine contaminants to wolverines. Analysis of elements in arctic fox and wolverine tissues indicates a moderate degree of exposure to toxic and essential elements, which is likely of natural origin. While OC concentrations, particularly ΣPCB, were highly variable, concentrations in the arctic fox and wolverines were generally below those associated with toxicological endpoints for adverse effects on mammalian reproduction. Further research is required to properly elucidate the potential wildlife health risk from OC exposure to these species.

Key Project Messages

1. Stable isotope data suggest that arctic fox feeding from the marine environment occupy a higher trophic level than foxes employing a terrestrial-oriented feeding strategy.
2. Contaminant profiles suggest that arctic fox and wolverines have similar ability to biotransform OC, and that marine mammals may represent a significant contribution to the overall exposure of persistent organochlorine contaminants to wolverines.
3. Preliminary results suggest that element concentrations in arctic fox and wolverines are low and comparable to other terrestrial arctic mammals.
4. While ΣPCB concentrations in arctic fox and wolverines are generally below those associated with adverse impact on mammalian reproduction, further research is required to properly elucidate the potential health impacts to this species from exposure to other OCs, such as chlordane-related compounds.

Objectives

1. To quantify the trophic ecology of the arctic fox via stable isotope analysis.
2. To determine tissue residue concentrations of OCs and elements in arctic fox and wolverine populations from the arctic coastal environment.
3. To assess whether or not OC residue levels found in arctic fox and wolverines pose a potential wildlife health risk.

Introduction

The arctic fox (*Alopex lagopus*) and the wolverine (*Gulo gulo*) are circumpolar species widely distributed across northern Canada and Alaska (Banfield, 1987). Arctic foxes are a socio-economically important species because of their valuable pelt (Banfield, 1987; Hiruki and Stirling, 1989) and a source of meat in some northern communities (Kassam, 1999). The arctic fox constitutes an important component of both the terrestrial and marine ecosystems as an efficient scavenger (Hiruki and Stirling, 1989) and its feeding strategy may seasonally shift between the marine and freshwater environment (Fay and Stephenson, 1989). In contrast, the omnivorous feeding strategy of wolverines is terrestrially based; primarily feeding upon birds, eggs, and terrestrial mammals, including ground squirrels and caribou carcasses (Magoun, 1987).

There are distinct differences in the summer and winter diets of inland versus coastal/island foxes. The feeding selection of this species in winter is necessarily different from those in summer based on the seasonal distribution and abundance of available prey (Fay and Stephenson, 1989). Inland, the diet of the arctic fox consists of small mammals, eggs and fledglings of ground-nesting birds and caribou remains (Banfield, 1987). Coastal foxes eat marine invertebrates (Kapel, 1999) and fish (Banfield, 1987) in summer and scavenge the remains of ringed seals and bearded seals killed by polar bears and actively prey on newborn seal pups in the winter and spring (Fay and Stephenson, 1989; Hiruki and Stirling, 1989; Kapel, 1999).

Stable isotope analyses can be used to distinguish populations feeding at different trophic levels, and between marine and terrestrial/freshwater-based diets. In single system studies, it is possible to use stable-nitrogen ratios ($^{15}N/^{14}N$; $\delta^{15}N$) to determine trophic relationships since nitrogen ratios increase by regular increments from one trophic level to the next. Measurements of naturally occurring stable isotopes in food webs can also be used to delineate relative inputs from freshwater and marine biomes (Kelly, 2000). Since ^{13}C is slightly enriched with increasing trophic level, the measure of $^{13}C/^{12}C$ ($\delta^{13}C$) in biological systems can describe trophic interactions by quantifying the relative contributions of marine versus terrestrial carbon sources (Kelly, 2000). While $\delta^{13}C$ values in arctic fox feeding from terrestrial and marine-based habitats have been recorded (Angerbjörn et al., 1994), the influence of feeding selection (marine versus terrestrial) on trophic position, as inferred from $\delta^{15}N$, had not been investigated prior to this study.

The accumulation of persistent organochlorine contaminants (OCs) in the terrestrial arctic environment has been

mainly focused on herbivores such as caribou, as they are an important food source of northern peoples. Due to the potential biomagnification of OCs, top trophic level carnivores, such as wolverines, may accumulate OCs at relatively high concentrations compared to other terrestrial biota. However, no reports of OC concentrations in wolverines have been published. Previous investigations have suggested that some arctic fox populations are exposed to ΣPCB at sufficient concentration to affect reproductive success. Brunström and Halldin (2000) concluded that ΣPCB concentrations in arctic fox liver from Svalbard exceeded to xicological endpoints for reproductive success in mink (*Mustela vison*) and OC exposure may be a concern for the arctic fox population.

Activities

In 2001–2003

As part of a project entitled *Human and Chemical Ecology of Arctic Pathways by Marine Pollutants* being conducted in Holman (Ulukhaqtuuq) as well as in communities in Alaska, arctic fox muscle and liver were collected in 1999–2001 by Inuit subsistence hunters and trappers from Ulukhaqtuuq, NT (n = 20, muscle and liver) along with North Slope Borough Public Health Office personnel in Barrow, AK, USA (n = 18 muscle and liver). During the winter of 2001, 50 carcasses of arctic foxes were collected with the help of local hunters and trappers from Arviat, NU. Foxes were collected by quick-kill techniques (i.e. shooting, quick-kill traps) and specimen data (i.e. sex, length, weight) was recorded by Department of Wildlife Management staff, Public Health Office personnel (Barrow); and local hunters (Ulukhaqtuuq and Arviat).

Wolverine (*Gulo gulo*) carcasses (n = 12) were collected from the coastal community of Coppermine (Kugluktuk), NU in 1998–1999 and were made available from the Government of the NWT for interspecies comparison. Fox and wolverine specimens collected in close proximity to human activity were omitted from this study to minimize the contribution of municipal waste on stable isotope and contaminant profiles. Tissues were stored at −20°C and homogenized prior to analysis. Age estimation for arctic fox and wolverines was quantified from cementum layers in canine teeth (Matson Laboratory, Milltown, MT).

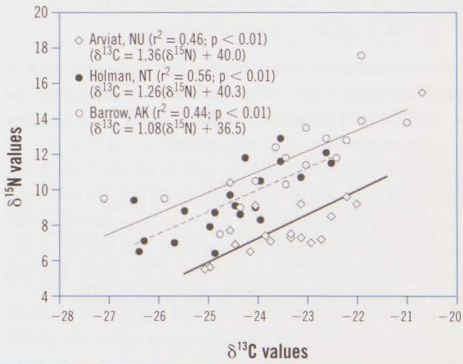
Arctic fox liver and muscle tissues from Ulukhaqtuuq, Barrow, and Arviat and wolverine livers from Kugluktuk were analyzed for various organochlorine analytes. A total of 100 PCB congeners and 30 organochlorine pesticides and related compounds were quantified by GC-ECD using a series of external standards. Toxaphene was analyzed by GC-MSD with electron capture negative ionization mode and was quantified using a single response factor based on technical toxaphene and a series of external chlorobornane standards. Detailed analysis of essential and non-essential elements (Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Tl, U, V, and Zn) in arctic fox and wolverine liver tissues was performed by ICP-MS. Additional mercury (Hg) and cadmium (Cd) analysis in liver and kidney was performed by GFAAS. Randomly selected arctic fox liver samples from Arviat were analyzed for monomethyl-Hg (MeHg) analysis. The results of these analyses were submitted for peer-reviewed publication in three scientific journals (see Hoekstra et al., 2003a, b, c) and are summarized herein.

Results and Discussion

Stable isotope profile

The $\delta^{15}N$ values in arctic fox muscle were positively correlated with $\delta^{13}C$ signatures at Ulukhaqtuuq, NT, Arviat, NU and Barrow, AK (Figure 1). As previously stated, the diet of arctic fox consists of small mammals such as lemmings, arctic hares, and ground squirrels as well as caribou carcasses and eggs and fledglings of ground-nesting birds. The stomach contents of arctic fox collected at Arviat revealed recent

Figure 1. Stable carbon ($\delta^{13}C$) versus nitrogen ($\delta^{15}N$) isotope ratios in artic fox muscle from Holman (Ulukhaqtuuq), NT (n = 20), Arviat, NU (n = 20) and Barrow, AK (n = 18). The regression for Ulukhaqtuuq and Barrow are the solid and dashed line, respectively. The thick solid line indicates linear regression for Arviat. The 1st order relationship was not significantly different between sites (t-test; $p > 0.05$) (Hoekstra et al., 2003b)



feeding on caribou and other terrestrial mammals and supports these reported field observations.

The relationship between $\delta^{13}C$ and $\delta^{15}N$ suggests that relative trophic position increases as the arctic fox at Holman, Barrow, and Arviat shift their relative terrestrial/freshwater-based feeding selection to the marine environment. The $\delta^{13}C$ signatures found in arctic fox border those $\delta^{13}C$ signatures found in other terrestrial and marine biota from Ulukhaqtuuq and Barrow. This is consistent with reported $\delta^{13}C$ values observed in other coastal and inland arctic fox populations from Iceland and previous field observations of arctic fox feeding behavior. However, arctic fox cannot be strictly classified as having predominantly marine or terrestrial-based diets. This species is considered a "highly opportunistic" scavenger, and its diet can vary tremendously over time and between individuals. As a result, the trophic level of food items, frequency and (or) magnitude of feeding events may be variable and stable isotope signatures in arctic fox will likely reflect a gradient between the marine and terrestrial ecosystems.

Organochlorine concentrations

The wet-weight concentrations of sum-group (Σ) OCs in arctic fox liver and muscle (by site) and wolverine liver are presented in Table 1. While concentrations for some OCs were significantly different between locations, the overall pattern of OC accumulation in arctic fox muscle and liver was similar at each community. ΣPCB and chlordane-related (CHLOR) compounds were the major organochlorines present in arctic fox and wolverines. At all sites, the rank order for OC groups in arctic fox muscle was ΣPCB > ΣCHLOR > ΣHCH > TOX > ΣClBz > ΣDDT. In liver, ΣCHLOR was the most abundant ΣOC group, followed by ΣPCB > TOX > ΣHCH > ΣClBz > ΣDDT. In wolverines, the rank order of hepatic concentrations were ΣPCB > ΣCHLOR > ΣDDT > ΣHCH. The most abundant OC analytes detected in arctic fox and wolverines were PCB-153, PCB-180, β-HCH, and oxychlordane.

OC concentrations were not significantly correlated with trophic position (as interpreted from $\delta^{15}N$) except for α- and β-HCH isomers ($p < 0.05$). We hypothesize that the disparity between OC concentrations and $\delta^{15}N$ may be attributed to different turnover rates in metabolically active tissue, the influence of maternal transfer of OCs and stable isotopes via lactation during early life-stage development, age, relatively high metabolic capacity, and (or) other factors influencing OC accumulation in the arctic fox that have not been accounted for in this investigation.

The biotransformation capacity of arctic fox and wolverines is an important factor governing the accumulation of OCs in this species. For example, the distribution of PCBs in arctic fox and wolverine liver was dominated by hexa- and hepta-Cl substituted congeners (35–40% and 25–30% of ΣPCB, respectively). However, these profiles are comprised of relatively few congeners and are similar among species (Hoekstra et al., 2003c). Concentrations of OCs in wolverines, particularly PCBs, were greater than values reported in other high trophic level terrestrial mammals, including wolves (*Canis lupus*), and comparable to marine mammals. A plausible explanation of these relatively high OC concentrations is that the feeding strategy of this wolverine population is similar to the arctic fox and has increased OC exposure due to the scavenging of marine mammals (Hoekstra et al., 2003c).

This hypothesis is further supported by the quantification of OC biomagnification factors (BMFs) to wolverines from terrestrial (e.g. caribou) and marine mammals (e.g. ringed seals). BMFs for a hypothetical caribou–wolverine food chain were generally greater than values reported for the caribou–wolf food chain. For example, the BMF of PCB-153 was approximately 16 from caribou to wolf (Kelly and Gobas, 2001), whereas the BMF of PCB-153 from caribou to wolverines was > 800. The BMF values determined for a seal–wolverine food chain ranged from 0.79 (for HCB) to 4.1 (for ΣPCB), and are in general agreement with the BMFs for OCs in other mammals, including arctic fox. These results suggest that caribou and other terrestrial mammals do not represent the major source of OCs to wolverines and that wolverines are consuming more contaminated prey items, such as marine mammals, along with a terrestrially oriented diet at this location (Hoekstra et al., 2003c).

Brustrom and Halldin (2000) observed that PCB levels in arctic fox liver samples from Svalbard were above the lowest-observed-adverse-effect-level (LOAEL) value for reproductive impairment in mink, suggested that this arctic fox population may be exposed to sufficient PCB concentrations to cause adverse reproductive effects. The ΣPCB concentrations in wolverines and arctic foxes from Barrow and Arviat were below the toxicological endpoints described therein. While ΣPCB concentrations in two liver samples exceeded the LOAEL for PCB-induced reproductive impairment in mink, the majority of liver and muscle samples quantified in this study contained lipid-normalized ΣPCB less than the concentrations associated with reproductive toxicity. However, the cumulative toxicological effects on wolverine and arctic fox reproduction, or other biological parameters, due to OC exposure cannot be assessed by only considering the

Table 1. Mean stable N and C values in muscle, lipid content, and concentrations (± 1 standard error) of ΣOC groups in arctic fox tissues and wolverine liver (ng g^{-1}, wet weight) by site

Tissue	Lipid (%)	$\delta^{13}C$	$\delta^{15}N$	ΣClBz[a]	ΣCHLOR[b]	ΣDDT[c]	ΣHCH[d]	ΣPCB[e]	TOX[f]
Arctic fox									
Barrow, AK									
Liver	7.7 ± 1.6	—	—	12 ± 1.7	236 ± 82	8.7 ± 0.9	22 ± 5.1	124 ± 32	28 ± 8.1
Muscle	7.1 ± 1.2	−23.5 ± 0.3	11.2 ± 0.4	9.9 ± 2.6	42 ± 17	5.8 ± 0.7	14 ± 5.0	81 ± 22	10 ± 2.6
Ulukhaqtuuq, NT									
Liver	9.2 ± 1.3	—	—	4.2 ± 1.0	219 ± 56	4.0 ± 0.8	11 ± 2.1	124 ± 39	17 ± 4.5
Muscle	5.6 ± 0.6	−24.5 ± 0.3	9.3 ± 0.4	4.4 ± 0.6	34 ± 8.9	1.9 ± 0.5	5.4 ± 0.9	48 ± 9.2	4.5 ± 1.2
Arviat, NU									
Muscle	9.1 ± 0.9	−23.5 ± 0.2	8.0 ± 0.5	17.6 ± 6.4	96 ± 27	8.5 ± 2.4	21 ± 12	156 ± 18	11 ± 1.9
Wolverine[g]									
Liver	3.8 ± 0.3	—	—	1.5 ± 0.3	14 ± 6.1	7.9 ± 3.9	1.5 ± 0.5	75 ± 18	—

[a] ΣClBz = sum of 1,2-diClBz, 1,2,3-triClBz, 1,2,4-triClBz, 1,3,5-triClBz, pentaClBz, and hexachlorobenzene; [b] ΣCHLOR = sum of sum of *cis*-chlordane, *trans*-chlordane, oxychlordane, *cis*-nonachlor, *trans*-nonachlor, heptachlor, and heptachlor *exo*-epoxide; [c] ΣDDT = sum of *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDT, and *p,p'*-DDT; [d] ΣHCH = sum of α-HCH, β-HCH, and γ-HCH; [e] ΣPCB = sum of 4/10, 7/9, 6, 8/5, 19, 12/13, 18, 15/17, 24/27, 16, 32, 54/29, 26, 25, 50, 28, 31, 33/21/53, 51, 22, 45, 46, 52, 49, 43, 47/48, 44, 59, 42, 64, 41/71, 40, 100, 63, 74, 76/98, 70, 95/66, 91, 55, 56/60, 92/84, 101, 99, 119, 83, 97, 87, 81, 85, 136, 110, 82, 151, 135, 144, 107/147, 149/133, 118, 114, 143, 141, 145, 153, 132, 105, 141/179, 137, 176/130, 163, 138, 158, 129/178, 175, 187, 182, 183, 128, 167, 185, 174, 177, 171, 156, 202/173, 172, 197, 180, 193, 191, 199, 170/190, 198, 201, 176/203, 189, 206, 195, 207, 194, 205, 208, and 209; [f] TOX = sum of all toxaphene components; [g] Wolverine livers from Kugluktuk, NU (Hoekstra et al., 2003b, c)

Table 2. Mean concentrations (μg g^{-1}, wet weight ± 1 standard error) of cadmium, mercury lead, arsenic, selenium, copper, zinc manganese and iron in arctic foxes and wolverines from the Canadian Arctic (reported in Hoekstra et al., 2003a)

Tissue	Kidney	Liver							
Site	Cd	Cd	Cu	Fe	Mn	Pb	Se	THg	Zn
Arctic fox									
Ulukhaqtuuq, NT (n=15)	NQ	0.21 ± 0.04	5.5 ± 0.64	285 ± 25	3.6 ± 0.35	< 0.18	0.79 ± 0.08	0.85 ± 0.22	29 ± 2.9
Arviat, NU (n=50)	1.08 ± 0.19	0.18 ± 0.03	7.1 ± 0.49	344 ± 16	3.7 ± 0.16	0.70 ± 0.10	0.88 ± 0.12	0.77 ± 0.25	29 ± 1.8
Wolverine									
Kugluktuk, NU (n=12)	0.67 ± 0.18	0.10 ± 0.01	32 ± 5.7	356 ± 25	3.6 ± 0.31	< 0.18	0.68 ± 0.04	0.13 ± 0.02	35 ± 3.3

impact of ΣPCB exposure. Further research is necessary to quantify the possible risk of OC exposure to the overall health of arctic fox and wolverine populations.

Heavy metal concentrations

Most trace elements (Ag, Al, As, B, Ba, Be, Co, Cr, Mo, Ni, Sb, Sn, Sr, Tl, U, and V) were below method detection limits. The concentrations of the measurable elements in arctic fox and wolverine liver are presented in Table 2. Concentrations of essential elements (Cu, Fe, Zn) in arctic fox and wolverines are likely within normal physiological limits and reflect the concentrations necessary for adequate biological function with each species. These results demonstrate that non-essential element concentrations are relatively low compared to marine biota and are similar to other terrestrial-based mammals, such as caribou and reindeer (AMAP, 1998), and arctic fox from Svalbard (Prestrud et al., 1994).

Hepatic total Hg (THg) concentrations in arctic fox from this study were not significantly different from specimens collected in 1973 from Ulukhaqtuuk suggesting that THg concentrations have not changed dramatically over the past 30 years. The mean (± 1 standard error) hepatic MeHg concentrations in arctic fox from Arviat (0.14 ± 0.07 μg g^{-1} wet weight) comprised 14% of THg. While the molar concentrations of THg were correlated

with Se in arctic foxes and wolverines, hepatic Hg/Se molar rations were consistently lower than unity suggesting that Se-mediated detoxification pathways of Hg are not overwhelmed at current exposure. However, ancillary mechanisms for Hg detoxification in these species may exist and need to be considered (Hoekstra et al., 2003a).

References

AMAP, 1998. AMAP Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway. xii + 859 pp.

Angerbjörn, A., P. Hersteinsson, K. Lidén, and E. Nelson. 1994. Dietary variation in arctic foxes (*Alopex lagopus*) — an analysis of stable carbon isotopes. *Oecologia.* 99: 226–232.

Banfield, A.W.F. 1987. The Mammals of Canada. National Museums of Canada, University of Toronto Press, Toronto, ON. pp. 295–298, 332–335.

Bruström, B., K. Halldin. 2000. Ecotoxicological risk assessment of environmental pollutants in the Arctic. *Tox Lett.* 112/113:111–118.

Fay, F.H. and R.O. Stephenson. 1989. Annual, seasonal, and habitat-related variation in feeding habits of the arctic fox (*Alopex lagopus*) on St. Lawrence Island, Bering Sea. *Can J Zool.* 67:1986–1994.

Hiruki, L.M. and I. Stirling. 1989. Population dynamics of the Arctic Fox, *Alopex lagopus*, on Banks Island, Northwest Territories. *Can Field-Nat.* 103:380–387.

Hoekstra, P.F., L.A. Dehn, J.C. George, K.R. Solomon, D.C.G. Muir, and T.M. O'Hara. 2002. Trophic ecology of bowhead whales (*Balaena mysticetus*) compared with that of other arctic marine biota as interpreted from C, N, and S isotope signatures. *Can J Zool.* 80:223–231.

Hoekstra, P.F., B.M. Braune, B. Elkin, F.A.J. Armstrong, and D.C.G. Muir. 2003a. Concentrations of selected essential and non-essential elements in arctic fox (*Alopex lagopus*) and wolverines (*Gulo gulo*) from the Canadian Arctic. *Sci Total Environ.* (in press).

Hoekstra, P.F., B.M. Braune, T.M. O'Hara, B. Elkin, K.R. Solomon, and D.C.G. Muir. 2003b. Organochlorine contaminant and stable isotope profiles in arctic fox (*Alopex lagopus*) from the Alaskan and Canadian Arctic. *Environ Pollut.* 122:423–433.

Hoekstra, P.F., B.M. Braune, C.S. Wong, M. Williamson, B. Elkin, and D.C.G. Muir. 2003c. Profile of persistent chlorinated contaminants, including selected chiral compounds, in wolverine (*Gulo gulo*) livers from the Canadian Arctic. *Chemosphere.* (in press).

Kapel, C.M.O. 1999. Diet of arctic foxes (*Alopex lagopus*) in Greenland. *Arctic.* 52:289–293.

Kassam, K. 1999. Report to Olokhaktomiut HTC (Holman, NT) by the Human and Chemical Ecology of Pollutants Project, May 1999. Arctic Institute of North America.

Kelly, B.C. and F.A.P.C. Gobas. 2001. Bioaccumulation of persistent organic pollutants in lichen-caribou-wolf food chains of Canada's Central and Western Arctic. *Environ Sci Technol.* 35:325–334.

Kelly, J.F. 2000. Stable isotopes of carbon and nitrogen in the study of avian and mammalian trophic ecology. *Can J Zool.* 78:1–27.

Magoun, A.J. 1987. Summer and winter diets of wolverines, *Gulo gulo*, in arctic Alaska. *Can Field-Nat.* 101: 392–397.

Prestrud, P., G. Norheim, T. Sivertsen, H.L. Daae. 1994. Levels of toxic and essential elements in arctic fox in Svalbard. *Polar Biol.* 14:155–159.

Retrospective Survey of Dioxins, Furans, Coplanar PCBs and Polybrominated Diphenyl Ethers in Arctic Seabird Eggs

Project leader

Birgit Braune, National Wildlife Research Centre, Canadian Wildlife Service, Environment Canada, Carleton University (Raven Road), Ottawa, ON K1A 0H3; phone: (613) 998-6694; fax: (613) 998-0458; e-mail: birgit.braune@ec.gc.ca

Project team

Bryan Wakeford, Mary Simon, and Abde Idrissi, DOE, CWS, NWRC.

Abstract

Archived arctic seabird eggs from Prince Leopold Island in the Canadian High Arctic collected as far back as the mid-1970s have been analyzed retrospectively to ascertain trends for organochlorine compounds as well as mercury, but compounds such as dioxins, furans and other halogenated organic compounds have never been analyzed in those eggs. Preliminary analysis of the data suggests that concentrations of dioxins and furans appear to have decreased in northern fulmars between 1975 and 1998 whereas in thick-billed murres, the pattern is less clear. Total non-*ortho* PCBs have decreased in both the fulmars and the murres whereas concentrations of polybrominated diphenyl ethers have increased dramatically in both those species. Stable isotope measurements, to determine if changes over time are due to contaminant changes in the environment or to changes in diet of the birds, have shown that the diets of the birds have not changed significantly over the period of the study. Therefore, the contaminant trends over time reflect changes in contaminant levels in the environment.

Key Project Messages

1. Dioxins and furans decreased in northern fulmars between 1975 and 1998 whereas in thick-billed murres, the pattern is less clear.
2. Total non-*ortho* PCBs decreased in both fulmars and murres whereas polybrominated diphenyl ethers increased in both those species.

Objectives

In order to identify contaminant temporal trends as described under Section 2.1 of the Monitoring Blueprint, it is proposed that archived arctic seabird egg contents be analyzed for polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), coplanar PCBs and polybrominated diphenyl ethers (PBDEs) in order to determine whether concentrations of those residues have changed over the period from 1975 to 1998.

Introduction

In the Canadian Arctic Contaminants Assessment Report, Muir et al. (1997) concluded that "*The lack of temporal trend information for most contaminants is perhaps the most significant knowledge gap at the present time.*" The Canadian Wildlife Service (CWS) seabird egg monitoring program was established to provide an index to contamination of the marine ecosystem and possible implications for seabird health. Eggs and livers of thick-billed murres, black-legged kittiwakes and northern fulmars collected from Prince Leopold Island in the Canadian High Arctic during 1975–1998 are archived in the CWS Specimen Bank. Analyses of livers from birds collected in 1975 and 1993 showed that concentrations of total PCDDs and PCDFs decreased while non-*ortho* PCBs increased in northern fulmars whereas in thick-billed murres, PCDDs and PCDFs increased and non-*ortho* PCBs decreased from 1975 to 1993 (Braune, 2001). The highest PBDE levels were detected in the 1993 egg and liver samples of kittiwakes, and the 1993 murre and fulmar samples also contained ng/g levels, whereas only a trace of PBDE-47 was detected in the 1975 kittiwake livers and no PBDEs were detected in the liver samples of thick-billed murres and black-legged kittiwakes from 1975 (Braune, 2001). Since the data suggest that exposure to PBDEs has increased from 1975 to 1993 in the three arctic seabird species analyzed, and that PCDDs and PCDFs have increased in thick-billed murres and non-*ortho* PCBs increased in northern fulmars (Braune, 2001), it was proposed that a detailed retrospective analysis be undertaken to examine temporal trends of PCDDs, PCDFs, non-*ortho* PCBs and PBDEs in Canadian arctic seabirds.

Activities

In 2001–2003

Archived egg homogenates of thick-billed murres (*Uria lomvia*) and northern fulmars (*Fulmarus glacialis*) collected from Prince Leopold Island in the Canadian High Arctic in 1975, 1987, 1993 and 1998 were retrieved from the CWS Specimen Bank and analyzed in pools of 5 eggs each for PCDDs, PCDFs, coplanar PCBs and PBDEs using HRGC/HRMS Selected Ion Monitoring (SIM) according to CWS Method No. MET-CHEM-PCDD-01C (Simon and Wakeford, 2000) in order to examine temporal trends of these compounds. The choice of species was based on results showing that the fulmars contained the highest levels of PCDDs and PCDFs, and the data for the murres suggests that concentrations may be increasing in that species (Braune, 2001).

Results

Preliminary analysis of the data suggests that concentrations of ΣPCDD and ΣPCDF appear to have decreased in northern fulmars between 1975 and 1998 (Figure 1) whereas in thick-billed murres, the pattern is less clear (Figure 2). Concentrations of total non-*ortho* PCBs (ΣNOPCB) have decreased in both the fulmars and the murres (Figure 3) whereas concentrations of ΣPBDE have increased dramatically in both those species (Figure 4).

Discussion and Conclusions

Dioxins (PCDDs) and Furans (PCDFs)

Polychorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) enter the environment as by-products of industrial processes. The tetra- to octa-chlorinated PCDD/Fs have lower vapour pressures and Henry's law constants than PCBs and are, therefore, not expected to undergo long-range transport to the same extent as PCBs (Mackay et al., 1992). The major sources of PCDD/Fs to air are: (i) low-temperature incineration of chlorine-containing waste such as plastics, particularly where incomplete combustion occurs, (ii) wood burning and other combustion, and (iii) metallurgical industries (de March et al., 1998). Such activities located in or near the Arctic are suspected as local sources of PCDD/Fs to the Arctic environment (de March et al., 1998). Dated sediment cores from a remote lake on Isle Royale in Lake Superior indicate that atmospheric deposition of PCDD/Fs has been declining there since the late 1970s (Baker and Hites, 2000). Concentrations of TCDD, PnCDD and HxCDD in herring gull eggs showed a decline in most colonies of the Great Lakes between 1981 and 1984 followed by no obvious temporal trends between 1984 and 1991 (Hebert et al., 1994). No significant change in concentrations of PCDD/Fs in ringed seals from the Canadian Arctic was observed during the period from 1981 to 1996 (Addison, 2000). Preliminary analysis of the data for Canadian Arctic seabirds suggests that concentrations of ΣPCDD and ΣPCDF appear to have decreased in northern fulmars between 1975 and 1998 (Figure 1) whereas in thick-billed murres, the pattern is less clear due mainly to a slight increase in concentrations in 1993 (Figure 2). Concentrations of total non-*ortho* PCBs (ΣNOPCB) have decreased in both the fulmars and the murres between 1975 and 1998 (Figure 3). Given the rather inconclusive results for the thick-billed murres, in particular, additional analyses for PCDDs and PCDFs in archived egg samples from 1976, 1977, 1988 as well as analysis of the proposed egg collections for 2003 may help to better define a trend for the murres.

Figure 1. Mean concentrations (pg/g wet weight) of total PCDDs (ΣPCCD) and total PCDFs (ΣPCDF) in eggs of northern fulmars collected from Prince Leopold Island

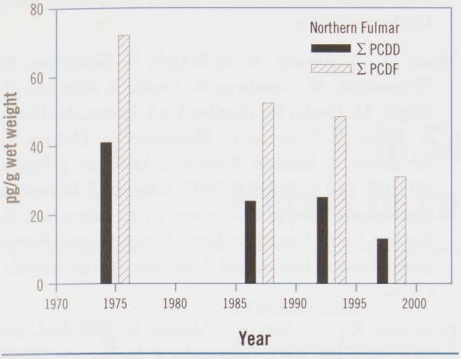


Figure 2. Mean concentrations (pg/g wet weight) of total PCDDs (ΣPCDD) and total PCDFs (ΣPCDF) in eggs of thick-billed murres collected from Prince Leopold Island

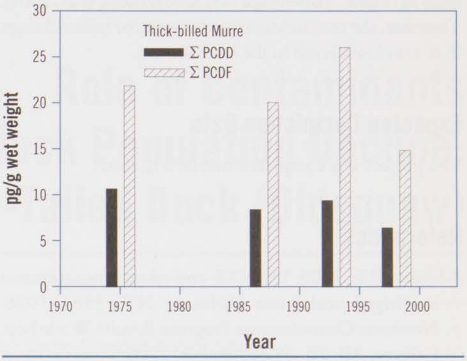


Figure 3. Mean concentrations (pg/g wet weight) of total non-*ortho* PCBs (sum of PCB-77, PCB-81, PCB-126, PCB-169) in eggs of thick-billed murres (TBMU) and northern fulmars (NOFU) collected from Prince Leopold Island

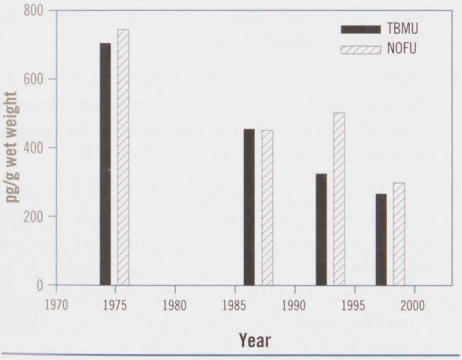
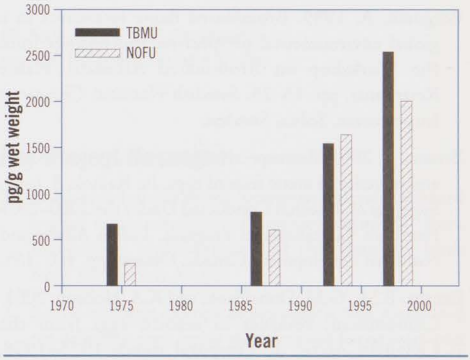


Figure 4. Mean concentrations (pg/g wet weight) of total PBDEs in eggs of thick-billed murres (TBMU) and northern fulmars (NOFU) collected from Prince Leopold Island



Polybrominated diphenyl ethers (PBDEs)

Polybrominated diphenyl ethers (PBDEs) are aromatic compounds that are structurally related to the PCBs but with bromine substitution instead of chlorine. Several brominated organic compounds are used as flame retardants in polymeric materials (Bergman, 1989). The increasing use of flame retardants in modern societies has led to increases of PBDEs in the environment (Sellström, 1996). Concerns for PBDEs are very similar to those for PCBs. Concentrations of 158.2 to 1909 ng/g lw in black guillemot eggs and 2140 ng/g lw in osprey muscle were reported by Sellström et al. (1993) for Swedish wildlife. Mean concentrations of ΣPBDE in northern fulmars and thick-billed murres from the Canadian Arctic (this study) were 17.9 and 20.3 ng/g lw, respectively, in 1998. There is evidence for increasing concentrations of PBDEs in black guillemot eggs from Sweden (Sellström et al., 1993), herring gull eggs from the Great Lakes (Norstrom et al., 2002), as well as in beluga (Stern and Ikonomou, 2000) and ringed seals (Addison 2000) from the Canadian Arctic. Recent concentrations of total PBDEs in Canadian Arctic beluga blubber range up to almost 18 ng/g lw (Stern and Ikonomou, 2000, 2001) and in Great Lakes herring gull eggs, up to 1400 ng/g ww in 2000 (Norstrom et al., 2002). Concentrations in the fulmars and murres from the Canadian Arctic were several orders of magnitude lower (maximum of 2.9 ng/g ww in thick-billed murre eggs in 1998) than

concentrations found in Great Lakes herring gull eggs in 2000. Stable-nitrogen isotope ratios ($^{15}N/^{14}N$) for archived egg content samples of fulmars and murres from the Canadian Arctic show that there have been no significant shifts in trophic relationships over time (Braune et al., 2001). Therefore, the contaminant trends over time reflect changes in contaminant levels in the environment.

Expected Completion Date

The project was completed March 31, 2003.

References

Addison, R.F. 2000. PCDD/F and related contaminants in ringed seal from Holman, NT, 1981–1996. Northern Contaminants Program Results Workshop, Calgary, AB, 26–28 September, 2000.

Baker, J.I. and R.A. Hites. 2000. Siskiwit Lake revisited: time trends of polychlorinated dibenzo-*p*-dioxin and dibenzofuran deposition at Isle Royale, Michigan. *Environ Sci Technol.* 34:2887–2891.

Bergman, A. 1989. Brominated flame retardants in a global environmental perspective. Proceedings from the Workshop on Brominated Aromatic Flame Retardants, pp. 13–23. Swedish National Chemicals Inspectorate, Solna, Sweden.

Braune, B. 2001. Retrospective survey of organochlorines and mercury in arctic seabird eggs. In: Kalhok, S. (ed.), Synopsis of Research Conducted Under the 2000–2001 Northern Contaminants Program. Indian Affairs and Northern Development Canada, Ottawa. pp. 160–165.

Braune, B.M., G.M. Donaldson, and K.A. Hobson. 2001. Contaminant residues in seabird eggs from the Canadian Arctic. I. Temporal trends 1975–1998. *Environ Pollut.* 114:39–54.

de March, B.G.E., C.A. de Wit, D.C.G. Muir, B.M. Braune, D.J. Gregor, R.J. Norstrom, M. Olsson, J.U. Skaare, and K. Stange. 1998. Chapter 6: Persistent Organic Pollutants. In: AMAP Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway. pp. 183–371.

Hebert, C.E., R.J. Norstrom, M. Simon, B.M. Braune, D.V. Weseloh, and C.R. Macdonald. 1994. Temporal trends and sources of PCDDs and PCDFs in the Great Lakes: herring gull egg monitoring, 1981–1991. *Environ Sci Technol.* 28:1268–1277.

Mackay, D., W.Y. Shiu, and K.C. Ma. 1992. Illustrated handbook of physical-chemical properties and environmental fates for organic chemicals. Volume II. Polynuclear aromatic hydrocarbons, polychlorinated dioxins, and dibenzofurans. Lewis Publishers, Chelsea, Michigan. 597 p.

Muir, D., B. Braune, B. de March, R. Norstrom, R. Wagemann, M. Gamberg, K. Poole, R. Addison, D. Bright, M. Dodd, W. Duschenko, J. Eamer, M. Evans, B. Elkin, S. Grundy, B. Hargrave, C. Hebert, R. Johnstone, K. Kidd, B. Koenig, L. Lockhart, J. Payne, J. Peddle and K. Reimer. 1997. Chapter 3. Ecosystem Uptake and Effects. In: Jensen, J., K. Adare, and R. Shearer, (eds), Canadian Arctic Contaminants Assessment Report, Indian and Northern Affairs Canada, Ottawa.

Norstrom, R.J., M. Simon, J. Moisey, B. Wakeford, and D.V. Weseloh. 2002. Geographical distribution (2000) and temporal trends (1981 to 2000) of brominated diphenyl ethers in Great Lakes herring gull eggs. *Environ Sci Technol.* 36:4783–4789.

Sellström, U. 1996. Polybrominated diphenyl ethers (PBDE) in the Swedish environment. M.S. Thesis, Dept. Environmental Chemistry, Stockholm University, Stockholm, Sweden.

Sellström, U., B. Jansson, A. Kierkegaard, C. de Wit, T. Odsjö, and M. Olsson. 1993. Polybrominated diphenyl ethers (PBDE) in biological samples from the Swedish environment. *Chemosphere.* 26:1703–1718.

Simon, M. and B.J. Wakeford. 2000. Multiresidue method for the determination of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and non-*ortho* substituted polychlorinated biphenyls in wildlife tissue by HRGC/HRMS. Technical Report Series No. 336E. Canadian Wildlife Service, Headquarters, Hull, Quebec, Canada. 41 p.

Stern, G.A. and M. Ikonomou. 2000. Temporal trends of polybrominated biphenyls and polybrominated and polychlorinated diphenyl ethers in southeast Baffin beluga. In: Kalhok, S. (ed.), Synopsis of Research Conducted Under the 1999–2000 Northern Contaminants Program. Indian Affairs and Northern Development Canada, Ottawa. pp. 227–232.

Stern, G.A. and M. Ikonomou. 2001. Temporal trends of organohalogen compounds in Canadian Arctic beluga. In: Kalhok, S. (ed.), Synopsis of Research Conducted Under the 2000–2001 Northern Contaminants Program. Indian Affairs and Northern Development Canada, Ottawa. pp. 237–242.

Role of Contaminants in Seaduck Population Decline: Metals in Long-Tailed Duck (Oldsquaw)

Project leader

Birgit Braune, National Wildlife Research Centre, Canadian Wildlife Service, Environment Canada, Carleton University (Raven Road), Ottawa, ON K1A 0H3; phone: (613) 998-6694; fax: (613) 998-0458; e-mail: birgit.braune@ec.gc.ca

Project team

Bryan Wakeford, NWRC, CWS, Ottawa, ON; Keith Hobson, CWS, Saskatoon, SK; Malone Associates, contractor, Ottawa, ON; Indian and Northern Affairs NCP, Hull, PQ.

Abstract

Western populations of long-tailed duck (oldsquaw) are in decline and although populations appear stable in the east, long-tailed duck is considered to be a *Species of Continental Conservation Concern*. A screening of trace elements in livers of adult males found detectable concentrations of arsenic, cadmium, iron, manganese, molybdenum and zinc to be higher in western arctic birds than eastern arctic birds. This is similar to the pattern previously found for cadmium in kidney and selenium in liver as well as cadmium and selenium in breast muscle for these birds. Some of the measured concentrations of cadmium, iron and manganese could be considered high based on threshold values cited in the literature. Stable-nitrogen isotope ratios suggest that males feed on different prey items than females for at least part of the year, and stable-carbon isotope ratios suggest that many of the birds breeding in the western Arctic overwinter in the Great Lakes whereas many of the birds breeding in the eastern Arctic overwinter along the Atlantic coast.

Key Project Messages

1. Long-tailed ducks from the western Arctic contained higher concentrations of arsenic, cadmium, iron, manganese, molybdenum and zinc than did birds from the eastern Arctic.
2. Stable-nitrogen isotope ratios suggest that males feed on different prey items than females for at least part of the year.
3. Stable-carbon isotope ratios suggest that many of the birds breeding in the western Arctic overwinter in the Great Lakes whereas many of the birds breeding in the eastern Arctic overwinter along the Atlantic coast.

Objectives

In order to determine the role of metals in declining populations of long-tailed duck, it is proposed that:

1. Archived samples of long-tailed duck collected from their Canadian arctic breeding grounds be analyzed for Hg, Se and Cu (in liver), Cd (in kidney), Pb (in

wing bone), and selected samples be screened for a wider range of metals (in liver).

2. Archived samples of oldsquaw wing bone be analyzed for stable isotopes ($^{13}C/^{12}C$; $^{15}N/^{14}N$, and $^{34}S/^{32}S$) and strontium (Sr) to discriminate whether birds from certain geographical areas of the Arctic are overwintering in freshwater (i.e. Great Lakes) or marine environments.

Introduction

North American populations of long-tailed duck or oldsquaw (*Clangula hyemalis*) are declining in the west, but are apparently stable in the east (CWS et al., 1997). Nevertheless, long-tailed ducks are considered to be a *Species of Continental Conservation Concern*. This species nests in greater numbers in the high Arctic than any other duck (Bellrose, 1980). Long-tailed ducks nesting in the eastern Canadian Arctic likely winter along the Atlantic coast whereas western Arctic birds winter in the Bering Sea and along the Pacific coast of Alaska and British Columbia (Bellrose, 1980). Considerable numbers also winter on the Great Lakes. It is unknown where the dividing line occurs between the two breeding populations.

Measurements of naturally occurring stable isotopes in foodwebs can be used to delineate relative inputs from freshwater and marine biomes (reviewed by Hobson et al., 1997). This is based on the fact that stable isotopes of carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$), sulfur ($\delta^{34}S$) and hydrogen (δD) are typically enriched in marine vs terrestrial/freshwater systems and these isotopic signatures are passed on to consumers. Upon arrival on the breeding grounds, metabolically active tissues of birds that wintered in freshwater environments can be distinguished isotopically from those that wintered in marine areas. Stable isotope values in bird tissues are in dynamic equilibrium with local foodwebs and so it is necessary to choose a tissue with slow turnover rate to delineate between freshwater and marine wintering ducks. Bone collagen was chosen because it has a turnover rate slow enough for isotope measurements to represent lifetime average values (Hobson and Sealy, 1991).

Metal residue data for breast muscle of long-tailed ducks collected from across the Canadian Arctic during 1991–94 suggest that western Arctic populations generally have higher levels of Cd and Se than eastern populations (Braune et al., 1999). Although it is not known whether or not the birds are more exposed to metal contamination on the arctic breeding grounds or on their overwintering grounds, analysis of metal levels in target organs would generate the data necessary to compare with known critical thresholds published in the literature. The stable isotope measurements should discriminate those birds which overwinter on the Great Lakes, a known contaminated area. As well, strontium measurements should help to corroborate stable isotope findings. It should then be possible to determine if those birds also contain higher tissue residue levels than the others. The connection between risk of exposure and overwintering area can then be investigated, if such a link exists. Alternatively, if no association between metal levels and overwintering area can be established, the source of contamination may, in fact, be in the Arctic.

Activities

In 2001–2002

Bone samples from 41 adult long-tailed ducks from the eastern Arctic (east of 95°W) and 38 from the western Arctic were analyzed for stable isotopes of carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$) and sulfur ($\delta^{34}S$) to discriminate between those individuals wintering in freshwater vs marine environments. Additionally, strontium (Sr) was analyzed in bone samples of 44 adult long-tailed ducks from the eastern Arctic and 41 from the western Arctic. Based on previous results (Braune, 2001), livers of 10 adult males (5 from the eastern Arctic, 5 from the western Arctic) with elevated levels of metals were analyzed using ICP-MS to screen for other elements.

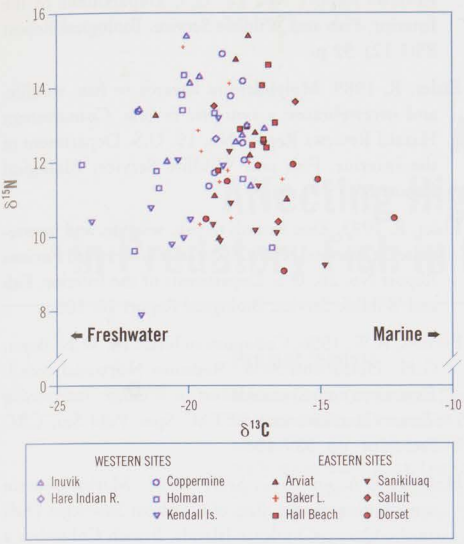
Results

Of the 24 elements analyzed by ICP-MS in the livers of the 10 adult males, residue levels were below detection limits for Ag, Al, An, B, Ba, Be, Co, Cr, Ni, Pb, Sn, Sr, Th, U and V. Detectable residue concentrations were found for arsenic (As), cadmium (Cd), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), molybdenum (Mo), selenium (Se) and zinc (Zn). Detection limits ranged from 0.02 to 2.5 mg/kg wet weight (ww), depending on the element. Residue concentrations for Hg, Se and Cu in livers of long-tailed ducks have been previously reported

Table 1. Mean metal concentrations (mg/kg wet wt) in livers of adult male long-tailed ducks from the Canadian Arctic

	# Birds	As	Cd	Fe	Mn	Mo	Zn
Western Arctic	5	0.95	10.6	1242	5.6	1	46
Eastern Arctic	5	0.40	4.6	792	4.2	1	33

Figure 1. $\delta^{15}N$ vs $\delta^{13}C$ in bone of long-tailed ducks collected from the Canadian Arctic, 1991–1994



(Braune, 2001) and so results for this subset of those samples will not be reported here. Concentrations of As, Cd, Fe, Mn, Mo and Zn were higher in birds from the western Arctic than from the eastern Arctic (Table 1).

Of the three stable isotopes ($\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$) measured in bone, only $\delta^{13}C$ varied significantly with collection location and longitude (Figure 1) whereas $\delta^{15}N$ varied significantly among collection locations and between sexes with higher values found in the males. Strontium and $\delta^{34}S$ values in bone did not vary significantly with either sex or location.

Discussion and Conclusions

In 2000–2001, liver, kidney and bone samples for 101 adult long-tailed ducks from the Canadian Arctic were retrieved from the CWS Specimen Bank and individually analyzed for Hg, Se and Cu in liver, Cd in kidney, and Pb in bone. Those results were reported in Braune (2001). Of the detectable elements measured in the subset of long-tailed duck livers from adult males, concentrations of As, Cd, Fe, Mn, Mo and Zn were higher in birds from the western Arctic than from the eastern Arctic (Table 1). This is similar to the pattern previously reported for Cd in kidney and Se in liver (Braune, 2001) as well as Cd and Se in breast muscle (Braune et al., 1999) of long-tailed duck.

Of the elements detected in measurable quantities in livers of long-tailed duck, Fe, Mn, Mo and Zn are all essential elements, and there is a growing body of evidence that suggests that As may be nutritionally essential or beneficial, as well (Eisler, 1988). Arsenic concentrations are usually low (<1 mg/kg fresh weight) in most living organisms (Eisler, 1988). Stanley et al. (1994) found liver concentrations of 6.6 mg/kg dry weight (~2.2 mg/kg ww) of As in mallards were associated with decreased weight gain, decreased liver weight and delayed egg-laying, and Puls (1988) considered 5–10 mg/kg ww of As in the liver to be toxic to poultry. Most of the long-tailed ducks in this study contained liver concentrations of As that were below the detection limit (<0.5 mg/kg ww), but a liver concentration of 3 mg/kg ww was measured in one bird from Kendall Island. Liver concentrations of 300–2000 mg/kg ww of Fe are considered to be high, and liver Mn concentrations of >9 mg/kg ww are considered to be toxic in poultry (Puls, 1988). Iron concentrations ranged from 520 to 1700 mg/kg ww in long-tailed ducks and the Mn concentrations ranged from 4 to 7 mg/kg ww. Although tissue residues are not yet reliable indicators of Zn contamination, Puls (1988) considers liver concentrations of 200–700 mg/kg ww to be toxic in poultry, and Eisler (1993) suggests that Zn poisoning usually occurs in birds when liver concentrations exceed 2100 mg/kg dry weight (~700 mg/kg ww). Zinc concentrations found in the livers of long-tailed duck were an order of magnitude lower than these threshold levels. Although data on Mo effects on avian wildlife are limited, Eisler (1989) suggests that birds are relatively resistant to Mo whereas Puls (1988) considers 6–10 mg/kg ww of Mo in the liver to be toxic in chickens. Low levels (1 mg/kg ww) of Mo were measured in livers of the long-tailed ducks. Based on a review of the literature, Furness (1996) suggests that about 40 mg/kg ww should be considered a tentative threshold for Cd poisoning in birds whereas Puls (1988) suggests that concentrations of 25–208 mg/kg ww in liver of waterfowl are considered toxic. Although most of the Cd levels measured in livers of long-tailed ducks ranged from 1 to 8 mg/kg ww, a single bird from Qurluqtuuq (Coppermine) contained a liver Cd concentration of 38 mg/kg ww.

There was a large range in the stable-nitrogen isotope ratios (Figure 1) which differed significantly between males and females suggesting that the males feed on different prey items than females for at least part of the year. Given that the $\delta^{13}C$ values varied significantly with collection location and longitude (Figure 1), and that ^{13}C is more enriched in marine environments, the $\delta^{13}C$ data suggest that birds from the western Arctic have a stronger

freshwater signal compared with birds from the eastern Arctic which have a stronger marine signal. The marine overwintering areas for North American long-tailed ducks include both the Atlantic and Pacific coasts whereas the only major freshwater overwintering region is in the Great Lakes (Bellrose, 1980). This would suggest that many of the birds breeding in the western Arctic overwinter in the Great Lakes whereas many of the birds breeding in the eastern Arctic overwinter along the Atlantic coast. Analyses of spatial relationships within the data are still in progress.

Expected Completion Date

The project should be completed by December 31, 2002.

References

Bellrose, F.C. 1980. *Ducks, geese and swans of North America.* Stackpole Books, Harrisburg, PA. pp. 385–393.

Braune, B. 2001. Role of contaminants in seaduck population decline: metals in oldsquaw. In: Kalhok, S. (ed.), Synopsis of Research Conducted Under the 2000–2001 Northern Contaminants Program. Indian Affairs and Northern Development Canada, Ottawa. pp. 166–168.

Braune, B.M., B. Malone, N.M. Burgess, J.E. Elliott, N. Garrity, J. Hawkings, J. Hines, H. Marshall, W.K. Marshall, J. Rodrigue, B. Wakeford, M. Wayland, D.V. Weseloh, and P.E. Whitehead. 1999. Chemical Residues in Gamebirds Harvested in Canada, 1987–95. Tech. Rep. Ser. No. 326. Ottawa: Canadian Wildlife Service.

Canadian Wildlife Service, U.S. Fish and Wildlife Service and U.S. Geological Survey. 1997. Conservation Issues for North American Sea Ducks: A Concept Paper for a Sea Duck Joint Venture under the North American Waterfowl Management Plan. 36 p.

Eisler, R. 1988. Arsenic hazards to fish, wildlife, and invertebrates: a synoptic review. Contaminant Hazard Reviews Report No. 12. U.S. Department of the Interior, Fish and Wildlife Service, Biological Report 85(1.12). 92 p.

Eisler, R. 1989. Molybdenum hazards to fish, wildlife, and invertebrates: a synoptic review. Contaminant Hazard Reviews Report No. 19. U.S. Department of the Interior, Fish and Wildlife Service, Biological Report 85(1.19). 61 p.

Eisler, R. 1993. Zinc hazards to fish, wildlife, and invertebrates: a synoptic review. Contaminant Hazard Reviews Report No. 26. U.S. Department of the Interior, Fish and Wildlife Service, Biological Report 10. 106 p.

Furness, R.W. 1996. Cadmium in birds. In: W.N. Beyer, G.H. Heinz and A.W. Redmon-Norwood (eds.). *Environmental Contaminants in Wildlife: Interpreting Tissue Concentrations*, SETAC Spec Publ Ser, CRC Press, Inc. pp. 389-404.

Hobson, K.A. and S.G. Sealy. 1991. Marine protein contributions to the diets of Northern Saw-whet Owls on the Queen Charlotte Islands, British Columbia: a stable isotope approach. *Auk.* 108:437-440.

Hobson, K.A., K.D. Hughes, and P.J. Ewins. 1997. Using stable-isotope analysis to identify endogenous and exogenous sources of nutrients in eggs of migratory birds: applications to Great Lakes contaminants research. *Auk.* 114:467-478.

Puls, R. 1988. Mineral Levels in Animal Health. Diagnostic Data. Sherpa International Press, Clearbrook, BC. 240 p.

Stanley, T.R., J.W. Spann, G.J. Smith, and R. Roscoe. 1994. Main and interactive effects of arsenic and selenium on mallard reproduction and duckling growth and survival. *Arch Environ Contam Toxicol.* 26:444–451.

An Investigation of Factors Affecting High Mercury Concentrations in Predatory Fish in the Mackenzie River Basin

Project leaders

Marlene Evans, Environment Canada, National Water Research Institute (NWRI), 11 Innovation Boulevard, Saskatoon, SK S7N 3H5; phone: (306) 975-5310; fax: (306) 975-5143; e-mail: marlene.evans@ec.gc.ca; Lyle Lockhart, Department of Fisheries and Oceans (DFO), Freshwater Institute, 501 University Crescent, Winnipeg, MB R3T 2N6; phone: (204) 983-7113; fax: (204) 984-2404; e-mail: lockhartl@dfo-mpo.gc.ca; Gary Stern, DFO, Freshwater Institute, 501 University Crescent, Winnipeg, MB R3T 2N6; phone (204) 984-6761; fax: (204) 984-2404; e-mail: sterng@dfo-mpo.gc.ca

Project team

George Low, DFO, Hay River, NT; Joanne Delaronde, Karen Kidd and Ross Tallman, DFO, Freshwater Institute, Winnipeg, MB; Derek Muir and Tog Jackson, Environment Canada, NWRI, Burlington, ON; Mike Whittle, DFO, Burlington, ON.

Abstract

Predatory fish in many lakes in the Mackenzie River Basin have high concentrations of mercury in their flesh. In 77–95% of surveyed lakes, predatory fish have mean mercury levels exceeding the 0.2 $\mu g \cdot g^{-1}$ guideline established for frequent consumers of fish. With Northern Contaminants Program funds, we have studied 9 lakes in the Fort Simpson area. Most are small with tea-coloured waters, although one lake (Cli Lake) has clear waters and another (Willow Lake) is relatively large. High mercury levels in predatory fish in these 9 lakes appear to be due to the relatively old age of these fish, the small lake sizes, and the tea-colored (high dissolved organic carbon) waters. We are further testing our fish age, lake area, and dissolved organic carbon hypotheses through the examination of larger data sets for Mackenzie River Basin lakes. Increased harvesting may lower average mercury levels in fish although additional research is required before such a strategy should be implemented. Sediment coring studies indicate that mercury fluxes have increased to lake sediments in recent years. Monitoring studies also have shown that mercury levels in burbot at Fort Good Hope are increasing. Additional research is required to: (1) develop predictive models describing how limnological variables affect mercury levels in fish; (2) investigate factors affecting time trends; (3) quantify mercury pathways in aquatic ecosystems; and (4) assess the impacts of global warming on mercury pathways.

Key Project Messages

1. Some 88–91% of lakes surveyed in the Mackenzie River Basin have mean mercury levels in predatory fish which exceed the 0.2 $\mu g \cdot g^{-1}$ guideline for frequent consumers of fish. Furthermore, some 25–45% of lakes surveyed have mean mercury levels in predatory fish which exceed the 0.5 $\mu g \cdot g^{-1}$ guideline for the commercial sale of fish. Consumption advisories have been issued for many of these lakes.
2. High mercury levels are associated with larger and older predatory fish, often more than 10 years in age. Increased fishing pressure may reduce average fish age and mercury levels in a lake, but this needs to be confirmed with further research. Excess fishing pressure could harm the fish populations or even increase mercury levels if fish diets change. Research is required to investigate this possible remedial action.
3. High mercury levels seem to be prevalent in small, tea-colored lakes, especially for lake trout populations. Additional studies are required to determine how lake features and watershed size effects mercury pathways into a lake and then through the food web.
4. Sediment coring studies suggest that mercury fluxes to lake sediments have been increasing since the turn of the century. Other studies show that mercury levels are increasing in burbot at Fort Good Hope. Research is needed to understand how these mercury time trends and how other perturbations such as global warming may affect mercury levels in predatory fish.

Objectives

1. Conduct limnological studies to determine why predatory fish inhabiting some lakes in the Mackenzie River Basin have elevated mercury levels while fish in other, apparently similar lakes, have lower mercury levels.
2. Investigate the role of food web structure in the biomagnification of mercury by predatory fish.
3. Investigate whether it is possible to develop lake-specific remedial actions to reduce mercury concentrations in harvested fish from high-mercury lakes.

Introduction

During the mid 1990s, evidence began to emerge that predatory fish in many of Canada's northern lakes had relatively high mercury levels in their flesh (Lockhart, 1999). In many instances, mercury levels exceeded both the 0.2 $\mu g \cdot g^{-1}$ guideline for frequent consumers of fish and the 0.5 $\mu g \cdot g^{-1}$ guideline for the commercial sale of fish. Consumption advisories were issued for many of these lakes. Mercury is subject to strong biomagnification in the food web, including humans, with the concomitant potential to adversely affect human health. Accordingly, mercury was a priority research area under the second Northern Contaminants Program (NCP). Two studies were conducted under this program to investigate mercury levels in freshwater fish in northern lakes. Lockhart and Evans (1999) continued to assess mercury levels in fish in a large number of Mackenzie River Basin (MRB) lakes, while Evans and Lockhart (1999) began to investigate fish biology and the limnological features of a subset of study lakes and aspects of fish biology which affected mercury levels. Highlights of these studies appear below.

During the mid 1990s to early 2000s, the Department of Fisheries and Oceans (DFO) played a major role in the management of fish populations in the north by performing stock assessment studies in the Deh Cho and Sahtu Settlement Areas. A total of 12 lakes in the Deh Cho and 13 lakes in the Sahtu were investigated during 1994–2000. Fish length, weight and age were determined as part of these assessments (Stewart et al., 2003a, 2003b). With NCP support, these fish were also analyzed for mercury and tissues were archived for later analyses (Lockhart and Evans, 1999). In 1998, we began a limnological study on lakes in the Fort Simpson area investigating the causal factors for elevated mercury levels in predatory fish (Evans and Lockhart, 1999). The study has since broadened to investigate why mercury levels are higher in some lakes than others and increasingly larger data sets have been incorporated into the study design.

It is not known what causes mercury levels to be high in predatory fish in some Northwest Territories (NWT) lakes. Because these lakes are in pristine environments, anthropogenic activities such as mining, pulp and paper mill operation, flooding with reservoir creation, and clear cutting cannot be the causal factors. Most lakes are located on glacial tills, and thus are not acidic as are many high mercury lakes in other pristine environments. Other natural factors such as lake size, watershed size, lake depth, and fish biology must be the primary factors affecting these levels (Cope et al., 1990; Bodaly et al., 1993; Shilts and Coker, 1995; Krabbenhoft et al., 1998).

Results of sediment coring studies in lakes such as Colville Lake and Great Bear Lake in the NWT, and Lake Laberge in the Yukon suggest that mercury fluxes to lake sediments are increasing (Lockhart et al., 1998; Stern et al., 2001a). We have observed a similar increase in mercury fluxes to Cli Lake, one of our NCP mercury study lakes (Evans and

Lockhart, 2000). Mercury levels in burbot collected at Fort Good Hope are also showing a trend of increasing concentrations (Stern et al., 2001b). It is possible that many lakes that currently support predatory fish with moderately high (0.2–0.5 $\mu g \cdot g^{-1}$) mercury concentrations may be impacted by these increased atmospheric mercury inputs and reach higher ($> 0.5\ \mu g \cdot g^{-1}$) mercury levels in their flesh. Therefore, it is important that we understand which lakes are most vulnerable to becoming high mercury lakes in the future.

Activities

In 2001–2003

As noted in our earlier studies, we initially hypothesized that elevated mercury levels in Cli Lake lake trout were related to high background mercury levels, possibly associated with fault lines which underlay the lake (Evans and Lockhart, 1999). The results of our first two field seasons did not support this hypothesis (Evans and Lockhart, 1999, 2000, 2001; Lockhart et al., 2001). Since then, we have focussed our efforts on investigating biological factors such as fish age and trophic feeding (Evans and Lockhart, 2001) and limnological factors such as lake depth, lake size, watershed size, water chemistry (pH, dissolved organic carbon, phosphorus, chlorophyll, etc.) and mercury and methyl mercury levels in water, sediment, invertebrates, and forage fish.

With NCP funding, we focussed our limnological studies on lakes in the Fort Simpson area, which had previously been included in the DFO stock assessment studies. These lakes included Cli Lake, Little Doctor Lake, Willow Lake, Sibbeston Lake, Ekali Lake, McEwan Lake, Tsetso Lake, Reade Lake, Deep Lake, Sanguez Lake, and McGill Lake (Table 1). In addition to our limnological studies, northern pike and walleye were collected from Cli Lake, Little Doctor Lake, Sibbeston Lake and Willow Lake to supplement the stock assessment collections.

With only three lake trout lakes (Cli Lake, Little Doctor Lake, and Willow Lake) in the Fort Simpson area, it is difficult to assess broad scale factors affecting the wide variation in mercury levels in MRB lake trout populations. Accordingly, we examined the larger lake trout data sets collected during the DFO stock assessment studies (Stewart et al., 2003a, 2003b) to investigate relationships between mercury levels, fish age, and lake size. We included other lakes in these analyses including Great Slave Lake (supported by NCP; Evans and Muir, 2001) and Trout Lake (Swyripa et al., 1993). In addition, we obtained funding which allowed us to expand our limnological sampling to lakes further north of the Fort Simpson area. With Northern Ecosystem Initiative (NEI) and Sahtu Renewable Resources Board (SRRB) funds we sampled 5 lakes in the Norman Wells and Colville Lake area: Great Bear Lake, Lac Ste. Therese, Kelly Lake, Mirror Lake, and Colville Lake. Thus, we now have limnological data for 9 of the 16 lake trout lakes sampled in the original DFO stock assessment studies. Further south, with Toxic Substance Research Initiative (TSRI) funds (Muir et al., 2001), we investigated mercury and organochlorine levels in lake trout populations in more than 20 lakes running from northern Alberta and Saskatchewan to Ontario, the Finger Lakes and into Labrador. This expanded data set allows us to extend our

Table 1. Mean ± standard deviation mercury concentrations (µg/g wet wt) in fish from lakes which were part of our limnological studies. Values in bold indicate that a consumption advisory has been issued

	Species		
Lake	Lake Trout	Northern Pike	Walleye
Cli Lake	**0.787 ± 0.749**	0.235 ± 0.133	–
Deep Lake	–	0.670 ± 0.196	1.105 ± 0.352
Ekali Lake	–	**0.300 ± 0.109**	**0.256 ± 0.063**
Little Doctor Lake	0.393 ± 0.081	**0.772 ± 0.367**	**0.753 ± 0.290**
McEwan Lake	–	0.331 ± 0.238	0.356 ± 0.158
McGill Lake	–	0.713 ± 0.365	1.125 ± 0.378
Reade Lake	–	0.430 ± 0.203	–
Sanguez Lake	–	**0.703 ± 0.179**	**0.539 ± 0.118**
Sibbeston Lake	–	0.165 ± 0.053	0.327 ± 0.120
Tsetso Lake	–	0.393 ± 0.155	0.485 ± 0.126
Willow Lake	0.380 ± 0.079	0.283 ± 0.147	–

spatial gradient in the examination of mercury levels in lake trout populations to much of northern Canada.

We are also examining the broad scale patterns of factors affecting elevated mercury levels in northern pike and walleye. We have investigated northern pike and walleye populations in 8 lakes in the Fort Simpson area. However, with NEI, SRRB and NCP-Great Slave Lake funding, we have increased our limnological data sets to include 14 of the 24 northern pike lakes, and 10 of the 12 walleye lakes originally sampled in the DFO stock assessment studies.

Results

Mercury levels as a function of species, geographic area, and guidelines

A total of 14 lakes have been sampled in the Deh Cho for mercury levels in fish. Only 14% of northern pike and 11% of walleye lake populations have mean mercury levels below 0.2 $\mu g \cdot g^{-1}$ (Fig. 1). None of the lake trout lake populations have mean mercury levels below 0.2 $\mu g \cdot g^{-1}$. Moreover, 20% of lake trout, 36% of northern pike, and 44% of walleye lake populations have mean mercury levels above 0.5 $\mu g \cdot g^{-1}$. In the Sahtu, a total of 15 lakes have been sampled. Only 18% of lake trout and 10% of northern pike lake populations have mean mercury levels below 0.2 $\mu g \cdot g^{-1}$. None of the walleye lake populations have mean mercury levels below 0.2 $\mu g \cdot g^{-1}$. Moreover, 27% of lake trout, 40% of northern pike, and 50% of walleye lake populations have mean mercury levels above 0.5 $\mu g \cdot g^{-1}$.

Lake trout length, age, and mercury relationships: Finger Lakes to the Mackenzie River Basin

A major factor affecting elevated mercury levels in lake trout is age. As fish reach ca. 10 years of age, mercury levels begin to approach 0.5 µg·g-1 (Evans and Lockhart, 2001). Furthermore, there is strong evidence that lake trout populations in the NWT are older on average than lake trout populations living further south (Fig. 2). Lake trout populations show no obvious latitudinal gradient in mean length.

Mercury concentrations in lake trout were highest in the NWT both in terms of population means and in length-standardized (600 mm) populations (Fig. 3). Lower mercury levels were observed in lake trout populations in northern Alberta and Saskatchewan; levels increased towards the Finger Lakes region.

Mercury and lake size relationships: Northwest Territories

Within the NWT, mercury levels appear to be higher in small lakes than larger lakes. To investigate this, mercury concentrations in length-adjusted fish were correlated against lake area (Fig. 4). This correlation was particularly strong for lake trout, a pelagic fish, and whitefish. Lower correlations were observed for northern pike and walleye, species that are more littoral in habitat than lake trout and whitefish.

Discussion and Conclusions

Elevated mercury levels in predatory fish in the NWT is a subject of much community concern. Approximately 27% of lake trout lakes, 38% of northern pike lakes, and

Figure 1. Frequency of lakes with mean mercury concentrations in fish above the guideline for frequent consumers of fish (0.2 ppm) and the guideline for the commercial sale of fish (0.5 ppm)

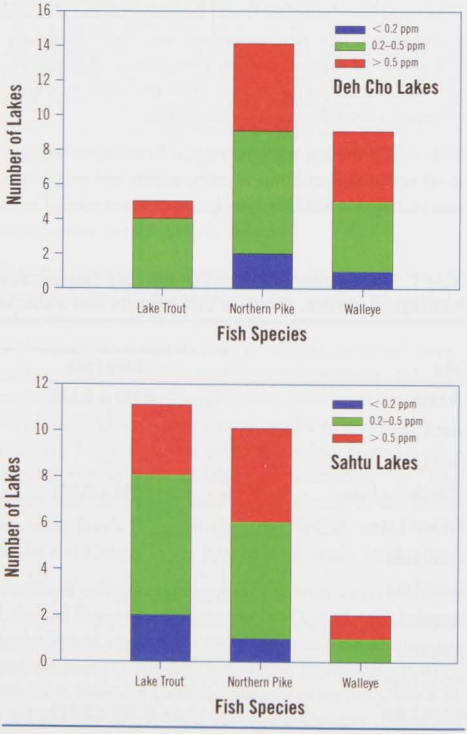
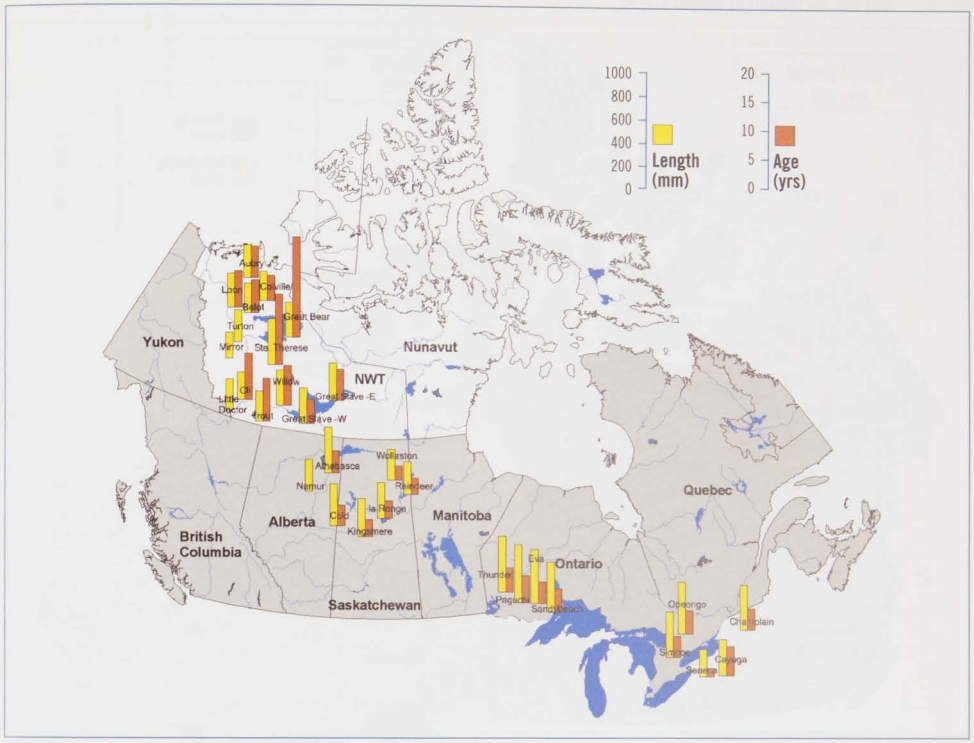


Figure 2. Mean length and age of lake trout caught in various lakes across Canada and the northeastern United States



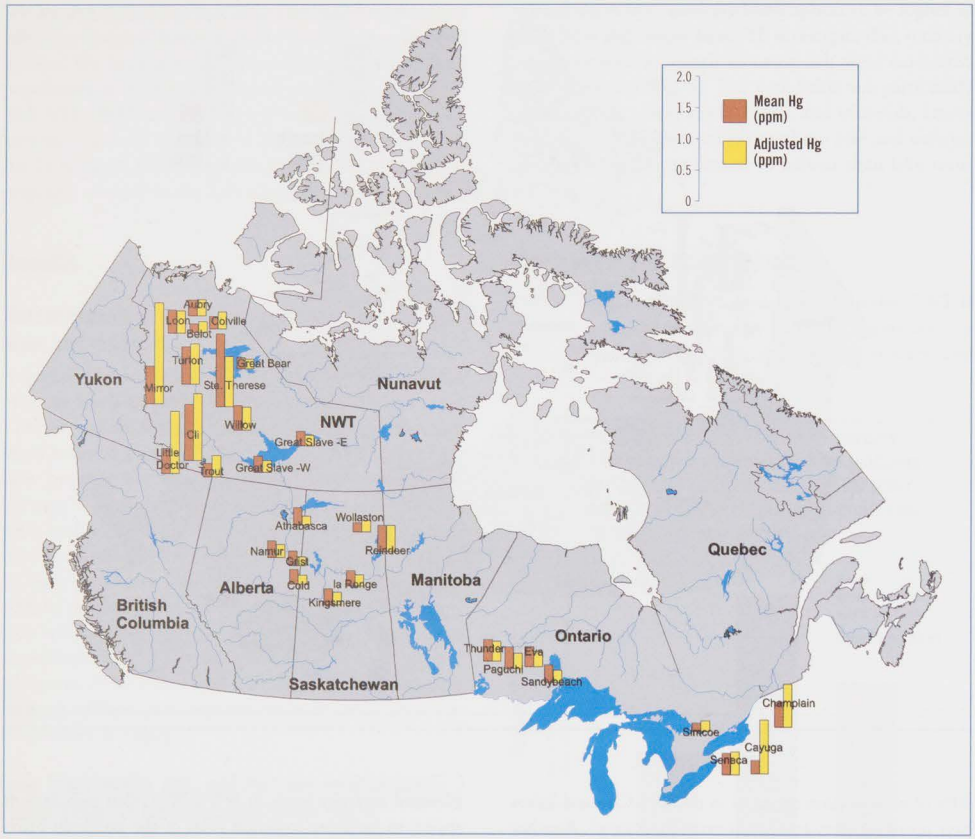
40% of walleye lakes surveyed in the Deh Cho and Sahtu have mean mercury levels that exceed 0.5 $\mu g \cdot g^{-1}$. Another 60% of lake trout lakes, 50% of northern pike lakes, and 42% of walleye lakes have mean mercury levels between 0.2 $\mu g \cdot g^{-1}$ and 0.5 $\mu g \cdot g^{-1}$. Consumption advisories have been issued for 16 of these 29 lakes with more anticipated as health assessments are completed and previous assessments revisited.

There are hundreds of lakes in the NWT. Clearly, it is not feasible to conduct stock assessment and mercury studies on all of these lakes. However, by identifying the factors affecting the high lake-to-lake variability in mercury levels, we will be able to identify which lakes are most likely to have predatory fish with high mercury concentrations. This is of special importance given community concerns regarding consumption advisories on lakes that have traditional and continued use.

Elevated mercury levels in NWT lake trout populations appear to be more common than in the northern provinces. We believe that this is due to a combination of factors including fish age, growth rates, and lake size. As previously noted, fish in the Fort Simpson area appear to approach mercury concentrations of 0.5 $\mu g \cdot g^{-1}$ as they reach 10 years of age. Harvesting rate is probably the major factor affecting the age structure of fish populations with mean age becoming younger as fishing pressures intensify and larger, older fish are removed.

For lake trout populations, the relationship between mean mercury concentration and latitude can be represented by a "U-shape" (Fig. 5). This is believed to be due to two factors: fish age (and fishing rate) and proximity to anthropogenic sources. Beginning in the south, mercury levels are relatively high in the Finger Lakes because of their close proximity to anthropogenic sources of mercury. Lake trout populations are young and fast growing: length

Figure 3. Mean and length-adjusted (600 mm) mercury concentrations in lake trout caught in various lakes across Canada and the northeastern United States



adjusted mercury levels are as high as in the NT. Mercury levels decrease northward into areas such as northern Alberta and Saskatchewan as distance from anthropogenic sources increases and fishing pressures remain significant. Mercury levels then increase moving further north, despite increasing distances from anthropogenic sources, because fishing pressures are less and lake trout populations are relatively old. These older fish have accumulated mercury over a longer time period than in the northern provinces. Levels remain high on a length-adjusted basis because a 600-mm lake trout in the NT is ca. 10–15 yr old versus 5–7 yr old in the Finger Lakes region.

With fish age, one of the primary factors affecting elevated mercury levels in predatory fish in the NWT, an increase in fishing pressure in lakes in the NWT to levels experienced in the northern provinces should result in a reduction in this limb of the curve (Fig. 5). Increased fishing pressure could lower the mean age of fish in a lake and improve growth rates as competition is reduced. Increased fishing pressure could occur with increased ecotourism in the area or through a deliberate harvesting (Verta, 1990). However, further research is required to confirm this and to determine the optimal level of fishing that will remove older fish, improve fish growth rates, yet still protect the fish population from over exploitation.

Mercury levels in fish are affected by other variables including lake size, watershed size, dissolved organic carbon (DOC), pH, trophic feeding, etc. (Miskimmen et al., 1992; Lange et al., 1993; St. Louis et al., 1994; Watras et al., 1995; Munn and Short, 1997). In general, we have

Figure 4. Length-adjusted mean mercury concentrations in four fish species as a function of lake area for lakes in the Mackenzie River Basin

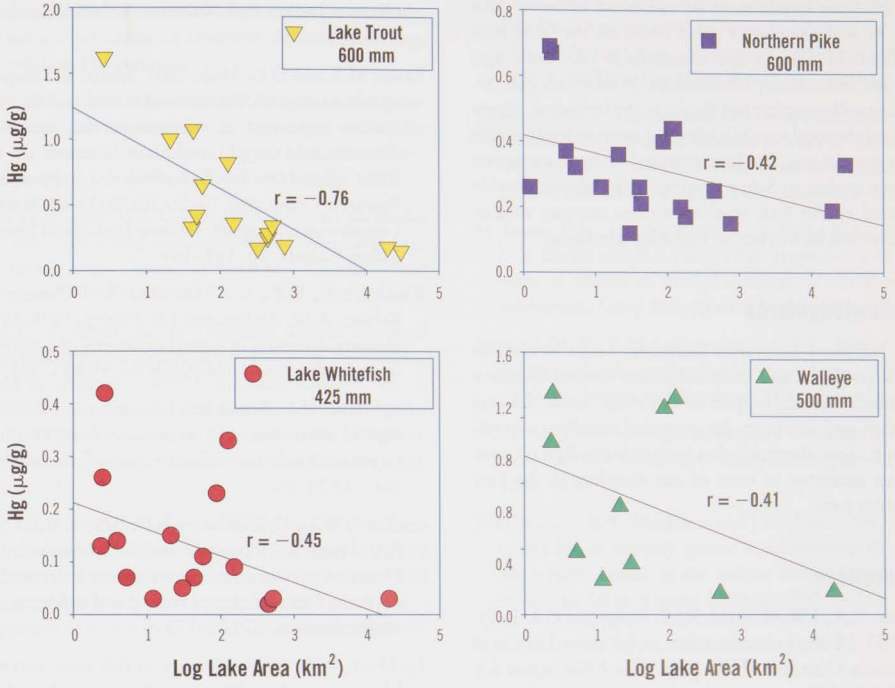
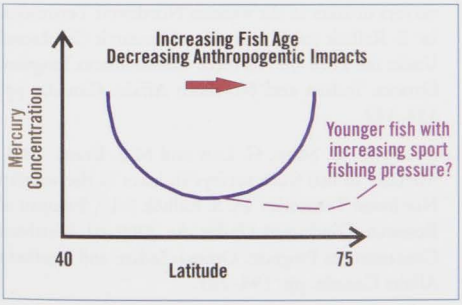


Figure 5. Mercury concentration as a function of fish age and latitude



found a negative relationship between lake size and length-adjusted (600 mm) mercury levels in fish. As lake area decreases, DOC, mercury, and methyl mercury concentrations increase. Small lakes, with their relatively more extensive littoral zone and wetland areas, may be greater sources of recently mobilized mercury and methyl mercury than larger lakes. Other analyses including mercury and methyl mercury concentrations in sediments, invertebrates and forage fish, and stable isotope analyses are being used to further elucidate relationships.

Various presentations have been given over the past years. In addition to the Northern Contaminants Program National Symposium, presentations based on the NCP, NEI, SRRB, and TSRI mercury studies were given in February 2003 for Great Slave Lake Deh Cho communities and to the SRRB. Scientific presentations have been given at the Society of Environmental Toxicology and Chemistry (SETAC) 2000, 2001, and 2002 meetings and the 2002 International Association for Great Lakes Research (IAGLR) annual conference.

Expected Completion Date

This study is ongoing with additional data to be collected and scientific questions to be addressed. However, this year we will complete a paper based on the latitudinal gradients in mercury concentrations in lake trout, age, lake size and mercury relationships. In addition, a M. Sc. student will complete her thesis on the biological, physical, and chemical variables affecting mercury levels in lake trout populations. We have provided preliminary reports on our studies to Sahtu communities and will provide updated and/or final reports on these mercury studies. Reports will be written on a lake-by-lake basis.

Acknowledgments

The Northern Ecosystem Initiative, Sahtu Renewable Resources Board, and Toxic Substances Research Initiative provided additional support for this study. South Nahanni Airways and Simpson Air provided excellent aircraft support. Special appreciation is extended to Ricky Tsetso for his assistance in most of our sampling in the Fort Simpson area.

References

Bodaly, R.A., J.W.M. Rudd, R.J.P. Fudge and C.A. Kelly. 1993. Mercury concentrations in fish related to size of remote Canadian Shield lakes. *Can J Fish Aquat Sci.* 50:980–987.

Cope, W.G., J.G. Weiner and R.G. Rada. 1990. Mercury accumulation in yellow perch in Wisconsin seepage lakes: relation to lake characteristics. *Environ Toxicol Chem.* 9:931–940.

Evans, M.S. and L. Lockhart. 1999. An investigation of the factors affecting high mercury concentrations in predatory fish in the Mackenzie River Basin. In: S. Kalhok (ed.), Synopsis of Research Conducted Under the 1998/99 Northern Contaminants Program. Ottawa: Indian and Northern Affairs Canada. pp. 103–110.

Evans, M.S. and L. Lockhart. 2000. An investigation of the factors affecting high mercury concentrations in predatory fish in the Mackenzie River Basin. In: S. Kalhok (ed.), Synopsis of Research Conducted Under the 1999/2000 Northern Contaminants Program. Ottawa: Indian and Northern Affairs Canada. pp. 172–175.

Evans, M.S. and L. Lockhart. 2001. An investigation of the factors affecting high mercury concentrations in predatory fish in the Mackenzie River Basin. In: S. Kalhok (ed.), Synopsis of Research Conducted Under the 2000–01 Northern Contaminants Program. Ottawa: Indian and Northern Affairs Canada. pp. 194–201.

Evans, M.S. and D.G. Muir. 2001. Spatial and long-term trends in organic contaminants and metals in fish species important to the commercial, sports, and domestic fisheries of Great Slave Lake and the Slave River ecosystem. In: S. Kalhok (ed.), Synopsis of Research Conducted Under the 2000–01 Northern Contaminants Program. Ottawa: Indian and Northern Affairs Canada. pp. 185–194.

Krabbenhoft, D.P., C.C. Gilmour, J.M. Benoit, C.L. Babiarz, A.W. Andren and J.P. Hurley. 1998. Methyl mercury dynamics in littoral sediments of a temperate seepage lake. *Can J Fish Aquat Sci.* 55:835–844.

Lange, T.R., H.E. Royals and L.L. Connor. 1993. Influence of water chemistry on mercury concentration in largemouth bass from Florida lakes. *Trans Amer Fish Soc.* 122:74–84.

Lockhart, W.L., P. Wilkinson, B.N. Billeck, R.A Danell, R.V. Hunt, J. DeLaronde and G.J. Brunskill. 1998. Fluxes of mercury to lake sediments in central and northern Canada inferred from dated sediment cores. *Biogeochemistry.* 40:163–173.

Lockhart, W.L. 1999. Mercury in fish from surveys in lakes in the western Northwest Territories. In: J. Jensen (ed.), Synopsis of Research Conducted Under the 1997–98 Northern Contaminants Program. Ottawa: Indian and Northern Affairs Canada. pp. 137–145.

Lockhart, L. and M.S. Evans. 1999. Mercury in fish from surveys in lakes in the western Northwest Territories. In: S. Kalhok (ed.), Synopsis of Research Conducted Under the 1998–99 Northern Contaminants Program. Ottawa: Indian and Northern Affairs Canada. pp. 133–142.

Lockhart, L., G. Stern, G. Low and M.S. Evans. 2001. Mercury in fish from surveys in lakes in the western Northwest Territories. In: S. Kalhok (ed.), Synopsis of Research Conducted Under the 2000–01 Northern Contaminants Program. Ottawa: Indian and Northern Affairs Canada. pp. 194–201.

Miskimmin, B.M., J.W.M. Rudd and C.A. Kelly. 1992. Influence of dissolved organic carbon, pH, and microbial respiration rates on mercury methylation and demethylation in lake water. *Can J Fish Aquat Sci.* 49:17–32.

Muir, D., R. Anderson, K. Drouillard, M. Evans, A. Fisk, W. Fairchild, S. Guildford, D. Haffner, K. Kidd, J. Pyne, M. Whittle and X. Wang. 2001. Spatial trends and trophic transfer of POPs and current use pesticides in fish across Canada: an Overview. Aquatic Toxicology Workshop Proceedings.

Munn, M.D. and T.M. Short. 1997. Spatial heterogeneity of mercury bioaccumulation by walleye in Franklin D. Roosevelt Lake and the Upper Columbia River, Washington. *Trans Amer Fish Soc.* 126:477–487.

Shilts, W.W. and W.B. Coker. 1995. Mercury anomalies in lake water and in commercially harvested fish, Kaminak Lake, District of Keewatin, Canada. *Water Air Soil Pollut.* 80:881–884.

Stern, G., P. Roach and M. Diamond. 2001a. Temporal and spatial trends of mercury in fish from Yukon lakes and in sediment cores from Lake Laberge. In: S. Kalhok (ed.), Synopsis of Research Conducted Under the 2000/01 Northern Contaminants Program. Ottawa: Indian and Northern Affairs Canada. pp. 243–250.

Stern, G., L. Lockhart and M. Ikonomou. 2001b. Temporal trends of organochlorine, organobromine, and heavy metal contaminants in burbot from Fort Good Hope, Northwest Territories. In: S. Kalhok (ed.), Synopsis of Research Conducted Under the 2000–01 Northern Contaminants Program. Ottawa: Indian and Northern Affairs Canada. pp. 230–236.

Stewart, D.B., P. Taylor and G. Low. 2002a. Biological data from experimental fisheries at lakes in the Deh Cho Settlement Area, Northwest Territories, 1994–2000. Can. Data Rep. Fish. Aquat. Sci. (draft).

Stewart, D.B., F. Taptuna and G. Low. 2002b. Biological data from experimental fisheries at lakes in the Sahtu Dene and Metis Settlement Area, Northwest Territories, 1993–2000. Can. Data Rep. Fish. Aquat. Sci. (draft).

St. Louis, V.L., J.W.M. Rudd, C.A. Kelly, K.G. Beaty, N.S. Bloom and R.J. Flett. 1994. Importance of wetlands as sources of methyl mercury to boreal forest ecosystems. *Can J Fish Aquat Sci.* 51:1065–1076.

Swyripa, M.W., C.N. LaFontaine and M.C. Paris. 1993. Water and fish quality from Trout Lake, N.W.T. 1990–91. Indian and Northern Affairs Canada.

Verta, M. 1990. Changes in mercury concentrations in an intensively fished lake. *Can J Fish Aquat Sci.* 47: 1888–1897.

Watras, C.J., K.A. Morrison and J.S. Host. 1995. Concentration of mercury species in relationship to other site specific factors in the surface waters of northern Wisconsin lakes. *Limnol Oceanogr.* 40:556–565.

Spatial and Long-Term Trends in Organic Contaminants and Metals in Fish Species Important to the Commercial, Sports, and Domestic Fisheries of Great Slave Lake and the Slave River Ecosystem

Project leaders

Marlene Evans, National Water Research Institute (NWRI), Environment Canada, 11 Innovation Boulevard, Saskatoon, SK S7N 3H5; phone: (306) 975-5310; fax: (306) 975-5143; e-mail: marlene.evans@ec.gc.ca; Gary Stern, Freshwater Institute, Department of Fisheries and Oceans (DFO), 501 University Crescent, Winnipeg, MB R3T 2N6; phone (204) 984-6761; fax: (204) 984-2404; e-mail: sterng@dfo-mpo.gc.ca; Derek Muir, NWRI, Environment Canada, Burlington, ON L7R 4A6; phone: (905) 319-6921; fax: (905) 336-6430; e-mail: derek.miur@cciw.ca

Project team

Lyle Lockhart, Freshwater Institute, DFO, Winnipeg, MB; George Low, DFO, Hay River, NT; Maurice Boucher, Akaitcho Territory Tribal Council, Fort Resolution, NT; Steve Ellis, Lutsel K'e Dene Band, Lutsel K'e, NT; Rob Tarboff, South Slave Métis Tribal Council, Fort Smith, NT; Mike Whittle, DFO, Burlington, ON; Juanetta Sanderson, Department of Indian and Northern Affairs, Yellowknife, NT.

Abstract

Our study was designed to determine whether contaminant levels are changing in Great Slave Lake and Slave River fish. Levels could be declining if fewer contaminants are entering the lake from the atmosphere and/or Slave River. During 1999–2002, community members collected lake trout, burbot (loche) and northern pike (jack) from two regions of the lake. The Lutsel K'e area was studied because it is in the East Arm, where the water is clear and where the atmosphere is the sole source of contaminants. The Fort Resolution area was studied because it is near the Slave River in the West Basin, where the water is muddy and where contaminant sources include both the atmosphere and Slave River. In addition, commercial fishermen collected lake trout from the Hay River area of the West Basin. Organochlorine levels in lake trout and burbot from the East Arm appear to be lower than in the mid 1990s, but levels appear to be the same in fish from the West Basin. Mercury levels in West Basin lake trout appear higher in 2000 and 2001 than in the late 1980s and early 1990s, while levels in northern pike may be

slightly lower. Mercury levels in West Basin burbot appear to have decreased from the early to the mid-to-late 1990s with higher values in the early 2000s. During the winters of 2000–2002, Fort Smith community members collected burbot from the Slave River; most organic contaminant levels appear lower than in the early 1990s. More extensive statistical analyses and final interpretations will be made after chemical analyses are complete.

Key Project Messages

1. Organochlorine (OC) levels were lowest in northern pike muscle followed by lake trout muscle. Highest levels were observed in burbot liver, a lipid-rich organ. Organochlorine levels were similar to levels observed in many other northern lakes and substantially lower than in contaminated areas such as the Laurentian Great Lakes.
2. Organochlorine levels in fish appear similar to (West Basin) or lower than (East Arm, Slave River) levels observed in the 1990s.
3. Mercury (Hg) levels in lake trout are possibly higher than in the late 1980s and early 1990s, while levels in northern pike may be slightly lower. Mercury levels in Great Slave Lake burbot may have increased since the mid 1990s, but such a pattern is not evident in Slave River burbot. Mercury levels in all three species of fish are below the 0.5 $\mu g \cdot g^{-1}$ guideline for the commercial sale of fish. However, northern pike and lake trout mercury levels are often above the 0.2 $\mu g \cdot g^{-1}$ guideline for frequent consumers of fish.
4. More thorough analyses and final interpretations of factors affecting differences in contaminant levels between species, years and locations will be made after all the chemical analyses have been completed.
5. As these interpretations are made, a cost-effective, long-term monitoring strategy will be developed for monitoring contaminant trends in Great Slave Lake and Slave River fish.

Objectives

1. Determine OC (PCBs, DDT, dieldrin, toxaphene, etc.) levels in key fish species inhabiting the Great Slave Lake ecosystem, including the Slave River, and compare these values with earlier levels to assess possible time trends.
2. As part of this program, assess regional differences (and similarities) in contaminant trends, including investigations of possible causal factors for these differences.
3. Work with First Nation communities and the commercial fisheries in sample collection, results interpretation, and long-term study design.
4. Develop the framework for a cost-effective, long-term monitoring program of contaminant trends in fish inhabiting the Great Slave Lake and Slave River ecosystem.

Introduction

Great Slave Lake (1999–2002) and the Slave River (2000–2002) are part of the Northern Contaminants Program (NCP) biomonitoring program of contaminant trends. This ecosystem was included in the biomonitoring program for the following reasons. First, organic contaminants were measured in predatory fish (and other organisms) in the West Basin and East Arm of Great Slave on various occasions during 1993–1996 (Evans, 1994, 1995; Evans et al., 1998a, 1998b; Lafontaine, 1997). Fish in the Slave River were monitored during 1990–1994 (Sanderson et al., 1997; McCarthy et al., 1997). A longer term, although less comprehensive, data set exists for metals in fish harvested during the commercial fisheries. Second, many of the NCP samples have been archived allowing for additional analysis under new research programs and objectives. Third, fish are harvested for domestic consumption by many communities including Fort Smith (Slave River), Fort Resolution (West Basin, near the Slave River mouth), and Lutsel K'e (East Arm, far removed from a direct Slave River influence). The West Basin has supported a commercial fishery since the late 1940s (Rawson, 1951). In recent years, a significant sports fishery has begun to emerge, particularly in the East Arm.

Great Slave Lake is a relatively pristine ecosystem with localised contamination (primarily metals and nutrients) largely limited to the Yellowknife and Back Bay areas (Jackson et al., 1996). It is strongly influenced by the Slave River, which brings tremendous volumes of water and suspended sediments into the West Basin (Evans et al., 1996). The Slave River is formed from the confluence of the Peace and Athabasca rivers, which originate in Alberta with some tributary inputs from British Columbia and Saskatchewan. The lake is a major depositional basin for sediments entering the lake via the Slave and ultimately the Peace and Athabasca rivers. Studies, especially the Northern River Basins Study (NRBS), conducted in these upstream reaches demonstrate the need for continued monitoring of the Great Slave Lake fisheries for contaminants entering the lake from the southern portion of its watershed.

NRBS was conducted during 1991–1994 and demonstrated that many activities were impacting the Peace and Athabasca river systems (NRBS, 1996). Elevated PCB, dioxin and furan concentrations were found in burbot liver (and other fish species) collected downstream of municipal and industrial discharges (Pastershank and Muir, 1996; Muir and Pastershank, 1997). Klaverkamp and Baron (1996) reported elevated concentrations of metallothionein in Slave River burbot liver; elevated levels were related to exposure to high concentrations of metals, although later studies provided no support for this hypothesis (Evans et al., 1996).

In 1999, two regions of Great Slave Lake were approved by the NCP for investigating temporal trends in contaminants: (1) the West Basin, with a focus on the Fort Resolution area; and (2) the East Arm, with focus on the Lutsel K'e area. Three species of predatory fish were selected for long-term biomonitoring. Lake trout was selected as a cold water fish, important in the domestic, commercial and sports fisheries. Burbot, with their prized lipid-rich liver, are important in the domestic fisheries. Burbot liver can contain very high levels of PCBs and toxaphene. Consumption advisories were considered, but not implemented for burbot liver from the Fort Smith and Lutsel K'e areas. Northern pike, the third species selected, is a warm-water, littoral zone fish. In 2000–2001, approval was obtained to add a third site, the Slave River, with sampling effort focused at Fort Smith. Only burbot were investigated in the Slave River.

Activities

In 2001–2003

The study design called for 20 replicate samples to be collected of each species, at each location and time. Community members collected the fish in waters and at times that the target species could readily be found. We sent each community fisherman coolers and instructions on the handling of the fish; the community member later shipped back the intact and frozen fish for initial processing. Northern pike, lake trout and burbot were collected from the Lutsel K'e area in autumn 2000, 2001 and 2002. Similarly, northern pike and burbot were collected from the Fort Resolution area in late summer 2000, 2001 and 2002; poor weather in the Fort Resolution area prevented burbot from being collected until winter 2003.

Lake trout are uncommon offshore of Fort Resolution although they are found elsewhere in greater abundance (Rawson, 1951). Lake trout were caught offshore of the Simpson Islands in 2000 in an area of strong Slave River influence. However, in 2001, lake trout were collected part way up the East Arm in an area of weakening Slave River influence and closer proximity to the Lutsel K'e site. Therefore, lake trout were collected from the domestic fisheries operating out of Hay River in autumn 2001 and then again in 2002. A community member from Fort Smith collected burbot from the Slave River in winter 2000, 2001 and 2002, generally in December.

All fish were catalogued (length, weight and given an identification number), without thawing, with a subset of 10 from each series selected for additional analyses. Specimens were selected to span a size range of medium to large fish with similar size ranges in all years of study. The subset of fish was sent to the Freshwater Institute (FWI) where they were thawed, remeasured, sex determined and ageing structures removed. A muscle subsample was removed from each of the fish and was analyzed for mercury, arsenic, selenium (FWI), and carbon and nitrogen stable isotopes (NWRI-Saskatoon). Lake trout muscle, northern pike muscle and burbot liver were analyzed for OCs (FWI), including toxaphene (FWI, NWRI-Burlington). Northern pike OC analyses were discontinued after 2000 because they have the lowest OC concentrations of all three species considered. Analyses for 2002 caught fish are ongoing as are some OC analyses for some fish caught in earlier years.

A subset of predatory fish, forage fish, benthic invertebrates and plankton from the 1993–1995 Great Slave Lake field seasons were selected for additional mercury analyses. The original studies focussed on OCs with only a subset analyzed for metals. These mercury analyses will allow us to quantify mercury biomagnification in the Great Slave Lake food web and compare this with our ongoing NCP mercury studies in smaller lakes in the Fort Simpson area, and other regions of the Northwest Territories (NWT).

Results

Organochlorine contaminants

Toxaphene was the predominant OC in fish tissue followed by PCBs, DDT, CBz and HCH. Burbot liver, a lipid-rich organ (mean 31.8% lipid), had the highest OC concentrations, while northern pike muscle, a very lean tissue (mean 0.1% lipid) had the lowest. Lake trout muscle, with a mean lipid content of 4.8%, had intermediate OC concentrations. Total PCB levels, for example, averaged 123.1 $ng \cdot g^{-1}$ in burbot, 4.4 $ng \cdot g^{-1}$ in northern pike and 18.6 $ng \cdot g^{-1}$ in walleye.

West Basin northern pike were analyzed for OCs in 1996 and have been analyzed for 1999 and 2000. Concentrations were similar during these 3 years, and during the 2 years

of sampling in the East Arm (Fig. 1). Concentrations tended to be higher in West Basin fish than in East Arm fish, although mean age and muscle lipid content were similar in both locations.

East Arm lake trout were analyzed for OCs in 1993 and have been analyzed for 1995, 1999 and 2000 (Fig. 2). Organochlorine levels were higher in 1993 and 1995 than in 1999 and 2000. This could suggest that OC levels are declining in East Arm lake trout. However, differences in OC levels may be lipid and/or age related. Mean lipid content and fish age were higher in 1993 and 1995 (7.6–16.0% lipid, age 15 yrs) than in 1999 and 2000 (2.4–4.9% lipid, age 7–8 yrs).

West Basin lake trout were analyzed for OCs in 1993 and have been analyzed for 1999–2001 (Fig. 2). Organochlorine levels were higher in 1999 than 1993 but lower in 2000 and 2001. Interpretation of possible temporal trends is confounded by the fact that some lake trout were summer caught (2000, 2001) in the Simpson Island and East Arm area and had lower mean lipid contents (3.6–5.3% lipid) than autumn (1993, 12.8% lipid) and winter (1999, 8.1% lipid) caught fish from the commercial fisheries operating in the Hay River area. On a lipid basis, PCB concentrations in lake trout are higher during 1999–2001 than in 1993.

East Arm burbot were analyzed for OCs in 1993 and have been analyzed for 1999–2001 (Fig. 3). Mean toxaphene concentrations were higher in 1993 than during 1999–2001. Chlordane and DDT concentrations were also somewhat lower during 1999–2001. Lower concentrations in more recent years may be age related with burbot averaging 8.2–9.5 yrs old in recent years versus 12.6 yrs old for 1993 caught fish.

West Basin burbot were analyzed for OCs in 1993, 1995 and have been analyzed for 1999–2001 (Fig. 3). PCB levels appeared to be increasing over 1993–2001 and CBz occurred in their highest concentrations in 2000 and 2001. Burbot mean ages ranged from 10.3 to 12.3 yrs old

Figure 1. Mean (+ one standard deviation) OC concentrations in West Basin and East Arm northern pike by sample year

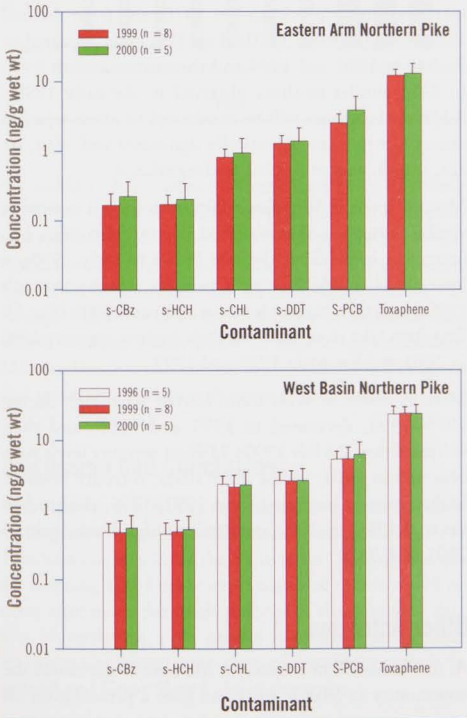


Figure 2. Mean (+ one standard deviation) OC concentrations in West Basin and East Arm trout by sample year

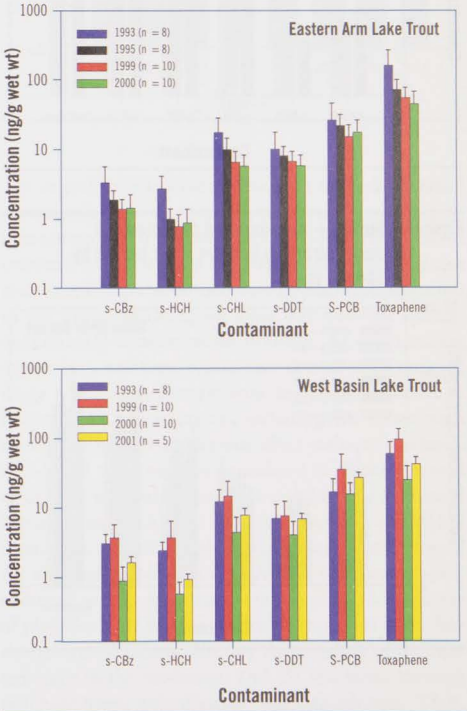


Figure 3. Mean (+ one standard deviation) OC concentrations in West Basin and East Arm burbot by sample year

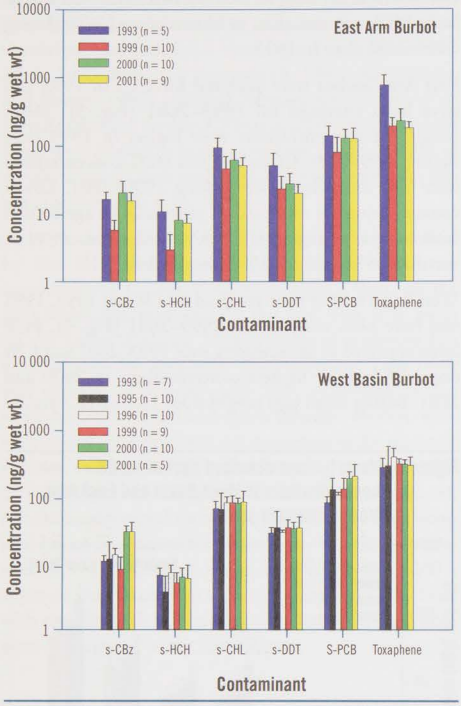
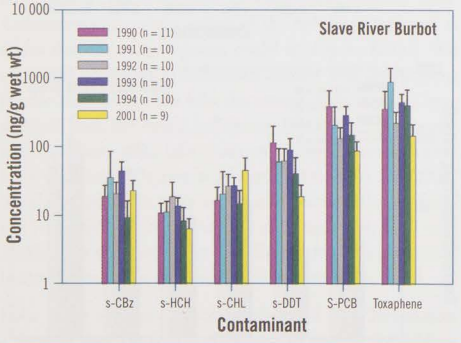


Figure 4. Mean (+ one standard deviation) OC concentrations in Slave River burbot by sample year



over the several years of collections suggesting that differences were not age related.

Slave River burbot were analyzed for OCs in 1990–1994 and have been analyzed for 2001 (Fig. 4). HCH, DDT, PCB and toxaphene concentrations were considerably lower in 2001 than in earlier years. In contrast, CBz and chlordane concentrations were higher in 2001 than earlier periods: more isomers were examined in the former than later period, possible accounting for some of these differences.

Mercury

Mercury levels have been measured at various times in the commercial fisheries. These data extend the long-term record for mercury trends in the West Basin.

Mean mercury concentrations in the muscle of all three species of fish were below the 0.5 $\mu g \cdot g^{-1}$ guideline for the commercial sale of fish, although a few large northern pike exceeded this value. Many northern pike exceeded the 0.2 $\mu g \cdot g^{-1}$ guideline for frequent consumers of fish, as did some lake trout and burbot (Fig. 5). West Basin northern pike and burbot tended to have higher mercury concentrations than East Arm fish.

In the West Basin, mercury levels in northern pike increased from the mid-to-late 1970s and from the mid 1980s into the early 1990s (Fig. 5). Levels appeared to decline in 1992 and 1994 and then increase with levels in 2001 similar to those observed in the early 1990s. Additional analyses will be conducted to assess whether these differences are statistically significant and, if so, are age, length, and/or trophic feeding related.

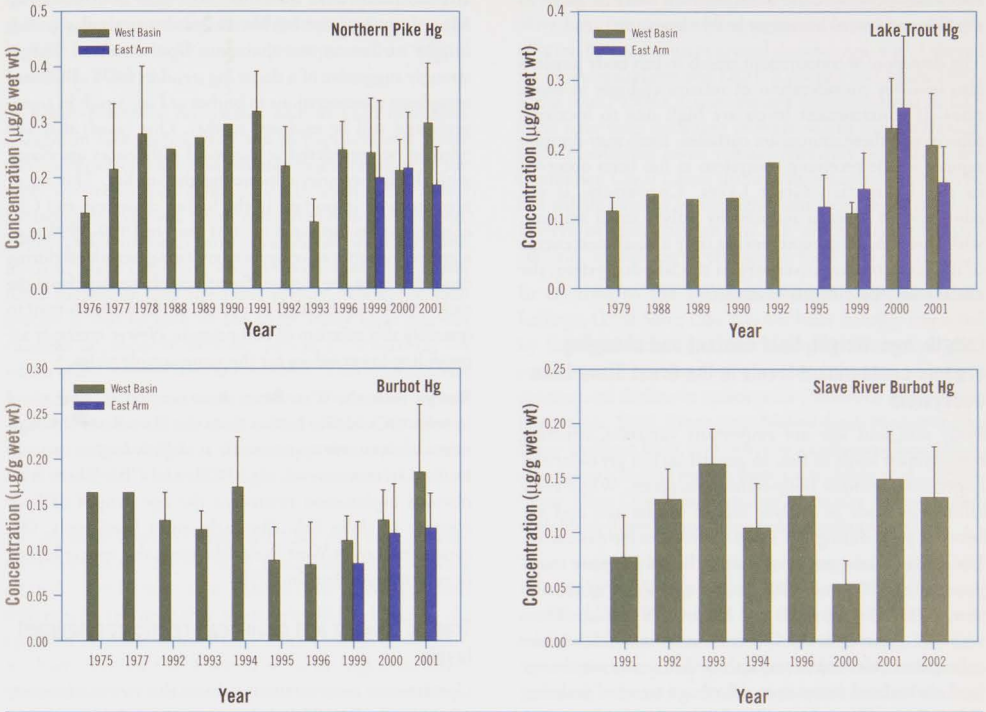
Mercury levels in West Basin lake trout show a somewhat similar pattern as that observed for northern pike, i.e., increasing levels from the late 1970s to early 1990s, a lower level in 1999 (with a possible decline through 1990s) and then highest levels in 2000 and 2001 (Fig. 5). East Arm lake trout also had their highest mercury level in 2001 and lowest in 1995 and 1999.

Mercury levels in West Basin burbot were high during 1975–1994, decreased in 1995 and 1996, and then increased over the late 1990s. Highest mercury levels were observed in 2001. In the Slave River, mercury levels in burbot muscle increased from 1991–1993, declined in the mid 1990s to 2000 and attained high levels again in 2001 and 2002.

Other Activities

At the invitation of Lutsel K'e, Marlene Evans visited the community in March 2001 and gave a presentation on

Figure 5. Mean (+ one standard deviation) mercury levels in West Basin, East Arm and Slave River fish by sample year



the results of her studies on Great Slave Lake, including earlier contaminant work. She participated in a community tour in March 2003, which included Hay River, Fort Resolution, Fort Smith, and Lutsel K'e. Maurice Boucher, from Fort Resolution, was an invited speaker in the Biology Department at the University of Saskatchewan, where Marlene Evans holds an adjunct professorship. Maurice Boucher participated in the Role Model Program and spoke on contaminant issues in the north.

Discussion and Conclusions

This study is designed to investigate long-term trends in contaminant levels in three species of fish in Great Slave Lake and one species in the Slave River. Sample analyses are ongoing and final interpretation of the data will be done after more thorough analyses of the complete data sets. Nevertheless, a few general statements can be made at this point about detecting contaminant trends in general and Great Slave Lake in particular.

The organic contaminants, which are the focus of these investigations, are persistent compounds, tending to bioaccumulate in biota. Each species has its own contaminant uptake and depuration rate. Where uptake rate exceeds depuration rate, contaminant concentration in the organism increases; when the converse occurs, contaminant concentration declines. As contaminant inputs into northern ecosystems decline with reduced usage worldwide, contaminant levels are expected to decline in all compartments, including fish. However, a number of other variables can affect contaminant levels in fish and these must be considered in assessing trends or the lack of trends in response to reduced contaminant inputs. These include (1) the characteristics of the fish themselves (length, weight, age, gender, lipid content); (2) the feeding behaviour of the fish (i.e., actual availability of prey, contaminant levels in prey, and intensity of predation); (3) trends in contaminant inputs into a lake ecosystem; (4) factors affecting the recycling of the contaminant in the ecosystem; and (5) loss terms through sedimentation, volatilisation and degradation. Thus,

although contaminant levels may differ in a fish between two study periods, close consideration must be given to the fish and its environment before assessing cause.

The detection of contaminant trends in fish body burdens also involves consideration of relative changes in input rates. If contaminant levels are high due to localized sources and these sources are curtailed, levels may decrease rapidly in the receiving ecosystem as has been observed in the Laurentian Great Lakes. Conversely, if the contaminant input is reduced by only a small amount, with this reduction representing only a small percentage of the contaminant inventory in the lake ecosystem, the decline may be difficult to detect.

Length, age, weight, lipid content and changing organic contaminant levels in the Great Slave Lake ecosystem

Body size and age are important variables affecting contaminant levels in fish. In general, as fish get older and larger, contaminant body-burden increases. While every effort was made to analyze fish of similar size and age between years during this study, differences have occurred. For example, lake trout collected at Lutsel K'e were much younger in 1999 and 2000 (mean ages 7.5–7.6 yrs old) versus 1993 (14.5 yrs old) and 1995 (15.5 yrs old). Thus, while we observed lower OC concentrations in lake trout collected in more recent years, these differences may be age (and size) related rather than reflecting a trend of declining OCs. We will explore this further by investigating contaminants, length, weight and age relationships for Lutsel K'e lake trout.

While some adjustments can be made for variations in the size of fish collected from one study period to another, size-contaminant relationships seem to vary between years. For example, PCB concentrations in burbot liver from Fort Smith are correlated with fish length. However, the correlation coefficient varied markedly between years from +0.62 for 1990, +0.75 for 1991, +0.07 for 1992, +0.42 for 1993, −0.70 for 1994, and +0.07 for 2002 caught fish. In addition, burbot caught in 1991 were considerably older for a given size than fish caught in 1990, i.e., a 700 mm fish in 1991 was ca. 13.2 yrs old versus 7.7 yrs old in 1990. This suggests that burbot caught in 1991 were slower growing than burbot caught in other years. They had more lipid-rich liver with lipid values 35.5 ± 8.4% versus 29.4 ± 11.0% in 1990. If OC levels generally increase with fish age and lipid content, 1991 would have been a year of relatively high OC concentrations. This, in fact, was observed for the 1990–1994 data set; the highest toxaphene and second highest PCB concentrations were observed in 1991.

DDT, PCB and toxaphene concentrations in burbot liver at Fort Smith were lower in 2001 than in 1990–1994. Mean length of the burbot analyzed was similar to fish caught earlier, as was the mean lipid content. This is strongly suggestive of a declining trend in DDT, PCB and toxaphene concentrations in burbot at Fort Smith in recent years and will be explored further. One caveat that will need to be considered is analytical differences associated with the laboratories conducting the studies. This factor appears to be important in the higher chlordane and CBz concentrations measured in 2001 than in 1990–1994, e.g., a greater number of congeners are being examined during our study than the former. Some toxaphene data from the early 1990s may be high as a result of the methods used to quantify this mixture of compounds. Newer methods are providing lower values for the same sample series.

Burbot from the West Basin show no obvious time trend in most OCs, unlike burbot from the Slave River although many compounds appear to be at slightly higher concentrations in recent years, e.g., PCBs and CBz. There is no obvious explanation related to the age, length or lipid content of these fish. Similarly, on a lipid basis, OC concentrations in West Basin lake trout also appear higher in recent years than in 1993.

Trophic feeding and changing organic contaminant levels

Contaminant concentrations in biota also vary as a function of trophic feeding. Fish that consume mainly invertebrates have lower levels of contaminants such as PCBs than fish that feed on benthic invertebrates (Kidd et al., 1998). Trophic feeding varies with the size of the fish, with larger fish generally being more predaceous and consuming larger (and older) prey. Within the Great Slave Lake ecosystem, species and regional differences exist between fish feeding behaviour, which in turn, may affect contaminant body burdens.

Rawson (1951) reported that fish made up 95% of the northern pike diet with the remainder mainly amphipods. However, fish made up only 75% of the burbot diet with mysids contributing approximately 20% and benthic invertebrates the remainder; Tallman (1996) reported that fish featured predominantly in the Slave River delta burbot diet. Regional differences occur in lake trout feeding behaviour in Great Slave Lake with fish contributing 90% of the lake trout diet in the West Basin, but only 38% in the East Arm (Rawson, 1951). These observations are supported by stable isotope analyses which suggest that lake trout, northern pike and burbot collected from the West Basin have a slightly richer fish diet than similar fish collected from the East Arm (Evans and Muir, 2001). Therefore, based on trophic feeding alone, West Basin

fish would tend to have slightly higher contaminant concentrations than East Arm fish. Northern pike, the most piscivorous species, would be expected to have the highest levels when OC levels are expressed on a lipid basis, as is observed.

In highly perturbed ecosystems such as Lake Michigan, changes in lake productivity and in plankton and forage fish composition can result in significant changes in the diets of predaceous fish. This, in turn, may affect contaminant levels and time trends (Borgman and Whittle, 1992). Stable nitrogen isotope values for predaceous fish in Great Slave Lake have shown no obvious change over time, suggesting that the main dietary habitats of each species of fish in each of the three study areas has not changed appreciably over the period (1995–2002) for which stable isotope data are available. This is in contrast to the Lake Laberge ecosystem where changes in organic contaminant concentrations in burbot and lake trout have, in part, been related to a changing commercial fisheries, food availability and habits of the harvested fish (Stern et al., 2001b).

OC levels are lower in Great Slave Lake than Lake Laberge fish (Stern et al., 2001b) with some differences possibly related to differences in food habits although such differences are probably more strongly related to the localized contamination of the Lake Laberge ecosystem. Similarly, burbot OC levels tend to be higher in Great Slave Lake than Mackenzie River at Fort Good Hope (Stern et al., 2001a). Some of these differences may be related to trophic feeding. Interestingly, mercury levels are higher in burbot at Fort Good Hope that Great Slave Lake. Mercury levels also are higher in fish in lakes in the Fort Good Hope area than Great Slave Lake but these differences are believed to be due to lake size.

Time trends in contaminant inputs

Detection of trends in contaminant levels in fish is also dependent on trends in contaminant inputs and losses to the lake. In the Laurentian Great Lakes, where localized sources of contaminant inputs were large, reductions in inputs are evident in the sediment core record with current levels considerably lower than in the 1960s, but still much higher than in more pristine areas such as Great Slave Lake (Wong et al., 1995). Contaminant levels in fish declined markedly during the late 1970s as contaminant inputs were reduced (Hesselberg et al., 1990; Suns et al., 1993; DeVault et al., 1996; Huestis et al., 1996). Declines are proceeding at a slower rate in recent decades as contaminants such as PCBs continue to recycle through the Great Lakes ecosystem from the sediments. Contaminants also continue to enter the lakes from watershed reserves and the atmosphere (Stow et al., 1995). Thus, OC levels remain much higher in Great Lakes fish than Great Slave Lake fish. Similarly, some Yukon lakes were strongly affected by local sources several decades ago, e.g., Laberge for PCBs, toxaphene and DDT (Lockhart and Muir, 1995; Muir et al., 1996). Contaminant concentrations in lake cores have been declining in more recent times although surface sediment levels remain relatively high. Like the Laurentian Great Lakes, declines in contaminant levels in fish will be affected by the significant recycling of the large reserve of contaminants in the sediments and water column in addition to changes in food web dynamics.

In contrast to the Laurentian Great Lakes and Lake Laberge, Great Slave Lake has not been strongly impacted by localized sources of contaminants. Therefore, OC concentrations in sediment cores have not shown a pronounced decline in recent years (Mudroch et al., 1992; Evans et al., 1996; Evans, unpublished data). Moreover, like many northern lakes, and as in the Laurentian Great Lakes, atmospheric inputs remain significant (Muir et al., 1996). Great Slave Lake also continues to receive contaminants with Slave River inflow from more southern reaches.

Three study locations are being investigated in the Great Slave Lake ecosystem and the question is whether all are necessary. We believe that the three study locations will exhibit different contaminant trends with time. The East Arm receives most of its contaminants from the atmosphere. Sediment rates are low in this region and much of the lake floor consists of dense clays. Sediment resuspension probably is low, especially since the East Arm is generally deep. Thus this site may show a relatively rapid response to decreased atmospheric inputs of contaminants. In contrast, the West Basin receives contaminants from the Slave River and represents the major depositional sink for fine sediments and associated contaminants transported into Great Slave Lake. Sediment resuspension and contaminant recycling are significant because much of the West Basin is shallow, fetch distances are large, and bottom topography irregular. Therefore, contaminant recycling probably is greater than in the East Arm and the West Basin may show a slower response to decreased inputs of contaminants from the atmosphere. As a shallower region, the West Basin may also experience a greater response to global warming than the East Arm. The Slave River has the shortest residence time of water and fine particulates. Therefore, in the absence of significant river borne contaminant inputs from the south, this region could show an early response to a decline in atmospherically derived contaminant inputs. However, most of its contaminants probably originate from the southern reaches of its watershed where anthropogenic activities are significant.

To conclude, preliminary examination of data collected over 1999–2002 suggest that OC levels have declined in East Arm lake trout and burbot and Slave River burbot while levels in West Basin burbot and lake trout (lipid basis) may have increased slightly. Mercury levels appear higher in recent years than over the past decade. However, additional study of the complete data sets are required to determine trends (or the lack of trends) and causal factors.

Expected Completion Date

Chemical analyses continue on samples collected in 2002–2003 with some analyses remaining to be conducted from 2001–2002 collections. Data interpretations will continue over a longer period.

Acknowledgments

The contributions of the Project Team are gratefully acknowledged and have been noted in this report. Special appreciation is extended to Ernest Boucher for collecting the fish from Lutsel K'e, Gab Lafferty and Kevin Boucher from Resolution Bay, Shawn Buckley from Hay River, and Fred McDonald and Fred Stirret from Fort Smith. Their close attention to detail and dedication in obtaining these fish is very much appreciated. Jonathan Keating and Geoff Koehler (NWRI-Saskatoon), Joanne Delaronde and Krystyna Koczanski (DFO-Winnipeg) provided excellent laboratory support during the various phases of this study.

References

DeVault, D.S., R. Hesselberg, P.W. Rodgers and T.J. Feist. 1996. Contaminant trends in lake trout and walleye from the Laurentian Great Lakes. *J Great Lakes Res.* 22:884–895.

Borgman, U. and D.M. Whittle. 1992. Bioenergetics of PCB, DDE, and mercury dynamics in Lake Ontario lake trout (*Salvelinus namaycush*): a model based on surveillance data. *Can J Fish Aquat Sci.* 49:1086–1096.

Evans, M.S. 1994. Biomagnification of persistent organic contaminants in Great Slave Lake. In: J.L. Murray and R.G. Shearer (eds.), *Synopsis of Research Conducted Under the 1993/94 Northern Contaminants Program.* Environmental Studies No. 72. Ottawa: Indian and Northern Affairs Canada. pp. 295–300.

Evans, M.S. 1995. Biomagnification of persistent organic contaminants in Great Slave Lake. In: J.L. Murray and R.G. Shearer (eds.), *Synopsis of Research Conducted Under the 1994/95 Northern Contaminants Program.* Environmental Studies No. 72. Ottawa: Indian and Northern Affairs Canada. pp. 215–220.

Evans, M.S. and D. Muir. 2001. Spatial and long-term trends in organic contaminants and metals in fish species important to the commercial, sports, and domestic fisheries of Great Slave Lake and the Slave River ecosystem. In: S. Kalhok (ed.), *Synopsis of Research Conducted Under the 2000–2001 Northern Contaminants Program.* Ottawa: Indian and Northern Affairs Canada. pp. 185–193.

Evans, M.S., R.A. Bourbonniere, D. Muir, L. Lockhart, P. Wilkinson and B. Billeck. 1996. *Spatial and Temporal Patterns in the Depositional History of Organochlorine Contaminants, PAHs, PCDDs, and PCDFs in the West Basin of Great Slave Lake.* Joint report to the Northern River Basins Study and Indian and Northern Affairs Canada, Water Resources Program. National Hydrology Research Centre Contribution 96001.

Evans, M.S., L. Lockhart and J. Klaverkamp. 1998a. *Metal Studies of Water, Sediments, and Fish from the Resolution Bay Area of Great Slave Lake: Studies Related to the Decommissioned Pine Point Mine.* Saskatoon: National Water Research Institute Contribution No. 98–87.

Evans, M.S., D. Muir, L. Lockhart and G. Stern. 1998b. *Metal and Persistent Organochlorine Pollutant (POP) Concentrations in Four Species of Predatory Fish from Resolution Bay, Great Slave Lake: Summer 1996 Studies.* Saskatoon: National Water Research Institute Contribution No. 98–93.

Hesselberg, R.J., J.P. Hickey, D.A. Nortrup and W.A. Willford. 1990. Contaminant residues in the bloater (*Coregonus hoyi*) of Lake Michigan, 1969–1986. *J Great Lakes Res.* 16:121–129.

Huestis, S.Y., M.R. Servos, D.M. Whittle and D.G. Dixon. 1996. Temporal and age-related trends in levels of polychlorinated biphenyl congeners and organochlorine contaminants in Lake Ontario lake trout (*Salvelinus namaycush*). *J Great Lakes Res.* 22:310–330.

Jackson, F.J., C.N. Lafontaine and J. Klaverkamp. 1996. *Yellowknife-Back Bay Study on Metal and Trace Element Contamination of Water, Sediment, and Fish.* Yellowknife: Indian and Northern Affairs Canada.

Kidd, K.A., D.W. Schindler, R.H. Hesslein and D.C.G. Muir. 1998. Effects of trophic position and lipid on organochlorine concentrations in fishes from subarctic lakes in Yukon Territory. *Can J Fish Aquat Sci.* 55:869–881.

Klaverkamp, J.F. and C.L. Baron. 1996. *Concentrations of Metallothionein in Fish: Peace, Athabasca, and Slave River Basins, September to December 1994.* Northern River Basins Study Project Report 93.

Lafontaine, C. 1997. Fort Resolution Monitoring Program (1992–1993): *Concentrations of Metals and Trace Elements in Muscle and Liver of Fish Collected from Great Slave Lake, Fort Resolution Area, NWT.* Yellowknife: Indian and Northern Affairs Canada, 141 pp.

Lockhart, W.L., and D. Muir. 1995. Food chain accumulation, biological effect and sediment contamination in Lake Laberge. In: J.L. Murray and R.G. Shearer (eds.), *Synopsis of Research Conducted Under the 1994–95 Northern Contaminants Program.* Environmental Studies No. 72. Ottawa: Indian and Northern Affairs Canada. pp. 199–208.

McCarthy, L.H., G.R. Stephens, D.M. Whittle, J. Peddle, S. Harbicht, C. Lafontaine and D.J. Gregor. 1997. Baseline studies in the Slave River, NWT, 1990–1994: Part II: Body burden contaminants in whole fish and livers. *Sci Total Environ.* 197:55–86.

Mudroch, A., R.J. Allan and S.R. Joshi. 1992. Geochemistry and organic contaminants in the sediments of Great Slave Lake, Northwest Territories, Canada. *Arctic.* 45:10–19.

Muir, D.C.G., A. Omelchenko, N.P. Grift, D.A. Savoie, W.L. Lockhart, P. Wilkinson and G.J. Brunskill. 1996. Spatial trends and historical deposition of polychlorinated biphenyls in Canadian midlatitude and Arctic lake sediments. *Environ Sci Technol.* 30:3609–3617.

Muir, D.C.G. and G.M. Pastershank. 1997. *Environmental Contaminants in Fish: Spatial and Temporal Trends of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans, Peace, Athabasca, and Slave River Basins, 1992–1994.* Northern River Basins Study Project Report 129.

Northern River Basins Study Board. 1996. *Report to the Ministers.* Edmonton: Northern River Basins Study.

Pastershank, G.M. and D.C.G. Muir. 1996. *Environmental Contaminants in Fish: Polychlorinated Biphenyls, Organochlorine Pesticides, and Chlorinated Phenols, Peace, Athabasca, and Slave River Basins, 1992 to 1993.* Northern River Basins Study Project Report 101.

Rawson, D.S. 1951. Studies of the fish of Great Slave Lake. *J Fish Res Board Can.* 8:207–240.

Sanderson (Peddle), J., J.C. Lafontaine and K. Robertson. 1997. *Slave River Environmental Water Quality Monitoring Program, 1990–1995.* Final Five Year Study Report. Yellowknife: Indian and Northern Affairs Canada, Water Resources Division. Three volumes.

Stern, G., L. Lockhart and M. Ikonomou. 2001a. Temporal trends of organochlorine, organobromine and heavy metal contaminants in burbot from Fort Good Hope, Northwest Territories. In: S. Kalhok (ed.), *Synopsis of Research Conducted Under the 2000–2001 Northern Contaminants Program.* Ottawa: Indian and Northern Affairs Canada. pp. 230–236.

Stern, G., P. Roach, and M. Diamond. 2001b. Temporal and spatial trends of mercury in fish from Yukon lakes and in sediment cores from Lake Laberge. In S. Kalhok (ed.), *Synopsis of research Conducted Under the 2000–2001 Northern Contaminants Program.* Ottawa: Indian and Northern Affairs Canada. pp. 243–250.

Stow, C.A., S.R. Carpenter, L.A. Eby, J.F. Amrhein and R.J. Hesselberg. 1995. Evidence that PCBs are approaching stable concentrations in Lake Michigan fishes. *Ecol Applic.* 5:248–260.

Suns, K.R., G.G. Hitchin and D. Toner. 1993. Spatial and temporal trends of organochlorine contaminants in spottail shiners from selected sites in the Great Lakes (1975–1990). *J Great Lakes Res.* 19:703–714.

Tallman, R.F. 1996. *Synthesis of Fish Distribution, Movements, Critical Habitat and Food Web for the Lower Slave River North of the 60th Parallel: a Food Chain Perspective.* Northern River Basins Study Synthesis Report 13.

Wong, C.S., G. Sanders, D.R. Engstrom, D.T. Long, D.L. Swackhamer and S.J. Eisenreich. 1995. Accumulation, inventory, and diagenesis of chlorinated hydrocarbons in Lake Ontario sediments. *Environ Sci Technol.* 29: 2661–2672.

Retrospective Analysis of Contaminants in Yukon Moose

Project leader

Mary Gamberg, Gamberg Consulting, Whitehorse, YT; phone: (867) 668-7023; fax: (867) 668-7024; e-mail: mary.gamberg@yt.sympatico.ca

Project team

Pat Roach, Department of Indian Affairs & Northern Development, Whitehorse, YT; Yukon Geology Program, Whitehorse, YT; Yukon Environment.

Abstract

The Yukon Contaminants Database and the Geological Survey of Canada database on stream sediments were used to analyze moose renal chemistry, stream sediment chemistry and their interrelationships. For some elements, moose renal chemistry is affected by the underlying geology of the moose home range. Renal cadmium, nickel and zinc had significant positive relationships with sediment concentrations. While nickel and zinc do not represent toxicity issues for Yukon moose, there is potential for older moose in some parts of the Yukon to be at risk of renal dysfunction due to high renal cadmium. These moose may, however, have a high level of cadmium tolerance. Health Canada has recommended limiting consumption of Yukon moose kidneys and livers to one·year^{-1}·person^{-1}. No limit has been set on the amount of moose meat recommended for consumption. Results are consistent with high concentrations of Cd found in Yukon moose coming from naturally occurring geological sources, via hyperaccumulating plants such as willows. However, the effect of local point sources on cadmium in Yukon moose has not yet been explored.

Key Project Messages

1. For some elements, moose renal chemistry is affected by the underlying geology of the moose home range.
2. Results are consistent with high concentrations of cadmium found in Yukon moose coming from naturally occurring geological sources, via hyperaccumulating plants such as willows.

Objectives

1. To further understand the dynamics of contaminants in moose as they relate to ecoregions and underlying geology.
2. To identify potential 'hot spots' for contaminants in Yukon moose.

Introduction

Moose represent a significant portion of the terrestrial country food consumed in the Yukon. The Yukon Contaminants Committee has recognized this and collected moose tissues for contaminant analysis since 1993. While moose are evaluated for contaminants of concern in the territory each year, there is potential for

much more to be learned from the information in the database. The Yukon Territory is a geographically and ecologically diverse land. A map of ecoregions in the Territory has been devised to enable wildlife managers to more meaningfully interpret data collected from diverse areas of the Territory. Analyzing existing contaminant data for moose on an ecoregion basis and relating that to the underlying geochemistry of the areas (data from Geological Survey of Canada) will increase our understanding of the dynamics of contaminants within the ecosystem. It will also highlight any geographical 'hot spots' of specific contaminants, such as cadmium, which is an ongoing concern in moose in the Yukon.

Activities

In 2002–2003

One hundred archived moose kidneys, obtained from the ongoing Hunter Survey Program, were analyzed for a suite of 26 elements by Elemental Research Inc., Vancouver, BC using ICP-MS. These data were added to the existing Yukon Contaminants Database for analysis. The resulting database and the Geological Survey of Canada database on stream sediments were used to analyze moose renal chemistry and stream sediment chemistry on an ecoregion basis, and subsequently on a hunting zone basis. The interrelationship between moose renal chemistry and stream sediment chemistry was also explored.

Results

Because age affects renal concentrations of some elements in moose (Gamberg, 2000), age was included as an independent factor in all General Linear Model (GLM) and regression analyses of moose kidney data. However, since the effect of age is not relevant to the interpretation of these analyses, it will not be included in the discussion of results. The following elements had more than 50% of the values below detection limits in the moose kidney database and were not included in the analyses: Sb, Be, Ag, Tl, and U. All significance levels in these analyses are considered to be $\alpha = 0.05$.

To determine whether moose renal chemistry differed among ecoregions, a K-Means Cluster analysis was used to classify the data into eight clusters based on renal chemistry. A chi-square test was then used to determine if there was an association between clusters and ecoregions. The resulting frequency table had too many cells that were < 5, invalidating the test. Data for clusters in which $N < 10$ were then removed, and the cluster analysis rerun. This procedure was repeated until all clusters had $N > 10$. As a result of this procedure, data in each cell (cluster) for the Pelly Mountains, Selwyn Mountains, Ruby Ranges and Yukon Plateau Central were < 5 and were deleted, leaving four regions in the analysis (Liard Basin, Klondike Plateau, Yukon Plateau North and Yukon Southern Lakes). The chi-square test on the resulting data showed that there was a significant association between cluster and ecoregion. The same procedure was followed for stream sediment chemistry except that data for clusters in which $N < 25$ were removed before performing the chi-square test (this was a much larger data set). No ecoregions were removed from this data set. The chi-square test showed that there was a significant association between cluster and ecoregion.

A GLM was used to determine whether specific elements in moose kidneys differed among all eight ecoregions, while an ANOVA was used to determine whether specific elements in stream sediments differed among ecoregions. Cd, Co and Ni were the only elements in moose kidneys that showed a significant difference among ecoregions whereas stream sediments showed a significant difference for As, Ba, Cd, Cr, Co, Cu, Fe, Pb, Mn, Hg and Mo. A regression performed for moose renal element against sediment element using average element concentrations for each ecoregion ($N = 8$ ecoregions), indicated no significant relationships.

As an alternative to ecoregions, the data were reanalyzed on a game management zone basis. Game management zones were delineated as a management tool by YTG, their borders usually following roads, rivers and/or mountain passes. Because these borders (including roads in the Yukon) follow natural contours of the land, it was considered a reasonable classification to consider in the context of these analyses. A GLM test on renal elements determined that Ba, Cd, Co and Pb differed among zones while Ba, Cd, Cr, Co, Fe, Pb, Hg, and Mo differed among zones when sediment elements were tested with an ANOVA. A regression was also performed between renal and sediment averages for hunting zones ($N = 9$ hunting zones) for each element. A significant relationship was found for renal and sediment Cd and Zn only (Figures 1 and 2), although the significance level for Zn was low compared to Cd.

To more closely examine the relationship of moose renal chemistry to sediment chemistry without artificially created categories (ecoregions or game management zones), a mean was taken of all sediment data for sediment collection points within a 20 km area circle around the collection point for each moose. The area of the circle was based on a mean winter home range size for Yukon moose (Keith, 1995).

Figure 1. Moose kidney and stream sediment Cd averages for hunting zone

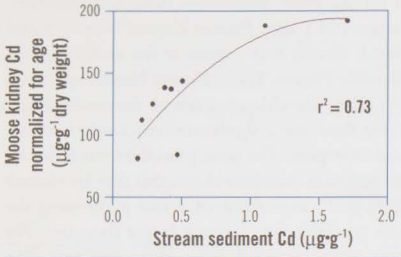
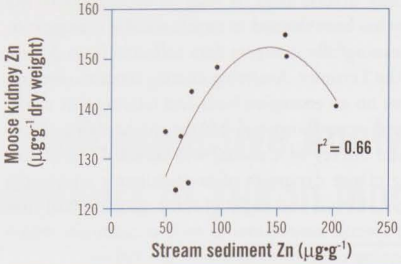


Figure 2. Moose kidney and stream sediment Zn averages for hunting zone



Mean sediment concentrations were then regressed against individual moose renal concentrations for each element using a linear regression model. Al, B, Ca, Mg sediment data were not available for these sites and were not included in the analysis. There was a significant relationship between moose renal concentration and sediment concentration for Cd and Ni only (Figures 3 and 4), although the relationship for Zn approached significance. Because there were obvious outliers in both cases, both regressions were rerun using age-corrected moose renal Ni concentrations ≤ 1.0 µg·g^{-1}, age-corrected moose renal Cd concentrations ≤ 400 µg·g^{-1} and sediment Cd concentrations ≤ 2.0 µg·g^{-1}. Both relationships remained significant.

Discussion and Conclusions

For some elements, moose renal chemistry is affected by the underlying geology of the moose home range. Renal cadmium and zinc both had a positive relationship with sediment concentrations when analyzed by game management zone and both renal cadmium and nickel were significantly affected by sediment concentrations in the area immediately surrounding the moose collection point.

The obvious mode of transfer of these elements from sediment to moose is via plants growing in the soil and being consumed by moose. Willows (*Salix* sp.) are a preferred food species for Yukon moose (Risenhoover, 1989), and have been shown to be hyperaccumulators of Cd and Zn (Vandecasteele et al., 2002). Although this effect has not (to the author's knowledge) been measured for Ni, it is reasonable to suppose that elements as similar chemically as Cd, Zn and Ni would act in the same manner, and that Ni would also accumulate in willows. It is likely that variation in renal elements that cannot be explained by sediment element or age may be explained, at least in part, by habitat variation. The presence or absence of hyperaccumulating plants that provide forage for moose will determine whether metals in the soil will be passed on to moose. Areas with high sediment elements, but no hyperaccumulating plants would not be expected to show high renal elements in moose as they would then browse on other species. Unfortunately, we have no quantitative measure of this variable to add to the analysis.

Nickel and zinc are both essential trace elements under homeostatic control, and concentrations in moose kidneys are similar to those considered adequate for cattle (Puls, 1994). Neither element represents a toxicity issue for Yukon moose. The same is not true of cadmium. This element has been named as a potential health threat to wildlife species (Larison et al., 2000), and there appears to be quite a large 'hot spot' in the central/southeastern part of the territory (Figure 5). Some of the moose measured in this study, particularly those from the southeastern Yukon have renal Cd concentrations that fall within, or even exceed the threshold range of 400–800 µg·g^{-1} (dry weight) at which renal tubule dysfunction has been shown to occur (Elliot et al., 1992, Kjellstrom, 1986). This indicates potential for older moose in some parts of the Yukon to be at risk of renal dysfunction due to high renal cadmium. The fact that these moose were alive, shot by hunters and apparently healthy at the time suggests that 1) moose in this area may have evolved a high level of natural cadmium tolerance, 2) moose in this area may have developed a high level of cadmium tolerance over their lifetimes, or 3) moose, as a species, have a high level of Cd tolerance. Health Canada has recommended limiting consumption of Yukon moose kidneys and livers to one·year^{-1}·person^{-1}. Because Cd does not accumulate in muscle tissue no limit has been placed on the amount of moose meat recommended for consumption.

These analyses show clearly that the high concentrations of Cd found in Yukon moose, that have prompted a health advisory on Yukon moose liver and kidneys, and may pose a health hazard to the moose themselves, is

Figure 3. Moose kidney and stream sediment Cd analyzed by moose location

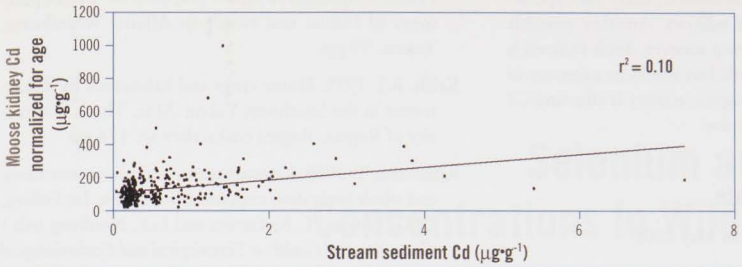


Figure 4. Moose kidney and stream sediment Ni analyzed by moose location

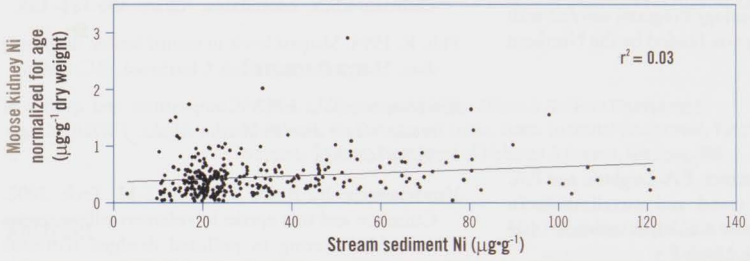
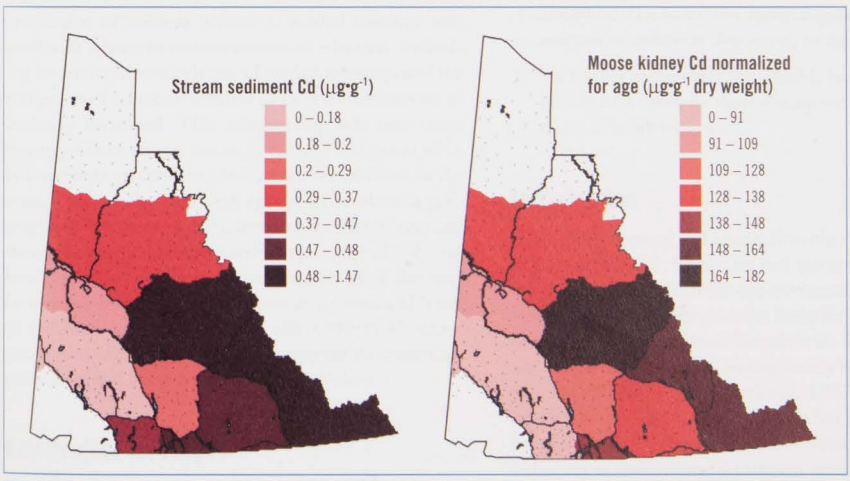


Figure 5. Average moose kidney and stream sediment Cd for hunting zones in the Yukon Territory



consistent with the hypothesis that the Cd is coming from naturally occurring geological sources, likely via hyperaccumulating plants such as willows. Another possible source of the Cd is local point sources. Such analysis is beyond the scope of this work, but would be necessary to determine whether anthropogenic activity is affecting Cd concentrations in Yukon moose.

Project Completion Date

The project was completed in May 2003

Acknowledgements

This project was generously supported by the Yukon Geology Program, and Emma Cunningham (DIAND) and Amy Stuart (Yukon Geology Program) assisted with the GIS work. The project was funded by the Northern Contaminants Program.

References

Elliot , J.E., A.M. Scheuhammer, F.A. Leighton and P.A. Pearce. 1992. Heavy metal and metallothionein concentrations in Atlantic Canadian seabirds. *Arch Environ Contam Toxicol.* 22:63–73.

Gamberg, M. 2000. Contaminants in Yukon Country Foods. Unpublished report prepared for the Department of Indian and Northern Affairs, Whitehorse, Yukon. 95 pp.

Keith, R.J. 1995. Home range and habitat use by female moose in the Southwest Yukon. MSc. Thesis. University of Regina, Regina Saskatchewan. 174 pp.

Kjellstrom, T. 1986. Critical organs, critical concentrations and whole body dose-response relationships. In: Friberg, C.-G. Elinder, T. Kjellstrom and G.F. Nordberg (eds.) *Cadmium and Health: a Toxicological and Epidemiological Appraisal, Vol. 2.* CRC Press, Boca Raton, Florida, pp. 231–246.

Larison, J.R., G.E. Likens, J.W. Fitzpatrick and J.G. Crock. 2000. Cadmium toxicity among wildlife in the Colorado Rocky Mountains. *Nature.* 406:181–183.

Puls, R. 1994. Mineral levels in animal health: diagnostic data. Sherpa International, Clearbrook, BC. 356 pp.

Risenhoover, K.L. 1989. Composition and quality of moose winter diets in interior Alaska. *J Wildl Manage.* 53(3):568–577.

Vandecasteele, B., B. De Vosa and F.M. Tack. 2002. Cadmium and zinc uptake by volunteer willow species and elder rooting in polluted dredged sediment disposal sites. *Sci Total Environ.* 299(1–3):191–205.

Selenium and Cadmium Concentrations in Wild Yukon Mink

Project leader

Mary Gamberg, Gamberg Consulting, Whitehorse, YT; phone: (867) 668-7023; fax: (867) 668-7024; e-mail: mary.gamberg@yt.sympatico.ca

Project team

Pat Roach, Department of Indian Affairs & Northern Development, Whitehorse, YT; Environment Yukon, Yukon Territorial Government; Yukon trappers; G. Stern, Department of Fisheries & Oceans, Winnipeg, MB.

Abstract

Mercury (total and methyl), cadmium and selenium concentrations were measured in tissues from mink trapped from the Yukon Territory. None of these metals were found at levels of toxicological concern. Total mercury concentrations were inversely related to the proportion of mercury present as methyl mercury, and positively related to concentrations of selenium, indicating increasing demethylation of methyl mercury, and the formation of mercuric selenide as total concentrations of mercury increased. This relationship was seen most strongly in mink liver, less so in kidneys and not at all in brains where most of the mercury was maintained in the methyl form. There did not appear to be obvious geographical 'hot spots' in mink mercury concentrations, and there was frequently a relatively large range of mercury levels found in mink from a given trapline. Mink diet may be a factor in this variation. Local environmental levels of cadmium do not appear to affect mink. Mercury, cadmium and selenium do not appear to constitute environmental hazards to mink in the Yukon.

Key Project Messages

1. Mercury, cadmium and selenium do not appear to constitute environmental hazards to Yukon mink.
2. No geographical 'hot spots' were found for mercury or cadmium in Yukon mink.

Objectives

1. To determine whether mink are exposed to high cadmium levels to the same degree as terrestrial animals in cadmium 'hot spots' in the Yukon.
2. To further understand the possible health impacts of mercury on mink by determining mercury/selenium ratios in mink tissues.

Introduction

In a review of spatial and temporal trends of contaminants in Canadian Arctic freshwater and terrestrial ecosystems, mercury was identified as the one contaminant found in fish that consistently exceeds guideline limits for commercial sale or subsistence consumption (Braune et al., 1999). Mink are top trophic level carnivores, feeding mainly on fish and small mammals (Gilbert and Nancekivell, 1982), and are thus exposed to the high levels of mercury found in freshwater fish. Furthermore, mink have been found to be sensitive indicators of environmental mercury, even at low levels of contamination (Kucera, 1983; Wren et al., 1986). Mercury levels in mink have been studied in NWT (Poole et al.,

1995), Manitoba (Kucera, 1983), Ontario (Wren et al., 1986) and northern Quebec (Langlois and Langis, 1995), but only tissues from three Yukon mink had been analyzed for mercury (Gamberg, 2000). Filling this knowledge gap will not only improve our understanding of the dynamics of mercury within the northern ecosystem, but in the implementation of this project, and in the communication of results, it will also increase public awareness of this environmental issue and of ecosystem health in general.

Activities

In 2002–2003

This project was initiated as an adjunct to an existing project funded by the Northern Ecosystems Initiative Program (Environment Canada) to study mercury in Yukon mink. In addition, Nil Basu, a graduate student working at McGill University under Dr. Laurie Chan, analyzed some of the mink brains for total Hg and methylmercury (MeHg) as part of his work on brain neurotransmitters. To keep the research in perspective, results from all three portions of the project are presented as an integrated whole.

A total of 98 mink carcasses were received from Yukon trappers over the two years of the project. All liver and kidney were analyzed for total mercury and selenium. Liver, kidney and brain tissue was analyzed for total Hg, MeHg and Se while only kidneys were analyzed for Cd. A lower canine was extracted from each mink and the age of the animal determined using the cementum technique at the Yukon Environment laboratory in Whitehorse. The stomach contents of each mink were analyzed at the same laboratory.

Results

Fish and mammals together made up 89% of the Yukon mink diet, with fish being slightly more prevalent (Table 1). Invertebrates were only found in two mink stomachs and were present in very small amounts (1–2% of total stomach contents). Unknown material was also found in two mink stomachs and in both cases appeared to be a synthetic fabric. None of age, sex or year of collection significantly affected levels of total Hg, MeHg or Se in any tissues measured. There was a negative relationship between total Hg concentrations and % MeHg in mink liver (Figure 1), but no significant relationship in either kidney or brain tissue. A positive relationship between total Hg and Se was found in mink liver and kidney, but not in brain (Figure 2). Kidney Cd was not affected by mink sex or year of collection, but was positively related to age, a relationship that is commonly seen in a variety of animals (Gamberg, 2000). The mink were assigned to one of two groups based on Yukon game management zones that were designated as high or low Cd areas. This designation was based on moose renal Cd and stream sediment Cd levels found in a previous study (Gamberg, 2003). There was no difference in mink renal Cd concentrations between the two areas. There did not appear to be obvious geographical 'hot spots' in mink Cd or Hg concentrations (Figure 3).

Discussion and Conclusions

Total concentrations of mercury in Yukon mink (Table 2) were similar to those found in mink from NWT (Poole et al., 1995), and generally lower than mink from Ontario (Wren et al., 1986; Evans et al., 2000) and Manitoba (Kucera, 1983). Total mercury levels in mink liver and brain were an order of magnitude lower than concentrations cited by Weiner et al. (2002) that would indicate lethal exposure (20–100 $\mu g \cdot g^{-1}$ in liver and > 10 $\mu g \cdot g^{-1}$ in brain on a wet weight basis). Selenium concentrations

Figure 1. Total and methyl mercury in Yukon mink liver

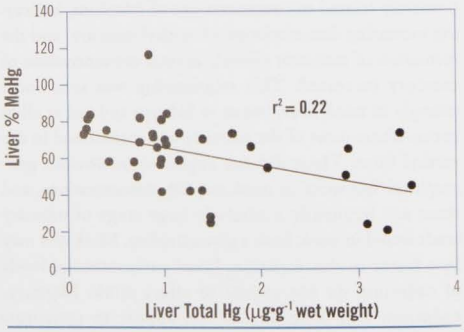
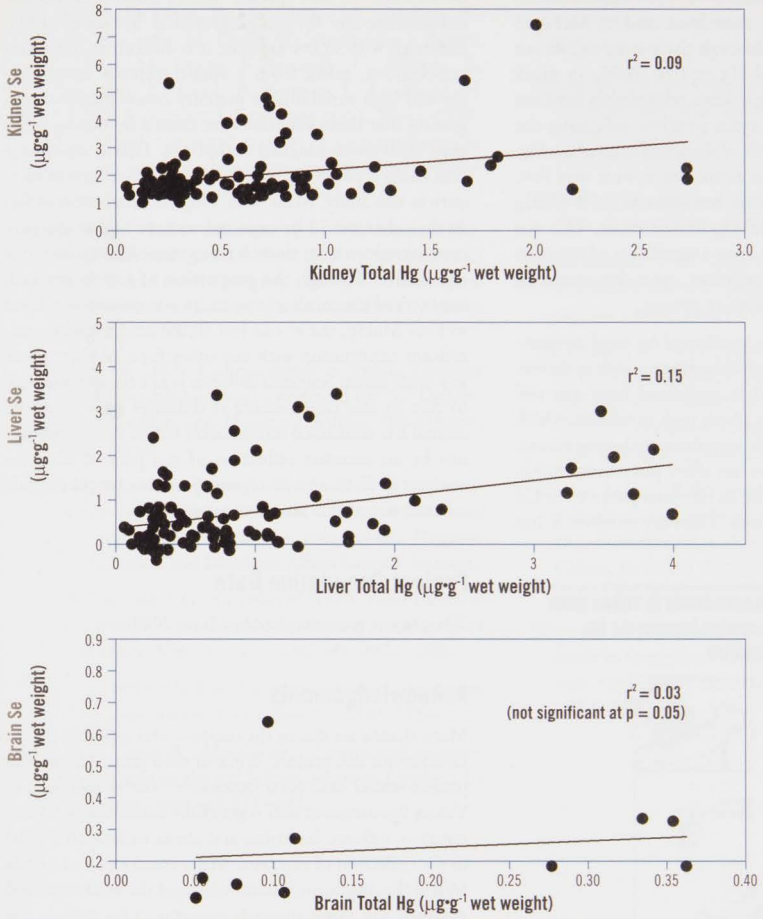


Table 1. Analysis of mink stomach contents from Yukon mink trapped 2001–3

	Fish	Mammal	Bird	Invertebrate	Vegetation	Unknown
Weighted Mean (%)	46	43	4	0	6	1
Frequency of Occurrence (%)	36	30	3	2	9	2

Figure 2. Total mercury and selenium in three tissues from Yukon mink



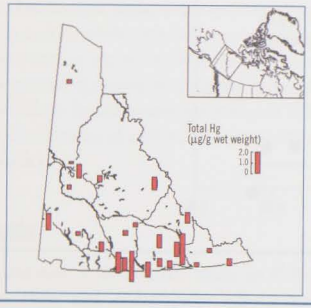
in these mink were somewhat higher than levels considered 'adequate' in mink by Puls (1994), but the mink did not show any signs of selenium toxicity. Kidney cadmium concentrations ranged from 0.034 to 1.84 $\mu g \cdot^{-1} g$ (wet weight) and did not approach levels that are thought to cause kidney dysfunction (100–200 $\mu g \cdot g^{-1}$ wet weight; Scheuhammer, 1991).

A significant relationship between total Hg and % MeHg has been explained in a variety of animals to be a threshold relationship where mercury consumed as MeHg remains in that form until a concentration of about 10 $\mu g \cdot g^{-1}$ is reached and the demethylation mechanism is activated (Weiner et al., 2002). The data from this project shows a similar relationship, but without the threshold effect. In fact the levels found in this study are consistently less than half that threshold concentration. The highest concentrations of total Hg are found in mink liver, where there is a significant inverse relationship between total Hg and % MeHg. This indicates the demethylation of MeHg in liver tissue occurring at a greater rate with increasing concentrations of total Hg. Wagemann (1999) has hypothesized that demethylation in the liver leads to the formation of Hg^{++} and finally the detoxification of that form to mercuric selenide (HgSe). Evidence supporting this hypothesis was offered from marine mammal data that indicated a positive relationship

between total Hg and Se in liver tissue. The same relationship is seen in the Yukon mink liver. Total Hg concentrations are lower in kidney than liver, and % MeHg is correspondingly higher. Although there is no significant relationship between total Hg and % MeHg in mink kidney tissue, there is a significant relationship between kidney total Hg and Se, again possibly indicating the formation of HgSe as a result of demethylation of MeHg. Total Hg concentrations in mink brains were very low, and virtually no demethylation was apparent, with MeHg making up 92% of the total Hg in that tissue. This was the only tissue that did not show a significant relationship between total mercury and selenium, again demonstrating the absence of the demethylation process.

Mink do not appear to be as affected by local environmental levels of Cd as terrestrial herbivores such as moose. In the latter case, the Cd is mobilized from the soil through hyperaccumulating plants such as willows, which are preferred forage for arctic ungulates, including moose. This process obviously does not affect piscivorous mink, and there doesn't seem to be an alternate pathway of Cd accumulating in their food web. There are no obvious 'hot spots' of Cd in Yukon mink, and Cd does not appear to be an issue for this species. Yukon mink also did not demonstrate any obvious geographical 'hot spots' of Hg. Although with so few samples, it is difficult to draw firm conclusions, mink from a single trapline frequently showed high variability in mercury concentrations, suggesting that these variations are caused by factors other than local environmental conditions. Diet is one factor that could account for some of the variation seen in mercury in this study. Mink with a higher proportion of fish in their diet would be expected to have higher mercury concentrations than those feeding more heavily on small mammals. Although the proportion of fish in stomach contents of the mink in this study was positively related to liver MeHg, the r^2 was low (0.06) and it had no significant relationship with any other form of mercury in any other tissue. Stomach contents is not the best measure of diet in this case because it indicates only what the animal has consumed immediately before death and may not be an accurate reflection of the general diet. An analysis of C-13 and N-15 isotope ratios would provide a better test of this potential relationship.

Figure 3. Total mercury concentrations in Yukon mink liver tissue. Each symbol represents the average for one trapline



Project Completion Date

The project was completed in June 2003

Acknowledgements

Many thanks are due to the trappers who submitted mink carcasses for this project. Without their participation, this project would have been impossible. The cooperation of Yukon Environment staff is gratefully acknowledged. Conservation officers, biologists and clerks were instrumental in the collection of carcasses. Many thanks also to Angela Milani (Environment Yukon) who aged the mink teeth and analyzed the mink stomach contents. This project was funded by the Northern Ecosystem Initiative (Environment Canada) and the Northern Contaminants Program.

Table 2. Metal concentrations in Yukon mink trapped 2001–3 (wet weight basis)

	Kidney				Liver				Brain			
	N	Mean		SD	N	Mean		SD	N	Mean		SD
Total Hg (µg/g)	98	0.66	±	0.54	98	0.92	±	0.90	30	0.22	±	0.16
MeHg (µg/g)	33	0.77	±	0.48	38	0.85	±	0.57	20	0.21	±	0.16
% MeHg	33	72	±	13	38	63	±	19	20	93	±	22
Cadmium (µg/g)	39	0.22	±	0.30								
Selenium (µg/g)	98	2.07	±	1.05	98	1.40		0.84	10	0.39	±	0.17
% Moisture	30	72	±	8	30	69	±	2	30	77	±	3

References

Braune, B., D. Muir, B. DeMarche, M. Gamberg, K. Poole, R. Currie, M. Dodd, W. Duschenko, J. Eamer, B. Elkin, M. Evans, S. Grundy, C. Hebert, R. Johnstone, K. Kidd, B. Koenig, L. Lockhart, H. Marshall, K. Reimer, J. Sanderson and L. Shutt. 1999. Spatial and temporal trends of contaminants in Canadian Arctic freshwater and terrestrial ecosystems: a review. *Sci Total Environ.* 230:145–207.

Evans, R.D., E.M. Addison, J.Y. Villeneuve, K.S. MacDonald and D.G. Joachim. 2000. Distribution of inorganic and methylmercury among tissues in mink (*Mustela vison*) and otter (*Lutra canadensis*). *Environ Res.* 84:133–139.

Gamberg, M. 2000. Contaminants in Yukon Country Foods. Unpublished report prepared for the Department of Indian and Northern Affairs, Whitehorse, Yukon. 95 pp.

Gamberg, M. 2003. Retrospective Analysis of Contaminants in Yukon Moose. *Synopsis of Research Conducted under the 1998/99 Northern Contaminants Program.* Ottawa: Indian and Northern Affairs Canada. In press.

Gilbert, F.F. and E.G. Nancekivell. 1982. Food habits of mink (*Mustela vison*) and otter (*Lutra canadensis*) in northeastern Alberta. *Can J Zool.* 60:1282–1288.

Kucera, E. 1983. Mink and otter as indicators of mercury in Manitoba waters. *Can J Zool.* 61:2250–2256.

Langlois, C. and R Langis. 1995. Presence of airborne contaminants in the wildlife of northern Quebec. *Sci Tot Environ.* 160/161:391–402.

Poole, K.G., B.T. Elkin and R.W. Bethke. 1995. Environmental contaminants in wild mink in the Northwest Territories, Canada. *Sci Tot Environ.* 160–161: 473–486.

Proulx, G., J.A. McDonnell and F.F. Gilbert. 1987. The effect of water level fluctuations on muskrat, *Ondatra zibethicus*, predation by mink, *Mustela vison. Can Field-Nat.* 101:89–92.

Puls, R. 1994. *Mineral levels in animal health: diagnostic data.* Sherpa International, Clearbrook, BC. 356 pp.

Scheuhammer, A.M. 1991. Effects of acidification on the availability of toxic metals and calcium to wild birds and mammals. *Environ Pollut.* 71:329–375.

Wagemann, R. 1999. Methylmercury and heavy metals in tissues of narwhal, beluga and ringed seals. In: S. Kalhok (ed.), *Synopsis of Research conducted under the 1997/98 Northern Contaminants Program.* Ottawa, ON: Indian and Northern Affairs Canada: 205–209.

Weiner, J.G., D.P. Krabbenhoft, G.H. Heinz and A.M. Scheuhammer. 2002. Ecotoxicology of Mercury. In: D.J. Hoffman, B.A. Rattner, G.A. Burton, Jr., and J. Cairns, Jr. (eds.), *Handbook of Ecotoxicology*, 2nd edition. CRC Press, Boca Raton, Florida.

Wren, C.D., P.M. Stokes and K.L. Fischer. 1986. Mercury levels in Ontario mink and otter relative to food levels and environmental acidification. *Can J Zool.* 64: 2854–2859.

Survey of Contaminants in Country Foods in the Selkirk First Nation Traditional Territory

Project leaders

Mary Gamberg, Research Biologist, Gamberg Consulting, Box 10460, Whitehorse, YT Y1A 7A1; phone: (867) 668-7023; fax: (867) 668-7024; e-mail: mary.gamberg@yt.sympatico.ca; Selkirk First Nation, Box 40, Pelly Crossing, YT Y0B 1P0; phone: (867) 537-3331; fax: (867) 837-3902; e-mail: klugies@selkirkfn.com

Project team

Styd Klugie, Selkirk First Nation; Selkirk First Nations members and elders; Mark O'Donoghue, Yukon Territorial Government Biologist, Mayo, YT.

Abstract

Whitefish and moose were sampled from the traditional territory of the Selkirk First Nation, near Pelly Crossing, Yukon, to address concerns of the First Nation regarding contaminants in their traditional foods and the safety of consuming those foods. Whitefish muscle was analyzed for total mercury, selenium and arsenic and a range of organochlorines. All contaminant concentrations were low and not of concern to people using these fish as a food source. Moose liver, kidney and muscle were analyzed for 26 elements. Elements of concern such as arsenic, lead and mercury were found at very low levels and should not be considered health issues. Cadmium levels in moose kidney and liver, while lower than levels found in moose from other parts of the territory, may still be a health concern. Consumers of these organs should note the Yukon Health and Social Services recommendation to limit consumption of moose liver and kidney to one/year. Cadmium does not accumulate in moose muscle (meat) and no limit has been placed on the amount of moose meat recommended for consumers.

Key Project Messages

1. Whitefish and moose from the Selkirk First Nation traditional area have generally low levels of contaminants and do not pose a health threat to consumers or to the animals themselves.
2. Those concerned about cadmium intake (especially smokers) should limit their intake of moose liver and kidney to one/year.

Objectives

1. To determine contaminant levels in country foods traditionally used by the Selkirk First Nation.
2. More specifically, to determine cadmium levels in moose in the Selkirk traditional area (human health issue).
3. To restore confidence in country foods within the Selkirk First Nation.

Introduction

The Northern Tutchone people of the Selkirk First Nation (SFN) continue to practice many aspects of their traditional lifestyle and consider it important to preserve this lifestyle for future generations. An important aspect of this lifestyle is hunting and gathering traditional foods throughout the SFN traditional territory. Over the past decade there has been much discussion and controversy about contaminants in the Canadian Arctic. This has caused some concern within SFN about the safety of consuming traditional foods from their traditional territory.

A survey of the Yukon Contaminants Database identified very few samples collected from the Selkirk traditional area. A survey of contaminants in Yukon country foods, conducted in 1995 under the Northern Contaminants Program, sampled only two ruffed grouse and two ground squirrels from this area. An ongoing survey of contaminants in Yukon moose and caribou has resulted in samples from seven moose and one caribou from the area, and an ongoing DIAND project sampling fish from around the Yukon for contaminants has only sampled one lake (Tatlemain) from the area. This constitutes a data gap in contaminants in country foods within the SFN traditional territory.

The purpose of this project was to determine if traditional foods from the SFN territory are safe to consume, and to restore the confidence of these First Nation people in their traditional lifestyle. SFN chose to sample moose and trout for contaminant analysis — two wildlife species commonly used as food and of concern with respect to contaminants. This addresses the identified data gap within the Yukon Contaminants Database.

Activities

In 2000–2001

Although the intent was for SFN to participate in the collection of fish for contaminant analysis, no members of the First Nation were available to assist. The Fish and Wildlife branch of Yukon Environment collected fish from Earn and Tadru Lakes, both near Pelly Crossing, Yukon, for this project. Trout were unavailable from these lakes, but 18 lake whitefish (*Coregonus clupeaformis*) were collected and analyzed in their place. Whitefish are also traditionally harvested by SFN as a food source. Fish were processed by DIAND staff in Whitehorse, and otoliths were extracted for aging. Whitefish muscle was analyzed for total mercury, selenium and arsenic and a range of organochlorines by Dr. Gary Stern at DFO, Winnipeg, using high resolution gas chromatography with electron capture detection.

Although every effort was made to obtain moose samples from SFN hunters during hunting season, none were submitted to the project. Muscle samples from 8 moose were obtained from hunters' freezers, and 5 liver, kidney and muscle samples from moose hunted in the SFN traditional territory were donated to this project from the ongoing Hunter Survey Program. Moose samples were processed at the DIAND laboratory in Whitehorse and were analyzed for a suite of 26 elements at Elemental Research Inc. in Vancouver using ICP-MS. Liver and kidney samples were analyzed individually, while the muscle samples were pooled into two groups for analysis, one group from SFN hunter freezers and one group from the hunter survey. Where teeth were available, they were aged using the cementum technique.

A full technical report on the project was written (Gamberg, 2003), and a brochure summarizing the findings of the project in a lay format was produced. The results of the project were also presented at the Annual Spring Gathering of SFN in May of 2003.

Results and Discussion

Arsenic and selenium concentrations were significantly lower in whitefish muscle samples from Tadru Lake as compared with those from Earn Lake, while mercury levels were significantly higher (Fig. 1). These differences may be the result of naturally occurring environmental levels of these elements. Selenium tends to concentrate in the black shales of the Selwyn Basin in the Yukon. Earn Lake is surrounded by these black shales whereas Tadru Lake is in a sedimentary geological type and would not be expected to have high selenium.

Total mercury in lake whitefish muscle was inversely related to selenium (Fig. 2; $p < 0.001$; $r^2 = 0.515$). It is

Figure 1. Average element concentrations (wet weight) in lake whitefish muscle from two Yukon Lakes

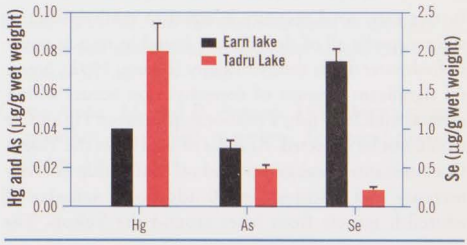


Figure 2. Relationship between Hg and Se in muscle from whitefish collected from two Yukon lakes

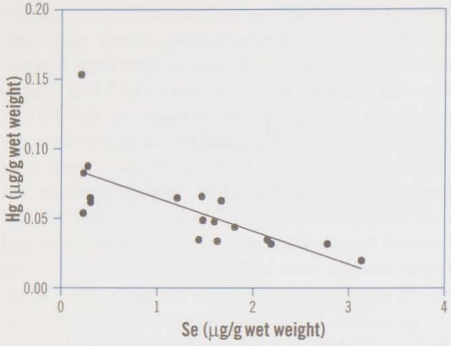
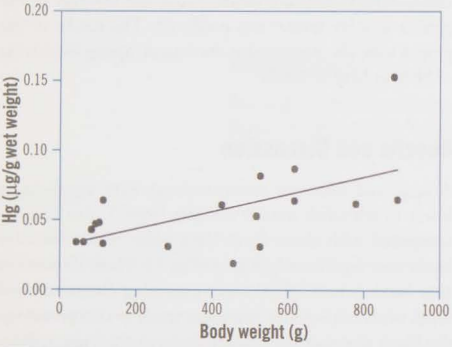
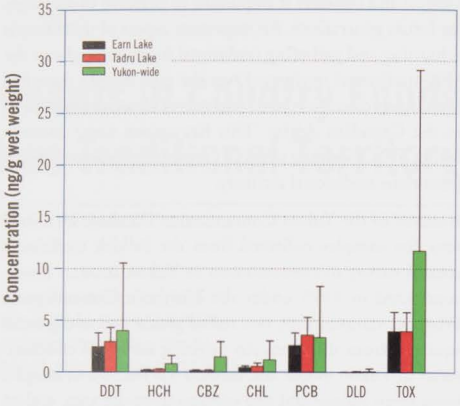


Figure 3. Relationship between muscle Hg and body weight in whitefish collected from two Yukon lakes



generally believed that selenium protects vertebrates against methylmercury poisoning (Cuvin-Aralar and Furness, 1991), but this has been shown largely in mammals and as a result of Hg-Se complexes being formed after the methylmercury has been demethylated (Wiener et al., 2002). In these cases, the relationship between Hg and Se is a positive one. Although methylmercury was not measured in this study, we assume that in this case, total mercury is equal to methylmercury, since virtually all of the mercury found in muscle tissue of freshwater fish is methylmercury (Bloom, 1992). Since, no significant amount of demethylation occurs within skeletal muscle of fish, a relationship between Hg and Se would not be expected. Analysis of data from the Yukon Contaminants Database revealed no relationship between mercury and selenium in 10 additional samples of whitefish muscle from lakes around the Yukon. The

Figure 4. Average organochlorine concentrations in whitefish muscle from Tadru and Earn Lakes and the average for Yukon lakes (data from the Yukon Contaminants Database)



DLD = dieldrin; CBZ = chlorobenzenes (include 1245- and 1234-tetrachlorobenzene, penta- and hexa-chlorobenzene); HCH = hexachlorocyclohexanes (include α,β,δ and γ-HCH); CHL = Chlordanes (include heptachlor, octachlorostyrene, oxychlordane, *trans*- and *cis*-chlordane, *trans*- and *cis*-nonachlor and heptachlor epoxide); DDTs include o,p- and p,p-DDE, o,p- and p,p-DDD and o,p- and p,p-DDT; PCBs include 91 PCB congeners; TOX = Toxaphene.

relationship seen in this study may be a reflection of local environmental levels of these metals.

Mercury in lake whitefish muscle was positively related to body weight (Fig. 3; $p = 0.008$; $r^2 = 0.025$). This relationship has been shown in many laboratory studies with fish (Wiener and Spry, 1996). Increasing concentrations of mercury with size or age indicate that the elimination of methylmercury is very slow relative to the uptake in fish. However, mercury levels in these fish do not approach concentrations that would be considered harmful to those using these whitefish as a food source. For those concerned about mercury in their diet, choosing smaller fish to eat would reduce the level of mercury intake.

Organochlorine concentrations in muscle from whitefish from the SFN area were consistently low and not a health concern for those consuming these fish. None of the organochlorines measured differed between SFN lakes, and most did not differ from concentrations found in whitefish Yukon-wide. Chlorobenzenes and HCHs, however, were lower in whitefish from the SFN area than the Yukon in general (Fig. 4). Note that although the average toxaphene level was higher Yukon-wide than in the SFN area, the high variability among individual concentrations resulted in no statistically significant difference between the Yukon in general and the SFN lakes.

Table 1. Average element concentrations ($\mu g \cdot g^{-1}$ dry weight) in tissues from moose collected from the Selkirk First Nation traditional territory (Mean ± standard deviation)

	Kidney			Liver			Muscle		
N	5			5			2 (Pooled)		
Aluminium	1.00	±	0.55	1.12	±	0.58	0.85	±	0.38
Arsenic	0.16	±	0.06	0.08	±	0.02	0.05	±	0.04
Cadmium	120.3	±	82.0	13.7	±	5.8	9.7	±	5.5
Copper	14.9	±	2.2	100.0	±	109.8	104.9	±	6.9
Lead	0.06	±	0.05	0.04	±	0.01	0.03	±	0.02
Mercury	< 0.05	±	0	< 0.05	±	0	< 0.05	±	0
Selenium	5.52	±	1.56	6.86	±	3.16	5.01	±	2.62
Zinc	127.6	±	24.3	72.6	±	23.8	48.2	±	34.5

Most element concentrations measured in moose kidneys, livers and muscle tissue from the SFN traditional area were not significantly different from those found in other parts of the Yukon (data from Yukon Contaminants Database). Arsenic, cadmium, calcium, strontium, vanadium and zinc were all lower in moose from the SFN area than in moose from other parts of the Yukon. Mercury concentrations tend to be low in Yukon moose, and were not detectable in any moose tissues analyzed from the SFN area. The low levels of some elements found in moose from this area likely reflect the local geology of the area.

Most elements measured in moose tissues were not at levels considered harmful to consumers. Elements of concern such as arsenic, lead and mercury were all found at very low levels and should not be considered health issues (Table 1). Cadmium levels in moose kidney and liver, while lower than levels found in moose from other parts of the territory, may still be cause for concern for those who have a preference for eating liver and kidney, especially if they are also smokers. Consumers of these organs should note the Yukon Health and Social Services recommendation to limit consumption of moose liver and kidney to one/year. Cadmium does not accumulate in moose muscle (meat) and no limit has been placed on the amount of moose meat recommended for consumers. Cadmium does accumulate over time, so that older animals would be expected to have higher levels in their organs than younger animals. Choosing to eat liver and kidney from younger animals would reduce the intake of cadmium.

Conclusions

Whitefish and moose from the Selkirk First Nation traditional area have generally low levels of contaminants and do not pose a health threat to consumers or to the animals themselves. Those concerned about cadmium intake (especially smokers) should limit their intake of moose liver and kidney to one/year.

Expected Completion Date

This project was completed in May 2003

Acknowledgements

The authors would like to gratefully acknowledge the assistance of Susan Thompson and Aaron Foos from Environment Yukon who collected fish for this project, and to Pat Roach and Rem Ricks from DIAND who processed the fish for analysis. Many thanks also, to the SFN hunters who donated moose meat samples from their freezers for analysis. This project was funded by the Northern Contaminants Program.

References

Bloom, N. 1992. On the chemical form of mercury in edible fish and marine invertebrate tissue. *Can J Fish Aquat Sci.* 46:1131–1140.

Cuvin-Aralar, M. and R. Furness. 1991. Mercury and selenium interaction: a review. *Ecotoxicol Environ Safety.* 21:348–364.

Gamberg, M. 2003. Survey of Contaminants in Country Foods in the Selkirk First Nation Traditional Territory. Unpublished report prepared for the Selkirk First Nation, Pelly Crossing, Yukon. 19 pp.

Wiener, J., D. Krabbenhoft, G. Heinz, A. Scheuhammer. 2002. Ecotoxicology of Mercury. In: D. Hoffman, B. Rattner, G. Burton and J. Cairns. (eds.), *Handbook of Ecotoxicology,* 2nd edition. CRC Press, Boca Raton, FL.

Wiener J. and D. Spry. 1996. Toxicological significance of mercury in freshwater fish in Environmental Contaminants. In: W. Beyer, G. Heinz, A. Redmon-Norwood (eds.), *Wildlife: Interpreting Tissue Concentrations.* Boca Raton, FL: Lewis Publishers. pp. 297–339.

Temporal and Spatial Trends of Contaminants in Canadian Polar Bears

Project leader

Robert Letcher, Great Lakes Institute for Environmental Research, University of Windsor, Windsor, ON; phone: (519) 253-3000 ext: 3753; fax (519) 971-3616; e-mail: letcher@uwindsor.ca; Derek Muir, National Water Research Institute, Environment Canada, Burlington, ON; phone: (905) 319-6921; fax: (905) 336-6430; e-mail: derek.muir@ec.gc.ca; Aaron Fisk, National Water Research Institute, Environment Canada, Burlington, ON; phone: (905) 336-6405; fax: (905) 336-6430; e-mail: aaron.fisk@ec.gc.ca; Ross Norstrom, National Wildlife Research Centre, Environment Canada, Hull, PQ; phone: (613) 859-6273; e-mail: ross.norstrom@sympatico.ca

Project team members

Birgit Braune and Bryan Wakeford, Canadian Wildlife Service, Environment Canada, Hull, PQ; Mitch Taylor, Department of Sustainable Development, Government Nunavut, Iqaluit, NU; John Nagy and Marsha Branigan, Department of Resources, Wildlife and Economic Development, Government of the Northwest Territories, Inuvik, NWT; Ian Stirling and Nick Lunn, Canadian Wildlife Service, Environment Canada, Edmonton, AB; Martyn Obbard, Ontario Ministry of Natural Resources, Government of Ontario, Peterborough, ON.

Abstract

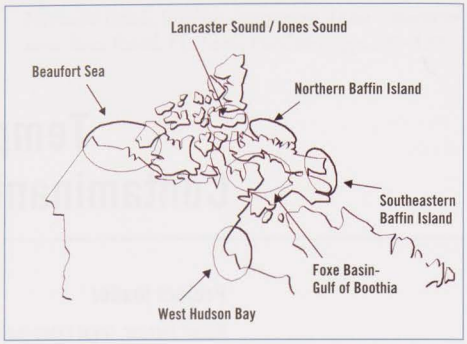
The polar bear (*Ursus maritimus*) is the apex predator of the Arctic marine ecosystem and an integral component of Inuit culture. Due to its position at the top of the marine food web, levels of contaminants in polar bears are among the highest observed in the Arctic. Significant concerns about the effect of these contaminants exist for both the polar bear and humans who consume them. Although the levels of organochlorine contaminants have been monitored in western Hudson Bay polar bears throughout the 1990s, there has not been a comprehensive study on the spatial distribution of contaminants, organics or metals in Canadian polar bears since the late 1980s and early 1990s. To address this data gap we determined a suite of persistent organic pollutants (POPs) and metals that have been identified as important contaminants in the environment, in tissues of individual polar bears (i.e., female bears between the ages of 5 and 15 years to reduce age effects) from populations spanning the Canadian Arctic. Samples of liver, muscle and fat were collected (2001–2002 season) from all polar bears harvested in Nunavut and some of the bears from the Northwest Territories.

Key Project Messages

1. Levels of arsenic, cadmium, mercury and selenium in polar bear liver in 2001–02 were similar to what they were in 1989–91.

2. The highest levels of mercury were found in polar bear livers from the southern Beaufort Sea. This is similar to geographic trends for mercury in Beluga.
3. Between 1989–91 and 2001–02, concentrations of chlordanes, DDTs, PCBs and PCB metabolites ($MeSO_2$-PCBs) showed a general decline.
4. For the first time, the flame retardant polybrominated diphenyl ether (PBDE) was measured in polar bear fat.
5. Perfluorinated acids, primarily perfluorooctane sulfonate (PFOS), were measured in polar bear liver. The highest concentrations of PFOS were measured in livers of Hudson Bay polar bears.

Figure 1. The regions of the Canadian Arctic that polar bears were chosen from for analysis of contaminants



Objectives

1. Determine spatial and temporal trends of persistent organic pollutants (POPs), including new potential POPs such as brominated flame retardants and perfluorinated acids, and metals in the tissues of polar bears collected throughout the Canadian Arctic in 2001–2002.
2. Measure stable isotopes of nitrogen and carbon in muscle tissue to determine the diet of the polar bears for use in assessing variation in contaminant levels.
3. To archive polar bear tissue samples for this project and future studies.
4. Provide information in a timely manner to each Inuit community participating in the study, on the levels and temporal trends of these contaminants in polar bear.

Introduction/Study Design

Collection of polar bear fat and liver samples was made during the 2001–2002 hunting season from what was initially considered 5 regions in the Canadian Arctic (Figure 1). However, after assessing the samples obtained, it was decided that the sets actually were comprised of bears from 6 populations. A large of number of samples was made available, and appropriate samples were selected (i.e., female polar bears between the ages of 5 and 15 years from each of the 6 regions). We have measured a suite of contaminants (organic and metals) in the fat and liver of the selected bears to assess spatial and temporal contaminant trends. Temporal trends can vary geographically and there has not been a comprehensive examination of contaminants in polar bears of Canada in more than 10 years. These locations were chosen based on the variability of OC concentrations observed in polar bear populations from the 1980s and early 1990s (Norstrom et al., 1998). Stable of isotopes of nitrogen and carbon in muscle are also in the process of being determined, and will be compared with ringed seal values available from other studies to assess if the feeding behavior of polar bears varies between regions. These results have been compared to past studies on OCs and metals in Canadian polar bears.

In the 2001 and 2002 hunting seasons, adipose samples from polar bears from several representative regions of the Canadian Arctic were gathered for contaminant analysis. In addition to the affiliation in the title, other Canadian government departments that participated in sample collection and distribution and/or sample analysis were NWRI (Environment Canada), NWRC (CWS, Environment Canada), Dept. of Sustainable Development (Government Nunavut), Dept. of Resources, Wildlife and Economic Development (Government of the NWT) and the Ontario Ministry of Natural Resources (Government of Ontario). Female polar bears were chosen from 5 regions in the Canadian Arctic (NWT and Nunavut, Figure 1). These locations were chosen based on the variability of PCB, OC and $MeSO_2$-PCB/-DDE concentrations observed in polar bear populations from the 1980s and early 1990s (Letcher et al., 1995; Norstrom et al., 1998). The number of samples was chosen to provide the necessary statistical power based on OC variability in polar bears. Norstrom et al. (1998) and Henriksen et al. (2001) concluded that a minimum sample size of 10 per location was required for statistical analysis of contaminant concentrations between locations. Due to the increase in concentrations with age in male polar bears and variability in concentrations encountered in young

bears, female polar bears between the ages of approximately 5 and 15 were chosen. Along with the samples, a tooth was collected and is currently being used for aging the bears. Stable isotopes of nitrogen and carbon in muscle is also being determined (Atwell et al., 1998; Hobson and Welch, 1998) and compared to ringed seal values available from other studies to assess if the feeding behavior of polar bears varies between regions. Adipose samples were stored at the NWRI (Environment Canada) and GLIER at –20°C or lower.

Results and Discussion

The main deliverable that was initially identified was to report on spatial and temporal trends in metal and POP concentrations in monitoring tissues of Canadian polar bears from areas of the NWT and Nunavut. The findings of these analyses are presently listed and discussed.

Metals

Liver samples were analyzed for mercury by cold vapour atomic absorption spectrometry (CVAAS) and for 24 elements using Inductively Coupled Plasma-low resolution mass spectrometry (ICP-MS) by NLET.

The toxicological significance of the *standard* suite of organochlorine contaminants (OCs) and metals in Arctic biota has been discussed in recent assessment reports (de March et al., 1998; Muir et al., 1997). The OCs include PCB congeners, DDT and metabolites, chlordane compounds, HCH isomers, chlorobenzens, toxaphene, and a number of miscellaneous compounds (e.g., mirex, endosulfan, etc.). Metals include Hg (organic and inorganic), Ag, As, Ba, Cd, Co, Cr, Cu, Ga, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sr, Tl, U, V, and Zn.

More than 20 elements were detected in the polar bear livers; for brevity only the elements As, Cd, Pb, Se and Hg will be discussed (Table 1). These elements were chosen based on concern about their toxicity and because they were listed as elements of concern by AMAP (AMAP, 1998). Concentrations of As, Cd, Pb, Se and Hg in the polar bear livers collected in 2001–2002 are similar to those reported in 1982 and 1984 (Norstrom et al., 1986; Braune et al., 1991). It is currently not possible to statistically evaluate the temporal trends of metals in polar bears because the age data is not yet available for the 2001–2002 samples. Concentrations of Cd and Pb were lower but As, Se and Hg were higher in the polar bears from the Southern Beaufort region. This trend was also observed for Cd, Se and Hg in polar bears in 1982 and 1984 (Braune et al., 1991). Levels of mercury in beluga livers were also higher in animals from the Beaufort Sea region (Fisk et al., 2003). More detailed analysis of these data requires age data, which is currently not available.

POPs

Fat samples were extracted and analyzed for traditional OCs and $MeSO_2$-PCBs and -DDEs using CAEAL accredited and published methods by gas chromatography with electron capture detection (GC/ECD). The levels and congener patterns of PCBs and OC pesticides were determined based on methods originally described by Norstrom and Won (1985) with modifications (Muir et al., 1998, 2000; Norstrom et al., 1988, 1998; Norstrom and Muir, 1994), especially for $MeSO_2$-PCB and -DDE determination (Letcher et al., 1995a, 1995b, 1998, 2000a, 2000b; Sandala et al., 2003). $MeSO_2$-PCB and -DDE standards were supplied by Dr. Å. Bergman (Department of Environmental Chemistry, Stockholm University, Sweden). PCBs (40 congeners including co-elutions) and major OCs were determined i.e., Σ-DDTs (*p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD), Σ-HCHs (α-HCH, β-HCH, γ-HCH), Σ-CHLs (oxychlordane, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, heptachlor epoxide), Σ-CBzs (1,2,4,5-TeCBz, PnCBz, HxCBz) and Σ-$MeSO_2$-PCBs (20 congeners). Tribromobenzene (PCB/OC) and 3-$MeSO_2$-2-Me-2',3',4',5,5'-Cl_5biphenyl (sulfones) were used as internals standards. Duplicate and blank analyses were analyzed with each block of 5 samples. Blank analysis indicated no background contribution, and duplicate polar bear fat analysis demonstrated 5% or less variation of contaminant levels. PCB, OC and aryl

Table 1: Concentrations (mean ± 1 SE, µg/g, wet weight) of five metals in the livers of polar bears collected in the Canadian Arctic in 2001–2002 (Figure 1)

Region	N	As	Cd	Pb	Se	Hg
Beaufort Sea	11	0.46 ± 0.07	0.35 ± 0.06	0.06 ± 0.01	21.8 ± 6.0	62.5 ± 16.0
Southeastern Hudson Bay	11	0.17 ± 0.02	1.06 ± 0.15	0.12 ± 0.02	3.31 ± 0.61	7.34 ± 1.58
Southeastern Baffin Bay	13	0.22 ± 0.03	0.62 ± 0.11	0.69 ± 0.41	9.16 ± 2.35	28.4 ± 8.47
Northern Baffin Bay	12	0.37 ± 0.02	1.02 ± 0.08	0.26 ± 0.05	11.6 ± 0.63	32.5 ± 2.71
Lancaster Sound	13	0.32 ± 0.03	0.87 ± 0.15	0.23 ± 0.06	14.4 ± 2.20	45.2 ± 7.78

sulfone contaminant recoveries were consistently > 90%. The participating GLIER and NWRI laboratories are CAEAL accredited for PCB and OC analysis, and are participating in the NCP QA/QC program. For brevity, only the Σ-PCBs, Σ-CHLs, Σ-HCHs, Σ-CBzs, Σ-DDTs and Σ-$MeSO_2$-PCBs are listed in Table 2 for the present NCP report. Other POPs determined were 3-$MeSO_2$-4,4'-DDE, dieldrin, octachlorostyrene and mirex. All sum PCB, OC and metabolite levels, as well as congener-specific data will be included in peer-reviewed scientific papers that are anticipated for the data generated by this study.

In addition to these POPs, there are a number of contaminant classes that are of emerging environmental relevance. The occurrence of persistent $MeSO_2$-PCB metabolites in wildlife tissues is of growing interest. $MeSO_2$-PCB levels and congener pattern have been reported in ringed seal, polar bear and beluga whale from the Canadian Arctic (Letcher et al., 1995a, 1995b, 2000a, 2000b). $MeSO_2$-PCB and -DDE metabolites have also been shown to be bioaccumulative contaminants in the cod-ringed seal-polar bear food chain (Letcher et al., 1998; Wiberg et al., 1998). Specifically in polar bear liver, $MeSO_2$-PCB and -DDE metabolites were found to be the third most significant class of OC contaminants, exceeded only by PCBs and chlordanes (Letcher et al., 1996). Exposure of arctic wildlife and native peoples to $MeSO_2$-PCB and -DDE metabolites, as well as other OC metabolites such as oxychlordane, constitutes a potential health risk. PCB metabolites have demonstrated endocrine-related and other toxicities *in vivo*, but mostly *in vitro* (e.g., estrogen, thyroid and glucocorticoid hormone-dependent processes) (Letcher et al., 2000a). Chronic and reproductive toxicity was observed in mink exposed *in vivo* to 16 environmentally relevant $MeSO_2$-PCBs. 3-$MeSO_2$-CB132, -CB141 and -CB149, and 4-$MeSO_2$-CB149 reduced thyroid hormone levels (T4 and T3) in blood and increased thyroid weight and hepatic CYP protein levels in rats. *In vitro* endocrine-related effects of persistent $MeSO_2$-PCBs include: *i)* increased binding affinity of congeners with 3 chlorines in *ortho*-positions and an $MeSO_2$-group in either the 4- or 4'-position to glucocorticoid receptor (GR) from mouse and human liver cytosol; *ii)* cytotoxicity of 3- and 4-$MeSO_2$-CB52, -CB70, -CB87 and -CB101 in human placental JEG-3 and JAR choriocarcinoma cells (Letcher et al., 1999); *iii)* competitive inhibition of CYP11B1 in the mouse Y1 adrenocortical cell line by 4-$MeSO_2$-CB64 and -CB110 (similar to 3-$MeSO_2$-4,4'-DDE); and *iv)* inhibition of CYP11β enzyme activity *in vitro* in grey seal adrenals. $MeSO_2$-PCBs were recently shown to be anti-estrogenic in several *in vitro* cell assays (Letcher et al., 2002).

For western Hudson Bay bears sampled in 2001–2002 (Table 2), results were consistent with the apparent non-decreasing trend of Σ-CHLs and Σ-DDTs, and the apparent declining trend for Σ-PCBs observed from 1991–1999 (Norstrom, 2001; Muir and Norstrom, 1999). Although variable between POP class and population, the 2001–2002 spatial distribution patterns of the arithmetic mean concentrations of Σ-CHLs, Σ-PCBs and Σ-DDTs were comparatively unchanged relative to distribution patterns reported for these populations in 1989–1991 (Norstrom et al., 1998). There was a general decrease in geometric mean concentrations of Σ-CHL and Σ-PCB, but especially for p,p'-DDE (i.e., Foxe Basin/Gulf of Boothia, Northern Baffin Island and Eastern Baffin Island) for the six bear populations from 1989–1991 (Norstrom et al., 1998) to 2001–2002.

Σ-$MeSO_2$-PCBs decreased by about 50–60% relative to 1989–1991 levels for comparable populations (Table 1) (Letcher et al., 1995b). However, the Σ-$MeSO_2$-PCB to Σ-PCB concentration ratios were virtually unchanged over approx. 10 years suggesting that Σ-$MeSO_2$-PCB and Σ-PCB concentrations are temporally co-variable in polar bears. Comparisons of mean 3-$MeSO_2$-*p,p'*-DDE concentrations and 3-$MeSO_2$-*p,p'*-DDE to *p,p'*-DDE ratios for 2001–2002 (not shown) with spatial assessments for

Table 2: Concentrations (arithmetic means (%RSD, ng/g, lipid wt.) of the sum (Σ) PCBs, several OCs and Σ-$MeSO_2$-PCBs) in adipose tissue of adult female polar bears from six Canadian Arctic populations collected in 2001–2002 (see Figure 1)

Population	n	Σ-PCB	Σ-$MeSO_2$-PCB	Σ-CHL	Σ-DDT	Σ-CBz	Σ-HCH
Beaufort Sea	12	2678 ± 50	154 ± 53	2225 ± 34	138 ± 68	213 ± 27	386 ± 43
Western Hudson Bay	15	2681 ± 30	126 ± 49	1768 ± 31	219 ± 41	174 ± 33	268 ± 24
Southeastern Baffin Bay	17	2991 ± 38	157 ± 50	2203 ± 47	139 ± 44	197 ± 41	312 ± 38
Northern Baffin Bay	9	2799 ± 43	168 ± 29	2554 ± 40	113 ± 37	346 ± 52	289 ± 18
Foxe Basin/Gulf of Boothia	9	1360 ± 59	90 ± 30	2391 ± 47	136 ± 109	331 ± 63	533 ± 60
Lancaster/Jones Sound	6	1966 ± 33	128 ± 28	1902 ± 34	79 ± 44	276 ± 69	337 ± 48

bear populations sampled in 1989–1991 were similar as for Σ-$MeSO_2$-PCBs (Table 1) (Letcher et al., 1995b). Overall the present 2001–2002 results for the concentrations of major POPs (Table 2) appear to be consistent with spatial and temporal trends over the 1990s. At present, interpretations of the present data should be made with caution since accurate aging of the female bears remains to be determined. OC, PCB and $MeSO_2$-PCB/-DDE data for the present Canadian bears will be compared with recent data for these contaminants in the adipose tissue of polar bear collected from East Greenland in 1999 and 2000 (Dietz et al., 2003; Sandala et al., 2003).

At NWRI, BDEs were analysed in Florisil eluates provided by GLIER using GC-MSD in the electron capture negative ion (ECNI) mode. Methodology for the work has been described by Luross et al. (2002).

To our knowledge, this is the first report of BDEs in the tissues of polar bear from any population (Law et al., 2003). In the blubber of Canadian Arctic ringed seal (*Phoca hispida*) collected from subsistence hunts in 1981, 1991, 1996, and 2000, sum BDE concentrations were recently shown to be increasing exponentially over this period in male ringed seals aged 0–15 years (Ikonomou et al., 2002). Penta- and hexa-BDEs were shown to be increasing at approximately the same rate (t_2 = 4.7 and 4.3 years, respectively) and more rapidly than tetra-BDEs (t_2 = 8.6 years) in this age/sex grouping. Levels found in ringed seal blubber were in the low ng/g (lipid weight) range. Based on these findings, we had predicted the BDE-47, -99 and -153/154 would likely dominate the BDE congener profile in Canadian polar bears. Our present finding for BDEs in polar bear fat (Table 3) demonstrates that Σ-BDE concentrations are higher than found recently in the blubber of ringed seal from the same regions (Ikonomou et al., 2002). Furthermore, the BDE-47 accounts for 50% or more of the Σ-BDE levels regardless of population. BDE-153 is the next most abundant congener followed by BDE-99. Ikonomou et al. (2002) found an even higher dominance of BDE-47 in Canadian ringed seal blubber. This may indicate that higher brominated BDE congeners are bioaccumulating in polar bear relative to ringed seal, and/or lower brominated BDE congeners are more rapidly metabolized in polar bear relative to ringed seal (Hakk and Letcher, 2003).

Perfluorinated acids (PFAs) in polar bear liver were analyzed using the method of Hansen et al. (2001). This method involves extraction with methyl tert-butyl ether in the presence of ion-pairing reagent tetrabutylammonium hydrogensulfate (TBAS). Liquid chromatography-tandem mass spectrometry (LC-MS/MS) was used for quantification of the PFAs. At the NWRI, experience exists with this method for the analysis of PFAs in fish (Moody et al., 2001a) and bioaccumulation studies with fish (Martin et al., 2003).

Perfluorooctane sulfonate (PFOS) was the predominant PFA in polar bear liver, detectable in all samples at concentrations ranging from 0.19 to 4.95 ug/g (Table 4). Other PFAs ranging from perfluorooctanoic acid (PFOA) to perfluoropentadecanoic acid were also detected at concentrations that were 5 to 10x lower than PFOS (Smithwick et al., 2003; Martin et al., 2003). PFOS concentrations were highest in samples from southwestern Hudson Bay (mean 2.12 ug/g ww) and lowest in samples from the southern Beaufort Sea (Table 4).

Concentrations of PFOS in the liver samples were generally higher than reported by Kannan et al. (2001) for samples from northern Alaska. There is a lot of concern about the presence of these compounds in the global environment because PFAs have no known route of degradation (Renner, 2001). PFAs are classed as non-mutagenic carcinogens and may cause other effects in wildlife such as liver enlargement and reduction of male sex hormones. Manufacturing of PFOS related compounds by 3M Co., the major producer, was recently phased out but production of related perfluorosulfonates continues. Many perfluorinated compounds are widely used to treat carpets and clothing and they may degrade to PFAs and thus the environmental burden of PFAs may increase over the next decade because of degrading commercial products and lack of environmental degradation.

Table 3: Concentrations (arithmetic mean ± %RSD, ng/g, lipid weight) of BDE congeners and the sum (Σ) of BDEs in the adipose tissue of adult female polar bears from six Canadian Arctic populations collected in 2001–2002 (see Figure 1)

Population	n	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	Σ-BDE
Beaufort Sea	12	7.7 ± 51	0.7 ± 55	2.9 ± 96	0.1 ± 0	1.3 ± 57	12.8 ± 60
Western Hudson Bay	15	15.3 ± 24	1.5 ± 30	5.2 ± 24	1.4 ± 378	11.4 ± 49	34.8 ± 36
Southeastern Baffin Bay	17	16.5 ± 6	1.1 ± 29	3.5 ± 23	0.1 ± 0	11.6 ± 151	32.8 ± 52
Northern Baffin Bay	9	7.5 ± 32	0.7 ± 56	2.1 ± 15	0.1 ± 0	2.2 ± 91	12.6 ± 34
Foxe Basin/Gulf of Boothia	9	6.8 ± 44	0.7 ± 52	3.1 ± 46	0.1 ± 0	1.6 ± 69	11.8 ± 41
Lancaster/Jones Sound	6	6.6 ± 25	0.6 ± 20	3.1 ± 18	0.4 ± 200	1.5 ± 84	12.2 ± 22

Table 4: Arithmetic mean concentrations (μg/g, wet weight) and range of concentrations of PFOS in the livers of adult female polar bears from four Canadian Arctic populations collected in 2001–2002 (see Figure 1)

Population	n	Mean	Minimum	Maximum
Beaufort Sea	7	1.04	0.46	1.92
Southeastern Baffin Bay	10	1.16	0.55	1.97
Lancaster/Jones Sound	9	1.19	0.19	2.39
Sanikiluaq	7	2.12	1.73	4.95

The implications for wildlife and people in the Canadian Arctic are unknown but should be investigated.

At the beginning of March 2003, a NCP Workshop was held in Ottawa. Partial POP and metabolite data was presented at this conference (Letcher et al., 2003). Results on the perfluorinated organics were also recently presented at the SETAC-Europe conference (Smithwick et al., 2003).

A number of papers in peer-reviewed scientific journals are expected from the results of this study. With completion of the stable isotope analysis for trophic level assessments, and aging of the bears, the writing of manuscripts will begin in earnest.

References

Atwell, L., K.A. Hobson, and H.E. Welch. 1998. Biomagnification and bioaccumulation of mercury in an arctic marine food web: insights from stable nitrogen isotope analysis. *Can J Fish Aquat Sci.* 55:1114–1121.

Addison, R. and M. Ikonomou. 2000. Presented at the NCP Results Workshop, White Rock, BC.

Braune, B.M., R.J. Norstrom, M.P. Wong, B.T. Collins, and J. Lee. 1991. Geographical distribution of metals in livers of polar bears from the Northwest Territories, Canada. *Sci Total Environ.* 100:283–299.

de March, B. et al. 1998. AMAP Assessment Report: Arctic Pollution Issues. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway. xii+859 pp.

Dietz, R., R.R. Rigit, C. Sonne-Hansen, R.J. Letcher, D.C.G. Muir, and E.W. Born. 2003. Polychlorinated biphenyls and organochlorine pesticides in East Greenland polar bears (*Ursus maritimus*), 1990–2001. *Sci Total Environ.* In preparation (invited).

Fisk, A.T., D.C.G. Muir, et al. 2003. Contaminant Levels, Trends and Effects in the Biological Environment. Northern Contaminants Program, Indian and Northern Affairs Canada, Ottawa, ON. 175 pp.

Hakk, H. and R.J. Letcher. 2003. Metabolism in the toxicokinetics and fate of brominated flame retardants — a review. *Environ Internat.* 29:801–828.

Henriksen, E.O., Ø. Wiig, J.U. Skaare, G.W. Gabrielsen, and A.E. Derocher. 2001. Monitoring PCBs in polar bears: Lessons learned from Svalbard. *J Environ Monit.* 3:493–498.

Hobson, K.A. and H.E. Welch. 1992. Determination of trophic relationships within a high Arctic marine food web using stable-isotope analysis. *Marine Ecology Progress Series.* 84:9–18.

Ikonomou, M.G., S. Rayne, and R.F. Addison. 2002. Exponential increases in the brominated flame retardants, polybrominated diphenyl ethers, in the Canadian arctic from 1981 to 2000. *Environ Sci Technol.* 36:1886–1892.

Kannan, K., J. Koistinen, K. Beckmen, T. Evans, J.F. Gorzelany, K.J. Hansen, P.D. Jones, E. Helle, M. Nyman, and J.P. Giesy. 2001. Accumulation of perfluorooctane sulfonate in marine mammals. *Environ Sci Technol.* 35:1593–1598.

Law, R.J., M. Alaee, C.R. Allchin, J.P. Boon, M. Lebeuf, P. Lepom, and G.A. Stern. 2003. Levels and trends of polybrominated diphenylethers and other brominated flame retardants in wildlife. *Environ Internat.* 29: 757–770.

Letcher, R.J., R.J. Norstrom, and Å. Bergman. 1995a. An integrated analytical method for determination of polychlorinated aryl methyl sulfone metabolites and polychlorinated hydrocarbon contaminants in biological matrices. *Anal Chem.* 67:4155–4163.

Letcher, R.J., R.J. Norstrom, and Å. Bergman. 1995b. Geographical distribution and identification of methyl sulfone PCB and DDE metabolites in pooled polar bear (*Ursus maritimus*) adipose tissue from the western hemisphere Arctic and subarctic regions. *Sci Total Environ.* 160/161:409–420.

Letcher, R.J., R.J. Norstrom, S. Lin, M.A. Ramsay, and S.M. Bandiera. 1996. Immunoquantitation and microsomal

monooxygenase activities of hepatic cytochromes P450 1A and P450 2B and chlorinated hydrocarbon contaminant levels in polar bear (*Ursus maritimus*). *Toxicol Appl Pharmacol.* 137:127–140.

Letcher, R.J., R.J. Norstrom, and D.C.G. Muir. 1998. Biotransformation versus bioaccumulation: Sources of methyl sulfone PCB and 4,4'-DDE metabolites in the polar bear food chain. *Environ Sci Technol.* 32:1656–1661.

Letcher, R.J., E. Klasson-Wehler, and Å. Bergman. 2000a. Methyl sulfone and hydroxylated metabolites of polychlorinated biphenyls. In: J. Paasivirta. (ed.), *Anthropogenic Compounds: New Types of Persistent Halogenated Compounds*, Vol. 3, Part K. Springer-Verlag: Heidelberg, pp. 315–359 (and references therein).

Letcher, R.J., R.J. Norstrom, D.C.G. Muir, C. Sandau, K. Koczanski, R. Michaud, S. De Guise, and P. Béland. 2000b. Methylsulfone PCBs and DDEs in beluga whale (*Delphinapterus leucus*) from the St. Lawrence river estuary and western Hudson Bay, Canada. *Environ Toxicol Chem.* 19(5):1378–1388.

Letcher, R.J., B. van der Burg, A. Brouwer, J. Lemmen, Å. Bergman, and M. van den Berg. 2002. In vitro antiestrogenic effects of aryl methyl sulfone metabolites of polychlorinated biphenyls and 2,2-bis(4-chlorophenyl)-1, 1-dichloroethene on 17β-estradiol-induced gene expression in several bioassay systems. *Toxicol Sci.* 69: 362–372.

Letcher, R.J., G.M. Sandala, A.T. Fisk, R.J. Norstrom, N. Lunn, B. Braune, M. Taylor, J. Nagy, M. Branigan, I. Stirling, M. Obbard, B. Wakeford, and D.C.G. Muir. 2003. Spatial and Temporal Trends (2001–2002) of Polychlorinated Biphenyl (PCBs), Methyl Sulfone PCBs and Organochlorine Pesticides in Polar Bears (*Ursus maritimus*) From Canadian Arctic Populations. Canadian Arctic Contaminants Assessment Symposium, Ottawa, March 4–7, 2003. Abstract # P-B11.

Luross, J.M., M. Alaee, D.B. Sergeant, C.M. Cannon, D.M. Whittle, and K.R. Solomon. 2002. Spatial distribution of polybrominated diphenyl ethers and polybrominated biphenyls in lake trout from the Laurentian Great Lakes. *Chemosphere.* 46:665–672.

Martin, J.W., S.A. Mabury, K.R. Solomon, and D.C.G. Muir. 2003. Dietary accumulation of perfluorinated acids in juvenile rainbow trout (*Oncorhynchus mykis*). *Environ Toxicol Chem.* 22:189–195.

Martin, J.W., M.M. Smithwick, B. Braune, P.F. Hoekstra, S.A. Mabury, and D.C.G. Muir. 2003b. Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. *Environ Sci Technol.* Submitted.

Moody, C.A., J.W. Martin, W.C. Kwan, D.C.G. Muir, and S.A. Mabury. 2001. Monitoring perfluorinated surfactants in biota and surface water samples following an accidental release of fire-fighting foam into Etobicoke Creek. *Environ Sci Technol.* In press.

Muir, D., G. Stern, and T. Bidleman. 1998. New Persistent and Bioaccumulative Chemicals in Arctic Air, Water/snow, and Biota. In: Synopsis of Research Conducted Under the 1997–98 Northern Contaminants Program, Environmental Studies No. 75. Ottawa: Indian and Northern Affairs Canada. pp. 165–170.

Muir, D., B. Braune, B. de March, R. Norstrom, R. Wagemann, M. Gamberg, K. Poole, R. Addison, D. Bright, M. Dodd, W. Duschenko, J. Eamer, M. Evans, B. Elkin, S. Grundy, B. Hargrave, C. Hebert, R. Johnstone, K. Kidd, B. Koenig, L. Lockhart, J. Payne, J. Peddle, and K. Reimer. 1997. Chapter 3. Ecosystem Uptake and Effects. In: Shearer, R. (ed.), Canadian Arctic Contaminants Assessment Report, Indian and Northern Affairs Canada, Ottawa. 199–207.

Muir, D.C.G. and R.J. Norstrom. 1999. Geographical differences and time trends of persistent organic pollutants in the Arctic. *Toxicol Lett.* In press.

Muir, D., F. Riget, M. Cleemann, L. Kleivane, J. Skaare, T. Severinsen, H. Nakata, and S. Tanabe. 2000. Circumpolar trends of PCBs and organochlorine pesticides in the Arctic marine environment inferred from levels in ringed seals. *Environ Sci Technol.* 34: 2431–2438.

Norstrom, R.J. and H. Won. 1985. Long term preservation of egg and tissue homogenates for determination of organochlorine compounds: freezing versus freeze-drying. *J Assoc Offic Anal Chem.* 68:130–135.

Norstrom, R.J., R.E. Schweinsberg, and B.T. Collins. 1986. Heavy metals and essential elements in livers of the polar bear (*Ursus maritimus*) in the Canadian Arctic. *Sci Total Environ.* 48:195–212.

Norstrom, R.J., M. Simon, D.C.G. Muir, and R.E. Schweinsburg 1988. Organochlorine contaminants in arctic marine food chains: identification, geographical distribution and temporal trend in polar bears (*Ursus maritimus*). *Environ Sci Technol.* 22:1063–1071.

Norstrom, R.J. and D.C.G. Muir. 1994. Chlorinated hydrocarbon contaminants in arctic marine mammals. *Sci Total Environ.* 154:107–128.

Norstrom, R.J., S. Belikov, E.W. Born, G.W. Garner, B. Malone, S. Olpienski, M.A. Ramsay, S. Schliebe, I. Stirling, M.S. Stishov, M.K. Taylor, and Ø. Wiig. 1998. Chlorinated hydrocarbon contaminants in polar bears from eastern Russia, North America, Greenland and Svalbard: Biomonitoring of Arctic pollution. *Arch Environ Contam Toxicol.* 35(2):354–367.

Norstrom, R. 2001. Effects and trends of POPs on polar bears. In: S. Kalhok (ed.). Synopsis of Research Conducted Under the 2000–01 Northern Contaminants Program. Indian and Northern Affairs Canada, Ottawa. pp. 215–226.

Sandala, G., C. Sonne-Hansen, D.C.G. Muir, R. Dietz, E. Bennett, K. Valters, and R.J. Letcher. 2003. Hydroxylated and methyl sulfone PCB metabolites in blood versus adipose tissue of Greenland polar bears. *Sci Total Environ.* In preparation (invited).

Smithwick, M.M., J.W. Martin, C. Sonne-Hansen, K.R. Solomon, S.A. Mabury, and D.C.G. Muir. 2003. Perfluorinated Organics in Polar Bears (*Ursus maritimus*) from the Canadian Arctic and Greenland. Presented at the Annual Meeting of Society of Environmental Toxicology and Chemistry — Europe, Hamburg Germany, May 2003.

Wiberg, K.A., R. Letcher, C. Sandau, J. Duffe, R. Norstrom, P. Haglund, and T. Bidleman. 1998. Enantioselective gas chromatography/mass spectrometry of methysulfonyl PCBs with application to Arctic marine mammals. *Anal Chem.* 70:3840–3844.

A Preliminary Assessment of Perfluorinated Compounds in the Canadian Arctic

Project leaders

Jonathan Martin and Scott Mabury, Department of Chemistry, University of Toronto, Toronto, ON; phone: (416) 978-1780; fax: (416) 978-3596; e-mail:, jmartin@chem.utoronto.ca; smabury@chem.utoronto.ca; Derek Muir, National Water Research Institute, Burlington, ON; phone: (905) 319-6921; fax: (905) 336-6430; e-mail: Derek.Muir@ec.gc.ca

Project members

Birgit Braune, Environment Canada, CWS, Ottawa, ON; Aaron Fisk, University of Georgia, Athens, Ga; Mary Gamberg, Gamberg Consulting, Whitehorse, YK; Lois Harwood, Fisheries and Oceans, Inuvik, NWT; Pat Roach, Indian and Northern Affairs, Whitehorse, YK; Marla Smithwick, Department of Environmental Biology, University of Guelph, Guelph, ON.

Abstract

Recently it was discovered that humans and animals from various urbanized and remote global locations contained a novel class of persistent fluorinated contaminants, the most pervasive of which was perfluorooctane sulfonate (PFOS). To provide a preliminary assessment of fluorinated contaminants in Canada, polar bears, ringed seals, arctic fox, mink, loons, fulmars, guillemots, and fish were collected at various locations in the circumpolar region for analysis of liver concentrations. PFOS was generally the dominant contaminant detected, and concentrations in polar bear liver were higher than any persistent organochlorine chemicals previously reported in polar bear fat such as PCB, chlordane, or hexachlorocyclohexanes, indicating the importance of this class of chemicals. Lower concentrations of perfluorooctanoic acid (PFOA) and heptadecafluorooctane sulfonamide (FOSA) were also detected. It was also discovered that all animals contained significant concentrations of long-chain perfluoroalkyl carboxylates (PFACs) ranging in length from 9 to 15 carbons. Confirmation of these analytes in biota was provided by two independent mass spectral methods. In general, odd-length PFACs exceeded the concentration of even-length PFACs. In mink, PFAC9 concentrations exceeded PFOS concentrations, indicating that PFACs should not be neglected in future monitoring efforts. By comparison of equivalent species between northern Canada and industrialized regions of the United States and Canada, it is evident that contamination by PFOS, and presumably PFACs, is much lower for animals living in the Canadian Arctic than near urban centers.

Key Project Messages

1. A novel series of perfluoroalkyl carboxylate contaminants, ranging from 9 to 15 carbons, were confirmed and quantified in animals collected from the Canadian Arctic.

2. Polar bear liver was the most contaminated tissue analyzed and concentrations of PFOS are higher than other contaminants previously reported in polar bear fat such as PCBs, chlordane, or hexachlorocyclohexane.
3. Fish and mink living in the United States (mid-latitude) are more contaminated than fish and mink living in the Canadian Arctic/subarctic, indicating that abiotic concentrations are lower in the remote Canadian environment than surrounding industrialized regions to the south.

Objective

Determine levels of PFOS and PFACs in livers of selected biota including mink, seabirds, and seals, for comparison with the same or similar species in the Great Lakes and other regions that have been reported by other investigators.

Introduction

The widespread contamination of wildlife (Geisy and Kannan, 2001; Kannan et al., 2001a, 2001b, 2002a, 2002b, 2002c, 2002d) and the general human population (Hansen et al., 2001; Taves, 1968) with perfluorinated acids and heptadecafluorooctane sulfonamide (FOSA) has been described in many recent publications. Perfluorooctane sulfonate (PFOS) is the dominant PFA in all biotic samples analyzed to date, while perfluorooctanoate (PFOA), perfluorohexane sulfonate (PFHxS), and FOSA are detected only occasionally in wildlife. In human serum, PFOA and PFHxS are generally present at much higher levels than in wildlife, indicating that exposure may be attributable to contact with commercial products containing these surfactants or their derivatives.

These observations in wildlife and humans quickly led to a voluntary manufacturing phase-out by the main producer of perfluorinated acids, and garnered the attention of national and international environmental protection agencies. Perfluorinated acids are a concern because they have no known route of degradation in the environment and are bioaccumulative when the perfluorinated chain reaches a length of between 6 and 7 carbons (Martin et al., 2003a, 2003b). The health effects associated with long-term exposure to perfluorinated acids for humans and wildlife is the subject of a present risk assessments US EPA (2003), though some perfluorinated acids are potent peroxisome proliferators (Berthiaume and Wallace, 2002), inhibitors of gap-junction intercellular communication in in vitro tests (Upham et al., 1998), and tumour promoters in animal studies (Biegel et al., 2001).

Perfluorinated acids ranging in chain-length from 2 to 13 carbons (some evidence for longer ones) have been confirmed as thermolysis products of polytetrafluoroethylene, yet the environmental impact of this observation has yet to be established. Furthermore, long-chain perfluoroalkyl carboxylates (PFACs), such as perfluorononanoic acid (PFAC9) and perfluorodecanoic acid (PFAC10) have been used in industry (Fluoropolymer Manufacturers Group, 2003), yet there are few reports of their environmental distribution. The only report of long-chain PFACs in biota are in fish collected following a spill of aqueous film forming foam (AFFF) into the Etobicoke Creek (Moody et al., 2002), however, given that long-chain PFACs are not listed as active ingredients in AFFF it seems prudent to examine for their presence in other environments. The unknown environmental distribution of long-chain PFACs represents a serious knowledge given their persistence, bioaccumulation potential, and potential to cause adverse toxicological effects.

In this study we look for the presence of fluorinated organics in the tissue of biological specimens collected from the Canadian circumpolar region. Liquid chromatography coupled with tandem and high-resolution mass spectrometry revealed that PFOS, FOSA, PFHxS, and PFOA are not the only fluorinated organic contaminants of biological significance. Using standardized criteria for identification we have confirmed and quantified several long-chain perfluoroalkyl carboxylates (PFACs) in animals from remote areas. The implications for wildlife and people in the Canadian Arctic are unknown, but are linked, given that many of these animals still serve as traditional foods for people in the Canadian north.

Methods

Sample Collection

All biota samples were collected by local subsistence hunters and trappers. Ringed seals from Holman were collected in 2001 with the assistance of Lois Harwood (DFO Inuvik), while seals from Qausuittuq/Grise Fjord were collected in spring of 1998 as part of the Northwater Study (Fisk et al., 2002). Loons were collected around Kuujjuarapik in 1992, while fulmars and guillemots were collected from Prince Leopold Island in 1993. Arctic fox were collected from trappers in Arviat in March 2001 (Hoekstra et al., 2003). Fish samples were collected from the mouth of the Great Whale River at Kuujjuarapik and in Lake Minto in July 2002 with the assistance of the local Cree Trappers Association. Samples of mink from the Yukon were collected by trappers in winter 2001/2002 from the southwestern part of the Territory east of Watson Lake, in the area of Blind Lake and

Crow River. Polar bears were collected February 2002 in eastern Hudson Bay near Sanikiluaq by Inuit hunters who supplied samples to Jackie Bourgeois and Mitch Taylor of the Department of Sustainable Development, Government of Nunavut Wildlife Service.

Analysis of perfluorinated acids

Analytical standards of potassium PFHxS (99.9%), and potassium PFOS (86.4%) were obtained from 3M Company (St. Paul, MN). Perfluoroheptanoic acid (99%), PFOA (98%), perfluorononanoic acid (PFAC9, 97%), perfluorodecanoic acid (PFAC10, 98%), perfluoroundecanoic acid (PFAC11, 95%), perfluorododecanoic acid (PFAC12, 95%), and perfluorotetradecanoic acid (PFAC14, 97%), were purchased from Sigma-Aldrich (Oakville, ON), and perfluorohexanoic acid (PFHxA, 95%) was obtained from Oakwood Research Chemicals (West Columbia, SC).

Sample extraction

A small amount of tissue (0.5 g) was removed from the whole liver, or partial liver, for analysis. To minimize potential contamination, whenever possible, the liver was cut open and an internal sample was removed for analysis. Liver tissue was then homogenized in 15 mL plastic (polypropylene copolymer) centrifuge tubes containing 3 mL of Na_2CO_3 (0.25 M), 1 mL of water, 1 mL of the ion-pairing agent TBAS (0.5 M adjusted to pH 10), and 100 μL (25 ng) of the internal standard, PFHpA. The resulting homogenates were extracted with 5 mL of MTBE by shaking vigorously for 10 min, followed by centrifugation to isolate the organic phase. The MTBE supernatant was collected in a separate plastic tube, and this extraction process was repeated once more, combining the supernatants. The MTBE was blown to dryness under high-purity nitrogen gas, and the analytes were taken up in 1 to 2 mL of 50:50 water/methanol by vortexing for 30 s. The solution was then filtered through 0.2 μm nylon filters into polypropylene vials for analysis.

LC/MS/MS

Routine quantitative instrumental analysis was performed by LC/MS/MS using previously described conditions. Water and methanol solvents (0.01 M ammonium acetate) were delivered at a total flow rate of 250 $\mu L \cdot min^{-1}$ by a Waters 600S controller, and samples were injected (10 μL) with a Waters 717 plus autosampler. Chromatography was performed on a Genesis C8 column (2.1 × 50 mm, Jones Chromatography, Lakewood, CO, USA). Initial mobile phase conditions were 80:10 water/methanol, followed immediately by an 8 min ramp to 0:100, a 2 min hold, and reverting to initial conditions at 10 min. The detector was a Micromass Ultima (Micromass, Manchester, UK) equipped with an electrospray interface operating in negative ion mode. Data was acquired by tandem mass spectrometry using a multiple reaction monitoring (MRM) method that monitored one to three transitions (parent → daughter ion) for each compound.

PFHpA was spiked into each homogenate as an internal standard before extraction and recovery was between 75 and 100% for all animals. PFHpA could not be detected in unspiked tissues. Quantification was performed based on the relative response of each analyte to PFHpA using a standard curve constructed from known quantities of standards extracted from water in the same manner as tissue samples. Standard injections were made every six to nine samples to monitor sensitivity drift, and the coefficient of determination for standard curves always exceeded 0.98 between 2.5 and 1000 pg of analyte injected. This range was appropriate for quantification of all analyte concentrations in all animals except for PFOS in polar bears. Detectable responses that resulted in concentrations below our lowest standard were reported as $< 0.5\ ng \cdot g^{-1}$, while any response having a signal to noise ratio less than 3 was reported as non-detectable (n.d.). For analysis of PFOS in polar bears it was necessary to add a higher standard (equivalent of 10 ng injected). Unfortunately, this resulted in non-linearity at high concentrations, thus any PFOS concentration exceeding the highest standard by 2-fold was reported as $> 4000\ ng \cdot g^{-1}$.

An instrumental blank response was always present for PFOA which made quantification difficult or impossible in most animals due to our resulting method detection limit of $2\ ng \cdot g^{-1}$. The background response could be minimized and stabilized, but not eliminated, by reducing the column equilibration time between sample injections. The precise source of the contamination is unknown, but was localized to the liquid chromatograph, and is presumably a result of PFACs leaching out from internal fluorinated polymers. For example, PFAC salts are reportedly utilized as fluoropolymer polymerization aids (Fluoropolymer Manufacturers Group, 2003).

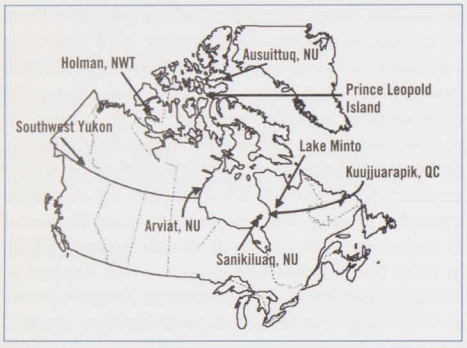
Results and Discussion

Confirmation of PFACs in biota

Confirmation of PFAC detection in polar bears was initially performed using liquid chromatography coupled to a triple quadrupole mass spectrometer by comparing the relative response of two secondary mass transitions

(i.e. parent → daughter) to the primary transition used for quantification. For all analytes, the relative response of all secondary mass transitions were close to those produced by injection of an authentic standard, and the error was within the tolerable limits defined by the European Communities (Table 1) (Commission of the European Communities, 2002). PFAC13 and PFAC15 could not be confirmed by this method due to a lack of authentic standards, however, secondary mass transitions analogous to other PFACs were detected for PFAC13, and retention times were appropriate relative to PFAC14 (Figure 2). Confirmation of PFACs was further achieved by accurate mass measurements using liquid chromatography coupled to a quadrupole-time-of-flight (QTOF) mass spectrometer. For most PFACs, the resultant accurate mass measurements were within 5 ppm of the calculated mass (Table 1). For PFAC13 and PFHxS, instrument response was near to detection limits, thus resulting in poor ion statistics and a relatively large error (i.e. 20 and 11 ppm, respectively). PFAC14 and PFAC15 could not be detected above background on the QTOF instrument. Overall, the weight of evidence suggests that long-chain PFACs, ranging from PFOA to PFAC15, are present in the Canadian circumpolar environment.

Figure 1. Map of Canada indicating the location of samples collected for fluorochemical analysis



Concentrations in biota

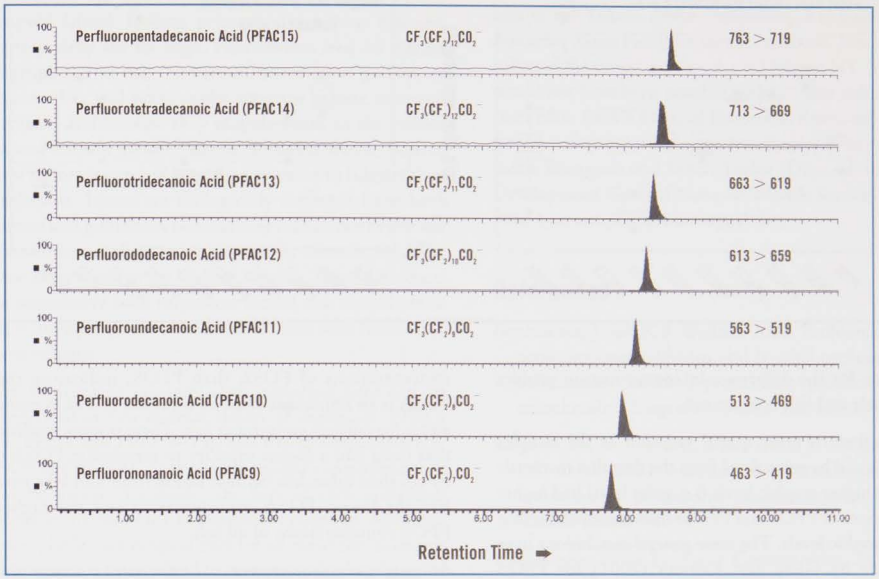
Polar bear livers had the highest concentration of each perfluorinated acid among all animals analyzed in this study. PFOS concentrations always exceeded 1 $ug \cdot g^{-1}$ (mean = 3.1 $ug \cdot g^{-1}$) in the liver. There are very few reports of organochlorine concentrations in polar bear liver with

Table 1. Confirmation criteria achieved by accurate mass determination and by monitoring of secondary mass transitions for all fluorinated contaminants.

	Accurate Mass Determination		Ratio of Secondary to Primary MS/MS Transitions				
Analyte	Calculated Mass	QTOF Mass (ppm Error)	Secondary Transitions	Polar Bear Ratio (n = 5)	Authentic Standard Ratio	% Error	% Allowed[a]
PFAC9	462.9631	462.9650	(419..219)	0.130	0.133	5.1%	30%
			(419..169)	0.047	0.050	6.2%	50%
PFAC10	512.9599	512.9606	(469..269)	0.169	0.169	0.28%	30%
			(469..219)	0.185	0.188	1.6%	30%
PFAC11	562.9567	562.9567	(519..269)	0.210	0.214	1.8%	25%
			(519..219)	0.159	0.164	3.3%	30%
PFAC12	612.9536	612.9564	(569..319)	0.199	0.186	6.6%	30%
			(569..269)	0.188	0.175	6.7%	30%
PFAC13	662.9505	662.9640	(663..319)	Present	Not Available		
			(663..269)	Present			
PFAC14	712.9472	< LOD	(669..219)	0.035	0.029	16%	50%
			(669..169)	0.014	0.014	1.5%	50%
PFAC15	762.9440	Not Detected	(763..169)	Not Detected	Not Available		
			(763..319)				
PFOS	498.9303	498.9278	Not Determined				
PFHxS	398.9365	398.9408	Not Determined				
PFOSA	497.9461	497.9477	(498..169)	0.028	0.035	26%	50%

[a] Tolerance according to Commission of the European Communities (2002) based on primary abundance relative to primary transition

Figure 2. LC MS/MS chromatogram of a polar bear liver extract showing a novel homologous series of perfluoroalkyl carboxylates

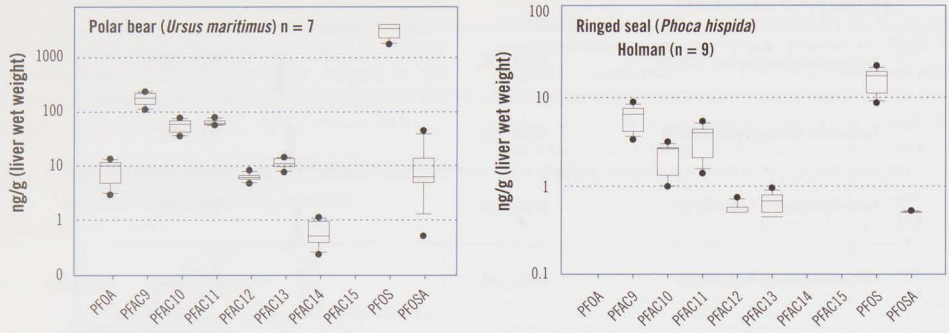


which to compare directly, however, PFOS liver concentrations exceed individual PCB, chlordane, and HCH-related chemical concentrations in blubber (Muir and Norstrom, 2001). These PFOS concentrations are also three-fold higher than those reported by Giesy and Kannan (2001) for polar bear liver collected in Alaska (mean = 350 $ng{\cdot}g^{-1}$), albeit Sanikiluaq is at a considerably lower latitude, perhaps closer to sources. Polar bears were the only animals to have quantifiable concentrations of PFOA, ranging from 2.9 to 8.6 ng·g-1. However, PFOA was not the only PFAC detected in polar bears, in fact, the entire homologous series of longer PFACs, ranging in length from 9 to 15 carbons were detected in these animals (Figure 2). The mean concentration of individual PFACs in polar bear liver ranged from < 0.5 $ng{\cdot}g^{-1}$ to 180 $ng{\cdot}g^{-1}$, and generally decreased with increasing perfluorinated chain-length. The concentration of these novel PFACs are all at least an order of magnitude lower than PFOS in polar bears, but PFAC9, PFAC10, and PFAC11 concentrations exceed PFOA and FOSA concentrations (Appendix 1).

The dominant PFAC detected in all mammals was PFAC9, and concentrations generally decreased for all other PFAC homologues as the perfluoroalkyl chain-length was increased. It has been shown that the bioaccumulation potential of PFACs increases with increasing perfluoroalkyl chain-length, suggesting that the abiotic environmental burden of PFACs is likely skewed towards PFAC9. PFOA was detectable in polar bear liver samples but not in any other organism, owing partially to the high limit of detection. Overall, it can be generalized that PFOA is a minor contributor to the overall burden of PFACs. For example, in polar bear liver PFOA concentrations were more than an order of magnitude lower than PFAC9.

Although PFAC concentrations generally decreased with increasing chain-length for mammals, a consistent trend was observed in all animals whereby odd chain-length PFAC concentrations exceeded the shorter, even chain-length PFAC concentration. For example, PFAC11 was usually higher than PFAC10, and PFAC13 was usually higher than PFAC12 concentrations. This contamination profile is shown most clearly for polar bears and ringed seals (Figure 3). The contamination profile for birds and fish was different from that observed in mammals. The most dominant PFAC in birds and fish was PFAC11, with lower concentrations of longer and shorter homologues alike. However, the same relative odd/even pattern that was shown in mammals (i.e. PFAC11 > PFAC10, and PFAC13 > PFAC12) was also apparent in all birds and fish, but was most evident in loons wherein concentrations were quantifiable for most PFACs (Appendix 1).

Figure 3. Contamination profile of fluorinated contaminants in polar bear and ringed seal



The reason for the difference in contamination profiles of mammals and fish is unknown.

Although there is great spatial variation in the samples analyzed, it can be generalized from the data that mammals feeding at higher trophic levels (i.e. polar bear) had higher concentrations of PFOS and PFACs than mammals feeding at lower trophic levels. The same general conclusions have been made by Giesy and Kannan (2001) for PFOS concentrations in a survey of wildlife around the globe.

There was very little variation in either ringed seal or polar bear liver concentrations within each population analyzed. For the most part, the difference between the maximum and minimum concentration was less than a factor of three. The same was not true for either arctic fox or mink liver. In these animals there was generally more than an order of magnitude separating the minimum from the maximum concentration (Appendix 1). This variation is presumably a function of feeding habits for these species. For example, arctic fox are opportunistic feeders that may be influenced by terrestrial and/or marine food webs, depending on food availability, and this can influence chlorinated contaminant concentrations (Hoesktra et al., 2003).

The only neutral fluorinated contaminant that was analyzed for was FOSA. Heptadeca-fluorooctane sulfonamide was detected in all animals except fulmar and guillemots, and ranged in concentration from < 0.5 to 110 $ng \cdot g^{-1}$. Surprisingly, arctic fox liver had a higher mean FOSA concentration than polar bears, despite having 5-fold lower concentrations of all perfluorinated acids. This may be a function of diet but could also indicate that polar bears have a greater metabolic capacity for degrading FOSA. FOSA concentrations were lower than PFOS in all mammals and birds, but not in fish. With the exception of brook trout and lake trout, all fish had higher concentrations of FOSA than PFOS, indicating that FOSA is an important route of exposure to PFOS equivalents for animals consuming fish. There is some evidence that trout had a higher capacity to metabolize FOSA to PFOS than other fish because brook trout and lake trout had the lowest FOSA concentrations and the highest PFOS concentrations of all fish.

Although polar bears appear to be the most contaminated organisms with respect to fluorinated contaminants, this is presumably a function of their diet and high feeding rate, rather than simple geography. When the concentration of PFOS is compared for the same species between the arctic and mid latitude environments, it is evident that animals living in mid-latitudes are much more heavily contaminated. For example, Giesy and Kannan (2001) reported a mean liver PFOS concentration of 2630 $ng \cdot g^{-1}$ for mink in the Midwest United States, compared to the mean value of 8.7 $ng \cdot g^{-1}$ reported here for the same species in the Yukon. Lake whitefish from Michigan waters had mean PFOS concentrations of 67 $ng \cdot g^{-1}$, compared to 12 $ng \cdot g^{-1}$ reported here for the same species in the Great Whale River, Kuujjuarapik. Common loon from North Carolina averaged 290 $ng \cdot g^{-1}$ in liver (Geisy and Kannan, 2001), compared to the same species in Kuujjuarapik having mean concentrations of 20 $ng \cdot g^{-1}$ PFOS. Ringed seals from the Baltic Sea had liver PFOS concentrations exceeding 400 $ng \cdot g^{-1}$ (Kannan et al., 2002b), compared to 16 and 19 $ng \cdot g^{-1}$ for ringed seal from Holman, and Grise Fjord, respectively.

The two bird species collected from Prince Leopold Island provided a unique opportunity to examine the influence of both diet and annual migration pattern on fluorinated contaminant concentrations. Guillemots had non-detectable concentrations of all analytes, whereas fulmars

have quantifiable concentrations of PFOS, and detectable/non-quantifiable concentrations of PFAC9, 11, 12, and 13. Guillemots are known to reside year round at Prince Leopold Island, feeding primarily on marine fish and amphipods at the ice edge. Fulmars also feed on marine amphipods and fish, but are different from guillemots because they will occasionally scavenge marine mammal carcasses, and because they migrate south to the eastern coast of Canada (North Atlantic Ocean) in winter; both of these factors may result in greater exposure to fulmars than guillemots. Loons are ecologically different from both fulmars and guillemots because they feed in the freshwater environment on fish and migrate great distance annually, some as far south as the Gulf of Mexico. These differences are presumably both important factors that contribute to the relatively high contamination of loons with fluorinated contaminants.

The fluorinated contaminants reported here can be categorized as two distinct classes of chemicals: PFACs (i.e. PFOA and PFAC9–15), and PFOS equivalents (i.e. PFOS and FOSA). As with chlorinated contaminants, it may be useful to consider the sum of each individual contaminant class for risk assessment purposes. Although there is little toxicological data for all these contaminants with which to perform a risk assessment, the sum of PFACs and sum of PFOS equivalents is shown in Appendix 1. The sum of PFOS equivalents is usually the dominant class of fluorinated contaminants; however, in mink PFAC9 exceeds the concentration of PFOS indicating that attention should also be paid to this class of contaminants in future monitoring efforts.

Conclusions

1. The elevated concentrations of PFOS in polar bear liver, which were higher than any persistent organochlorine chemicals previously reported in polar bear fat such as PCB, chlordane, or hexachlorocyclohexanes, indicates the importance of this chemical in particular and the perfluoro acid class of chemicals in general in Canadian arctic marine ecosystems.
2. The presence of low but readily detectable levels of PFOS in mink and arctic fox, as well as lake trout, indicate that this contaminant is important in terrestrial and freshwater food webs as well.
3. These and other fluorinated contaminants require future attention through monitoring and risk assessment given that the magnitude of contamination is similar to total PCBs and that their toxicity is not yet understood.

Acknowledgements

We thank the hunters and trappers from the Watson Lake area in the Yukon, Arviat, Sanikiluaq, Kuujjuarapiq, and Ausuittuq (Grise Fiord) for sample collection. John Alikamik collected the ringed seal samples at Holman NT. This study would not have been possible without their collaboration. Brett Elkin (NWT Dept. of Renewable Resources) arranged for the collection of the arctic fox samples from Arviat and Jackie Bourgeois and Mitch Taylor (Dept. of Sustainable Development, Gov't of Nunavut Wildlife Service) provided polar bear samples and biological data.

References

Berthiaume, J. and K.B. Wallace. 2002. Perfluorooctanoate, perfluorooctanesulfonate, and N-ethyl perfluorooctanesulfonamido ethanol; peroxisome proliferation and mitochondrial biogenesis. *Toxicol Let.* 129:23–32.

Biegel, L.B., M.E. Hurtt, S.R. Frame, J. O'Connor, and J.C. Cook. 2001. Mechanism of extrahepatic tumor induction by peroxisome proliferators in male rats. *Toxicol Sci.* 60:44–55.

Commission of the European Communities. 2002. Commission Decision 2002/657/EC implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results.

Fisk, A.T., M. Holst, K.A. Hobson, J. Duffe, J. Moisey, and R.J. Norstrom. 2002. Comparison of persistent organic pollutants (POPs) and enantiomeric signatures of chiral pollutants in ringed seals feeding on the east and west side of the Northwater Polynya. *Arch Environ Contam Toxicol.* 42:118–126.

Fluoropolymer Manufacturers Group. 2000. Detecting and quantifying low levels of fluoropolymer polymerization aids. Society of the Plastics Industry Inc., Washington, DC.

Giesy, J.P. and K. Kannan. 2001. Global distribution of perfluorooctane sulfonate in wildlife. *Environ Sci Technol.* 35:1339–1342.

Hansen, K.J., L.A. Clemen, M.E. Ellefson, and H.O. Johnson. 2001. Compound specific quantitative characterization of organic fluorochemicals in biological matrices. *Environ Sci Technol.* 35:766–770.

Hoekstra, P.F., B.M. Braune, T.M. O'Hara, B. Elkin, K.R. Solomon, and D.C.G. Muir. 2003. Organochlorine contaminant and stable isotope profiles in arctic fox (*Alopex lagopus*) from the Alaskan and Canadian Arctic. *Environ Pollut.* 122:423–433.

Kannan, K., J.-W. Choi, N. Iseki, K. Senthilkumar, D.H. Kim, et al. 2002a. Concentrations of perfluorinated acids in livers of birds from Japan and Korea. *Chemosphere.* 49:225–231.

Kannan, K., S. Corsolini, J. Falandysz, G. Oehme, S. Focardi, and J.P. Giesy. 2002b. Perfluorooctanesulfonate and related fluorinate hydrocarbons in marine mammals, fishes, and birds from coasts of the Baltic and the Mediterranean seas. *Environ Sci Technol.* 36: 3210–3216.

Kannan, K., J.C. Franson, W.W. Bowerman, K.J. Hansen, P.D. Jones, and J.P. Giesy. 2001a. Perfluorooctane sulfonate in fish-eating birds including bald eagles and albatrosses. *Environ Sci Technol.* 35:3065–3070.

Kannan, K., K.J. Hansen, T.L. Wade, and J.P. Giesy. 2002c. Perfluorooctane sulfonate in oysters, *Crassostrea virginica*, from the Gulf of Mexico and the Chesapeake Bay, USA. *Arch Environ Contam Toxicol.* 42:313–318.

Kannan, K., J. Koistinen, K. Beckmen, T. Evans, J.F. Gorzelany, et al. 2001b. Accumulation of perfluorooctane sulfonate in marine mammals. *Environ Sci Technol.* 35:1593–1598.

Kannan, K., J. Newsted, R.S. Halbrook, and J.P. Giesy. 2002d. Perfluorooctanesulfonate and related fluorinated hydrocarbons in mink and river otters from the United States. *Environ Sci Technol.* 36:2566–2571.

Martin, J.W., S.A. Mabury, K.R. Solomon, and D.C.G. Muir. 2003. Dietary accumulation of perfluorinated acids in juvenile rainbow trout (*Oncorhynchus mykiss*). *Environ Toxicol Chem.* 22:189–195.

Martin, J.W., S.A. Mabury, K.R. Solomon, and D.C.G. Muir. 2003. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (*Oncorhynchus mykiss*). *Environ Toxicol Chem.* 22:196–204.

Moody, C.A., J.W. Martin, W.C. Kwan, D.C.G. Muir, and S.A. Mabury. 2002. Monitoring perfluorinated surfactants in biota and surface water samples following an accidental release of fire-fighting foam into Etobicoke Creek. *Environ Sci Technol.* 36:545–551.

Muir, D.C.G. and R. Norstrom. 2001. Geographical differences and time trends of persistent organic pollutants in the Arctic. *Toxicol Lett.* 112–113:93–101.

Taves, D.R. 1968. Evidence that there are two forms of fluoride in human serum. *Nature.* 217:1050–1051.

U.S. Environmental Protection Agency. 2003. Preliminary risk assessment of the developmental toxicity associated with exposure to perfluorooctanoic acid and its salts. Office of Pollution Prevention and Toxics, Risk Assessment Division.

Upham, B.L., N.D. Deocampo, B. Wurl, and J.E. Trosko. 1998. Inhibition of gap-junctional intercellular communication by perfluorinated fatty acids is dependent on the chain length of the fluorinated tail. *International Journal of Cancer.* 78:491–495.

APPENDIX 1. Fluorinated Organic Contaminant Concentrations (ng·g^{-1} wet weight) in Canadian Arctic biota

	Site and Year		PFOA	PFAC9	PFAC10	PFAC11	PFAC12	PFAC13	PFAC14	PFAC15	PFOS	PFOSA	SUM PFAC	SUM PFOS
MAMMALS														
Polar Bear (n = 7)	Sanikiluaq	Mean	8.6	180	56	63	6.2	11	0.51	< 0.5	3000	12	325	3012
Ursus maritimus	2002	Min	2.9	108	35	56	4.7	7.5	< 0.5	< 0.5	1700	< 0.5		
		Max	13	230	76	78	8.2	14	1.1	< 0.5	4900	44		
Arctic Fox (n = 10)	Arviat	Mean	n.d.	22	14	13	1.5	2.2	< 0.5	n.d.	250	19	53	269
Alopex lagopus	2001	Min	n.d.	2.2	1.9	0.78	< 0.5	< 0.5	< 0.5	n.d.	6.1	< 0.5		
		Max	n.d.	86	72	55	4.8	7.1	1.9	n.d.	1400	110		
Ringed Seal (n = 9)	Holman	Mean	n.d.	5.9	2.1	3.3	0.44	0.57	< 0.5	n.d.	16	0.36	12	16
Phoca hispida	2001	Min	n.d.	3.3	0.98	1.4	< 0.5	< 0.5	< 0.5	n.d.	8.6	< 0.5		
		Max	n.d.	8.8	3.1	5.4	0.74	0.94	< 0.5	n.d.	23	0.52		
Ringed Seal (n = 10)	Qausuittuq	Mean	n.d.	4.9	2.9	3.8	0.76	0.95	n.d.	n.d.	19	2.0	13	21
Phoca hispida	1998	Min	n.d.	2.4	2.1	2.0	0.56	0.68	n.d.	n.d.	10	< 0.5		
		Max	n.d.	8.1	3.8	5.9	1.3	1.6	n.d.	n.d.	37	5.5		
Mink (n = 10)	Yukon	Mean	n.d.	16	3.7	4.3	< 0.5	< 0.5	n.d.	n.d.	8.7	1.4	24	10
Mustela vison	2001/2002	Min	n.d.	2.0	0.69	< 0.5	< 0.5	< 0.5	n.d.	n.d.	1.3	< 0.5		
		Max	n.d.	35	9.0	12	0.76	0.83	n.d.	n.d.	20	2.4		
BIRDS														
Common Loon (n = 5)	Kuujjuarapik	Mean	n.d.	< 0.5	< 0.5	1.3	< 0.5	0.88	< 0.5	< 0.5	20	5.9	2	26
Gavia immer	1992	Min	n.d.	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	11	2.0		
		Max	n.d.	< 0.5	0.55	2.2	0.74	1.5	< 0.5	< 0.5	26	13		
Northern Fulmar (n = 5)	Prince Leopold Isl.	Mean	n.d.	< 0.5	n.d.	< 0.5	< 0.5	< 0.5	n.d.	n.d.	1.3	n.d.		1
Fulmarus glacialis	1993	Min	n.d.	< 0.5	n.d.	< 0.5	< 0.5	< 0.5	n.d.	n.d.	1.0	n.d.		
		Max	n.d.	0.50	n.d.	< 0.5	< 0.5	< 0.5	n.d.	n.d.	1.5	n.d.		
Black Guillemot (n = 5)	Prince Leopold Isl.	Mean	n.d.	n.d.	n.d.	< 0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		
Cepphus grylle	1993	Min	n.d.	n.d.	n.d.	< 0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		
		Max	n.d.	n.d.	n.d.	< 0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.		

APPENDIX 1. Fluorinated Organic Contaminant Concentrations ($ng \cdot g^{-1}$ wet weight) in Canadian Arctic biota (continued)

	Site and Year		PFOA	PFAC9	PFAC10	PFAC11	PFAC12	PFAC13	PFAC14	PFAC15	PFOS	PFOSA	SUM PFAC	SUM PFOS
FISH														
White Sucker (n = 3)	Kuujjuarapik	Mean	n.d.	1.0	2.6	6.2	1.3	2.7	0.76	n.d.	7.6	13	15	21
Catostomus commersoni	2002	Min	n.d.	0.61	1.7	3.9	0.65	1.4	< 0.5	n.d.	6.5	10		
		Max	n.d.	1.7	3.1	8.5	1.8	3.7	1.2	n.d.	8.6	18		
Northern Pike (n = 1)	Kuujjuarapik	Mean	n.d.	< 0.5	2.0	2.9	0.83	1.3	0.35	n.d.	5.7	8.7	7	14
Esox lucius	2002													
Arctic Sculpin (n = 1)	Kuujjuarapik	Mean	n.d.	2.2	0.52	1.1	0.55	1.7	< 0.5	n.d.	12	18	6	30
Myoxocephalus scorpioides	2002													
Brook Trout (n = 2)	Kuujjuarapik	Mean	n.d.	6.2	2.5	5.7	1.5	1.4	0.27	n.d.	39	2.8	18	42
Salvelinus fontinalis	2002	Min	n.d.	5.9	2.3	4.9	0.83	1.1	0.22	n.d.	29	2.0		
		Max	n.d.	6.5	2.8	6.5	2.2	1.7	0.32	n.d.	50	3.5		
Lake Whitefish (n = 2)	Kuujjuarapik	Mean	n.d.	3.2	1.5	3.7	1.2	5.5	1.7	n.d.	12	14	17	27
Coregonus clupeaformis	2002	Min	n.d.	2.4	1.2	2.7	0.69	2.7	1.1	n.d.	12	14		
		Max	n.d.	4.0	1.8	4.7	1.8	8.3	2.3	n.d.	12	15		
Lake Trout (n = 1)	Lake Minto	Mean	n.d.	3.4	2.0	6.1	2.30	4.8	0.63	n.d.	31	6.8	19	38
Salvelinus namaycush	2002													

Temporal Trends of Persistent Organic Pollutants and Metals in Landlocked Char

Project leaders

Derek Muir, National Water Research Institute (NWRI), Environment Canada, Burlington, ON L7R 4A6; phone: (905) 319-6921; fax: (905) 336-6430; e-mail: derek.muir@ec.gc.ca; Günter Köck, Institute of Zoology and Limnology, University of Innsbruck, Technikerstr. 25, A-6020 Innsbruck, Austria; phone +43 512 507 6196; fax +43 512 507 2930; e-mail: Guenter.Koeck@uibk.ac.at

Project team

Qausuittuq (Resolute Bay) Hunters and Trappers Association, Resolute, NU; Doug Bright, UMA Engineering, Victoria, BC; Gino Sardella, Christina Cannon, Mike Comba, Sean Backus and Xiaowa Wang, NWRI, Burlington, ON; Jim Reist, Dept. of Fisheries and Oceans, Winnipeg, MB.

Abstract

This study has examined temporal trends of persistent organic pollutants and metals, especially mercury, in landlocked Arctic char from lakes near the community of Qausuittuq (Resolute) by analysis of annual sample collections. Concentrations of mercury in the char in Resolute Lake were found to have declined significantly from 1993 to 2002. However, mercury concentrations have actually increased in Char Lake and Amituk Lake over the same period and mean concentrations in char from these lakes are above guidelines for subsistence consumption of 0.2 $\mu g \cdot g^{-1}$ wet wt. The reasons for increasing concentrations in Char and Amituk Lakes are unknown and need to be investigated. PCBs did not decline significantly in char from Resolute (1997 to 2002) or in Char and Amituk Lakes over the period 1992/93 to 2002. However, chlorinated pesticides (chlordane and hexachlorocyclohexanes) as well as chlorobenzenes declined significantly between 1992 and 2002 in Amituk Lake and in Char Lake from 1993 to 2000. Concentrations of endosulfan and polybrominated diphenyl ethers increased significantly in char in Resolute Lake from 1997 to 2002. This illustrates that the lake is responding to increases in global emissions of these chemicals which have been shown to be increasing in Arctic air (endosulfan) and biota. The lack of a trend for PCBs in char is also consistent with results from Arctic air during the mid-1990s.

Key Project Messages

- Mercury concentrations have declined significantly in landlocked char from Resolute Lake from 1993 to 2002 but have increased in char from Char and Amituk Lakes over the same period.
- PCB levels have not declined significantly in char from Resolute, Char or Amituk lakes while concentrations of the pesticide endosulfan and brominated flame retardants have increased.
- The reasons for increasing mercury in two of the three lakes for which there is long term data need to be investigated.

Objectives

1. Determine temporal trends of persistent organic pollutants (POPs) and metals in landlocked Arctic char from lakes in the Canadian High Arctic islands by analysis of annual sample collections.
2. Investigate factors influencing contaminant levels in landlocked char such as the influence of sampling time, water temperature and diet.
3. Determine levels of current POPs and metals as well as "new" potential POPs in fish from lakes of importance to the community of Qausuittuq and provide this information on a timely basis.

Introduction

Small lakes in the high Arctic are replenished annually with snowmelt runoff and direct precipitation, which represent significant fractions of their water budgets. Declining concentrations of POPs, or increasing levels of previously unstudied POPs, in air and precipitation should be reflected relatively quickly in changes in levels in food webs and top predator fishes, compared to the vast marine environment. We know this to be the case from the sedimentary record of POPs and mercury (Hg) in small Arctic lakes (Muir et al., 1996; Lockhart et al., 1998; Muir et al., 2003).

The value of annual long-term sampling of fish for measurement of temporal trends of contaminants was well illustrated by studies in Sweden. Arctic char have been collected since 1980 in Lake Abiskojaure, 200 km north of the Arctic circle, and northern pike were collected from Lake Storvindeln, a forest lake in northern Sweden since 1978. Samples were collected annually and were selected for consistency in sex, age, size and sampling season. Each annual sample at a given location was represented by 10–25 specimens, thus within-year variation could be estimated. Declines in levels of ΣDDT (DDT + DDD + DDE), PCBs and hexachlorobenzene (HCBz) but not hexachlorocyclohexane (HCH) isomers, were noted in fish from the Arctic locations (Olsson and Reutergårdh, 1986; DeMarch et al., 1998). The char data provided a more accurate temporal trend than pike muscle since the char has a higher concentration of fat. Because of annual sampling, the Swedish program was also able to detect increases in DDT inputs due to the use of DDT in East Germany in 1984 (Bignert et al., 1993).

The assessment of contaminants conducted by the NCP (Jensen et al., 1997) found that there was limited information on temporal trends in fish especially in the eastern and High Arctic. This study was designed to help fill that knowledge gap. Lakes near Qausuittuq (Resolute) were selected for study of temporal trends of POPs and metals in fishes. Many of the lakes, e.g. Amituk, Char, Resolute, Meretta, are well studied limnologically and the food chain in Char Lake has been well documented (Hobson and Welch, 1995). Char from Char Lake and Amituk Lake have been previously analysed for organochlorine contaminants and metals (Muir and Lockhart, 1994, 1996). This study, which began in 1999, has collected fish annually from 1997 to 2002 and compared contaminant concentrations with older data from Resolute and Char Lakes in order to examine temporal trends.

Activities

In 2001–02 and 2002–03

Sample collection

Samples were successfully collected in August 2002 from Resolute, Aqiatusuk, Amituk, Boomerang and Sapphire Lakes by Dr. Guenter Köck and colleagues (University of Innsbruck) working with Debbie Iqaluk of Resolute, using either hand methods or gill netting. Unfortunately only 5 fish were obtained from Amituk Lake. However, 19 fish were collected from Resolute and 25 from Boomerang Lake. These collections add to previous collections by members of the project team as outlined in Table 1.

Samples (skin on fillets) were frozen in Resolute and then shipped to the National Water Research Institute (NWRI), Burlington, Ontario, and stored at −20°C until analysis. Subsamples were also shipped to J. Reist (DFO Winnipeg). Aging of the char was done by J. Babaluk (DFO Winnipeg).

Chemical analysis

Metals

Arctic char muscle was subsampled and acid-digested in a high-pressure microwave oven. Hg was analysed by cold vapour atomic absorption spectrophotometry (CVAAS), and 22 elements (Ag, As, Ba, Cd, Ca, Cr, Cu, Ga, La, Li, Mn, Mo, Ni, Pb, Pt, Sb, Se, Sr, Tl, U, V, Zn) were detemined by inductively coupled plasma mass spectrometry (ICP-MS) (PQ-2, VG Elemental). All analyses were performed by the National Laboratory for Environmental Testing (NLET) at NWRI, Burlington.

Organochlorines

Char (muscle plus skin) samples were homogenized, mixed with pre-cleaned Na_2SO_4 and Soxhlet extracted with dichloromethane:hexane (1:1). Organochlorines were isolated by gel permeation chromatography (GPC)

Table 1. List of lakes and Arctic char samples collected and analysed or available for analysis

Lake	Island	Latitude	Longitude	Years
Amituk[1]	Cornwallis	75° 03'N	93° 49'W	1992, 2001, 2002
Aqiatusuk	Cornwallis	74° 42'N	94° 14'W	2002
Boomerang	Somerset	73° 57'N	92° 59'W	1999, 2001, 2002
Char[1]	Cornwallis	74° 42'N	94° 53'W	1993, 1999, 2000, 2001
North	Cornwallis	74° 46'N	95° 06'W	2000
Resolute[1]	Cornwallis	74° 41'N	94° 55'W	1993, 1997, 1998[2], 1999, 2000, 2001, 2002
Sapphire	Devon	75° 21'N	89° 29'W	1999, 2001, 2002

[1] Reported by Muir and Lockhart 1994; 1996

[2] Livers analysed for cadmium only; muscle samples lost in freezer failure

followed by silica gel cleanup. Lipid was determined using the GPC lipid fraction. The chromatography on silica gel was used to separate PCBs and *p,p'*-DDE from more chlordane and toxaphene components, *p,p'*-DDT and HCH isomers. The two fractions from the silica gel column were then analysed by gas chromatography with electron-capture detection (GC-ECD). Separation was accomplished on a HP 6890 GC using a 30 m DB-5 column with H_2 carrier gas. ΣPCBs represented the sum of 103 congeners. Toxaphene and PBDEs were analysed by low resolution GC-negative ion MS using a HP 5973 MSD. Selected samples of Fraction 1 were also run to check quantification of toxaphene congener P26. PBDEs were quantified using an external standard consisting of 32 congeners. Gas chromatographic conditions for the PBDEs were as described by Luross et al. (2002).

Co-planar PCBs (77, 126 and 169) were determined in the lipid-free extracts. They were spiked with ^{13}C-labelled surrogates, subjected to silica-gel cleanup and carbon column enrichment prior to analysis by high resolution MS. Coplanar PCB analyses were performed by AXYS Analytical (Sidney, BC).

Stable isotope analyses

Muscle from all fish analysed for mercury were analysed for stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) at NWRI (Saskatoon) in muscle samples using isotope ratio MS.

Quality assurance (QA)

QA steps included the analysis of certified reference materials for heavy metals and organochlorines, reagent blanks and duplicate samples. A reference material (NIST [National Institute of Standards and Technology, Gaithersburg MD; http://ois.nist.gov/srmcatalog] 1588 cod liver, NIST 1974 mussels or Cambridge Isotopes Ltd, lake trout 2525) and a blank were run with each sample batch of 10 samples. NLET organics and metals labs are participants in the NCP Quality Assurance Program. The NLET organics lab is a participant in the Quality Assurance for Marine Environmental Monitoring in Europe (QUASIMEME) programs for PCBs and toxaphene. NLET is certified by the Canadian Environmental Analytical Laboratory program of the Canadian Standards Association.

Statistical analyses

Recent mean concentrations of metals and organochlorines in char from Resolute Lake and other lakes were compared with results from 1992–93 using t-tests. Results were first tested for normality using skewness and kurtosis tests. Statistical analysis showed that concentration data for most elements in char muscle from Resolute Lake was normally distributed. Therefore, arithmetic means were reported and correlation analysis was conducted with untransformed data. Organochlorine data were lipid corrected and log transformed prior to testing significant differences among years using the t-test.

Results and Discussion

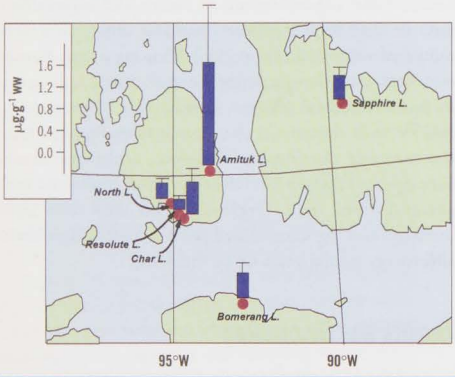
Spatial trends of mercury and other metals

Mean concentrations of mercury in landlocked Arctic char from Resolute, North, Sapphire, Boomerang and Char Lakes ranged from 0.14 to 0.55 ug g^{-1} wet wt based on the most recent collections from each lake. Higher mean concentrations (1.3 ug g^{-1} ww) were seen in char from Amituk Lake (Figure 1; Table 1). The sample size from Amituk was small and therefore may not be representative, however, previous results (Muir and Lockhart, 1994) also showed relatively high mercury in char from this lake compared to other lakes in the area. Mercury was strongly correlated with fish length and weight, as well as with thallium (Tl), rubidium (Rb) and selenium (Se) ($P < 0.05$) in all lakes, but not consistently with any of the other 18 other elements that were measured. Mercury

was also significantly correlated with stable nitrogen isotope ratios ($\delta^{15}N$). This suggests that biomagnification of mercury is occurring within the char population due to the presence of piscivorous char.

Concentrations of mercury and 10 other elements, including the toxic metals Pb, Cd, As and Tl, in Resolute, Boomerang, Sapphire and Amituk Lakes are shown in Table 1. We have previously reported these same elements in Char and North Lakes, as well as Resolute Lake (Muir et al., 2001). Lead and cadmium concentrations were uniformly low, approaching detection limits of about 0.001 ug/g. Thallium and arsenic showed more lake-to-lake variation. Thallium was higher in Sapphire and Amituk char than in Resolute, Boomerang, Char or North Lakes (see Muir et al., 2001; Table 1). Arsenic and chromium were higher in Sapphire Lake than in all other lakes. Sapphire Lake is in the area of the Haughton meteor crater and may have unusual geology relative to the other lakes on Cornwallis Island.

Figure 1. Mercury concentrations in muscle of landlocked Arctic char from six lakes in the central Arctic archipelago. Vertical bars represent 95% confidence intervals. Results are from 1999 (Sapphire), 2000 (North), 2001 (Char), and 2002 (Resolute, Boomerang and Amituk)



Temporal trends of mercury

Mercury concentrations in char from Resolute Lake in 1999 through to 2002 were about 20–25% lower than those from 1993 and 1997 (Figure 2). The decline from 1997 to 2002 was statistically significant (t-test; P = 0.001) in 2002. In contrast, mercury concentrations in char from Char Lake and Amituk Lake were significantly higher (P = 0.03) in recent samples (Amituk 01–02; Char 00–01) compared to 1992–93. The 2–3 fold increases in mercury in Arctic char from Char and Amituk Lakes are within the range seen in seabirds and ringed seals in the Canadian Arctic archipelago during the 1990s (Fisk et al., 2003). The slow declining trend in Resolute Lake suggests that these trends can vary widely among lakes. Differences in water residence time and watershed characteristics may help explain this.

In other work, we have found mercury concentrations in a dated sediment core from Resolute Lake have also declined during the past 15–20 years, while concentrations in a core from Amituk Lake mercury reached a maximum in the early 1980s and are now declining (Muir et al., 2003 — this volume). Thus, the changes in concentrations in Arctic char in both lakes do not coincide well with total mercury deposition to sediments. They may be related to inputs from methyl mercury which has been shown to be formed in wetland areas on Cornwallis Island during spring snow melt (Losetto et al., 2003).

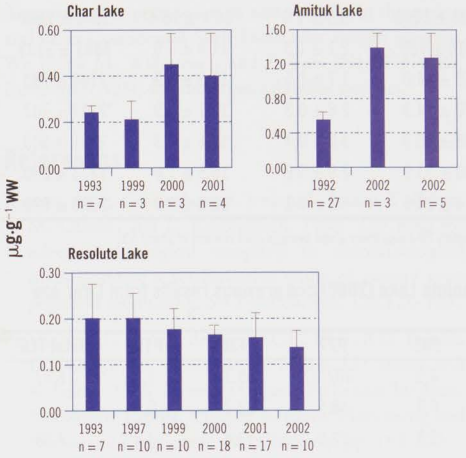
Persistent organochlorines (OCs)

Char (skin on muscle) samples had detectable levels of about 85 PCB congeners and 30 OC pesticides and

Table 2. Mean concentrations and standard deviation of mercury and other major elements ($\mu g \cdot g^{-1}$ wet wt) detected in muscle of landlocked Arctic char from lakes in the area of Qausuittuq (Resolute)

Lake	N		Weight (g)	As	Cd	Cr	Ni	Pb	Rb	Tl	V	Se	Hg
Resolute	10	mean	370	0.021	0.002	0.032	0.115	0.007	0.641	0.004	0.002	0.714	0.138
(2002)		SD	101	0.014	0.001	0.021	0.053	0.007	0.112	0.002	0.003	0.078	0.059
Boomerang	5	mean	465	0.009	0.001	0.030	0.072	0.001	0.432	0.004	0.001	0.664	0.213
(2002)		SD	138	0.007	0.000	0.011	0.011	0.001	0.230	0.003	0.000	0.069	0.183
Sapphire	8	mean	864	0.046	0.001	0.135	0.025	0.007	0.360	0.016	0.031	0.670	0.291
(1999)		SD	1063	0.012	0.001	0.022	0.013	0.003	0.056	0.007	0.005	0.053	0.189
Amituk	5	mean	688	0.012	0.002	0.042	0.076	0.002	0.832	0.017	0.001	1.65	1.30
(2002)		SD	533	0.004	0.001	0.016	0.029	0.002	0.167	0.007	0.000	0.210	0.834

Figure 2. Mercury concentrations (means ± 95% confidence interval) in landlocked Artic char from Char, Amituk, and Resolute Lakes (1992/93–2002)



related compounds. Mean concentrations in Resolute Lake char were virtually identical over the five year period. ΣPCB concentrations showed no significant decline (t-test, $P > 0.05$) in Char Lake (1993–2000), Amituk Lake (1992–2002) or Resolute Lake (1997–2002). Total chlordane (ΣCHL), total tetra-, penta- and hexachlorobenzenes (ΣCBZ), and total hexachlorocyclohexanes (ΣHCH) declined significantly between 1992–02 (Amituk) and 1993–2000 (Char) (Table 2). ΣDDT (total DDT-related compounds) also declined but the trend was not statistically significant due to small sample sizes. Endosulfan concentrations increased significantly ($P < 0.01$) in Amituk and Resolute Lakes but showed no significant trend in Char Lake (Table 1). The observation that endosulfan is increasing in two of the three lakes is interesting because Hung et al. (2002) have found increasing concentrations of this pesticide in Arctic air over the period 1993 to 1998. The lack of a trend for PCBs is also consistent with the observation that PCBs did not decline in Arctic air during the mid-1990s (Hung et al., 2001).

Results for stable isotope analysis of the Resolute Lake char from 1997–2001 showed that $\log_{10}$ΣPCB (lipid weight) was significantly correlated with $\delta^{15}N$ ($r^2 = 0.29$; $P < 0.01$). Each year, 1–3 fish out of 10–12 analysed from Resolute Lake had $\delta^{15}N$ values 3.5‰ or more higher than others indicating they are feeding at a higher trophic level, probably on other char. Hobson and Welch (1995) associated $\delta^{15}N$ values of 13.7‰ with piscivory in char. They also found a significant increase in the $\delta^{15}N$ of these fish with size which they attributed to cannibalism within the population. There were no significant correlations of $\delta^{15}N$ with length or weight in Resolute Lake char.

Co-planar PCBs

These congeners were measured in 6 char samples from Resolute Lake (2000). We chose to analyse all 209 PCB congeners (including all 16 non-ortho and mono-ortho congeners for which there are toxic equivalent factors) using high resolution mass spectrometry (HRMS). The HRMS work confirmed the presence of low pg/g levels of co-planar PCBs (Table 3). Concentrations and TEQs were, in most cases, similar to those reported previously from other landlocked char (by low resolution MS), however, PCB77 concentrations were higher than measured previously. Most of the TEQs were due to PCB 126 which has a TEF of 0.1 compared to 0.0001–0.0005 for most of the other planar congeners. PCB 169 was not detected (< 0.1 pg/g) in char samples.

Polybrominated diphenyl ethers (PBDEs)

Because of the increasing concentrations of BDPEs reported in ringed seals from the Canadian Arctic (Ikonomou et al., 2002) we decided to examine the trends in our Arctic char samples. There are no previous results on BDPEs in Arctic char to our knowledge. While total PBDEs were relatively low (1.1–5.5 ng g^{-1} wet weight) the concentrations of congeners 47 and 99 are within the range of the 30 most prominent PCB congeners in the same samples (Figure 3). BDE 47 and 99 have doubled in concentration in Resolute Lake char (selected with $\delta^{15}N$ from 10–13‰) between 1997 and 2001 (Figure 3). Mean concentrations of these PBDEs were significantly higher in 2001 and 2002 than in 1997 (t-test, $P < 0.05$).

Conclusions

Concentrations of mercury in the char in Resolute Lake have declined significantly from 1993 to 2002. However, mercury concentrations have increased in Char Lake and Amituk Lake over the same period and mean concentrations are above guidelines for subsistence consumption of 0.2 ug g^{-1} wet wt. The 2–3 fold increases in mercury in Arctic char from Char and Amituk Lakes are within the range seen in seabirds and ringed seals in the Canadian Arctic archipelago during the 1990s (Fisk et al., 2003). The slow declining trend in Resolute Lake suggests that

Table 3. Geometric mean concentrations (ng g^{-1} lipid wt) of major OCs in landlocked Arctic char[1]

Lake	N	ΣCBz	ΣCHL	ΣDDT	α–endo-sulfan	ΣHCH	ΣPCB
Amituk (1992)	12	149 ± 30	1220 ± 372	833 ± 315	4.5 ± 1.1	44.0 ± 4.2	1823 ± 724
Amituk (2002)	4	48.7 ± 2.6	567 ± 256	416 ± 196	9.9 ± 3.3	13.0 ± 2.3	1262 ± 556
Char (1993)	5	66.8 ± 24.0	361 ± 138	2108 ± 1040	3.5 ± 1.0	60.1 ± 16.4	5546 ± 2602
Char (2000)	4	42.9 ± 8.6	39.2 ± 10.2	1310 ± 789	2.1 ± 1.3	11.4 ± 1.5	4883 ± 3133
Resolute (1997)	10	29.3 ± 5.3	84.3 ± 29.8	119 ± 44.0	1.7 ± 0.5	11.3 ± 1.9	2144 ± 783
Resolute (1999)	10	39.1 ± 5.3	121 ± 30.4	170 ± 44.3	2.8 ± 0.3	17.1 ± 1.9	2347 ± 707
Resolute (2000)	8	38.0 ± 4.6	30.5 ± 6.2	148 ± 40.9	3.0 ± 0.4	12.6 ± 0.3	2281 ± 603
Resolute (2001)	10	32.3 ± 5.9	91.2 ± 32.3	109 ± 33.9	2.9 ± 0.6	10.5 ± 1.6	1373 ± 230
Resolute (2002)	9	36.5 ± 6.9	89.4 ± 11.9	114 ± 20.6	3.2 ± 0.3	12.6 ± 0.5	2323 ± 529

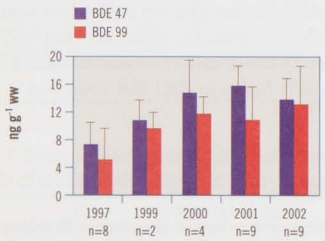
[1] These are lipid weight concentrations. Wet or fresh weight concentrations are approximately 20-times lower given average lipid content of about 5%

Table 4. Co-planar PCB concentrations in Arctic char from Resolute Lake (2000) and previous results from Char and Amituk Lakes

Location	Year	N	% lipid	P37	P81	P77	P126	P169	Total TEQ[1]
Resolute Lake	2000	6	5.6	14.2	4.3	107.9	56.3	1.3	8.47
			1.7	5.2	4.3	48.5	23.3	0.0	
Char Lake	1993	5	4.3	1.1	2.3	22.0	73.4	3.4	7.38
			1.9	1.3	0.9	8.7	31.1	1.2	
Amituk Lake	1993	12	4.4	0.4	0.6	7.1	9.3	1.1	0.95
			2.1	0.7	0.5	3.5	5.6	1.2	

[1] TEQs based on congeners 77, 81, 105, 114, 118, 123, 126, 156/157, 167, 169, 189

Figure 3. Concentrations of PBDEs in landlocked Arctic char from Resolute Lake (1997 – 2002). Bars are average lipid weight concentrations and vertical lines are 95% confidence intervals.



these trends can vary widely among lakes. Resolute Lake has a much higher sedimentation rate than the two other lakes, and this may influence exposure of char to mercury. Differences in water residence time and watershed characteristics may help explain this.

The reasons for increasing concentrations in Char and Amituk Lakes need to be investigated. Climate warming and the destruction of the ozone layer could be resulting in increased exposure of biota to mercury in high Arctic lakes.

PCBs have not declined significantly in char from Resolute, Char or Amituk Lakes over the period 1992–93 to 2002. PCB TEQs in char muscle, calculated with all dioxin-like PCB congeners, average 8 pg/g which is relatively low.

Concentrations of endosulfan and PBDEs increased significantly in char in Resolute Lake from 1997 to 2002. This illustrates that the lake is responding to increases in global emissions of these chemicals which have been shown to be increasing in Arctic air (endosulfan) and biota. The lack of a trend for PCBs is also consistent with results from Arctic air during the mid-1990s.

PCBs and mercury have been shown to vary with trophic level of the char in Resolute Lake. Stable isotope signatures of the fish are thus important in helping to interpret temporal trends. Only fish with a similar narrow range of $\delta^{15}N$ can be compared among years.

Acknowledgements

Lyle Lockhart (DFO Winnipeg, retired) provided results for mercury in char from 1992/93. We thank the Qausuittuq (Resolute Bay) Hunters and Trappers Association for permission to sample lakes in the region and Polar Continental Shelf Project for aircraft support. We thank M. Williamson and P. Low (NLET/NWRI, Burlington, ON) for the organochlorine analysis.

References

Bignert, A., A. Göthenberg, S. Jensen, K. Litzén, T. Odsjö, M. Olsson, and L. Reutergårdh. 1993. The need for adequate biological sampling in ecotoxicological investigations: a retrospective study of twenty years pollution monitoring. *Sci Total Environ.* 128:121–139.

de March, B.G.E., C.A. de Wit, D.C.G. Muir, B.M. Braune, D.J. Gregor, R.J. Norstrom, M. Olsson, J.U. Skaare, and K. Stange. 1998. Persistent Organic Pollutants. In: Arctic Assessment Report, Chapter 6. Arctic Monitoring and Assessment Programme. Oslo, Norway. pp. 183–372.

Fisk, A.T., K.E. Hobbs, and D.C.G. Muir (eds.). 2003. Contaminant Levels and Trends in the Biological Environment, Canadian Arctic Contaminants Assessment Report II. Indian and Northern Affairs Canada. 202 pp.

Hobson, K.A. and H.E. Welch. 1995. Cannibalism and trophic structure in a high arctic lake: Insights from stable-isotope analysis. *Can J Fish Aquat Sci.* 52: 1195–1201.

Hung, H., C.J. Halsall, P. Blanchard, H.H. Li, P. Fellin, G. Stern, and B. Rosenberg. 2001. Are PCBs in the Canadian Arctic atmosphere declining? Evidence from 5 years of monitoring. *Environ Sci Technol.* 35:1303–1311.

Hung, H., C.J. Halsall, P. Blanchard, H.H. Li, P. Fellin, G. Stern, and B. Rosenberg. 2002. Temporal trends of organochlorine pesticides in the Canadian Arctic atmosphere. *Environ Sci Technol.* 36:862–868.

Ikonomou, M.G., S. Rayne, and R.F. Addison. 2002. Exponential increases of the brominated flame retardants, polybrominated diphenyl ethers, in the Canadian Arctic from 1981–2000. *Environ Sci Technol.* 36:1886–1892.

Jensen, J., K. Adare, and R. Shearer (eds.). 1997. Canadian Arctic Contaminants Assessment Report. Ottawa: Indian and Northern Affairs Canada. 460 pp.

Lockhart, W.L., P. Wilkinson, B.N. Billeck, R.A. Danell, R.V. Hunt, J. Delaronde, and V. St. Louis. 1998. Fluxes of mercury to lake sediments in central and northern Canada inferred from dated lake sediment cores. *Biogeochemistry.* 40:163–173.

Losetto, L., S.D. Siciliano, and D. Lean. 2003. Methyl mercury production in high arctic wetlands. *Environ Toxicol Chem.* Accepted for publication.

Luross, J.M., M. Alaee, D.B. Sergeant, C.M. Cannon, D.M. Whittle, K.R. Solomon, and D.C.G. Muir. 2002. Spatial distribution of polybrominated diphenyl ethers and polybrominated biphenyls in lake trout from the Laurentian Great Lakes. *Chemosphere.* 46: 665–672.

Muir, D., D. Halliwell, T. Jackson, and V. Cheam. 2003. Spatial trends in loadings and historical inputs of mercury inferred from Arctic lake sediment cores. In: S. Smith (ed.). Synopsis of Research Conducted Under the 2001–2002 and 2002–2003 Northern Contaminants Program. In press.

Muir, D.C.G., G. Köch, J. Reist and D. Bright. 2001.Temporal trends of persistent organic pollutants and metals in landlocked char. In: S. Kalhok (ed.). Synopsis of Research Conducted Under the 2000–01 Northern Contaminants Program. Ottawa: Indian and Northern Affairs Canada. pp. 202–207.

Muir, D.C.G., A. Omelchenko, N.P. Grift, D.A. Savoie, W.L. Lockhart, P. Wilkinson, and G.J. Brunskill. 1996. Spatial Trends and Historical Deposition of Polychlorinated Biphenyls in Canadian Mid-latitude and Arctic Lake Sediments. *Environ Sci Technol.* 30: 3609–3617.

Muir, D.C.G. and W.L. Lockhart. 1996. Contaminant trends in freshwater and marine fish. In: J.L. Murray and R.G. Shearer (eds.). Synopsis of Research Conducted Under the 1994–95 Northern Contaminants Program, Environmental Studies Report, No. 73. Ottawa: Indian and Northern Affairs Canada. pp. 189–194.

Muir, D. and L. Lockhart. 1994. Contaminant trends in freshwater and marine fish. In: Synopsis of Research Conducted Under the 1993/1994 Northern Contaminants Program. Indian and Northern Affairs Canada, Environmental Studies Report, No. 72. pp. 264–271.

Olsson, M. and L. Reutergårdh. 1986. DDT and PCB pollution trends in the Swedish aquatic environment. *Ambio.* 15:103–109.

Temporal Trends of Persistent Organic Pollutants and Metals in Ringed Seals from the Canadian Arctic

Project leaders

Derek Muir, National Water Research Institute, Burlington ON; phone: (905) 319-6921; fax (905) 336-6430; e-mail: derek.muir@ec.gc.ca;
Michael Kwan, Kuujjuaq Research Centre, P.O. Box 179, Kuujjuaq, QC J0M 1C0; phone: (819) 964-2951; fax: (819) 964-2230; e-mail: m_kwan@makivik.org

Project team (2001–02–03)

2001 — Hunters and Trappers Associations of Sachs Harbour and Paulatuk
2002 — Hunters and Trappers Associations of Inukjuaq, Kangiqsujuaq (Wakeham), Kangiqsualujjuaq (George River) and Quaqtaq; John Alikamik, Holman, NT; Sean Backus and Mike Comba, NWRI, Burlington, ON; Aaron Fisk, University of Georgia, Athens, GA; Paul Hoekstra, University of Guelph, Guelph, ON; Lyle Lockhart, Winnipeg, MB; Eric Loring, Inuit Tapiriit Kanatami, Ottawa; Lois Harwood, Fisheries and Oceans, Inuvik, NWT; Ian Stirling, Canadian Wildlife Service, Edmonton.

Abstract

Temporal trends of mercury, PCBs, DDT, and other persistent organic pollutants (POPs) in ringed seals were studied by comparing results from samples collected in the 1970–early 1990s with results from recent collections. Significant declines of ΣPCB10 (sum of 10 major PCB congeners) and ΣDDT (sum of DDT related compounds) were seen in female ringed seals from 7 of 9 locations in the Canadian Arctic and there was a shift to more recalcitrant residues, i.e. *p,p'*-DDE and CB153, reflecting older "weathered" or degraded sources at all locations. ΣHCH and ΣCHL concentrations in seals showed greater annual % declines (up to 6% per year) than PCBs and ΣDDT at some locations. ΣDDT and PCBs were found to be declining at 1–5% per year at 7 locations during the 1990s/early 2000s. However, two eastern Arctic locations (Pangnirtung and Ungava Bay) show no significant trend. These results suggest that there are regional differences in temporal trends of persistent organochlorines possibly because of exposure to different water masses, e.g. Atlantic Ocean influence in the eastern Arctic, and because of differences in atmospheric deposition between the eastern and western Arctic. During the 1990s/early 2000s, mercury concentrations increased from 2- to 3-fold at 3 locations, declined by 1.5–2x at 3 locations and showed no change at two others. Therefore, it appears that there is no clear increasing trend of mercury in ringed seals in the Canadian Arctic. The observation of both increases and declines in mercury in seal liver points to the need for increased frequency of sampling for this contaminant.

Key Project Messages

1. Temporal trends of POPs and mercury were examined in female ringed seals over a 25-year period at 2 locations and over 12 to 15 years at 8 other locations.
2. Concentrations of most POPs were lower in the late 1990s/early 2000s compared to the 1970/80s and early 1990s, however, the extent of declines varied widely. ΣDDT had the largest decline (1.7x to 3.3x) while PCBs declined 1.6–2.4x over 25 years.
3. Mercury increases were also quite variable. Mercury increased 2–3x at three locations (Mittimatalik, Hudson Strait and Holman) and declined by 1.5–2x at Qausuittuq, Ungava Bay and Sachs Harbour and showed no change at Arviat and Inukjuaq.
4. Overall there appears to be no geographically widespread increase in mercury in ringed seal liver. Year to year variation in mercury in seals makes assessment of temporal trends difficult.

Objectives

1. Determine temporal trends of persistent organic pollutants (POPs) and mercury in ringed seals from locations previously studied in the 1980s and early 1990s.
2. Provide the information on levels and temporal trends of these contaminants to each community participating in the study on a timely basis.

Introduction

The ringed seal is the most abundant Arctic pinniped with a circumpolar distribution, making this species an ideal candidate for examining spatial trends of persistent organic pollutants (POPs) and heavy metals in the Arctic. It is identified as a key species for monitoring by the Arctic Monitoring and Assessment Program (AMAP) and for temporal trends monitoring in the NCP "Blueprint" (INAC 1999). As a top predator in nearshore pelagic food webs, the ringed seal prefers land fast ice or multiyear ice. The ringed seal diet consists of fish, mainly Arctic cod (*Boreogadus saida*), polar cod (*Arctocadus glacialis*) and crustaceans (amphipods, mysids and euphausids) (Holst et al., 2001). Ringed seals are relatively sedentary and male ringed seals may occupy the same under ice habitat for up to 9 months (Smith, 1987). Ringed seals are hunted virtually throughout all coastal communities of the Canadian Arctic and it is therefore relatively easy to obtain samples with the help of local hunters and trappers associations.

The original rationale for this project was that there could be differences in the temporal trends of POPs and Hg in marine mammals across the Canadian Arctic. Recent seawater measurements show large spatial differences of HCH, toxaphene and PCBs concentrations in seawater between the Beaufort Sea and Baffin Bay and between those areas and Hudson Bay (Hoekstra et al., 2002; Macdonald et al., 2000). These differences in seawater levels may give rise to differences in contaminant levels in marine food webs and ultimately in marine mammals. In the case of HCH for example, much higher levels are found in ringed seal blubber from the central high Arctic than in waters influenced by the Atlantic Ocean (Muir et al., 2000). PCB153 shows fewer regional differences after adjusting for the effects of age and sex using analysis of covariance (Muir et al., 2000) but levels of PCBs are generally higher in seals in the eastern Arctic (Muir et al., 1997).

Regional differences in concentrations are even more pronounced for mercury (Hg) than for persistent organochlorines (OCs) in seals with higher levels in the western Arctic (Muir et al., 1997; Wagemann et al., 1996). This may be due to greater sources of natural Hg in the sedimentary rocks of the western Arctic. When this project began, information on temporal trends in Hg in ringed seals was limited, however, results to the mid-1990s showed increasing levels with time (Wagemann et al., 1996) but the rates of increase did not seem to be the same in the eastern and western Arctic.

Results for OCs (in blubber) and Hg (in liver) were available from previous NCP and pre-NCP studies of ringed seals from several communities in the eastern Arctic and western Arctic (Muir et al., 1997; Weis and Muir, 1997; Wagemann et al., 1996). Results for mercury in liver were available for several communities in the eastern Arctic (Resolute, Pangnirtung, Inukjuaq, Kangiqsujuaq) and western Arctic (Holman, Sachs Harbour) from the 1970s to 1990s although they had been presented only on a regional basis by Wagemann et al. (1996).

Activities

In 2001–02 and 2002–03

In 2001–02 ringed seal samples were successfully collected with the help of our HTA partner organizations in Sachs Harbour and Paulatuk as part of the spring/summer hunt. Lois Harwood of Fisheries and Oceans (Inuvik) arranged for collection of ringed seals from Holman. Collection at Tuktoyaktuk was unsuccessful due to limited hunting and the lack of a freezer

at the HTA office which prevented storage of samples. In 2002–03 ringed seal samples were collected successfully by the HTAs of 4 northern Québec communities, Inukjuaq, Kangiqsujuaq (Wakeham), Kangiqsualujjuaq (George River) and Quaqtaq. These collections added to samples collected and analysed from Mittimatalik (Pond Inlet), Qausuittuq (Resolute) and Ikpiarjuk/Tununirusiq (Arctic Bay) in 2000 (Muir et al., 2001).

Hunters were provided with a kit and video prepared in Inuktitut and English by the Kuujjuaq Research Centre (KRC). Collections consisted of blubber, liver, muscle, kidney, tooth/lower jaw (for aging) from 25 seals, most being adults and about half female. Essential data on length, girth, blubber thickness at the sternum, and sex was provided for all locations except Mittimatalik. All samples were shipped to KRC for processing. Large subsamples of all tissues were archived in walk-in freezers at −35°C in sealed plastic bags (double bagged). Aging was performed on tooth sections at KRC.

Chemical analyses

OC pesticides and PCBs in seal blubber were determined with the following general procedure: Blubber samples were homogenized with sodium sulfate and Soxhlet extracted with dichloromethane:hexane (1:1). Following lipid removal by gel permeation chromatography, OCs were fractionated on an activated silica gel column, then analysed by gas chromatography with electron-capture detection (GC-ECD). Separation was accomplished on a HP 6890 GC using a 30m DB-5 column with H_2 carrier gas. Toxaphene was analysed by low resolution GC-negative ion MS using a HP 5973 MSD in negative ion mode. All OC analyses were conducted by the National Laboratory for Environmental Testing (NLET) Organics Analysis Laboratory. This lab is certified by Canadian Standards Association and has participated successfully since 1998 in more than 12 QUASIMEME interlab comparisons on PCBs/OC pesticide analysis as well as in toxaphene intercomparisons.

Liver and kidney samples were analysed for heavy metals (cadmium, mercury, lead, selenium and arsenic) at KRC (Kuujjuaq) using atomic absorption spectrometry (AAS). Methyl mercury was determined (by NLET) in a subset of liver samples by GC-atomic emission detection (AED) to examine the speciation of Hg.

Quality assurance steps included the analysis of reference materials for heavy metals and organochlorines, reagent blanks and duplicate samples. The KRC metals lab and the NLET organics lab were participants in the NCP Quality Assurance Program (Stokker, 2003).

Organochlorines concentrations in ringed seals were normalized to 100% lipid. Results for both mercury and organochlorines were first tested for normality using skewness and kurtosis tests. All mercury data were $\log_{10}$ transformed to give coefficients of skewness and

Table 1. Collection of ringed seal samples for OCs and Hg temporal trends 1998–2002

Location	Year of Collection	Year analysed			Chemicals
		2000–01	2001–02	2002–03	
Nunavut					
Arviat	1998	3			Hg & OCs
Ausuittuq (Grise Fiord)	1998	3			Hg & OCs
Pangnirtung	1999	3			Hg & OCs
Mittimatalik (Pond Inlet)	2000	3			Hg
Qausuittuq (Resolute)	2000		3		Hg & OCs
Ikpiarjuk/Tununirusiq (Arctic Bay)	2000		3		Hg & OCs
NWT					
Sachs Harbour	2001		3		Hg & OCs
Holman	2001		3		Hg & OCs
Paulatuk	2001			3	Hg
Nunavik					
Kangiqsujuaq (Wakeham)	2002			3	Hg & OCs
Kangiqsualujjuaq (George River)	2002			3	Hg & OCs
Quaqtaq	2002			3	Hg & OCs
Inukjuaq	2002			3	Hg & OCs

kurtosis < 2 while OC data were not log transformed because of relatively low coefficients of skewness and kurtosis. Geometric means (back transformed log data) and arithmetic means were calculated for mercury in liver. Selected comparisons between years were made with the Students t-test (two tailed, unequal variances) (Excel, 2000).

Results and Discussion

Organochlorines

Samples from female seals only were selected for analysis in order to minimize the influence of age in the interpretation of temporal trends of OCs (Addison and Smith, 1974). Results are available for all 10 communities from which we originally planned to analyse seal blubber samples based on the availability of previous data. In addition, a small number of samples from Holman (5 males and 5 females) were analysed for OC pesticides and PCBs in order to provide additional temporal trend information for the Canadian Arctic Assessment Report (P. Hoekstra, unpublished data).

Arithmetic mean concentrations (95% confidence limits; $ng \cdot g^{-1}$ lipid weight) for ΣPCB10 (sum of CB 28, 31, 52, 101, 105, 118, 138, 153, 156 and 180) and CB153/ΣPCB ratios in blubber of female ringed seals are shown in Figure 1. This figure combines the results from this study of 10 locations with historical results. In order to make this comparison some communities were combined. Results for Quaqtaq and Kangiqsujuaq in Nunavik were combined as a "Hudson Strait" group because the communities are relatively close together. Previous OC results for this area were from Salluit and Kangiqsujuaq. Older results from Rankin Inlet (Kangiqliniq) in 1986 were used for comparison with Arviat for 1992 and 1998. The seals hunted by these two communities are considered to be from the same western Hudson Bay population (I. Stirling, personal communication). For comparison with earlier data ΣPCB10 was used rather than all congeners because the results from the early 1980s and

Figure 1. Temporal trends of ΣPCB10 (sum of 10 congeners) and ratio of CB153 to ΣPCB10 in female ringed seal blubber from 9 locations in the Canadian Arctic. Bars represent arithmetic mean concentrations ($ng \cdot g^{-1}$ lipid weight) ± 95% confidence limits

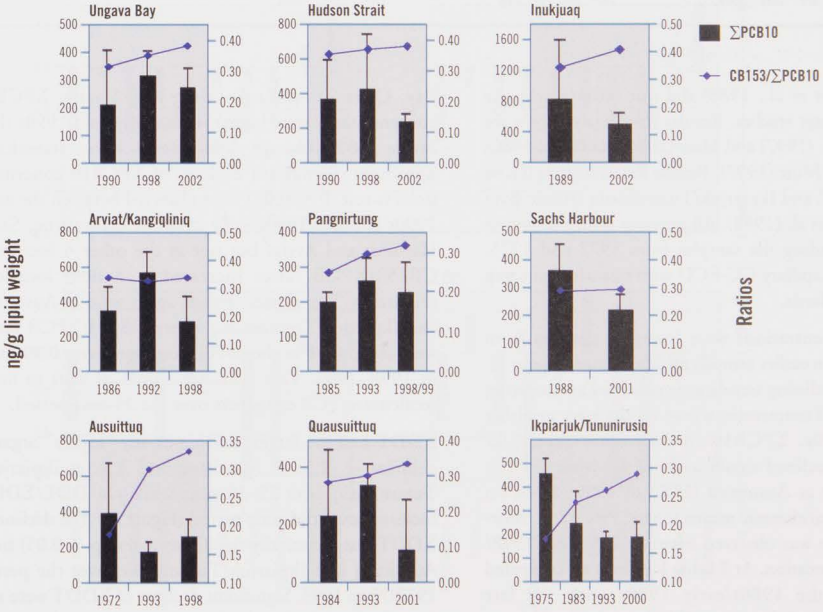
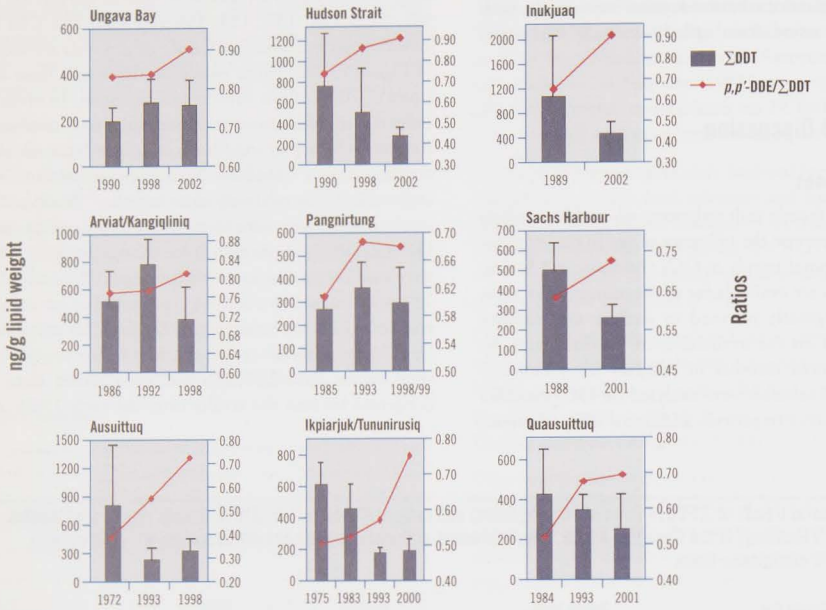


Figure 2. Temporal trends of ΣDDT and the ratio of p,p'-DDE to ΣDDT in female ringed seal blubber from 9 locations in the Canadian Arctic. Bars represent arithmetic mean concentrations (ng·g^{-1} lipid weight) ± 95% confidence limits



1970s (in Muir et al., 1988) did not include as many congeners as later studies. Results from early 1990s are from Muir et al. (1997) and Muir (1996), and from 1980s from Weis and Muir (1997). Results for Ausuittuq (Grise Fiord) for 1972 and Ikpiarjuk/Tununirusiq (Arctic Bay) are from Muir et al. (1988). All previous results shown in Figure 1, including the samples from 1972 and 1975, were based on capillary GC-ECD with quantitation using authentic standards.

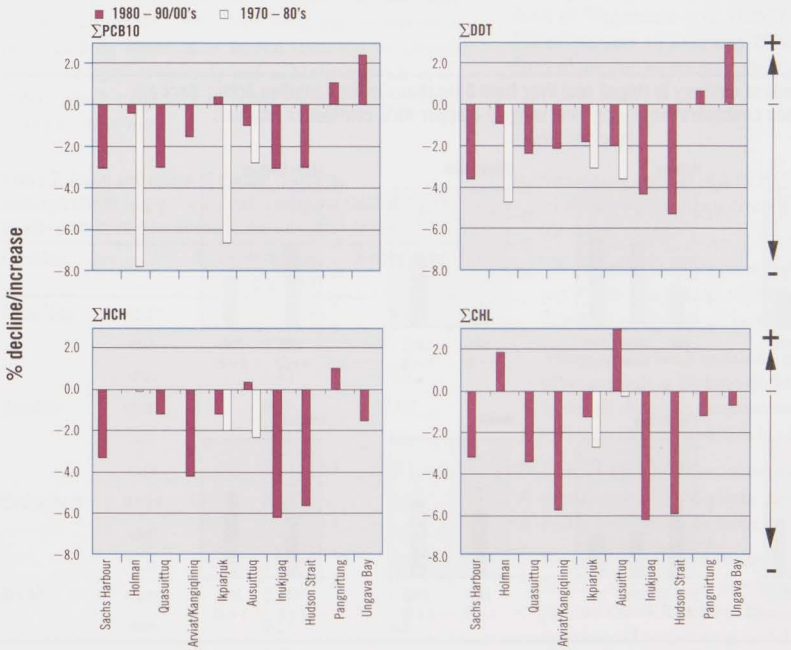
ΣPCB10 concentrations were lower in samples from 1998–2002 than earlier samples at all locations (Figure 1). The clearest declining trends were observed at Ausuittuq and Ikpiarjuk/Tununirusiq where results were available from the 1970s. ΣPCB10 in seals from Ikpiarjuk/Tununirusiq declined significantly (2.4x) from 1975 to 2000 and 1.5x at Ausuittuq (1972 to 1998) based on comparison of arithmetic means (t-test, $P < 0.05$), however no decline was observed between 1993 and 1998/2000 at either location. At 7 other locations we compared results from the 1980s/early 1990s with the late 1990s/2000s. At 5 locations (Hudson Strait, Ungava Bay, Qausuittuq, Pangnirtung and Arviat), ΣPCB10 concentrations were higher in the early/mid 1990s than in the 1980s although differences were not statistically significant. Significant declines of ΣPCB10 concentrations (t-test, $P < 0.05$) were observed between the early 1990s and late 1990s/early 2000s at Qausuittuq, Sachs Harbour and Arviat but not at the other 4 locations. CB153/ΣPCB ratios increased at 8 of 9 locations (Figure 1). The clearest trends again were at Ausuittuq and Ikpiarjuk/Tununirusiq where CB153/ΣPCB ratios were about 0.18 in the 1970s, compared with 0.30–0.33 in 1998–2000. This indicates a gradual shift to more recalcitrant PCB congeners over the 25-year period.

ΣDDT had the largest decline of any "legacy" organochlorine — 2.5x at Ausuittuq and 3.3x at Ikpiarjuk/Tununirusiq ,over 25–30 years while *p,p'*-DDE/ΣDDT increased over the same period (Figure 2). The decline in ΣDDT was statistically significant (t-test, $p < 0.05$) from Ausuittuq and Ikpiarjuk/Tununirusiq over the period 1972/75 to 1993. Significant declines of ΣDDT were also found at 5 of the 7 other locations. At Pangnirtung and

Ungava Bay, no significant differences were found for ΣDDT between samples from 1985, 1993 and 1999, although mean levels were higher in the samples from the 1990s. At Pangnirtung one explanation for the higher levels in the 1999 animals is that their average age was older (12 yrs) compared to the 1985 group (2 yrs). However, this was not the case in the samples from Ungava Bay which had similar mean ages for each sampling year. Although concentrations of major OCs generally do not vary with age in reproductively active females, there is a gradual increase from young to very old animals (Fisk et al., 2001). *p,p'*-DDE/ΣDDT ratios generally increased from the 1980s to the 1990s/2000s at all locations. This trend towards more recalcitrant DDT components was most evident at Ausuittuq, Ikpiarjuk/Tununirusiq, Qausuittuq, and Sachs Harbour and not significant at Pangnirtung and Ungava Bay.

The geographic variation in temporal trends of ΣPCB, ΣDDT, ΣCHL and ΣHCH in female ringed seals is illustrated in Figure 3 by plotting the annual percent decline in the 1970s to 1980s or 1980s to 1990s/2000s. The annual percent decline was calculated by expressing the difference in mean concentrations between sampling years as a percentage and dividing by the number of years. Results from Holman were also included by using mean concentrations reported by Addison and Smith (1998) combined with recent results of Hoekstra (2001, unpublished). The results show a decline for all four persistent OC groups at 8 locations. Interestingly the two most easterly locations, Pangnirtung and Ungava Bay, show low annual percent declines for ΣCHL and ΣHCH and small increases for ΣPCB10 and ΣDDT. Ringed seals from Holman had comparable rates of decline of ΣPCB10 and ΣDDT in the 1970s and '80s to those from Ikpiarjuk/Tununirusiq. Neither location had a significant decline of ΣPCB10 during the 1990s while the annual decline of ΣDDT at Holman (0.9%) was much less than at Ikpiarjuk/Tununirusiq (-1.8%). ΣCHL and ΣHCH also had different trends at Holman (negligible decline or

Figure 3. Average percent annual declines or increases of ΣPCB, ΣDDT, ΣCHL, and ΣHCH in female ringed seal blubber from 10 locations in the Canadian Arctic. Locations are arranged longitudinally from west to east. Bars represent % decline calculated by expressing the difference in concentrations between sampling years as a percentage and dividing by the number of years. Not all declines or increases shown are statistically significant



actual increases) compared to other locations including nearby Sachs Harbour (Figure 2). The uncertainties in the estimation of the annual % declines were not investigated in this preliminary assessment of the data but they are probably similar to the relative standard deviations of the mean concentrations, i.e. in the range of 30–100%. Therefore the annual % declines reported in Figure 3 should be used with caution.

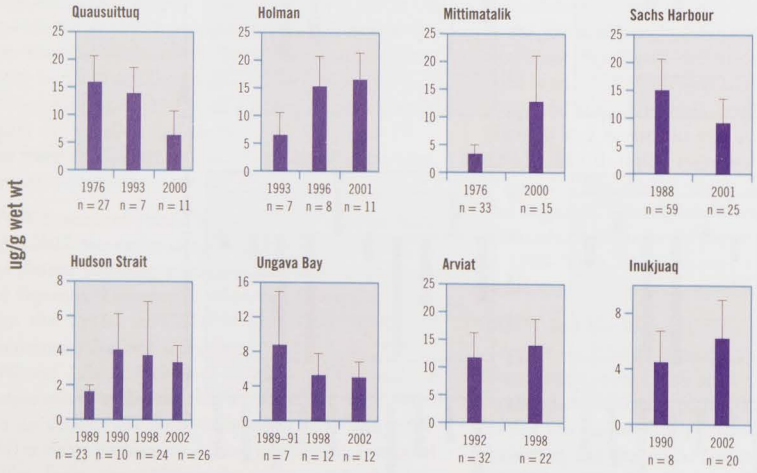
Addison and Smith (1998) found a 3-fold decline for ΣDDT at Holman between 1972 and 1991, which is in general agreement with results from Ausuittuq and Ikpiarjuk/Tununirusiq. In the case of PCBs, there are greater uncertainties in the trends from 1972–1981 at Holman because archived samples are not available from 1972 and analytical methodologies have changed (packed columns to capillary GC columns), nevertheless, through reanalysis of 1981 samples by both packed column and capillary column GC, the authors have been able to compare results over the 18-year period. In the present case, the results from 1972 from Ausuittuq consist of samples analysed by capillary GC with ECD detection on 60 m 5% phenylmethyl silicone bonded columns (0.25 μm film thickness) with automated split-splitless injection system and are therefore comparable to present day analyses.

Stern and Addison (1999) conducted a temporal trend study on PCBs and other POPs in beluga from Cumberland Sound using archived blubber for 4 sampling times from the mid-1980s to late 1990s. Their results showed a small but significant decline in PCBs, DDT group and α-HCH, but none for β- and γ-HCH over the 15-year period (Stern and Addison, 1999). The seals, collected from the same area (Pangnirtung) do not show a significant decline for PCBs, DDT or HCH isomers. These results illustrate differences due to species feeding behavior and migratory pattern. The adult ringed seals are more likely full-time residents of Cumberland Sound while the beluga are migratory, spending winter in offshore ice of Baffin Bay and the Davis Strait.

Mercury

Results for both male and female ringed seals were used for Hg in liver because Analysis of Covariance showed no effect of gender of the animals on Hg concentrations. Concentrations of Hg in liver of ringed seals from 8 locations are shown in Figure 4. Results for Quaqtaq and Kangiqsujuaq in Nunavik were combined as a "Hudson Strait" group as discussed for the OCs. Hg concentrations ranged widely in adult seals and were highly skewed; however, log transformation reduced skewness and yielded normally distributed data. To further improve the

Figure 4. Temporal trends of mercury in ringed seal liver from 8 locations in the Canadian Arctic. Bars are geometric mean concentrations (μg·g^{-1} wet weight) + upper 95% confidence intervals



comparison among years, only the 5–15 year age class was selected where possible (all data except Mittimatalik/Pond Inlet 1976).

Temporal trends of Hg in ringed seal liver varied widely among locations. Hg increased 3x in seals at Pond Inlet from 1976 to 2000; and 2x in Hudson Strait and 2.5x at Holman during the 1990s. Arithmetic mean concentrations of mercury in adult seals from Pond Inlet (2000) were 3-fold higher than results reported by Smith and Armstrong (1978) for the same average aged animals. This difference was statistically significant ($p < 0.05$), however, the assumption that the data are normally distributed may not be correct. The raw data from the Mittimatalik samples of 1976 are not available (L.Lockhart, personal communication) and therefore there will always be great uncertainty in the conclusion regarding the size of the increase. On the other hand, the two groups of seals were comparable in age, which is an important co-variate for mercury in adult seals. Also, the mercury measurements in seal tissues have been conducted using the same analytical methodology (cold vapor atomic absorption spectroscopy), therefore analytical differences are not likely to be an issue. Results for Arviat and Pangnirtung could not be compared with previous data as there are no published results to our knowledge. Hg concentrations declined by 1.5–2x at Resolute, Ungava Bay and Sachs Harbour during the 1990s. Significant year to year variation has been observed at several sites, e.g. at Ungava 1989 and 1990 (Figure 4) and at Holman (Fisk et al., 2003), which suggests that ringed seals can vary annually in Hg levels in liver.

Table 2. Mean and range of methyl mercury concentrations ($\mu g \cdot g^{-1}$ ww), and fraction of total mercury, in seal liver from 4 locations in the Canadian Arctic

Location		N	Methyl Hg $\mu g \cdot g^{-1}$ ww	% of total Hg
Arctic Bay	mean	7	0.79	4.9
	min		0.24	1.1
	max		1.43	9.6
Resolute	mean	8	0.30	13.8
	min		0.04	0.6
	max		0.53	26.1
Sachs Harb	mean	10	0.48	11.5
	min		0.11	0.9
	max		1.00	30.0
Arviat	mean	5	0.44	7.8
	min		0.17	1.2
	max	7	0.75	21.3

A further illustration of the complexity of the Hg temporal information comes from the work on seabird eggs from Prince Leopold Island in Lancaster Sound. Braune et al. (2001) found a significant, approximately two-fold, increase in Hg in thick-billed murre eggs, a 50% increase in northern fulmar eggs and no significant increase in black-legged kittiwake eggs over approximately the same period as several of the ringed seal populations in this study. The explanation for this may be that kittiwakes overwinter at lower latitudes while the murres and fulmars overwinter in northern waters that may not have experienced a decline in Hg. The results for eggs of northern resident seabirds are in accord with the increasing Hg result for ringed seal liver from Mittimatalik. Results for ringed seals from Avanersuaq in northwest Greenland also show a significant increase in mercury from 1984 to 1998 (Riget, 2002). However, ringed seals from Qausuittuq, which feed in the same area as the seabirds, showed declining trends.

Methyl mercury

Concentrations of methyl Hg in ringed seal liver were examined at 4 locations (Table 2). Methyl Hg concentrations were in the low or sub $\mu g \cdot g^{-1}$ range at all locations. These values represented from 0.6 to 30% of total mercury in seal liver. These results are in agreement with those of Wagemann et al. (1997) who found that about 5% of mercury in liver and 20% in kidney was in the form of organic mercury, probably methyl mercury.

Conclusions

1. Significant declines of ΣPCB10 and ΣDDT were seen in female ringed seals from 7 of 9 locations in the Canadian Arctic.
2. There was a shift to more recalcitrant residues, i.e. p,p'-DDE and CB153 reflecting older "weathered" or degraded sources at all locations.
3. These results for 9 locations agree with observations in ringed seals at Holman (Addison and Smith, 1998), however, they also demonstrate that there is regional variation in temporal trends of POPs.
4. ΣHCH and ΣCHL concentrations in seals showed greater annual % declines (up to 6% per year) than PCBs and ΣDDT at some locations.
5. Expressed as annual % declines, the results suggest ΣDDT and PCBs are presently declining at 1–5% per year at the 7 locations. However, 2 eastern Arctic locations (Pangnirtung and Ungava Bay) show no significant trend. These results suggest that there are

regional differences in temporal trends of persistent organochlorines possibly because of exposure to different water masses (e.g. Atlantic Ocean influence in the eastern Arctic) and to differences in atmospheric deposition between the eastern and western Arctic.

6. During the 1990s/early 2000s, mercury concentrations increased from two- to three-fold at 3 locations, declined by 1.5–2x at 3 locations and showed no change at two others. Therefore, it appears that there is no clear increasing trend of mercury in ringed seals in the Canadian Arctic.

7. The observation of both increases and declines in mercury in seal liver indicates that discerning short term trends in mercury in this species is difficult. The results point to the need for increased frequency of sampling for mercury trends.

8. Methyl mercury concentrations in seal liver were generally a small fraction of total mercury in the same samples (0.6 to 30%). The reason for the variation in % methyl mercury among individual animals is unknown.

Acknowledgments

We thank Sheryl Tittlemier for the analysis of some of the blubber samples from Pangnirtung for organochlorines. Dr. T. Kunito and S. Tanabe, Ehime University, Japan provided ringed seal samples from Pangnirtung (1999) and Ms. Natsuko Kajiwara carried out aging of the seals. We thank Alex Gordon for sample kit preparation and Chesley Mesher (both of KRC in Kuujjuaq) for aging of seals.

Mary Williamson, Peter Lowe, Camilla Teixeira and Maxim Chigak of NWRI conducted the sample extraction and much of the GC data analysis during 2000/02/03.

References

Addison, R.F. and T.G. Smith. 1998. Trends in organochlorine residue concentrations in ringed seal (*Phoca hispida*) from Holman NWT, 1972–1991. *Arctic.* 51: 253–261.

Addison, R.F. and T.G. Smith. 1974. Organochlorine residue levels in Arctic ringed seals: variation with age and sex. *Oikos.* 25:335–337.

Braune, B.M., G.M. Donaldson, and K.A. Hobson. 2001. Contaminant residues in seabird eggs from the Canadian Arctic. I. Temporal trends 1975–1998. *Environ Pollut.* 114:39–54.

Hoekstra, P.F., T.M. O'Hara, C. Teixeria, S. Backus, A.T. Fisk, and D.C.G. Muir. 2002. Spatial trends and bioaccumulation of organochlorine pollutants in marine zooplankton from the Alaskan and western Canadian Arctic. *Environ Toxicol Chem.* 21:575–583.

Holst, M., I. Stirling, and K.A. Hobson. 2001. Diet of ringed seals (*Phoca hispida*) on the east and west sides of the North Water Polynya, northern Baffin Bay. *Mar Mammal Sci.* In press.

INAC. 1999. Indian and Northern Affairs Canada. Northern Contaminants Program. Blueprints for Phase II of the Northern Contaminants Program. Nov. 1999.

Macdonald, R., L. Barrie, T. Bidleman, M. Diamond, D. Gregor, R. Semkin, W. Strachan, M. Alaee, S. Backus, M. Bewers, C. Gobeil, C. Halsall, J. Hoff, A. Li, L. Lockhart, D. Mackay, D. Muir, J. Pudykiewicz, K. Reimer, J. Smith, G. Stern, W. Schroeder, R. Wagemann, F. Wania, and M. Yunker. 2000. Sources, occurence and pathways of contaminants in the Arctic. *Sci Total Environ.* 254:93–234.

Muir, D., A. Fisk, and M. Kwan. 2001. Temporal trends of persistent organic pollutants and metals in ringed seals from the Canadian Arctic. In: S. Kalhok (ed.), Synopsis of Research Conducted Under the 2000–2001 Northern Contaminants Program. pp. 208–214.

Muir, D., F. Riget, M. Cleemann, L. Kleivane, J. Skaare, T. Severinsen, H. Nakata, and S. Tanabe. 2000. Circumpolar trends of PCBs and organochlorine pesticides in the Arctic marine environment inferred from levels in ringed seals. *Environ Sci Technol.* 34: 2431–2438.

Muir, D., B. Braune, B. DeMarch, R. Norstrom, R. Wagemann, M. Gamberg, K. Poole, R. Addison, D. Bright, M. Dodd, W. Duschenko, J. Eamer, M. Evans, B. Elkin, S. Grundy, B. Hargrave, C. Hebert, R. Johnstone, K. Kidd, B. Koenig, L. Lockhart, J. Payne, J. Peddle, and K. Reimer. 1997. Chapter 3. Ecosystem Uptake and Effects. In: R. Shearer (ed.), Canadian Arctic Contaminants Assessment Report. Indian and Northern Affairs Canada, Ottawa 1996. pp. 199–207.

Muir, D.C.G. 1996. Spatial and temporal trends of organochlorines in Arctic marine mammals. In: J.L. Murray and R.G. Shearer (eds.). Synopsis of Research Conducted Under the 1994/95 Northern Contaminants Program. Environmental Studies No. 73. Ottawa: Indian and Northern Affairs Canada. pp. 135–146.

Muir, D.C.G., R.J. Norstrom, and M. Simon. 1988. Organochlorine contaminants in Arctic marine food chains: Accumulation of specific PCB and chlordane-related compounds. *Environ Sci Technol.* 22:1071–1079.

Riget, F. 2002. POPs in Greenland biota. Unpublished data. Department of Arctic Environment, National Environmental Research Institute, Denmark.

Smith, T.G. 1987. The ringed seal, *Phoca hispida,* of the Canadian western Arctic. *Can Bull Fish Aquat Sci.* No. 216, 81 pp.

Smith, T.G. and F.A.J. Armstrong. 1978. Mercury and selenium in ringed and bearded seal tissue from Arctic Canada. *Arctic.* 31:75–84.

Stern, G. and R. Addison. 1999. Temporal trends of organochlorines in southeast Baffin beluga and Holman ringed seal. NCP Synopsis Report on 1998–99. pp. 203–212.

Stokker, Y. 2003. Interlaboratory Quality Assurance for the Northern Contaminants Program. In: Part II. Contaminant Levels and Trends in the Biological Environment, Canadian Arctic Contaminants Assessment Report II. Indian and Northern Affairs Canada. pp. 111–127.

Wagemann, R., E. Trebacz, R. Hunt, and G.Boila. 1997. Percent methylmercury and organic mercury in tissues of marine mammals and fish using different experimental and calculation methods. *Environ Toxicol Chem.* 16:1859–1866.

Wagemann, R., S. Innes, and P.R. Richard. 1996. Overview and regional and temporal differences of heavy metals in Arctic whales and ringed seals in the Canadian Arctic. *Sci Total Environ.* 186:41–67.

Weis, I.M. and D.C.G. Muir. 1997. Geographical variation of persistent organochlorine concentrations in blubber of ringed seal (*Phoca hispida*) from the Canadian Arctic: Univariate and multivariate approaches. *Environ Pollut.* 96:321–333.

Heavy Metal Trends in Yukon Caribou, Over 6500 Years, Using Teeth Recovered from a Melting Ice Field

Project leader(s)

Pat Roach, Department of Indian Affairs & Northern Development, Whitehorse, Yukon; phone (867) 667-3139; fax (867) 667-3271; e-mail: roachp@inac.gc.ca (representing the Yukon Contaminants Committee); Peter Outridge, Geological Survey of Canada, 601 Booth St., Ottawa, ON K1A 0E8; phone (619) 996-3958; fax (613) 996-3726; e-mail: outridge@nrcan.gc.ca; Richard Farnell, Department of the Environment, Box 2703, Whitehorse, Yukon Y1A 2C6; phone (867) 667-5465; fax (867) 393-6263; e-mail: rick.farnell@gov.yk.ca

Project team

Yukon Contaminants Committee; Champagne Aishihik First Nation; Carcross Tagish First Nation; Kwanlin Dun First Nation; Department of Indian Affairs & Northern Development, Whitehorse, Yukon; Department of the Environment, Yukon Government; Yukon Heritage; and adjunct, Geological Survey of Canada.

Abstract

The transport of heavy metals to the North appears to be increasing, but the available temporal databases available are limited in their range. In the Yukon, mountain ice fields have began melting and revealing large numbers of human artifacts and faunal remains. These sites were sampled by the Yukon Government and dated to 8000 ybp. The materials recovered included quantities of caribou mandibles and teeth summer, which range in age from 310 to 6320 ybp. The analysis of carbon and nitrogen isotopes, and metal concentrations, is in progress.

Key Project Message

It is important to determine the trend in metal transport into the North.

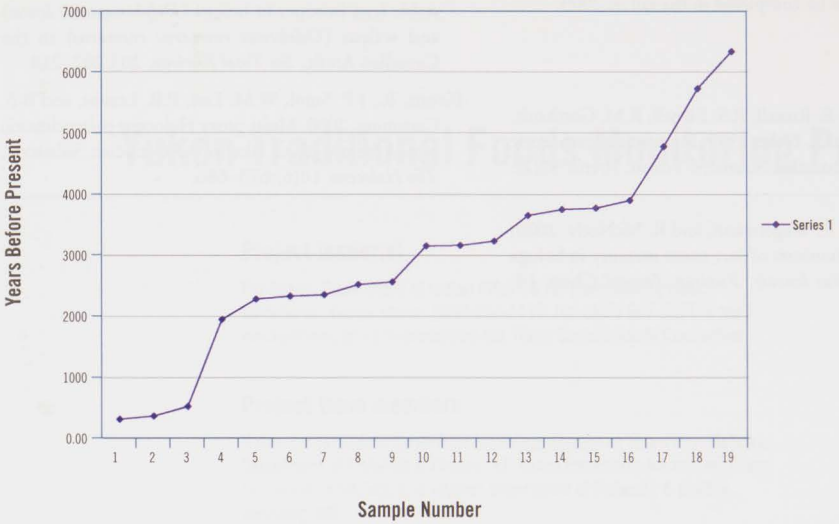
Objectives

1. To determine the historical levels of heavy metals, such as cadmium, in the tissues of caribou through examination of recently discovered fossil teeth.
2. Compare this historical record with modern teeth from extant herds in the same geographic region, to develop a long-term trend for heavy metal transport and bioaccumulation in caribou in the southwest Yukon.

Introduction

The transport of heavy metals to the North appears to be increasing, mostly through the analysis of sediment cores. To what extent anthropogenic sources have increased or if changes in global climate are generating increased

Figure 1. Carbon dating for Yukon caribou teeth



transport of metals is unclear. The northern temporal databases available are often limited to ten years or less. Recently, mountain ice fields in the Yukon have been melting and revealing large areas of caribou, other faunal remains, and human artifacts (Kuzyk et al., 1999). The ice fields were summer refuge areas for caribou in historic times, and were occupied seasonally over thousands of years. The Yukon Government's Renewable Resources program formed the Ice Patch Research Group to examine these sites. Recently, the Yukon Northern Contaminants Program has joined this Group and obtained the samples for this current project.

Dating has determined that the areas were occupied from 8000 ybp to 160 ybp (R. Farnell, unpublished data). The recovered caribou remains included quantities of mandibles and teeth, which can be both aged and used for the analysis of metal exposure through diet. These teeth offer an opportunity to measure trend for metals transported into the Yukon, from the pre-industrial era to present.

Activities

In 2001–2002

Twenty-seven teeth (17 ancient, 10 modern) have been collected. Carbon dating of the teeth has been completed, yielding a chronology of from 310 to 6320 ybp. The results for metal analysis and the carbon and nitrogen isotopes are still in progress. A trend chart showing heavy metal bioaccumulation rates for Yukon caribou, through the mid to late Holocene, will be generated after reception of these results. Carbon and nitrogen isotopes will be analyzed by MS and will provide a check on the potential for changes in diet to have influenced the intake of metals over time. These methods will be similar to those previously employed to determine geologic versus anthropogenic sources in marine mammals (Outridge et al., 1997, 2000).

Results and Discussion

The analysis of samples, from this natural archive, will improve our understanding of the temporal trends for metal deposition in the Yukon. The metals analysis of the historical and modern samples, coupled with the carbon and nitrogen isotopes, will allow us to chart the trend in heavy metal bioaccumulation in caribou going back to the mid-Holocene. Recent research in the Yukon has produced a palaeoclimatic record for this period of the Holocene (Pienitz et al., 2000), which will allow us to compare the carbon and nitrogen isotope data from the faunal samples, with the reported climate. The metal trends, coupled with the climatic data, may provide direction for local climate change research.

Project Completion Date

This project is to be completed in the fall of 2003.

References

Kuzyk, G.W., D.E. Russell, R.S. Farnell, R.M. Gotthardt, P.G. Hare, and E. Blake. 1999. In pursuit of prehistoric caribou on Thandlat, Southern Yukon. *Arctic.* 52(2): 214–219.

Outridge, P.M., R. Wagermann, and R. McNeely. 2000. Teeth as biomonitors of sort tissue mercury in beluga (*Delphinapterus leucas*). *Environ Toxicol Chem.* 19: 1517–1522.

Outridge, P.M., R.D. Evans, R. Wagermann, and R.E.A. Stewart. 1997. Historical trends of heavy metals and stable lead isotopes in beluga (*Delphinapterus leucas*) and walrus (*Odobenus rosmarus rosmarus*) in the Canadian Arctic. *Sci Total Environ.* 203:202–219.

Pienitz, R., J.P. Smol, W.M. Last, P.R. Leavitt, and B.F. Cumming. 2000. Multi-proxy Holocene palaeoclimatic record from a saline lake in the Canadian Subarctic. *The Holocene.* 10(6):673–686.

Yukon Traditional Foods Monitoring Program

Project leader(s)

Pat Roach, Department of Indian Affairs & Northern Development, Whitehorse, Yukon; phone: (867) 667-3139; fax: (867) 667-3271; e-mail: roachp@inac.gc.ca (representing the Yukon Contaminants Committee)

Project team members

Yukon Contaminants Committee including: Council of Yukon First Nations; Department of Fisheries & Oceans, YT; Yukon Renewable Resources; Yukon Conservation Society; and adjunct Department of Fisheries & Oceans, Winnipeg, MB.

Abstract

Forty caribou kidneys from seven Yukon herds were analyzed for 26 elements. Concentrations of renal arsenic, copper, lead, mercury, selenium and zinc should be considered normal, background levels. None of these elements occurred at levels at which toxicological effects in the caribou would be expected. Renal cadmium concentrations in Porcupine caribou were not significantly affected by year, indicating a stable situation with respect to cadmium dynamics in that environment. The barren-ground caribou in this study had concentrations of renal cadmium similar to other Arctic barren-ground caribou, while the woodland caribou tend to be much more variable. This may be attributable to differences in dietary habits between the two subspecies. There is potential for older caribou in some Yukon herds to be at risk of renal dysfunction due to high renal cadmium. Health Canada has recommended limiting consumption of caribou kidneys based on previously collected data.

Key Project Messages

1. Most elements measured in caribou kidneys were at normal background levels, and are stable over time.
2. Some Yukon caribou herds have high levels of cadmium in their kidneys. This cadmium is likely from natural mineralizations rather than industrial pollution.

Objectives

1. To investigate the fate and effects of contaminant deposition and transport to the Yukon, allowing Northerners to better manage the issue of contaminants.
2. To determine levels of contaminants for use in long-term trend monitoring.
3. To provide additional information for use in updating health advisories.

Introduction

The issue of contaminants in traditional foods is an ongoing concern for the many Yukoners that use fish and wildlife as a food source. Over the last 10 years the Yukon Contaminants Committee (YCC) has studied contaminants in traditional foods throughout the Territory. While this research has, in large part, provided confidence that Yukon traditional foods are safe and healthy food choices, it has also given rise to two health advisories: one on fish from Lake Laberge and Atlin Lake for toxaphene, and one on

kidney and liver from wild game, including moose and caribou, for cadmium. It is one of the goals of YCC to continue to monitor contaminants in Yukon traditional foods to maintain public confidence in these food sources, to determine if contaminant concentrations are changing over time, and to determine if there are local 'hot spots' for contaminants of concern.

Burbot and lake trout have been selected as the two freshwater fish indicator species for contaminants in the Yukon. These fish are commonly used as traditional foods and have been extremely important as a long-term window for producing relevant information for consumers. Kusawa and Quiet Lakes have been selected as sampling sites for burbot and trout. These lakes have been sampled in the past and can sustain a yearly sampling protocol, making them excellent choices for temporal trend monitoring in these fish.

Although previous data indicate low levels of POPs in salmon, the 1998 CINE Dietary Study recommends that toxaphene and chlordane levels in all species of salmon and trout consumed by Yukon First Nations be monitored over time to ensure they do not rise above current levels. These food species are consumed often and a small increase in contaminant concentration would result in significant increase in exposure levels in the population. Tolerable daily intakes are already exceeded in some instances. Salmon, therefore, will also be monitored for contaminants on an ongoing basis.

Moose and caribou are the most commonly used terrestrial traditional foods in the Yukon. A small cost-effective annual hunter collection program of caribou and moose kidneys, liver, and muscle tissue, has been carried out since 1993 through YCC. Samples have been analyzed for metals, and duplicate samples archived for possible future analysis. This year the focus for analysis was on caribou to compare to previous years and thus monitor possible temporal trends in contaminants.

Activities

In 2000–2001

Results of the fish sampling program are not available at this time.

The hunter survey program received samples from 90 moose, 34 caribou and one mule deer from the 2001 hunting season. All moose and deer samples, as well as the caribou liver and muscle samples were archived for potential future contaminant analysis. In order to complete the sample of 40 caribou kidneys targeted for this project, 6 kidneys were added from the tissue archive. Because of the opportunistic nature of the hunter survey, it was not possible to target one caribou herd only. Considerable effort was made to solicit samples from the Finlayson caribou herd, which had been sampled extensively in 1992 and again in 1993. However, the population of this herd is now declining, licensed hunting has been reduced to a permit hunt and the local First Nation has voluntarily reduced its harvest. As a result, only one sample was received from this herd. In total the sample of 40 caribou kidneys covers 7 herds, only one of which has a sample size > 3. Fortunately, we received the greatest number of kidneys (17) from the Porcupine herd, for which we have reasonable sample sizes on an annual basis dating from 1991. This makes it an excellent herd to examine temporal trends in contaminants.

All caribou kidneys were analyzed for a suite of 26 elements by Elemental Research Inc., Vancouver, BC, by the inductively coupled plasma with mass spectroscopy technique (ICP-MS). Results for all elements analyzed are available in Gamberg (2002), but only the following elements of interest will be discussed in this report: arsenic, cadmium, copper, lead, mercury, selenium and zinc. Results are expressed on a dry weight basis. Remaining homogenate was archived for potential future analysis. Each caribou for which a tooth was submitted was aged using the cementum technique. The effect of age and year were determined using Porcupine caribou data collected through this program since 1991 for all elements except arsenic, lead and selenium. For these elements, different analytical techniques before 1994 resulted in detection limits greater than measured values in later years. Accordingly, only data from 1994–2001 were used in the statistical analysis of these three elements.

Results

There was little variation in renal arsenic and copper measured in this study (Table 1). Kidney samples from the Finlayson and Carcross caribou were notably higher in cadmium than samples from other herds, although low sample sizes precluded statistical analysis of this difference (Figure 1). Renal lead concentrations were generally low and usually less than 0.50 $g{\cdot}g^{-1}$. Exceptions to this included two Porcupine caribou with 0.63 and 1.22 $g{\cdot}g^{-1}$ lead in their kidneys. Renal mercury concentrations varied among herds, and although sample sizes were too low to allow the statistical comparisons of caribou herds, Figure 2 suggests that some herds (Carcross, Finlayson and Little Rancheria in particular) may have higher mercury concentrations than others. This pattern is supported by previously collected data that indicate average renal mercury levels of 4.18, 3.36 and 2.48 $g{\cdot}g^{-1}$ respectively for the Carcross, Finlayson and Little Rancheria caribou herds (Gamberg, 2000).

Table 1. Average renal concentrations ($g \cdot g^{-1}$ dry weight) of elements in Yukon caribou from the 2001 collection. Effects of age of caribou and year of collection on renal concentrations within the Porcupine caribou herd are expressed as NS (non-significant), + (positive) or − (negative) at a significance level of $\alpha = 0.05$

Element	Average	Range	Effect of Age	Effect of Year
Arsenic	0.34	0.21–0.64	NS	NS
Cadmium	54	10–381	+	NS
Copper	23.5	18.2–31.1	NS	NS
Lead	0.2	0.06–1.22	+	NS
Mercury	1.96	0.86–6.48	+	−
Selenium	1.6	3.1–6.9	NS	+
Zinc	115	85–181	+	NS

Figure 1. Renal cadmium concentrations in seven Yukon caribou herds. Samples collected in 2000 and 2001

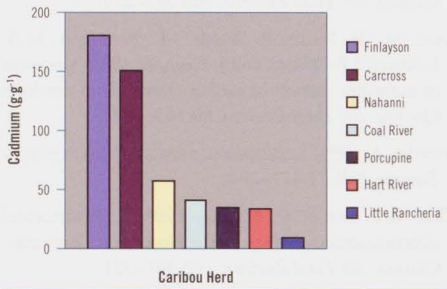
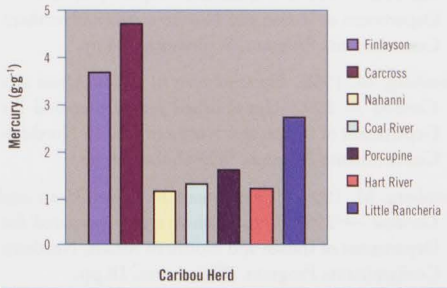


Figure 2. Renal mercury concentrations in seven Yukon caribou herds. Samples collected in 2000 and 2001



Discussion and Conclusions

Concentrations of renal arsenic, copper, lead, selenium and zinc are similar to those found in caribou from Northwest Territories (Elkin and Bethke, 1995) and should be considered normal, background levels. Although there were significant positive relationships between age and renal lead, mercury and zinc in the Porcupine caribou, the absolute increases in each element from age 0 (fetus) to 11 were slight and of little toxicological significance. It should be noted that even the highest lead concentrations found in this study were well below the threshold level of 80 $g \cdot g^{-1}$ that is thought to be indicative of lead poisoning (Scheuhammer, 1991). It is questionable whether the positive relationship between year of collection and renal selenium is an actual trend. The absolute change in selenium was slight and the significance level was not high ($r = 0.13$; $p = 0.04$). Continuing research may confirm or refute this apparent trend.

All mercury concentrations found in this study were low relative to those found in caribou from the Northwest Territories (Elkin and Bethke, 1995), and the highest mercury level measured in this study, (6.48 $g \cdot g^{-1}$ dry weight or 1.3 $g \cdot g^{-1}$ wet weight in a Carcross caribou) is far below the threshold level of 30 $g \cdot g^{-1}$ wet weight cited by Scheuhammer (1991) at which neurological effects might be expected to occur. Braune et al. (1991) suggested that high mercury levels in the Canadian Arctic reflect naturally occurring geological sources rather than industrial pollution. Mercury levels found in this study should be considered natural background levels. Although year was negatively correlated with mercury in the Porcupine caribou, if the notably higher 1991 data are removed, there is no significant correlation between renal mercury and year. It is unclear why the 1991 data are higher than the ensuing years, but it seems likely that mercury levels in the Porcupine caribou are relatively stable over time.

The relationship between renal cadmium and age has been extensively described in the literature (Crete et al., 1989; Gamberg and Scheuhammer, 1994), and has been seen in previous work of this type in the Yukon (Gamberg, 1993, 1997, 1998, 1999, 2000, 2001). It is important to consider age as a factor when comparing cadmium levels among herds or species. Renal cadmium concentrations in Porcupine caribou were not significantly affected by year, indicating a stable situation with respect to cadmium dynamics in that environment.

The barren-ground caribou in this study (Porcupine herd) had concentrations of renal cadmium similar to those found in five barren-ground herds studied in the Northwest Territories (Elkin and Bethke, 1995). The woodland caribou (all the other Yukon herds) tend to be much more variable in cadmium levels (Figure 1). This may be attributable to differences in dietary habits between the two subspecies. Barren-ground caribou feed mainly on lichen, which absorb contaminants along with necessary nutrients from the air. Having no root system, lichens do not absorb anything from the soil on which they grow. Arctic lichens are blanketed with low concentrations of cadmium brought to the north by long-range transport via large air masses. In the absence of local point sources of airborne cadmium, this is virtually the only route of cadmium contamination for barren-ground caribou, and it tends to be fairly consistent across the Arctic.

Woodland caribou habitat is much more wooded than the tundra preferred by barren-ground caribou. Woodland caribou are also less migratory, inhabiting a much smaller home range. They feed on lichens, but also have a variety of browse available to them in their wooded habitat. One of the preferred species of browse is willow (*Salix* sp.), which absorbs cadmium very effectively from the soil in which it grows (Crowder, 1991). Woodland caribou inhabiting a home range naturally high in cadmium, then, would be exposed to much higher levels of cadmium over their lifetime than barren-ground caribou feeding primarily on lichen. Conversely, woodland caribou inhabiting an area low in natural cadmium would have far less of this particular contaminant accumulating in their organs.

Although average renal cadmium for all herds measured in this study is well below the critical threshold value (400–800 $g \cdot g^{-1}$ dry weight) at which renal tubule dysfunction has been shown to occur (Kjellstrom, 1986), one Finlayson caribou did have renal cadmium (381 $g \cdot g^{-1}$) approaching the critical range. This indicates potential for older caribou in some Yukon herds to be at risk of renal dysfunction due to high renal cadmium.

Health Canada has recommended limiting consumption of caribou kidneys based on previously collected data. Because cadmium levels have not changed over time, the recommendations should still be relevant.

Expected Completion Date

The caribou portion of this project has been completed. Fish results are expected February 2003.

Acknowledgements

This project was funded by the Northern Contaminant Program, administered by the Yukon Conservation Society, and conducted in cooperation with Renewable Resources branch of the Yukon Territorial Government and the Department of Northern Affairs. Many thanks to the Conservation Officers, clerks and biologists who assisted in collecting samples for the project, to Philip Merchant who also assisted with sample collection and to Angela Milani who aged the caribou teeth. Alpine Aviation Ltd. of Whitehorse also generously supported this project. Much gratitude is also due to the hunters who provided the samples for analysis — without their support this project would not have been possible.

References

Braune, B.M., R.J. Norstrom, M.P. Wong, B.T. Collins, and J. Lee. 1991. Geographical distribution of metals in livers of polar bears from the Northwest Territories, Canada. *Sci Total Environ.* 100:283–299.

Crete, M., R. Nault, P. Walsh, J.L. Benedetti, M.A. Lefebvre, J.P. Weber, and J. Gagnon. 1989. Variation in cadmium content of caribou tissues from northern Quebec. *Sci Total Environ.* 80:103–112.

Crowder, A. 1991. Acidification, metals and macrophytes. *Environ Poll.* 71:171–204.

Elkin, B.T. and R.W. Bethke. 1995. Environmental contaminants in caribou in the Northwest Territories, Canada. *Sci Total Environ.* 160:307–321.

Gamberg, M. 1993. *Survey of contaminants in the Finlayson Caribou Herd, Ross River, Yukon Territory.* Technical Report TRC-93-2. Dept. of Renewable Resources, Whitehorse, Yukon. 64 pp.

Gamberg, M. 1997. *Contaminants in Yukon Moose and Caribou — 1996.* Unpublished report prepared for Department of Indian and Northern Affairs, Northern Contaminants Program, Whitehorse. 24 pp.

Gamberg, M. 1998. *Contaminants in Yukon Moose and Caribou — 1997.* Unpublished report prepared for Department of Indian and Northern Affairs, Northern Contaminants Program, Whitehorse. 16 pp.

Gamberg, M. 1999. *Contaminants in Yukon Moose and Caribou — 1998.* Unpublished report prepared for Department of Indian and Northern Affairs, Northern Contaminants Program, Whitehorse. 18 pp.

Gamberg, M. 2000. *Contaminants in Yukon Country Foods.* Unpublished report prepared for Department of Indian and Northern Affairs, Northern Contaminants Program, Whitehorse. 95 pp.

Gamberg, M. 2001. *Contaminants in Yukon Moose and Caribou — 2000.* Unpublished report prepared for Department of Indian and Northern Affairs, Northern Contaminants Program, Whitehorse. 5 pp.

Gamberg, M. 2002. *Contaminants in Yukon Moose and Caribou — 2001.* Unpublished report prepared for Department of Indian and Northern Affairs, Northern Contaminants Program, Whitehorse. 16 pp.

Gamberg, M. and A.M. Scheuhammer. 1994. Cadmium in caribou and muskoxen from the Canadian Yukon and Northwest Territories. *Sci Total Environ.* 143: 221–234.

Kjellstrom, T. 1986. Critical organs, critical concentrations and whole body dose-response relationships. In: Friberg, C., G. Elinder, T. Kjellstrom, and G.F. Nordberg (eds.), *Cadmium and Health: a Toxicological and Epidemiological Appraisal.* Vol. 2. CRC Press, Boca Raton, Florida. pp. 231–246.

Scheuhammer, A.M. 1991. Effects of acidification on the availability of toxic metals and calcium to wild birds and mammals. *Environ Pollut.* 71:329–375.

Uptake of Contaminants in Beaver and Muskrat of the Mackenzie River Delta

Program leader

Norman Snowshoe, Gwich'in Tribal Council, Box 1509, Inuvik, NT X0E 0T0; phone: (867) 777-4869; fax: (867) 777-4538; e-mail: snowshoe@inuvik.net

Project team members

John Nagy, GWNT Resources, Wildlife and Economic Development, Inuvik, NT; Brett Elkin, GWNT Resources, Wildlife and Economic Development, Yellowknife, NT; Liz Wright, Tetlit Gwich'in Renewable Resource Council, Fort Macpherson, NT; Wayne Cardinal, Gwichya Gwich'in Renewable Resource Council, Tsiigehtchic, NT; Neil Firth, Nihtat Gwich'in Renewable Resource Council, Inuvik, NT; George Nerysoo, Ehdiitat Gwich'in Renewable Resource Council, Aklavik, NT; Laurie Chan, Centre for Indigenous Peoples Nutrition and Environment (CINE), Montreal, QC; Alan Ehrlich, Indian and Northern Affairs Canada, Yellowknife, NT (to August 2001).

Abstract

Beaver and muskrat meat are an important part of the diet of the Gwich'in people in the Mackenzie Delta region of the Northwest Territories. In 2001, beaver and muskrat samples were collected by local trappers, and analysis was completed to determine levels of organochlorines and heavy metals. For organochlorine analysis, beaver and muskrat liver samples were pooled by species, sex and location. PCBs, DDT and chlordane levels were very low and well below available guideline levels. Chlorobenzene, mirex, heptachlor and toxaphene were below detection limits. Beaver and muskrat muscle, liver and kidney were analyzed for heavy metals. Levels of metals in beaver and muskrat meat were very low or considered normal for terrestrial wildlife. Levels of cadmium in beaver liver (10.32 µg/g d.w.) and kidney (55.46 µg/g d.w.) were comparable with those found in Fort Resolution (liver = 6.6 µg/g d.w.) (Kennedy, 1999) and the Yukon (liver = 12.94 µg/g d.w., kidney = 95.12 µg/g d.w.) (Gamberg, 2000). As beaver liver and kidney are not consumed by residents of the GSA, a health assessment was not necessary for these organs (Snowshoe, 2002, pers. comm.). The key message for residents of the Gwich'in Settlement Area is that beaver and muskrat meat are safe to eat and can continue to form part of the traditional diet.

Key Project Messages

1. Beaver and muskrat meat are safe to eat.
2. Beaver livers and kidneys have levels of cadmium which reflect natural background levels and are consistent with other terrestrial wildlife levels.

Photo 1. Norman Snowshoe, GTC

Objectives

1. To determine the presence and quantity of contaminants in country foods consumed in the Gwich'in Settlement Area (GSA).
2. To measure the uptake of metals and organochlorines into beaver and muskrat of the Mackenzie River Delta.
3. To identify potential health risks to Gwich'in consuming beaver and muskrat.
4. To identify potential health problems in wildlife populations.
5. To train community members in environmental sampling.
6. To develop baseline data on contaminant levels in muskrat and beaver in the Mackenzie Delta.
7. To compare data with similar studies completed, e.g. Slave River Delta.

Introduction

Muskrat and beaver are consumed by Gwich'in residents in the Mackenzie Delta area as a staple of their spring and summer diet. The consumers reported eating both beaver and muskrat for 0.4 day/week, and 14% and 18% reported that they consumed beaver meat and muskrat meat, respectively (Receveur et al., 1996). Only one other study has been completed on beaver and muskrat in the NWT, taking place in 1998 in the Slave River Delta near Fort Resolution at the southern end of the Mackenzie Basin (Kennedy, 1999). One of the objectives of the present study is to gather data at the north end of the Mackenzie River Basin, around Inuvik and Aklavik. The results of the present study will provide a snapshot at either end of the basin. As there has never been any work of this nature in the Mackenzie River Delta, the study also provides important baseline data for the region, as well as reflecting the importance of beaver and muskrat in the diet of the Gwich'in people.

Activities

In 2001–2002

Sampling locations were selected in areas regularly trapped for beaver and muskrat. These were determined through meetings with the Nihtat, Tetlit and Ehdiitat Gwich'in Renewable Resource Councils.

Between May 30 and June 15, 2001, trappers from the Gwich'in Settlement Area harvested 27 beavers and 12 muskrats for this study. The whole animal was collected and later dissected in Inuvik. The date of collection was recorded along with the name of the trapper, the species collected, the sex of the animal and the approximate age of the animal (juvenile or adult). Samples were taken from both the east and west side of the Mackenzie River. Approximate sampling locations are presented in the following map.

Norman Snowshoe (Gwich'in Tribal Council) and Alan Ehrlich (DIAND) worked with Liz Gordon (GNWT), John Lucas Jr. (GNWT) and Dennis Thompson (local hunter and trapper), to measure, weigh and skin the animals. The livers and left and right kidneys were also weighed. It was noted that some body measurements were estimated as the head or tail of the animal was occasionally missing. Muscle, liver and kidney samples were sent for contaminants analysis. In

Photo 2. Norman Snowshoe (GTC), John Lucas Jr. (GNWT) and Liz Gordon (GNWT)

Figure 1. Beaver & muskrat sample locations

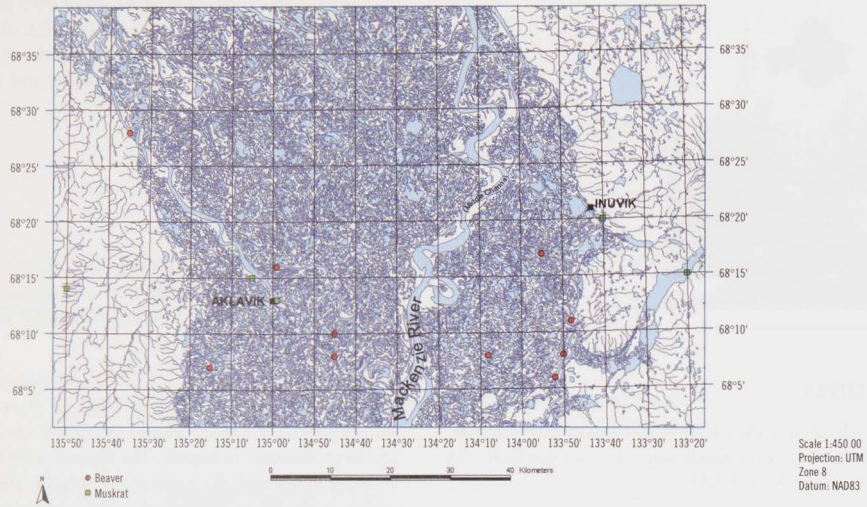


Photo 3. Norman Snowshoe (GTC) and Dennis Thompson (trapper)

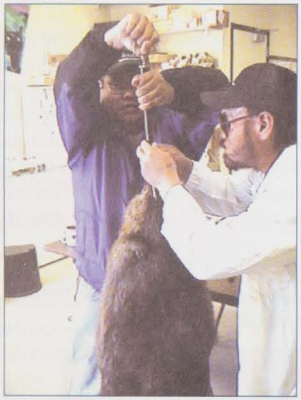
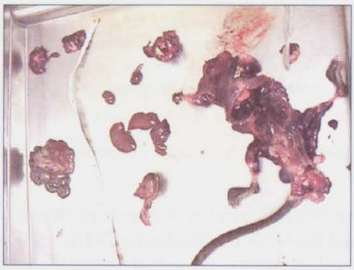


Photo 4. Dissected muskrat



addition, the lower jaw, stomach contents and a fat sample were collected. Sample processing took place at the GNWT Department of Resources, Wildlife and Economic Development laboratory in Inuvik.

Liver samples from 14 beavers and 12 muskrats were sent to Laurie Chan at Centre for Indigenous Peoples' Nutrition and Environment (CINE) laboratory at McGill University in Montreal for organochlorine analysis by GC-Mass Spectrometer (these were pooled into 7 samples according to sex and collection location). The following were analyzed: total PCBs (the sum of 51 congeners) and chlorinated pesticides (chlorobenzene (CBZ), hexachlorocyclohexane (HCH), heptachlor epoxide (HE), chlordane (CHL), dichloro-diphenyl-trichloroethane (DDT) and mirex (MIR)). As muscle can be reasonably expected to be lower in organochlorines than liver, it was decided that it would not be analyzed if the liver results were low. Strict quality control measures were built into all the analyses.

Muscle, liver and kidney samples were sent to Taiga Environmental Laboratory in Yellowknife for metals analysis for arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn),

nickel (Ni) and zinc (Zn) by ICP-Mass Spectrometer. Ten muscle, ten liver and ten kidney samples were analyzed for both beavers and muskrats.

Muscle, liver, kidney and tail samples were also archived in Inuvik if required for further analysis in the future.

In the lab, M1 molars were removed from each beaver and muskrat and sent to Matson's Laboratory in Montana for cementum analysis to age the animals.

All laboratory analysis was completed by March 2002.

Results

All beaver and muskrat samples were cementum-aged by analyzing a vertical section of the M1 molar for growth patterns. All muskrats were aged one year or less. The ages of beavers varied between one and five years, with an average age of approximately three years. Differences in ages of beavers between the east and west side of the Mackenzie River were not evident.

Organochlorines

Levels of total PCBs (the sum of 51 congeners) and chlorinated pesticides (chlorobenzene, hexachlorocyclohexane (HCH), heptachlor epoxide, chlordane, dichlorodiphenyl-trichloroethane (DDT), mirex and toxaphene) were determined. These results are presented in Table 1. Also included for comparison are guideline levels used by Health Canada.

Liver samples were pooled by species, sex and location, for a total of seven pools. Since organochlorines were only detected at low levels in the Slave Delta study, research interests were satisfied by analyzing fewer samples and by pooling samples. The results showed very small amounts of organochlorine contaminants, with the majority of the results below the 0.1 ng/g (ppb) wet weight detection limit (see Table 1).

Total PCBs were detected in only three of the seven pools analyzed. The highest concentration was approximately 20 ng/g, which is about 100 times below Health Canada guidelines for human consumption. DDT levels were over 200 times below Health Canada guidelines for human consumption. The only other pesticides detected in some pools were chlordane and HCH, and all were below levels considered normal for any food purchased in a store (Kennedy, 1999). Chlorobenzene, mirex, heptachlor epoxide and toxaphene were below detection levels in all samples analyzed.

As with the beaver and muskrat study which took place in the Slave River Delta, there were no clear differences between species, sex or location (Kennedy, 1999). Results are quite similar to the Slave River Delta sites with results well below guideline level. Results are also similar to a study of beaver and muskrat in the Yukon, with very low levels found in liver (Gamberg, 2000).

Following his analysis, Dr. Laurie Chan of CINE stated the following: "all organochlorine data are relatively low and should not pose any health concern for people consuming them [beavers and muskrats]". This statement was very similar to that made in the Slave River Delta study (Kennedy, 1999).

Table 1: Data summary of organochlorines in beaver and muskrat liver in the Gwich'in Settlement Area (ng/g or ppb wet weight)

	West side of Mackenzie River			East side of Mackenzie River				
	Beaver		Muskrat	Beaver		Muskrat		
Organochlorine*	Males	Females	Unknown	Males	Females	Males	Females	Guideline level**
Total PCB	nd	nd	1.14*	6.09	20.26	nd	nd	2000
DDT	17.27	8.82	18.88*	13.19	10.67	23.77	4.22	5000
Chlordane	2.78	1.12	4.39*	1.93	0.79	2.14	nd	not available
HCH	nd	nd	nd	nd	8.14	nd	0.47	not available
Chlorobenzene	nd	nd	nd	nd	nd	nd	nd	300
Mirex	nd	nd	nd	nd	nd	nd	nd	100
Heptachlor	nd	nd	nd	nd	nd	nd	nd	not available
Toxaphene	nd	nd	nd	nd	nd	nd	nd	not available

*Detection limit for all organochlorines is 0.1 ng/g

**Guidelines provided by CINE (originally provided to CINE by Health Canada)

nd = not detected

Based on the low or undetectable results of dioxins and furans in the Slave River Delta study, these organochlorines were not tested in the present study.

Heavy Metals

Muscle, liver and kidney in beavers and muskrats were analyzed for heavy metals (As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Zn). These results are presented in Table 2. The metal levels in tissues were generally low and representative of natural background levels (Elkin, 2002, pers. comm.). There were no significant differences between the means of the samples taken east of the Mackenzie River, compared to those taken west of the river.

Levels of iron and zinc are naturally quite variable, and the results are considered normal (Elkin, 2002, pers. comm.). Levels of arsenic, chromium, cobalt, lead, manganese and nickel were very low in all samples. These results were similar to the Slave River Delta results (Kennedy, 1999), as well as the results from a study of Yukon beaver and muskrat (Gamberg, 2000). Levels of copper in the samples were also within the same range as both these studies.

Cadmium levels in muskrat muscle, livers and kidneys were quite low, and sometimes undetectable. These results mirrored the Slave River Delta data (Kennedy, 1999) and the Yukon data (Gamberg, 2000). As with muskrat muscle, cadmium in beaver muscle was not detected. This

Table 2. Mean concentrations of metals in beaver and muskrat in the Gwich'in Settlement Area (μg/g or ppm dry weight)

	As [0.5]	Cd [0.1]	Cr [0.3]	Co [0.1]	Cu [0.2]	Fe [3]	Pb [0.1]	Mn [0.1]	Ni [0.1]	Zn [10]
Beaver muscle (n = 10)										
Mean	**0.83**	**nd**	**0.33**	**nd**	**5.78**	**300.1**	**nd**	**0.98**	**nd**	**161.2**
Standard deviation					1.12	90.81		0.74		51.19
Percent detection	50%		10%		100%	100%		100%		100%
Beaver liver (n = 10)										
Mean	**0.78**	**10.32**	**0.54**	**0.12**	**14.75**	**1244.4**	**0.33**	**13.02**	**0.21**	**152.6**
Standard deviation	0.31	5.88			2.31	336.12	0.17	7.05		38.71
Percent detection	60%	100%	50%	20%	100%	100%	100%	100%	10%	100%
Beaver kidney (n = 10)										
Mean	**0.86**	**55.46**	**0.52**	**0.16**	**16.89**	**319.4**	**0.35**	**9.12**	**0.14**	**180.8**
Standard deviation	0.49	33.76	0.35		2.58	62.91		2.28		60.22
Percent detection	60%	100%	60%	40%	100%	100%	30%	100%	20%	100%
Muskrat muscle (n = 9)										
Mean	**0.53**	**nd**	**0.87**	**nd**	**4.89**	**357.78**	**nd**	**1.01**	**0.34**	**91.56**
Standard deviation					1.44	186.65		0.56		23.83
Percent detection	11%		44%		100%	100%		100%	22%	100%
Muskrat liver (n = 10)										
Mean	**0.62**	**0.13**	**0.05***	**0.17**	**11.50**	**2365**	**0.11**	**6.80**	**0.11**	**73.70**
Standard deviation				0.05	3.25	616.90		1.95		11.27
Percent detection	30%	10%	20%	70%	100%	100%	10%	100%	10%	100%
Muskrat kidney (n = 9)										
Mean	**0.64**	**0.26**	**0.37***	**0.18**	**10.52**	**637.78**	**nd**	**10.02**	**0.16**	**72.89**
Standard deviation			0.39	0.07	1.75	151.89		10.50		10.40
Percent detection	22%	22%	67%	67%	100%	100%		100%	33%	100%

* For these samples the detection limit was 0 instead of 0.3

[ ] number in bracket represents the detection limit for each metal analyzed

n = the number of samples analyzed

nd = not detected (results were below the detection limit)

result is identical to that of the Slave River Delta study (Kennedy, 1999).

The mean cadmium level in beaver livers was 10.32 µg/g dry weight (d.w.). This is slightly higher than the mean level of 6.60 µg/g d.w. calculated for the Slave River Delta (Kennedy, 1999), and lower than the mean level of 12.94 µg/g d.w. calculated for the Yukon study (Gamberg, 2000). These levels are comparable to other terrestrial wildlife and are reflective of local geological conditions (CACAR, 1997; Elkin, 2002, pers. comm.). The mean level of cadmium in beaver kidneys in the Mackenzie River Delta was calculated to be 55.46 µg/g. This is about half the amount measured in beaver kidneys from the Yukon, which averaged 95.12 µg/g d.w. (Gamberg, 2000). Beaver kidneys were not analyzed in the Slave River Delta study therefore comparisons can not be made.

There was a positive correlation between levels of cadmium in beaver liver and kidney and the fresh weight of the organs and length/size of the animal. The correlation between levels of cadmium in beaver organs and the age of the animal was established by Kennedy (1999), but was not as pronounced in the present study.

While metal levels were variable among animals, the concentrations in both beaver and muskrat were generally below those associated with toxicological effects in different mammalian species (CEPA, 1994).

Discussion and Conclusion

This study involved numerous residents of the Gwich'in Settlement Area, from trappers to lab technicians, to Gwich'in Tribal Council staff. By conducting preliminary laboratory procedures in Inuvik, several individuals were able to gain valuable experience in basic scientific techniques. These individuals will also be in an ideal position to communicate the results back to Gwich'in residents.

This study has resulted in useful baseline data on beaver and muskrat in the Mackenzie Delta. It complements both the Fort Resolution and Yukon studies. Overall levels in the Mackenzie Delta (north end of the Mackenzie Basin), were similar to those in Fort Resolution (southern end of the basin). This information is very valuable to Gwich'in residents, and will aid them in making informed decisions about their food choices.

It should be emphasized that although liver and kidneys of certain land mammals can be a very small source of cadmium, the largest source of cadmium to humans is cigarette smoke. Smokers have 20 to 30 times higher average levels of cadmium in their blood then non-smokers (CACAR, 1997).

Beaver and muskrat are an excellent source of iron, protein and vitamin B (GNWT HSS, 1995). Animals such as beaver and muskrat are very nutritious, and an important part of a diet including a variety of traditional foods. It is also important to remember that hunting and trapping of these animals contributes to social, economic, cultural and spiritual well-being.

Acknowledgements

The following trappers are thanked for providing beavers and/or muskrats for analysis: Linly Day, Brad Firth, Leonard Debastien, JoJo Arey, Buster McLeod, Peter Kasook, Edward McLeod, Dean McLeod, Dean Arey and Sam McLeod.

References

Canadian Arctic Contaminants Assessment Report (CACAR). 1997. Department of Indian Affairs and Northern Development, Ottawa, ON.

Canadian Environmental Protection Act (CEPA). 1994. Priority Substances List Assessment Report: Cadmium and its Compounds. Government of Canada.

Elkin, B. 2002. Disease/Contaminants Specialist. Government of the Northwest Territories, Resources, Wildlife and Economic Development, Yellowknife, NT.

Gamberg, M. 2000. Contaminants in Yukon Country Foods. Unpublished report prepared for Indian and Northern Affairs Canada, Whitehorse, YK. 95 pp.

Government of the Northwest Territories, Health and Social Services (GNWT HSS). 1995. Contaminants and Your Health: NWT Fact Sheets.

Kennedy, D. 1999. Metals and Organic Contaminants in Beaver and Muskrat in the Slave River Delta Area, NWT, Canada. In: Synopsis of Research Conducted Under the 1998/99 Northern Contaminants Program. Indian and Northern Affairs Canada, Ottawa, ON.

Receveur, O., M. Boulay, C. Mills, W. Carpenter, and H. Kuhnlein. 1996. Variance in Food Use in Dene/Metis Communities. The Centre for Indigenous Peoples' Nutrition and Environment, Montreal, QC.

Mercury and Organochlorines in Lake Trout from Selected Yukon Lakes: A Temporal and Spatial Study

Project leader(s)

Gary A. Stern, DFO, Freshwater Institute, Winnipeg, MB; phone: (204) 984-6761; fax: (204) 984-2403; Pat Roach, DIAND, Whitehorse, YT; phone: (867) 667-3139; fax: (867) 667-3271; Miriam Diamond, University of Toronto, Department of Geography, Toronto, ON; phone: (416) 978-1586; fax: (416) 946-3886.

Project team members

DFO — Mike Ryan, Lyle Lockhart, Melanie Croft, Bruno Rosenberg, Paul Wilkinson, Joanne Delaronde and Gail Boila; U of T, Sarah Gewurtz; WR Ricks Consulting, Rem Ricks.

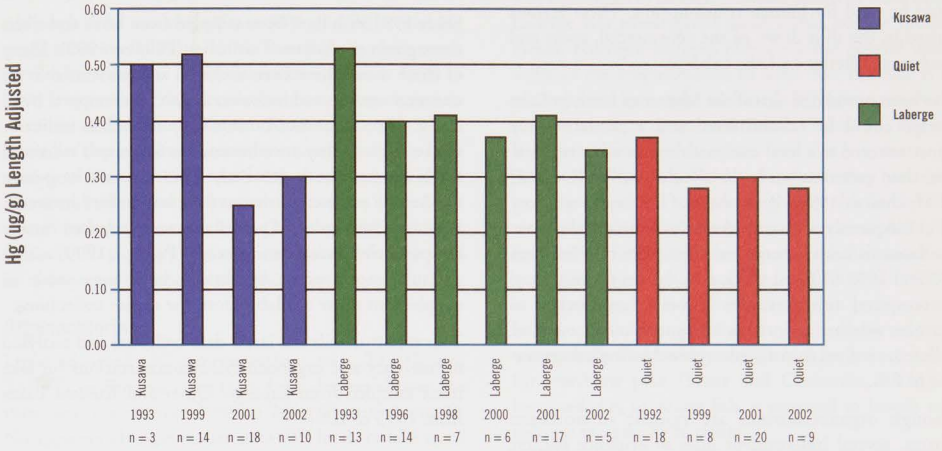
Abstract

This research is aimed at documenting and accounting for the temporal and spatial trends of mercury and organochlorine contaminants in the ecosystem of several Yukon lakes with a focus on Lake Laberge. Although there was a significant 30% decline in total Hg concentrations (1993 to 1996) from Laberge lake trout, there is no evidence of significant change from 1996 to 1998 (Figure 1). A 50% decline in mercury concentrations was measured in lake trout from Kusawa Lake after 1999. A smaller decrease was observed in trout from Quiet Lake sometime between 1993 and 1999. OC concentrations in trout from Kusawa Lake have decreased over the three-year period from 1999 to 2002. No apparent changes or trends in OC levels in lake trout from Quiet Lake were observed and levels remain significantly lower than those in trout from Kusawa and Laberge. Laberge lake trout have displayed a significant downward trend in OC levels over the eight-year period from 1993 to 2001. Unlike Kusawa, the downward trend in the Laberge trout OC levels may, at least in part, be attributed to increases in overall fish populations (since the closure of the fishery) offsetting various ecosystem parameters such as trophic status of prey biota.

Key Project Messages

1. Mercury concentrations in lake trout muscle from Lake Laberge and Quiet Lake have decreased since the early 1990s with no distinctive pattern since the declines. Kusawa Lake also shows an Hg decline post-1999. All average (and length adjusted) levels of Hg from lake trout muscle from these 3 lakes still exceed recommended health guidelines for subsistence fisheries (0.20 μg/g).
2. Lake Laberge had the highest mercury concentrations in lake trout muscle followed closely by Kusawa and Quiet Lake as of 2002.
3. Organochlorines still appear to be decreasing in lake trout from Lake Laberge and Kusawa Lake. OC levels in

Figure 1. Length adjust (ANCOVA) muscle mercury concentrations in lake trout from Kusawa, Laberge and Quiet Lakes (1992–2002)



Quiet Lake remain relatively unchanged at concentrations significantly less than Kusawa and Laberge fish.

4. Fulton (K) condition factors in Lake Laberge trout show a mild pattern of change potentially caused by changing fish populations.

5. Lake Laberge trophic structure has shown little change from 1993 to 2001 with the exception of Northern pike, Tricopterans and snails, as characterized by stable nitrogen isotope analyses.

Objectives

1. To document the temporal and spatial trends of OC (organochlorines such as PCBs, DDT, toxaphene) and Hg (mercury) in fish from Yukon lakes to determine whether contaminant levels in the fish and thus exposure to people who consume them, are increasing or decreasing with time.

2. To determine the underlying factor(s) responsible for the observed decline of organochlorines and patterns of mercury concentrations in Lake Laberge fish.

Introduction

Very few studies exist on direct temporal trend information of organochlorine contaminants and heavy metals in fish from either the Arctic marine or freshwater environments. Data variability in available studies is derived from short sampling periods and confounded by changes in analytical methodology as well as variability due to fish age/size, or dietary and population shifts (CACAR, 1997; AMAP, 1998). By comparison, temporal trend data for contaminants in Lake Ontario lake trout (Borgmann and Whittle, 1991) and in pike muscle from Storvindeln, Sweden (AMAP, 1998) are available over a 15- to 30-year period.

A temporal trend study of contaminants in fish from Lake Laberge is of particular interest because of the unusually high organochlorine contaminant levels found in the lake trout (muscle) and burbot (liver) in 1991 (Kidd et al., 1993, 1995). As a result of the high historical levels of commercial exploitation, Lake Laberge has a relatively low abundance of lake trout and a high abundance of species such as burbot and sucker as compared to other regional lakes (Thompson, 1996). Because of reduced competition and an increased forage base, it is hypothesized that Laberge lake trout have switched from an insectivorous to a strict piscivorous diet, resulting in faster growth and more fat accumulation than lake trout from other non-exploited systems such as Kusawa and Fox Lakes. This hypothesis will be reviewed by examining the trophic structure (food web) of Lake Laberge by using stable isotopes of carbon and nitrogen to characterize food sources (Hesselein et al., 1993) and predator hierarchy (Kidd et al., 1998) within the lake. In response to the

high toxaphene concentrations, Health Canada issued a public health advisory, recommending that consumption of lake trout flesh be limited and that no burbot livers should be used for human consumption. These actions resulted in the shut down of the commercial, sport and subsistence fisheries on Lake Laberge.

It has been postulated that if the lake trout stock in Lake Laberge could be rehabilitated and a predator/prey balance restored to a level comparable with other regional lakes, then contaminant levels should decline (DeGraff and Mychasiw, 1994). As a result of the health advisory and consequently a decreased rate of fishing, lake trout abundance in Lake Laberge has almost doubled between 1991 and 1999 (A.Foos, YTG, pers. comm.) This part of our temporal trend studies is being conducted to determine whether an increase in trout abundance has, as predicted, resulted in reduced organochlorine concentrations in fish.

Although organochlorines are evident in northern climates, several independent lines of evidence suggest that inputs of mercury to northern Canada have increased over pre-industrial levels. With a few exceptions, minimal or no direct temporal trend information on mercury is available in biota from either the Arctic marine or freshwater environments. NCP noted this as a significant knowledge gap.

Mercury levels in Arctic seals and whales have increased since the 1970s (Wagemann et al., 1996) and more recently, Stern et al. (2000, 2001) have reported that mercury levels in burbot muscle from Fort Good Hope, on the Mackenzie River, have increased by 36% over the 15-year time period from 1985 to 2000. Muir et al. (2000) reported no significant changes in mercury concentrations in Arctic char from Resolute and Char Lakes over the 7-year period from 1992 to 1999.

Since 1991, fish have been sampled from lakes and rivers throughout the Yukon Territories (Palmer, 1999). Many of these tissues have been archived and are available for chemical analysis and inclusion as part of a temporal trend study. Lake trout and burbot were chosen as indicator species because they are consumed as Country/Traditional foods and have been extremely important as a long-term window for producing relevant information for consumers. Kusawa, Laberge and Quiet Lakes were selected for the temporal trend study on mercury (Palmer, 1999) and as a result, more recent collections have been made to supplement those available from the earlier collections.

This report details the latest data collected and analysed on mercury and organochlorine concentrations for lake trout sampled from Laberge, Quiet and Kusawa Lakes from 1993 to 2001.

Activities

In 2002–03

Collection of lake trout and burbot from Kusawa, Laberge and Quiet Lakes has continued. Extractions and chromatogram analysis are nearly completed for all biotic samples and some abiotic samples. Statistical analyses for all biotic samples are presently underway. All stable isotope analysis has been completed.

Table 1. Mean (S.D.) muscle mercury levels (μg/g wet wt.) in lake trout from Kusawa, Laberge and Quiet Lakes (1992–2002)

Kusawa	1992	1993	1996	1998	1999	2001	2002
n	–	3	–	–	14	18	10
Length	–	535.0 (72.6)	–	–	514.6 (106.0)	550.6 (114.3)	500.0 (78.2)
Hg	–	0.54 (0.21)	–	–	0.57 (0.39)	0.29 (0.11)	0.29 (0.10)
Laberge	**1992**	**1993**	**1996**	**1998**	**1999**	**2001**	**2002**
n	–	13	14	7	6	17	5
Length	–	482.8 (110.3)	489.3 (95.0)	700.0 (125.4)	590.0 (107.7)	646.2 (103.1)	570.0 (121.1)
Hg	–	0.44 (0.13)	0.33 (0.10)	0.61 (0.24)	0.43 (0.21)	0.55 (0.26)	0.38 (0.15)
Quiet	**1992**	**1993**	**1996**	**1998**	**1999**	**2001**	**2002**
n	18	–	–	–	8	20	9
Length	522.6 (135.0)	–	–	–	561.3 (48.2)	499.5 (185.2)	595.0 (174.1)
Hg	0.44 (0.28)	–	–	–	0.31 (0.08)	0.35 (0.27)	0.39 (0.21)

Results and Discussion

Mercury

Although there was a significant 30% decline in total Hg concentrations (1993 to 1996) from Laberge lake trout, there is no evidence of significant change from 1996 to 1998 (Figure 1). A 50% decline in mercury concentrations was measured in lake trout from Kusawa Lake after 1999. A smaller decrease was observed in trout from Quiet Lake sometime between 1993 and 1999. A summation of the data used in statistical analyses can be found in Table 1. All trout muscle samples exceeded the Health Canada guideline level of 0.20 μg Hg/g (tissue) recommended for fish used for subsistence fisheries as of 2002.

Organochlorines

Lipid adjusted OC concentrations (e.g. ΣCHB and ΣDDT) in Kusawa Lake trout have decreased over the three-year period from 1999 to 2002 (Figures 2 and 3). No apparent changes or trends in OC levels in lake trout from Quiet Lake were observed and levels remain significantly lower than those in trout from Kusawa and Laberge. Laberge lake trout have displayed a significant downward trend in OC levels over the eight-year period from 1993 to 2001. Unlike Kusawa, the downward trend in the Laberge trout OC levels may, at least in part, be attributed to increases in overall fish populations (since the closure of the fishery) offsetting various ecosystem parameters such as trophic status of prey biota.

The hypothesis of changing trophic status of biota in Lake Laberge was investigated using stable isotope measurements. Nitrogen isotopes indicate some general upward shifts in the trophic status of some fish but this is also accompanied by a slight increase in $\delta^{15}N$ for primary food sources such as clams and snails (Table 2). The only significant change in fish was for northern pike (NP; $p < 0.05$) whose $\delta^{15}N$ level indicates they have shifted by 1.5 parts per mil towards a higher trophic level. Tricopterans have also shown a significant increase in $\delta^{15}N$ levels from 1993 to 2001. All other species have maintained their general trophic levels as described in Kidd et al. (1993). It is hypothesized that with increasing fish populations in Laberge, more young of the year are available as prey in warm, shallow and weedy areas, which are known habitats for northern pike (Scott and Crossman, 1973). An increased diet of young fish as opposed to insects could increase the pike $\delta^{15}N$ values.

Snails are the only organisms to have a significant difference in stable carbon isotopes from 2001 as compared to 2000 data ($p = 0.04$, Table 3). $\delta^{13}C$ did not change significantly in trout over the 8-year period from 1993 to 2001. More comparisons of other organisms with earlier years may be possible if the data can be located for further study.

Figure 2. Lipid adjusted (ANCOVA) ΣDDT concentrations in lake trout muscle from Kusawa, Laberge, and Quiet Lakes (1992–2002)

Figure 3. Lipid adjusted (ANCOVA) ∑DDT concentrations in lake trout muscle from Kusawa, Laberge and Quiet Lakes (1992–2002)

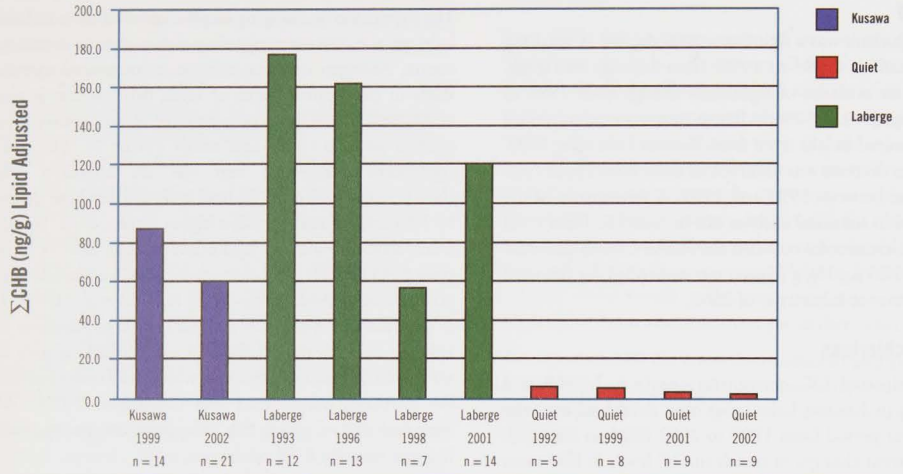


Table 2. Stable nitrogen isotopes ($\delta^{15}N$ in parts per mil) for all biota collected from Lake Laberge in 2000–2001. 1993 isotope values are from Kidd (1996). Snails and northern pike $\delta^{15}N$ values are significantly different between 1993 and 2001

$\delta^{15}N$

	2001			2000			1993*	
Species	n	Mean	SD	n	Mean	SD	n	Mean	SD
LT	17	13.18	0.39	6	13.49	0.33	32	12.36	0.85
BB	30	12.41	0.41	18	12.34	0.41	32	12.06	0.59
INC	6	11.73	0.33	2	11.48	0.35	0	n/a	n/a
NP	5	11.09	0.21	5	10.83	0.52	10	9.62	0.75
LWF	13	9.38	0.71	15	9.27	0.45	36	8.22	1.15
CIS	2	8.99	0.61	22	8.68	0.39	14	7.87	0.47
AG	1	8.97	N/A	0					
LNS	6	8.62	0.75	14	8.15	0.56	12	7.57	0.92
RWF	20	7.65	0.85	6	8.05	0.87	8	7.16	0.76
BWF	0	n/a	n/a	7	7.85	0.44	3	6.55	1.10
Tricoptera	3	5.18	1.02	0			9	2.55	1.38
Chironomids	1	4.20		0			8	4.02	1.14
Snails (family Lymnaeidae)	18	3.21	0.56	17	1.96	1.36	6	2.05	1.01
Snails (family Planorbidae and Valvatidae)							4	1.26	1.39
Clams	1	2.48		1	3.11		1	2.19	n/a
Dipterans (other than chironomids)	3	2.18	0.38	0					
Ephemeroptera	1	1.65		0					
Plankton	0	n/a	n/a	9	4.95	0.69	6	4.94	1.22

* from Kidd (1996)

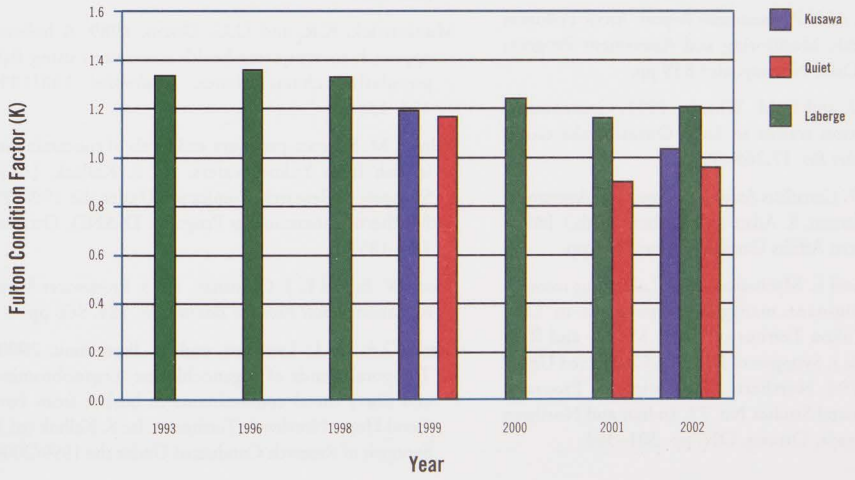
Table 3. Stable carbon isotopes ($\delta^{13}C$ in parts per mil) for all biota collected from Lake Laberge in 2000–2001. 1993 isotope values are from Kidd (1996)

$\delta^{13}C$

	2001			2000			1993*	
Species	n	Mean	SD	n	Mean	SD	n	Mean	SD
LT	17	−28.21	1.39	6	−29.51	2.36	10	−27.57	1.88
BB	30	−27.41	0.47	18	−27.45	0.80			
INC	6	−27.40	0.61	2	−26.07	0.09			
NP	5	−25.34	0.73	5	−24.71	0.71			
LWF	13	−24.69	1.41	15	−25.04	1.37			
CIS	2	−29.95	0.29	22	−29.65	0.37			
AG	1	−23.23	n/a						
LNS	6	−21.18	0.54	14	−21.39	0.83			
RWF	20	−25.25	3.17	6	−24.36	2.64			
BWF	0	n/a	n/a	7	−21.75	1.17			
Tricoptera	3	−32.61	3.29	0					
Chironomids	1	−22.54		0					
Snails	18	−24.27	1.69	17	−20.38	2.78			
Clams	1	−28.32		1	−27.69				
Dipterans (other than chironomids)	3	−25.20	2.94	0					
Ephemeroptera	1	−29.58		0					
Plankton				9	−33.03	1.26			

* from Kidd (1996)

Figure 4. Fulton's condition factor (K) based on [weight*100000/length^3] for lake trout from Laberge, Kusawa and Quiet Lakes between 1993 and 2002



Fulton's condition factor was used to estimate overall fish health and to predict any change that may be occurring in weight to length ratios. Fish that have a smaller K value are considered less robust indicating that they are becoming slimmer. Fish condition factors for Laberge follow a general decrease from 1993 to 2001 with a slight increase in 2002. This pattern is similar to the trend in OC levels but has not been correlated. Condition factors for Quiet Lake and Kusawa lake trout have also shown mild decreases from previous years to present (Figure 4). The patterns in condition factors of Laberge lake trout are similar to two generalized response patterns as described by Munkittrick and Dixon (1989) and thus may be attributed to changes in the fish populations. These changes would have created a broader or perhaps a lesser food base (depending on the species) for foraging. The fish population and lake biomass data are limited at this time due to a 2 point 'curve' and changes in sampling methodology from 1991 to 1999. An additional study (3rd time point) is planned for either the summer of 2003 or 2004.

Expected Completion Date

Temporal trend studies are long-term propositions and thus annual sampling is projected until at least 2005. Present sample collection extractions and chromatography is near completion and data analyses should be finished by late 2003.

References

AMAP. 1998. AMAP Assessment Report. Arctic Pollution Issues, Arctic Monitoring and Assessment Program (AMAP), Oslo, Norway. xii+859 pp.

Borgmann, U. and D.M. Whittle. 1991. Contaminant concentration trends in Lake Ontario lake trout. *J Great Lakes Res.* 17:368–381.

CACAR. 1997. Canadian Arctic Contaminants Assessment Report. J. Jensen, K. Adare and R. Shearer (eds.). Indian and Northern Affairs Canada, Ottawa. 460 pp.

DeGraff, N. and L. Mychasiw. 1994. Lake trout recovery and contaminant management program in Lake Laberge, Yukon Territory. In: J.L. Murray and R.G. Shearer (eds.), Synopsis of Research Conducted Under the 1993/94 Northern Contaminants Program. Environmental Studies No. 72. Indian and Northern Affairs Canada, Ottawa, ON. pp. 301–304.

Hebert, C.E. and K.A. Keenleyside. 1995. To normalize or not to normalize? Fat is the question. *Environ Toxicol Chem.* 14(5):801–807.

Hesslein, R.H., K.A. Hallard, and R. Ramlal. 1993. Replacement of sulfur, carbon and nitrogen in tissue of growing broad whitefish (*Coregonus nasus*) in response to a change in diet traced by S34, C13 and N15. *Can J Aquatic Sci.* 50:2071–2076.

Kidd, K.A. 1996. Use of stable nitrogen isotope ratios to characterize food web structure and organochlorine accumulation in subarctic lakes in Yukon territory. University of Alberta, Doctoral thesis.

Kidd, K.A., D.W. Schindler, D.C.G. Muir, W.L. Lockhart, and R.H. Hesslein. 1995. High concentrations of toxaphene in fishes from a sub-arctic lake. *Science.* 269: 240–242.

Kidd, K.A., D.W. Schindler, R.H. Hesslein, and D.C.G. Muir. 1998. Effects of trophic position on organochlorine concentrations in fishes from sub-arctic lakes in Yukon Territory. *Can J Aquatic Sci.* 55:869–881.

Kidd, K.A., J.E. Eamer, and D.C.G. Muir. 1993. Spatial variability of chlorinated bornanes (toxaphene) in fishes from Yukon lakes. *Chemosphere.* 27:1975–1993.

Muir, D.C.G., G. Köck, J. Reist, and D. Bright. 2000.Temporal trends of persistent organic pollutants and metals in landlocked char. In: S. Kalhok (ed.), Synopsis of Research Conducted Under the 1999/2000 Northern Contaminants Program. DIAND, Ottawa. 202–207.

Munkittrick, K.R. and D.G. Dixon. 1989. A holistic approach to ecosystem health assessment using fish population characteristics. *Hydrobiol.* 188/189: 123–135.

Palmer, M. Sources, pathways and levels of contaminants in fish from Yukon waters. In: S. Kalhok, (ed.), Synopsis of Research Conducted Under the 1998/99 Northern Contaminants Program. DIAND, Ottawa. 183–185.

Scott, W. B. and E. J. Crossman. 1973. Freshwater fishes of Canada. *Bull Fish Res Board Can.* 184. 966 pp.

Stern, G.A., W.L. Lockhart, and M. Ikonomou. 2000. Temporal trends of organochlorine, organobromine and heavy metal contaminants in burbot from Fort Good Hope, Northwest Territories. In: S. Kalhok (ed.), Synopsis of Research Conducted Under the 1999/2000

Northern Contaminants Program. DIAND, Ottawa. 233–236.

Stern, G.A., W.L. Lockhart, and M. Ikonomou. 2001. Temporal trends of organochlorine, organobromine and heavy metal contaminants in burbot from Fort Good Hope, Northwest Territories. In: S. Kalhok (ed.), Synopsis of Research Conducted Under the 2000/01 Northern Contaminants Program. DIAND, Ottawa. In press.

Thompson, S.W. 1996. Fish Stock Assessment of Kusawa, Laberge and Teslin Lakes. Fish and Wildlife Branch Internal Report, Yukon Territorial Government.

Wagemann, R., S. Innes, and P.R. Richard. 1996. Overview and regional and temporal differences of heavy metals in arctic whales and ringed seals in the Canadian Arctic. *Sci Total Environ.* 186:41–66.

Temporal Trends of Mercury in Beluga, Narwhal and Walrus from the Canadian Arctic

Project leader(s)

Gary A. Stern, Department of Fisheries & Oceans, 501 University Crescent, Winnipeg, MB R3T 2N6; phone: (204) 984-6761; fax: (204) 984-2403; e-mail: SternG@dfo-mpo.gc.ca; Peter Outridge, Geological Survey of Canada, 601 Booth St., Ottawa, ON K1A 0E8; phone: (613) 996-3958; fax: (613) 943-1286; e-mail: outridge@nrcan.gc.ca; Rob Stewart, Department of Fisheries & Oceans, 501 University Crescent, Winnipeg, MB R3T 2N6; phone: (204) 983-5023; fax: (204) 984-2403; e-mail: StewartRE@dfo-mpo.gc.ca

Project team

Lyle Lockhart (retired), Rudolf Wagemann (retired), Gail Boila, Joanne DeLaronde and Blair Dunn, Department of Fisheries & Oceans, Winnipeg, MB.

Abstract

Samples of liver of beluga from the eastern Arctic have been analyzed for mercury sporadically since 1984. These results offer some opportunities to estimate temporal changes and these opportunities will grow as future collections add more recent data. Mercury levels in beluga liver have increased since the mid-1980s in Arviat and Pangnirtung and since the early 1980s in the western Arctic. Collections from Iqaluit, Kimmirut and Sanikiluaq appear to have increased levels but there are fewer than 10 years between the earliest and latest collections. There have been no clear changes in Grise Fiord and Coral Harbour. One set only of narwhal data spans more than 10 years; narwhal from Pond Inlet have been collected on four occasions between 1978 and 1999 and mean levels ranged from 6.3 to 12.6 $ug \cdot g^{-1}$ with the highest values in the collections of 1992 and 1994. Mercury levels found in walrus are lower than those measured in either beluga or narwhal. Probably this difference reflects different feeding habits between walrus and both species of whales.

Key Project Messages

1. Total mercury levels in beluga, narwhal and liver are much higher than levels used to regulate the sale of commercial fish ($0.5ug \cdot g^{-1}$).
2. Levels of mercury in liver of walrus are lower than those in the whales but they still exceed the guideline.
3. Only a small fraction of the mercury in beluga liver is present as methyl mercury although even the methyl mercury concentrations exceed the consumption guidelines for fish.
4. There are regional differences with beluga from the western Arctic generally having higher levels of mercury in liver than those from the eastern Arctic. The reverse is true for levels of cadmium.
5. The proportion of mercury present as methyl mercury in eastern Arctic beluga were somewhat higher (~19%) than those measured in the western Arctic animals (~11%).

6. While there is considerable variation from place to place, the data suggest that levels of mercury have increased since the mid-1980s. The data from some locations also suggest that levels may have peaked in the mid-1990s and have declined slightly since then. However, few data extend over long periods of time and there are some inconsistencies among locations making it difficult to be confident about trends yet.

Objectives

1. To define temporal trends in concentrations of mercury in tissues of narwhal, beluga and walrus from the eastern Canadian Arctic.
2. To develop the data from which to track trends in the levels of mercury on a stock-by-stock basis of beluga, narwhal and walrus from which to project future levels.

Introduction

The levels of mercury in organs of northern marine mammals generally exceed the two guidelines used to regulate the sale or domestic consumption of fish ($0.5ug{\cdot}g^{-1}$ for sale of commercial fish and $0.2ug{\cdot}g^{-1}$ for subsistence consumption). The extent to which this results from natural processes acting on the northern geological settings, climate change or from the import of industrial mercury with air and water movements is not clear. Studies of sediment cores suggest that about half the mercury coming into northern lakes is of anthropogenic origin (Lockhart et al., 1998). Mercury has been increasing in air over the North Atlantic (Slemr and Langer, 1992) and mercury has been measured in air and in snow in the Arctic (Lu et al., 2001). There seems little doubt that some industrial mercury has reached Arctic ecosystems.

A previous study of mercury in northern animals pooled data from different locations in the eastern and western Arctic and reported a trend to higher levels in both regions (Wagemann et al., 1996). With growing recognition that Arctic populations of marine mammals are composed of multiple stocks that are hunted separately in different communities, the need is for trend data on a stock-specific basis.

Whales may range considerable distances from the communities where they are hunted, but the hunting itself is usually relatively close to the communities. For this study, the stocks are not described biologically but are rather simply described by the communities where the samples were obtained. Hence two or more communities may hunt the same stock if those communities are relatively near each other. For example, Igloolik and Repulse Bay may hunt the same stocks.

The raw data from several investigations are archived in the Freshwater Institute and comprise records from about 1800 marine mammals, mostly beluga, ringed seals, narwhal and walrus with a few bowhead. Biologists concerned with stock management obtain various samples from hunter kills and those samples form the basis of most of our analyses. Over time, the accumulated data will offer the means to detect any regional or temporal trends. This report has been generated from the raw data exclusively, not from previously published accounts.

Activities

In 2001–2003

No report was made for this project in 2002 and so this report covers data accumulated throughout 2001 and into early 2003. The collection of samples is done independently of this project and is not described here. The analytical methods have been described in previous reports and have been continued to date. While the project is concerned with mercury, the same samples have also been analyzed for selenium and cadmium. The reason for inclusion of selenium is that it generally ameliorates the toxicity of mercury and it may be useful in evaluation of the risks of consuming marine mammals with high levels of mercury. Cadmium is included because its concentrations sometimes reach high levels, notably in kidneys, and consumption advisories have been issued to restrict consumption of kidneys of some land animals.

Only 8 animals from Sanikiluaq and 2 from Iqaluit were collected in 2002, additional collections from these 2 locations will be conducted in 2003. Analysis of these animals (2002 and 2003) will be completed in the 2003–2004 fiscal year. Collections of walrus samples beyond 1996 have not as of yet been successful.

For comparing collections of beluga and walrus taken at different times from a single location, the mercury levels were log-transformed and then analyzed by the General Linear Models procedure of SAS with age as a covariate. The age-corrected levels of mercury were examined for statistical differences at a probability of 0.05. With narwhal, ages are not known and so total length was used instead of age.

In some instances, the original analyses were reported on a dry weight basis. In these cases, the dry weight unit was converted to wet weight using the formula:

Concentration (wet weight) = [dry weight]·(100·(100% moisture)$^{-1}$)$^{-1}$.

Results

Beluga

The results are summarized in Tables 1–3. Table 1 lists the average ages and the mercury, selenium and cadmium concentrations in the livers of belugas from a number of communities for all the samples available. The data is tabulated as arithmetic mean values. Parallel data is available for kidney and more restricted data is available for a number of other organs. The results in Table 1 show total mercury since it is that value that is used by Health Canada for assessment and since we have methyl mercury data on only a small fraction of the samples.

Mercury in liver of beluga is usually related to the age of the whales with older animals having higher levels (Figure 1). For that reason, statistical comparisons were made using age-adjusted means. The two collections at Arviat differed significantly with higher levels of mercury in liver in 1999 (12.7ug·g^{-1}) than in 1984 (6.6ug·g^{-1}). There were no statistical differences among the age-adjusted mean concentrations of total mercury in the samples of liver from the Coral Harbour (1993, 1997, 2000) and Grise Fiord animals (1984, 2001). Levels in beluga liver from Iqaluit appear to have increased significantly from 7.6ug·g^{-1} in 1993 to 16.3ug·g^{-1} in 1994. While this increase is statistically meaningful, it is probably an artifact since the two sampling periods were only one year apart and the change seems too large to have occurred over a single year. The 8 Iqaluit samples collected in 2002 will be analyzed after the planned 2003 collection has been completed. Age-adjusted mercury levels in beluga liver from the Lake Harbour/Kimmirut animals show a steady increase over the three sampling periods in 1994, 1997 and 2001. In the Pangnirtung animals the highest levels were observed in the 1994 and 2002 samples. The mean levels of mercury in the liver of the Sanikiluaq animals appears to have increased greatly between 1994 and 1998, however, the statistical interpretation of this data is complex because of a strong interaction term between age and year of sampling. A more rigorous interpretation will await the inclusion of the 2002 and 2003 results. Mean liver concentrations of mercury are higher in the western Arctic and have increased since the early 1980s. They appear to have reached a peak in the mid-1990s and to have declined somewhat since then.

The methylmercury data available to date on beluga livers are shown in Table 2. Comparing the levels of methylmercury with levels of total mercury in beluga from the same sources and times (Table 1), it is clear that only a small fraction of the total mercury is present as methylmercury. However, although the proportion present as methylmercury is small, the levels of methylmercury are still well above the consumption guideline for commercial fish. Previous studies with beluga and ringed seals has shown that generally less than 20% of total mercury in livers of those species is present as methylmercury. Surprisingly, the proportion of mercury present as methylmercury in the beluga from the eastern Arctic was somewhat higher (about 19%) than in those from the western Arctic (about 11%).

Levels of selenium in liver of beluga from the western Arctic seem to parallel the levels of mercury (Table 1), as might be expected from the observation that seals and whales store liver mercury as a selenide (Wagemann et al., 2000). There is a correlation between mercury and selenium in several whale organs, notably those with a low proportion of methylmercury; the relationship between mercury and selenium in beluga liver is shown in Figure 2 without regard for time or place of collection.

Cadmium was not formally part of this project and is not discussed fully here, but a regional trend in levels of cadmium is apparent with higher levels in most collections from the eastern Arctic than in those from the western Arctic. With the exception of Arviat, there appears to be no obvious increase in levels of cadmium in liver of beluga over time. Curiously, levels in Sanikiluaq appear to have fallen considerably between 1994 and 1998. The apparent increase in Iqaluit is probably an artifact since the two collections were only one year apart.

Narwhal

Levels of mercury in liver of narwhal are summarized in Table 3. There was some correlation between mercury in liver and whale length (Figure 3). For comparing among years at a given location, log-transformed values for mercury concentrations were used in the General Linear Models procedure of SAS to allow adjustment for the relationship between mercury and length. The age-adjusted levels of mercury in liver did not change over the 1993–1996 period. However, a significant increase in mercury was observed in the samples collected from the 2001 whales (Table 3). The most extensive narwhal samples we have are from Pond Inlet. Statistically, there is a significant interaction term between year and length but the sample taken in 1978 had somewhat lower levels than those from 1992 ($p = 0.087$) or 1994 ($p = 0.036$),

Table 1. Mean ages and concentrations of total mercury, selenium and cadmium (all $\mu g \cdot g^{-1}$ wet weight) in liver of beluga whales from the Canadian Arctic

Species	Location	Year	N Age	Mean Age	N Total Hg ($\mu g \cdot g^{-1}$)	Mean Total Hg ($\mu g \cdot g^{-1}$)	St Dev Total Hg ($\mu g \cdot g^{-1}$)	N Selenium ($\mu g \cdot g^{-1}$)	Mean Selenium ($\mu g \cdot g^{-1}$)	St Dev Selenium ($\mu g \cdot g^{-1}$)	N Cadmium ($\mu g \cdot g^{-1}$)	Mean Cadmium ($\mu g \cdot g^{-1}$)	St Dev Cadmium ($\mu g \cdot g^{-1}$)
Beluga	Arviat	1984	22	11.2	23	6.6	6.9	23	4.2	2.4	23	6.7	6.7
Beluga	Arviat	1999	37	11.2	37	12.7	9.9	37	8.5	6.8	37	11.9	6.7
Beluga	Coral Harbour	1993	11	16.1	11	6.5	3.0	11	4.0	2.3	11	9.0	5.2
Beluga	Coral Harbour	1997	19	13.1	20	13.4	28.6	20	9.1	15.3	20	8.4	3.8
Beluga	Coral Harbour	2000	24	8.9	25	3.9	2.5	25	4.2	2.5	25	9.2	5.8
Beluga	Grise Fiord	1984	17	5.6	17	2.0	1.7	17	2.3	1.1	17	3.1	3.8
Beluga	Grise Fiord	2001	5	4.1	5	2.1	1.5	5.0	4.0	1.2	5	2.7	1.0
Beluga	Igloolik	1995	35	11.5	35	10.6	8.5	35	8.2	3.1	35	6.6	4.1
Beluga	Iqaluit	1993	23	12.9	23	7.6	4.9	23	4.2	1.6	23	4.4	1.9
Beluga	Iqaluit	1994	7	12.9	7	16.3	8.9	7	8.8	4.7	7	14.5	5.5
Beluga	Kimmirut	1994	19	10.8	20	9.3	6.4	20	7.2	4.0	20	5.5	4.7
Beluga	Kimmirut	1997	10	16.1	9	11.7	4.2	9	5.9	1.7	9	6.9	4.0
Beluga	Kimmirut	2001	13	14.2	13	16.4	9.8	13	9.8	4.3	13	5.9	2.2
Beluga	Nastapoka	1984	14	13.2	15	10.7	13.7	10	4.6	2.3	15	5.1	2.7
Beluga	Pangnirtung	1984	11	11.1	11	5.0	4.4	11	2.8	1.5	11	6.4	6.4
Beluga	Pangnirtung	1993	12	7.8	11	8.5	7.0				11	8.9	4.5
Beluga	Pangnirtung	1994	27	8.4	27	10.7	13.4				27	6.5	2.9
Beluga	Pangnirtung	1997	24	13.0	25	8.6	4.6	25	4.8	2.1	25	5.5	4.4
Beluga	Pangnirtung	2002	10	15.3	16	11.6	7.6	16	6.7	3.6	16	5.3	2.8
Beluga	Repulse Bay	1993	2	8.0	2	3.4	3.1	2	4.8	2.1	2	9.7	5.2
Beluga	Sanikiluaq	1994	30	13.7	30	12.9	9.5	30	9.8	4.8	30	7.6	4.0
Beluga	Sanikiluaq	1998	22	13.0	22	21.1	25.3	22	16.0	14.9	22	1.3	0.6
Beluga	East Whitefish	1993	13	23.7	13	33.4	31.4	13	19.9	17.9	13	2.0	1.4
Beluga	East Whitefish	1994	12	18.8	13	17.8	19.3	13	13.3	11.5	13	1.6	0.7

Table 1. Mean ages and concentrations of total mercury, selenium and cadmium in liver of beluga whales from the Canadian Arctic (continued)

Species	Location	Year	N Age	Mean Age	N Total Hg ($\mu g \cdot g^{-1}$)	Mean Total Hg ($\mu g \cdot g^{-1}$)	St Dev Total Hg ($\mu g \cdot g^{-1}$)	N Selenium ($\mu g \cdot g^{-1}$)	Mean Selenium ($\mu g \cdot g^{-1}$)	St Dev Selenium ($\mu g \cdot g^{-1}$)	N Cadmium ($\mu g \cdot g^{-1}$)	Mean Cadmium ($\mu g \cdot g^{-1}$)	St Dev Cadmium ($\mu g \cdot g^{-1}$)
Beluga	Hendrickson Isl.	1993	9	20.9	11	33.3	21.7	11	21.2	9.8	11	2.3	0.7
Beluga	Hendrickson Isl.	1994	29	17.3	32	35.1	29.3	32	19.0	14.4	32	2.4	0.9
Beluga	Hendrickson Isl.	1995	16	15.6	18	44.0	35.1	18	19.4	10.7	18	2.3	0.5
Beluga	Hendrickson Isl.	1996	10	14.6	15	33.9	29.1	15	18.2	13.1	15	2.3	1.2
Beluga	Hendrickson Isl.	2001	24	15.5	24	38.9	41.7	24	12.2	8.6	24	2.6	1.9
Beluga	Hendrickson Isl.	2002	23	14.1	24	26.5	27.6	24	14.7	9.7	24	2.3	0.8
Beluga	Mack Delta	1981	26	12.3	34	10.7	10.9	35	5.6	4.4	35	2.3	1.5
Beluga	Mack Delta	1984	8	21.1	8	17.8	16.5	8	9.8	8.2	8	2.5	1.6
Beluga	Paulatuk	1993	3	14.3	3	8.6	10.0	3	7.1	2.8	3	1.1	0.2
Beluga	Shingle Point	1993	3	19.7	5	32.1	23.0	5	29.7	15.7	5	4.2	2.3

Figure 1. Mercury in liver of beluga whales from communities in the eastern Arctic as a function of whale age

Figure 2. Mercury and selenium in liver of beluga whales regardless of location or time of collection

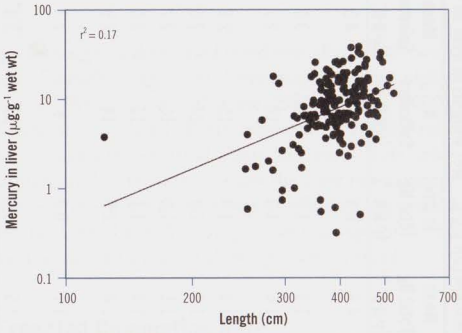
but did not differ from the sample taken in 1999 ($p = 0.41$). The pattern suggests peak values in the 1990s, similar to some of the beluga collections.

The sample from Repulse Bay in 1993 consisted of four animals only with a mean level of $7.9 \mu g \cdot g^{-1}$. The sample from 1999 was larger (Table 3, N = 18) with an apparently higher mean ($11.4 \mu g \cdot g^{-1}$) in spite of the fact that the mean length was smaller in 1999. Statistically the two length-corrected means failed to meet the statistical criterion of $p = 0.05$ to differ ($p = 0.12$). Future samples from Repulse Bay are desirable to test whether levels there are changing. Selenium in narwhal liver generally tracks the pattern of

Table 2. Mean concentrations of methylmercury ($\mu g \cdot g^{-1}$ wet weight) in liver of beluga whales

Species	Location	Year	Organ	N (MeHg)	Mean (MeHg) $\mu g \cdot g^{-1}$	St. Dev. (MeHg)
Beluga	Arviat	1999	Liver	7	1.20	0.50
Beluga	Coral Harbour	1993	Liver	11	1.12	0.19
Beluga	Iqaluit	1993	Liver	23	1.47	0.37
Beluga	Iqaluit	1994	Liver	7	1.70	0.27
Beluga	Repulse Bay	1993	Liver	2	0.65	0.06
Beluga	Sanikiluaq	1994	Liver	30	1.47	0.68

Figure 3. Narwhal, mercury in liver ($\mu g \cdot g^{-1}$ wet wt) as a function of length (cm)



mercury in that organ suggesting that in this species, as in beluga, the selenium might be used to detoxify mercury. Cadmium levels are high in liver but are even higher in kidney. Cadmium levels in liver of narwhal are considerably higher than those in liver of beluga.

Walrus

The levels of mercury in walrus liver (Table 4) are much lower than in narwhal or beluga, although they still exceed the consumption guidelines for fish. The few samples from Akulivik stand out from the other walruses with higher values. Beluga from Igloolik in 1995 had a mean level of $10.6 \mu g \cdot g^{-1}$ mercury in liver but walrus from the same area in 1996 had a mean level of only $2.4 \mu g \cdot g^{-1}$. Presumably the lower levels in walrus are caused by feeding lower in the trophic pyramid. Samples from Hall Beach and Igloolik offer some potential for estimating temporal trends since they were sampled in the 1980s and again in the 1990s. The effect of age of mercury levels is relatively weak in walrus (Figure 4), the regression equation having an r^2 value of only 0.08. Nonetheless, the same statistical analysis used for beluga was used for walrus from Igloolik and Hall Beach. The values from Igloolik were all similar except for the results in 1996 which were considerably higher than any from the 1980s, although the animals were older in 1996. Statistically, the age-adjusted means failed to differ at the 0.05 level of probability. The same applies to the two collections from Hall Beach. Although the mean recorded in 1996 was somewhat higher than that from 1988, older animals were taken in 1996 and the difference in levels of mercury was not significant statistically.

Discussion and Conclusion

Levels of mercury in liver of three species of marine mammals (beluga, narwhal and walrus) have been determined at intervals since the 1970s. Generally the levels of mercury exceed greatly the levels allowed in commercial fish sold in Canada. However, the toxicological significance of the high levels in beluga and narwhal liver are not clear. The predominant form of mercury is not methylmercury as it is in fish. It appears that beluga and narwhal store liver mercury as a selenide that is not likely to be toxic either to the whales or to people eating them. We have little information on the speciation of mercury in narwhal or walrus. There are regional differences in levels found in beluga with generally higher levels of mercury in the western Arctic than in the Eastern Arctic. There are also species differences with levels found in walrus lower than levels found in either beluga or narwhal. Probably this difference reflects different feeding habits between walrus and both species of whales.

In some instances, more than one collection was made from a community and those instances offer some opportunity to detect temporal change. The data from beluga and narwhal generally show either increased levels since the 1980s or no statistically clear change. The same is true of walrus but the means failed to differ significantly over the years for which data were available. No data from any

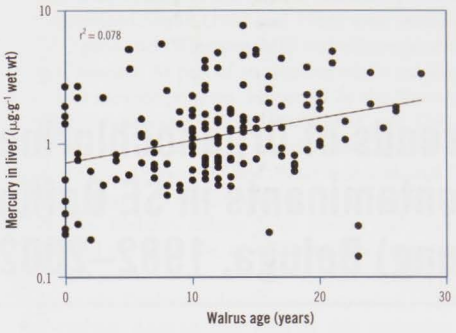
Table 3. Mean lengths (cm) and concentrations of total mercury, selenium and cadmium (all $\mu g \cdot g^{-1}$ wet weight) in liver of narwhal from the Canadian Arctic

Species	Location	Year	N Length	Mean Length (cm)	N Total Hg ($\mu g \cdot g^{-1}$)	Mean Total Hg ($\mu g \cdot g^{-1}$)	St Dev Total Hg ($\mu g \cdot g^{-1}$)	N Selenium ($\mu g \cdot g^{-1}$)	Mean Selenium ($\mu g \cdot g^{-1}$)	St Dev Selenium ($\mu g \cdot g^{-1}$)	N Cadmium ($\mu g \cdot g^{-1}$)	Mean Cadmium ($\mu g \cdot g^{-1}$)	St Dev Cadmium ($\mu g \cdot g^{-1}$)
Narwhal	Arctic Bay	1999	27	411.4	27	12.2	8.1	27	6.5	3.3	27	6.5	3.3
Narwhal	Broughton Isl.	1993	13	455.2	14	9.4	5.7	14	8.5	5.4	14	15.4	7.8
Narwhal	Broughton Isl.	1995	27	414.7	28	13.0	9.2	28	7.1	3.7	28	24.8	21.0
Narwhal	Broughton Isl.	1996	8	395.0	8	11.6	7.4	8	6.2	3.0	8	18.1	14.3
Narwhal	Broughton Isl.	2001	25	425.0	25	17.8	24.1	25	9.8	5.3	25	25.2	18.2
Narwhal	Clyde River	1993			5	11.7	12.4	5	7.3	4.7	5	15.8	12.8
Narwhal	Grise Fiord	1993			3	9.3	6.1	3	3.8	0.9	3	66.9	58.8
Narwhal	Pond Inlet	1978	35	376.0	38	6.3	3.2	38	4.2	2.0	38	34.1	33.5
Narwhal	Pond Inlet	1992	9	381.3	9	10.0	5.9	9	5.4	2.6	9	46.1	37.2
Narw hal	Pond Inlet	1994	19	387.5	20	12.6	9.7	20	8.4	5.2	20	30.0	20.9
Narwhal	Pond Inlet	1999	17	393.0	17	9.6	8.4	17	5.8	4.4	16	39.8	36.7
Narwhal	Repulse Bay	1993	3	397.7	4	7.9	6.8	4	5.4	4.3	4	30.7	27.9
Narwhal	Repulse Bay	1999	16	364.7	18	11.4	7.2						

Table 4. Mean ages and concentrations of total mercury, selenium and cadmium (all $\mu g \cdot g^{-1}$ wet weight) in liver of walrus from the Canadian Arctic

Species	Location	Year	N Length	Mean Length (cm)	N Total Hg ($\mu g \cdot g^{-1}$)	Mean Total Hg ($\mu g \cdot g^{-1}$)	St Dev Total Hg ($\mu g \cdot g^{-1}$)	N Selenium ($\mu g \cdot g^{-1}$)	Mean Selenium ($\mu g \cdot g^{-1}$)	St Dev Selenium ($\mu g \cdot g^{-1}$)	N Cadmium ($\mu g \cdot g^{-1}$)	Mean Cadmium ($\mu g \cdot g^{-1}$)	St Dev Cadmium ($\mu g \cdot g^{-1}$)
Walrus	Akulivik	1990	4	5.7	4	4.9	0.8	4	4.0	0.6	4	11.0	2.6
Walrus	Hall Beach	1988	16	9.7	16	1.3	1.2	16	3.0	1.2	16	11.2	5.0
Walrus	Hall Beach	1996	16	14.7	16	1.6	1.3	16	2.7	1.6	15	10.8	6.7
Walrus	Igloolik	1982	13	11.7	16	1.3	1.4	15	2.8	0.9	15	12.3	5.7
Walrus	Igloolik	1983	27	12.6	25	1.3	1.0	24	2.6	1.0	25	9.8	3.8
Walrus	Igloolik	1987	16	8.8	16	1.1	1.0	16	2.7	1.4	15	13.8	8.3
Walrus	Igloolik	1988	15	8.5	13	1.4	1.1	13	3.0	1.5	11	13.3	10.3
Walrus	Igloolik	1996	14	16.6	14	2.4	2.0	14	2.9	1.9	14	12.0	4.7
Walrus	Inukjuaq	1990	8	12.4	9	1.1	0.9	9	2.3	1.1	9	5.3	5.8
Walrus	Iqaluit	1984	30	11.5	31	1.5	1.0	30	3.0	0.9	30	11.2	6.2

Figure 4. Mercury in liver of walrus from communities in the eastern Arctic as a function of walrus age



species suggest a downward trend over the period. Some sets of samples suggest that levels may have been higher in the 1990s than in either the 1980s or early 2000s. Sediment core data indicate increased inputs to Arctic lakes since pre-industrial times and cores from mid-latitudes in North America show the same trend, except that very recent inputs have begun to decline (e.g. north/central USA, Lake Winnipeg). Some groups of Arctic marine mammals may be showing a similar trend.

Expected Completion Date

This project officially ended March 2003. Any remaining analysis (e.g. 2002 and 2003 samples from Sanikiluaq and Iqaluit beluga) will be completed by March 2004. Additional collections and analysis will be done in future years with funding from DFO, FJMC, NWMB, NIF and programs such as ArcticNet. No future funding from NCP is anticipated.

References

Lockhart, W.L., P. Wilkinson, B.N. Billeck, R.A. Danell, R.V. Hunt, G.J. Brunskill, J. Delaronde, and V. St. Louis. 1998. Fluxes of mercury to lake sediments in central and northern Canada inferred from dated sediment cores. *Biogeochem.* 40:163–173.

Lu, J.Y., W.H. Schroeder, L.A. Barrie, A. Steffen, H.W. Welch, K. Martin, W.L. Lockhart, R.V. Hunt, and G. Boila. 2001. Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry. *Geophys Res Lett.* 28:3219–3222.

Slemr, F. and E. Langer. 1992. Increase in global atmospheric concentrations of mercury inferred from measurements over the Atlantic Ocean. *Nature.* 355:434–437.

Wagemann, R., S. Innes, and P.R. Richard. 1996. Overview and regional and temporal differences of heavy metals in arctic whales and ringed seals in the Canadian Arctic. *Sci Total Environ.* 186:41–66.

Wagemann, R., E. Trebacz, G. Boila, and W.L. Lockhart. 2000. Mercury species in the liver of ringed seals. *Sci Total Environ.* 261:21–32.

Temporal Trends of Organochlorine Contaminants in SE Baffin (Pangnirtung) Beluga, 1982–2002

Project leader(s)

Gary A. Stern, Freshwater Institute, Winnipeg, MB R3T 2N6; phone: (204) 984-6761; fax: (204) 984-2403;
M. Ikonomou, DFO, Institute of Ocean Sciences, Sidney, BC; phone: (250) 363-6804; fax (250) 363-6808; e-mail: IkonomouM@dfo.mpo.gc.ca

Project team members

DFO; K. Koczanski, Bruno Rosenberg, and B. Dunn.

Abstract

Blubber samples from male Pangnirtung beluga, collected over 20 years at five time points, were analysed for organochlorine contaminants. A significant decline in concentration of major OC groups such as HCH, DDT, CHL and toxaphene was observed in the blubber over this time period while the level of the current use pesticide endosulfan steadily increased (3.2-fold).

Key Project Messages

1. A significant decline in concentration of major OC contaminant groups such as HCH, DDT, CHL and toxaphene was observed in the blubber of Pangnirtung beluga over the 20-year time period from 1982 to 2002.
2. Endosulfan sulfate levels have steadily increased over the same time period (3.2-fold).

Objectives

To document the temporal trends of bioaccumulating substances such as for polychlorinated dibenzodioxins (PCDD), dibenzofurans (PCDF), PCBs, DDT, toxaphene, coplanar PCBs and selected current use chemicals such as polybrominated diphenyl ethers (BDPEs) in Arctic marine ecosystems. This will help determine whether contaminant levels in marine mammal tissues, and thus exposure to people living in Arctic communities who consume them as part of their traditional diet, are increasing or decreasing with time. Also, to equip Canadian delegations involved in international controls with appropriate information to formulate Canadian positions.

Activities

In 2001–2002 and 2002–03

In July 2002, 8 blubber samples from male Pangnirtung beluga were collected by community residents. As samples were not received until December 2002, only the OC analyses and aging have now been completed. PBDE and *n*PCB analysis are still underway.

Results

Blubber samples from beluga in the Clearwater Fjord area of Cumberland Sound (1982 and 1986) were obtained by DFO personnel (Winnipeg, MB) with the cooperation of local hunters. As part of an ongoing whale sampling and stock identity program, supported by the Nunavut Wildlife Management Board (NWMB) and DFO, samples from the southern coastline in Cumberland Sound (1992, 1996, 1997 and 2002) were collected by hunters during their subsistence hunts using standardized whale kits. Blubber, kidney, liver, ovaries and uterus, muscle and the lower jaw, as well as morphometric data were collected for each animal. All samples were shipped frozen to the Freshwater Institute and stored at −20°C until analysis. Animals were aged by thin sectioning a canine tooth from the rear of the lower jaw and counting growth layer groups (GLG) in the dentine using transmitted light (Heide-Jørgensen, 1994).

All univariate analyses were performed with lipid normalized $\log_{10}$ transformed data to adjust for skewness. ANCOVA was used to assess the effects of year to year collections (temporal trends), age of the animals and age*year interactions (homogeneity of slope between age and [OC]) using the model [OC] = year age age*year, where [OC] = log concentration of either individual contaminants or major OC groups. Differences between collection years were examined with paired comparisons of age adjusted least squared mean concentrations (SAS Institute, 1989–1996). Only results for animals older than two years of age were included in the analysis of covariance because of the large variations in concentrations seen in younger animals (Stern et al., 1994).

Significant declines in α- and β-HCH concentrations, 2.0 and 1.7-fold respectively, over the 20-year interval from 1982 to 2002 were observed. ΣHCH levels declined by 1.8-fold. (Table 1, Figure 1). The decreasing trend in α-HCH concentrations is consistent with the 9-fold decline in Arctic airborne concentrations over the 14-year period from 1979 to 1993 and with the significant but much smaller reduction (3% per year) of ΣHCH in surface seawater (Jantunen and Bidleman, 1995; Bidleman el al., 1995). In the beluga blubber, the α/γ ratio decreased from 3.75 to 2.47 over the 20-year time period. This result is consistent with decreased usage of technical HCH (α-HCH (60–70%), β-HCH (5–12%) and γ–HCH (10–15%)) since the early 1980s (Li et al., 1997).

While ΣDDT concentrations varied substantially over the 20-year time period, 2002 levels were 1.5-fold lower than those measured in the 1982 animals (Table 1, Figure 2). Significant declining trends were observed for both *p,p'*-DDT (4.8-fold) and its metabolite *p,p'*-DDE (2.3-fold). The *p,p'*-DDE/ΣDDT ratio changed from 0.37 to 0.44 suggesting "old" rather than recent DDT inputs.

Concentrations of the most abundant congeners in technical chlordane, *cis*- and *trans*-nonachlor, peaked in the 1992 blubber samples and declined to their lowest levels in the 2002 animals (Table 1). The same trend was observed for ΣCHL, with an overall 2.1-fold decline over the 20-year time period. *Cis*- and *trans*-CHL levels consistently declined and increased, respectively, over the 20-year time period. Peak concentrations in the 1992 animals most likely reflects the fact that the use of chlordane was not banned in Canada and the United States until the

Figure 1. Temporal trends of age adjusted concentrations of ΣHCH, α-HCH, β-HCH, γ-HCH in blubber from male Pangnirtung beluga (1982–2002)

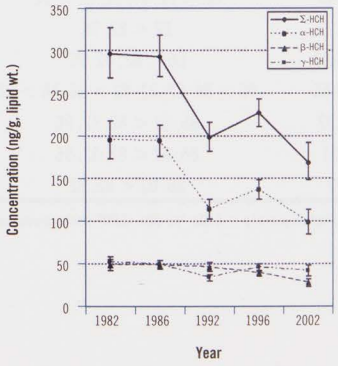


Figure 2. Temporal trends of age adjusted concentrations of ΣDDT, *pp*-DDE, *pp*-DDT, *pp*-DDD in blubber from male Pangnirtung beluga (1982–2002)

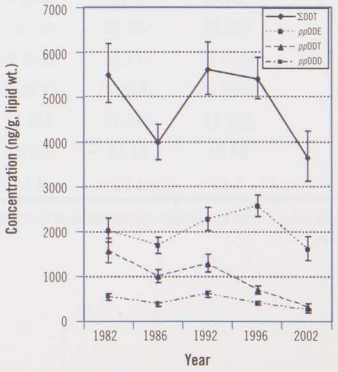


Table 1. Age adjusted concentrations of OCs in male Pangnirtung beluga blubber samples (only results from animals > 2 years were included in the analysis of covariance because of the large variations in concentrations seen in younger animals) (ng/g, lipid wt.)

	1982	1986	1992	1996	2002	Year[a]
ΣHCH	295.52	292.28	198.30	226.60	168.58	82, 86 > 92, 96, 02; 96 > 02
α-HCH	194.29	193.37	113.57	136.80	98.19	82, 86 > 92, 96, 02; 96 > 02
β-HCH	48.40	48.79	46.24	39.02	27.82	82, 86, 92, 96 > 02
γ-HCH	52.02	48.99	33.95	45.68	41.74	82, 86, 96 > 92
ΣDDT	5481.47	3980.63	5606.60	5400.62	3638.48	86, 02 < 82, 92, 96
op-DDE	79.70	59.08	79.52	60.55	33.28	02 > 82, 86, 92, 96; 92 > 96
pp-DDE	2020.54	1683.73	2269.27	2562.50	1601.81	96 > 86, 02
op-DDD	198.97	126.83	259.39	317.05	245.50	86 < 82, 92, 96, 02; 82 < 96
pp-DDD	552.58	385.53	610.63	416.24	248.06	86 < 82, 92, 96; 86 > 02
op-DDT	–	–	–	–	–	–
pp-DDT	1566.08	1000.12	1283.69	702.53	328.08	02 < 82, 86, 92, 96; 82 > 86, 96; 92 > 96
Ratio[b]	0.37	0.43	0.41	0.47	0.44	82 < 86, 92, 96, 02
ΣCHL	1817.29	1663.13	2089.57	1521.40	876.08	02 < 82, 86, 92, 96; 92 > 96
c-CHL	112.97	85.08	81.28	72.46	35.34	02 < 82, 86, 92, 96; 82 > 96
t-CHL	13.57	6.18	14.35	17.81	20.93	86 < 82, 92, 96, 02
c-Nona	182.52	123.98	211.34	154.64	96.41	82 > 86, 02; 92 > 86, 02; 96 > 02
t-Nona	603.31	596.71	930.79	640.82	365.40	02 < 82, 86, 92, 96; 92 > 82, 86, 96
oxychlor	306.58	313.84	410.23	224.66	139.02	02 < 82, 86, 92, 96; 96 < 92
ΣCBz	503.95	426.62	332.49	702.85	552.46	96 > 82, 86, 92; 92 < 82, 02
ΣCHB	11257.59	9924.86	9646.01	10383.95	5641.96	02 < 82, 86, 92, 96
B8-1413 (T2)	3383.89	2954.22	2717.72	2903.16	1711.46	02 < 82, 86, 92, 96
B9-1679 (T12)	6625.97	5881.52	5756.66	6279.22	3464.48	02 < 82, 86, 92, 96
Dieldrin	688.27	531.98	391.18	547.71	335.43	02 < 82, 86, 92, 96
Endosulfan	4.31	4.65	9.72	13.50	13.95	82, 86 < 92, 96, 02
Mirex	6.64	5.26	13.65	10.80	14.97	82, 06 < 92, 96, 02
ΣPCB	4575.92	3089.44	4053.17	4464.72	3554.29	86 < 82, 92, 96; 02 > 96
Mono/di-CB	198.91	139.87	201.23	71.83	59.32	82, 92 > 86, 96, 02; 86 > 96, 02
Tri-CB	124.75	74.22	89.14	113.11	122.43	86 < 82, 96, 02; 82 > 92
Tetra-CB	641.86	540.94	452.60	622.73	555.27	92 < 82, 96
Penta-CB	1343.80	873.26	1218.95	1281.24	1106.00	86 < 82, 92, 96
Hexa-CB	1630.13	1042.98	1439.76	1765.49	1310.55	96 > 86, 92, 02; 82 > 86; 86 > 92
Hepta-CB	550.25	348.39	544.17	516.03	352.92	86, 02 < 82, 92, 96
Octa-CB	64.04	47.85	60.90	66.49	44.11	86, 02 < 82, 92, 96
Nona-CB	4.42	1.93	4.68	3.15	1.77	86, 02 < 82, 92

[a] Significant differences in least square mean concentrations of individual OCs and groups for all five collection years ($p < 0.05$); [b] *pp*-DDE /ΣDDT (ratio values were not log transformed)

late 1980s, and that countries such as Mexico continued, until very recently, to import over 45 tons of chlordane annually from the United States where it is still legal to manufacture (Environ Health Perspectives 105, 1997).

Endosulfan is currently used in the United States, Canada and other countries for insect control on high value crops. Like DDT, endosulfan is also used to combat disease carrying insects such as mosquitoes, flies and lice. In 1988, the worldwide production of endosulfan was estimated to be approximately 107 kg·year^{-1} (World Health Organization. Environmental Health Criteria 40-Endosulfan; WHO: Geneva, 1984). Total usage of endosulfan in the US during 1992–93 is estimated to be 814,000 kg. In Ontario and Quebec, Canada, usage is comparable to that in the high-application areas of the United States. Technical endosulfan contain two isomers, endosulfan I and endosulfan II, in approximately a 7:3 ratio along with impurities and degradation products. In the beluga blubber only endosulfan sulfate, the degradation product of endosufan, is present and levels appear to have increased steadily (Table 1) over the 20-year time period from 1982 to 2002. Conversely, ΣCHB, B8-1413 (T2), B9-1679 (T12) and dieldrin concentrations have declined by ~2-fold between 1982 and 2002. No clear trends were observed for PCBs.

Expected Completion Date

As a result of this study we now have OC temporal trend covering 20 years and 5 time points. PBDE and *n*PCB analysis should be completed by fall. Based on five year sampling intervals, an additional collection should occur in 2007.

References

Bidleman, T.F., L.M. Jantunen, R.L. Falconer, L.A. Barrie, and P. Fellin. 1995. Decline of hexachlorocyclohexanes in the Arctic atmosphere and reversal of air-sea gas exchange. *Geophys Res Lett.* 22:219–222.

Heide-Jørgensen, M.-P., J. Jensen, A.H. Larsen, J. Teilmann, and B. Neurohr. 1994. Age estimation of white whales (*Delphinapterus leucas*) from Greenland. Meddelelser om Grønland. *Bioscience.* 39:187–193.

Jantunen, L.J. and T.F. Bidleman. 1995. Reversal of the air-water gas exchange direction of hexachlorocyclohexane in the Bering and Chuckchi Seas: 1993 versus 1988. *Environ Sci Technol.* 27:1081–1098.

Li, Y.F., T.F. Bidleman, and L.A. Barrie. (1997). Global HCHs usage trends and their impact on the Arctic. *Geophy Res Let.* 25:39–41.

SAS Institute. 1989–1996. Release 6.12 TS Level 0045. SAS Institute Inc., SAS Campus Drive, Cary, NC.

Stern, G.A., D.C.G. Muir, M.D. Segstro, R. Dietz, and M.-P. Heide-Jørgensen. 1994. PCBs and other organochlorine contaminants in white whales (*Delphinapterus leucas*) from West Greenland: variations with age and sex. Meddelelser om Grønland. *Bioscience.* 39:243–257.

Temporal Trends of Organochlorine, Organobromine and Heavy Metal (Hg, As, Se) Contaminants in Burbot from Fort Good Hope, N.W.T.

Project leader(s)

Gary A. Stern, Freshwater Institute, Winnipeg, MB R3T 2N6; phone: (204) 984-6761; fax: (204) 984-2403; M. Ikonomou, DFO, Institute of Ocean Sciences, Sidney, BC; phone: (250) 363-6804; fax: (250) 363-6808; e-mail: IkonomouM@dfo.mpo.gc.ca

Project team members

DFO — W.L. Lockhart, G. Low, K. Koczanski, J. DeLaronde, P. Lyng, Fort Good Hope Renewable Resource Council and community members.

Abstract

Tissues from burbot collected at Fort Good Hope (Rampart Rapids) in 2001 were analysed for organochlorine contaminants, mercury, selenium and arsenic. Data from this time point was combined with the existing metal (1985, 1989, 1993, 1995, 1999 and 2000) and OC (1988, 1994, 1999 and 2000) data covering time spans of 16 and 13 years, respectively. No significant correlation between length and mercury concentration was observed with muscle or liver for either sex. In the males, mean mercury concentrations in muscle increased by 35% over the 16-year time period. Mean Hg concentrations in muscle and liver over the entire data sets were 0.302 ± 0.121 (n = 128) and 0.067 ± 0.056 (n = 122) $\mu g \cdot g^{-1}$, respectively. Muscle mercury levels are below the recommended guideline level of 0.50 $\mu g \cdot g^{-1}$ for commercial sale but are at, or exceed, the guideline level of 0.2 $\mu g \cdot g^{-1}$ recommended for fish used for subsistence. Levels of most major OC groups in liver from Fort Good Hope burbot have declined over the 13-year period from 1988 to 2001.

Key Project Messages

1. Mean mercury concentrations in muscle from male Fort Good Hope burbot have increased by 35% over the 16-year time period from 1985 to 2001.
2. Muscle mercury levels are below the recommended guideline level of 0.50 $\mu g \cdot g^{-1}$ for commercial sale but are at, or exceed, the guideline level of 0.2 $\mu g \cdot g^{-1}$ recommended for fish used for subsistence.
3. Levels of most major OC groups in liver from Fort Good Hope burbot have declined over the 13-year period from 1988 to 2001.

Objectives

To document the temporal trends of bioaccumulating substances such as heavy metals (mercury, selenium, arsenic), organochlorine contaminants (e.g. PCBs, DDT, toxaphene, coplanar PCBs) and selected current use chemicals such as short chain polychlorinated-*n*-alkanes

(PCAs) and polybrominated diphenyl ethers (BDPEs) in burbot liver (and muscle for metals) from Fort Good Hope, so as to determine whether contaminant levels in the fish and thus exposure to people living in Arctic communities who consume them as part of their traditional diet, are increasing or decreasing with time. These results will also help to test the effectiveness of international controls.

Introduction

With a few exceptions, minimal or no direct temporal trend information on organochlorine contaminants and heavy metals in fish are available in either the Arctic marine or freshwater environments. Much of the temporal trend data that is available are too limited to be scientifically credible because they are based on 2 or at most 3 sampling times. In addition, much of this is confounded by changes in analytical methodology as well as variability due to age/size, or dietary and population shifts (CACAR, 1997; AMAP, 1998). By comparison, temporal trend data for contaminants in Lake Ontario lake trout (Borgmann and Whittle, 1991) and in pike muscle from Storvindeln, Sweden (AMAP, 1998) are available over a 15- to 30-year period.

Very few measurements have been made of the toxic coplanar (or *non-ortho* substituted) PCBs and other planar OCs in Arctic fish, however, where coplanar PCBs have been measured along with PCDD/Fs, PCNs and CDPEs, calculations of TCDD TEQs show that the coplanar PCBs, especially CB126, account for most of the TEQs (CACAR, 1997). As a result, one of the priorities outlined in both CACAR (1997) and AMAP (1998) is for additional measurements of coplanar PCBs in Arctic fish. Measurements of PCDD/F were not recommended unless specific sources are suspected. Because of their toxicological significance, analysis of new chemical contaminants (i.e. those not currently identified in the UN-ECE LRTAP protocols) such as PCAs and BDPEs are essential and will provide a "baseline" against which future measurements can be compared.

Burbot is a predatory, bottom-feeding species of fish. Their sedentary nature and high lipid content of the liver make the species very suitable for monitoring lipophilic contaminants (CACAR, 1997; AMAP, 1998). As outlined in the Northern Contaminants Program Phase II, Call for Proposals (Blueprint for International Activities, and Blueprint for Monitoring the Health of Arctic Peoples and Ecosystems), some of the most comprehensive temporal trend data that exists is for OCs in burbot liver from Fort Good Hope (Wagemann, 1985; Lockhart et al., 1989; Stern et al., 2000, 2001).

Activities

In 2001–2002 and 2002–03

In December 2001 and 2002, 20 and 35 burbot, respectively, were collected from the Mackenzie River at Fort Good Hope (Rampart Rapids) by community residents. The heavy metal and OC analyses for the 2001 samples now been completed and analyses of the 2002 samples are underway (burbot were not shipped to FWI until late March, 2002).

Results

Hg, Se, As

Mean mercury, selenium and arsenic concentrations for burbot muscle and liver samples collected between 1985 and 2001 are shown in Table 1 and 2, respectively. No significant correlation between length and mercury concentration was observed with muscle or liver for either sex. In the males, mean mercury concentrations in muscle increased by 35% over the 16-year time period from 1985 to 2001 (Table 1 and Figure 1). For selenium, weak negative correlations exist between concentration and length for liver and muscle in male fish. The length adjusted mean selenium concentrations in liver (ANCOVA) were 1.55, 1.17, 0.92, 1.55 and 1.56 ($\mu g \cdot g^{-1}$) for the 1985, 1988, 1999, 2000 and 2001 time points, respectively. The highest measured As concentration, 17.16 $\mu g \cdot g^{-1}$, occurred in a muscle sample from a female burbot collected in 1999.

Organohalogens

Table 3 lists the mean wet weight major OC group concentration for five collection periods between 1988 and 2001. Table 4 summarizes the ANCOVA results used to assess the effects of year to year collections (temporal trends), % lipid and lipid*year interactions (homogeneity of the slope between % lipid and [OC]) of OCs in liver samples collected from Fort Good Hope burbot in 1988, 1994, 1999 and 2001. Comparison with the 2000 results could not be made as age*year interactions were significant for most major OC groups. Significant declines, 1.4- and 2.5-fold, were observed for both α- and γ-HCH over this 13-year time period. β-HCH concentrations were below the detection limit in all samples. Interestingly, the α/γ-HCH ratio has increased from 4.3 to 8.2 which is opposite to what one might have expected based on the decreased usage of the technical

Table 1. Mean (standard deviation) concentrations of mercury, selenium and arsenic in Fort Good Hope burbot muscle ($\mu g \cdot g^{-1}$)

Collection	Sex	n	Length (mm)	Hg	Se	As
Apr-85[1]	M	10	633 (84)	0.222 (0.035)	0.358 (0.087)	–
Dec-93	M	7	677 (109)	0.231 (0.113)	0.534 (0.163)	2.291 (3.151)
Sept-95	M	2	–	0.265 (0.035)	–	–
Dec-99	M	21	676 (107)	0.286 (0.095)	0.395 (0.107)	0.637 (0.637)
Dec-00	M	21	699 (104)	0.345 (0.097)	0.478 (0.136)	1.333 (1.944)
Dec-01	M	10	720 (164)	0.342 (0.151)	0.295 (0.352)	3.106 (3.897)
Apr-85[1]	F	6	714 (140)	0.337 (0.136)	0.480 (0.126)	–
Dec-93	F	3	812 (133)	0.297 (0.035)	0.321 (0.009)	6.450 (0.984)
Sept-95	F	2	–	0.180 (0.085)	–	–
Dec-99	F	21	735 (101)	0.259 (0.108)	0.219 (0.104)	2.626 (3.815)
Dec-00	F	15	732 (127)	0.364 (0.140)	0.460 (0.175)	1.929 (1.621)
Dec-01	F	10	747 (122)	0.336 (0.180)	0.128 (0.161)	1.098 (1.821)

[1] Wagemann 1985; [2]n = 20

Table 2. Mean (standard deviation) concentrations of mercury, selenium and arsenic in Fort Good Hope burbot liver ($\mu g \cdot g^{-1}$)

Collection	Sex	n	Length (mm)	Hg	Se	As
Apr-85[1]	M	9	643 (82)	0.044 (0.019)	1.759 (0.558)	–
Dec-88	M	8	706 (84)	0.054 (0.026)	1.230 (0.555)	3.119 (1.725)
Dec-93	M	7	677 (109)	–	–	1.016 (1.328)
Dec-99	M	21	676 (107)	0.046 (0.024)	1.071 (0.628)[2]	0.607 (0.326)
Dec-00	M	21	699 (104)	0.064 (0.026)	1.646 (0.733)	0.585 (0.412)
Dec-01	M	10	720 (164)	0.063 (0.048)	1.434 (1.278)	0.839 (0.822)
Apr-85[1]	F	6	714 (140)	0.097 (0.098)	1.272 (0.715)	–
Dec-88	F	2	623 (86)	0.072 (0.035)	1.460 (1.529)	1.280 (1.018)
Dec-93	F	3	812 (129)	–	–	1.062 (0.546)
Dec-99	F	20	749 (77)	0.064 (0.069)	0.687 (0.552)[2]	1.353 (0.811)
Dec-00	F	15	732 (127)	0.094 (0.056)	1.203 (0.469)	0.632 (0.349)
Dec-01	F	10	747 (122)	0.098 (0.108)	1.235 (0.720)	1.074 (1.227)

[1] Wagemann 1985; [2]n = 19

mixture (α-HCH (60–70%), β-HCH (5–12%) and γ-HCH (10–15%)) and corresponding increase in the usage of lindane since the early 1990s (Li et al., 1997). The most plausible explanation for this result is that γ-HCH is being transformed by sunlight into α-HCH during long range transport (Muir et al., 2000; Barrie et al., 1992; Oehme, 1991). γ-HCH was reported to be declining at a faster rate than α-HCH in air samples collected at Alert, Nunavut, from January 1993 to December 1997 (Blanchard, 2000).

Lipid adjusted ΣDDT concentrations were at their highest in the 1994 samples and declined by over 2-fold by 2001. The *p,p'*-DDE/ΣDDT ratios increase from 0.39 in 1988 to 0.57 in 2001 suggesting "old" rather than recent inputs of DDT.

Overall, a 1.9-fold decline in the lipid adjusted mean concentrations of ΣCHL was observed. Oxychlordane, the principal metabolite of *cis*- and *trans*-chlordane, and second only to *trans*-nonachlor as the most abundant chlordane-related residue in the Fort Good Hope burbot liver, did not change significantly over this 13-year period. The decreasing *t/c*-CHL ratio suggests "old" rather than recent chlordane inputs. *t*-nonachlor, and heptachlor

Figure 1. Mean Hg concentrations in muscle samples from male Fort Good Hope burbot

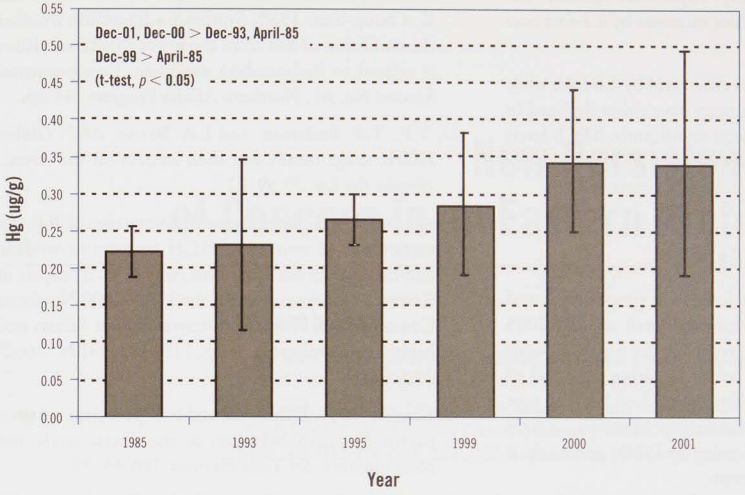


Table 3. OCs in Burbot liver from Fort Good Hope (mean and standard deviation, ng/g, ww)

Year	Sex	n	% Lipid	ΣCBz	ΣHCH	ΣCHL	ΣDDT	ΣPCB	ΣCHB	HCBz	Dieldrin
1988	M + F	10	30.20 (13.47)	13.63 (4.21)	5.53 (1.71)	23.83 (7.37)	16.17 (5.25)	58.11 (18.45)	60.83 (19.31)	13.07 (4.06)	2.38 (0.74)
1994	M + F	9	30.56 (11.59)	8.63 (2.63)	5.13 (1.53)	17.34 (6.14)	18.96 (8.28)	50.05 (17.55)	46.85 (14.46)	8.17 (2.48)	2.02 (0.62)
1999	M + F	21	42.10 (13.31)	10.04 (3.81)	3.78 (1.38)	21.00 (8.04)	22.84 (8.59)	62.77 (22.29)	54.03 (20.37)	5.43 (2.17)	2.38 (0.93)
2000	M + F	20	36.22 (15.22)	8.72 (5.24)	3.29 (1.98)	19.02 (12.50)	21.24 (14.92)	54.62 (36.25)	47.01 (29.04)	4.78 (2.89)	2.21 (1.57)
2001	M + F	20	30.14 (15.00)	6.36 (3.06)	3.79 (1.67)	13.68 (6.99)	8.99 (5.96)	41.88 (21.26)	37.68 (24.27)	4.33 (1.90)	2.37 (1.31)

Table 4. Lipid adjusted (ANCOVA) OC concentrations in liver of Fort Good Hope burbot. All concentrations are in ng/g

Year	Sex	n	ΣCBz	ΣHCH	ΣCHL	ΣDDT	ΣPCB	ΣCHB	HCBz	Dieldrin
1988	M + F	10	15.12	6.05	26.68	18.48	64.47	68.90	14.41	2.67
1994	M + F	9	9.56	5.59	19.02	20.50	54.45	52.52	9.00	2.26
1999	M + F	21	7.46	2.89	15.37	16.25	46.78	38.80	4.05	1.72
2001	M + F	20	6.79	4.07	14.46	8.96	44.44	37.83	4.71	2.44

concentrations declined by 2.0- and 2.4-fold fold over this time period. Conversely, heptachlor epoxide, the oxidation product of heptachlor increased by 2.2-fold over the same time period.

ΣTri-PCB concentrations have increased by 1.8-fold, while all other PCB homologue groups have either declined in concentration or did not change significantly. ΣPCB levels have declined by 1.5-fold. ΣCHB and ΣCBz concentrations decreased by 1.8- and 2.2-fold, respectively.

Expected Completion Date

Temporal trend studies are long-term propositions and thus annual sampling is projected until at least 2005 (8 time points covering 17 years for the organohalogen compounds and 10 time points covering a period of 21 years for mercury). While Phase II of NCP is now finished, and no further funding is expected, sample collections will continue (funded by DFO) and analysis will be done as funding permits.

References

AMAP. 1998. AMAP Assessment Report: Arctic Pollution Issues, Arctic Monitoring and Assessment Program (AMAP). Chapter 6. Oslo, Norway. xii+859 pp.

Barrie, L.A., D. Gregor, B. Hargrave, R. Lake, D. Muir, R. Shearer, B. Tracey, and T. Bidleman. 1992. Arctic contaminants: sources, occurrences and pathways. *Sci Total Environ.* 122:1–74.

Blanchard, P. 2000. Northern Contaminants Air Monitoring and Interpretation. In: Synopsis of Research Conducted under the 1990–2000 Northern Contaminants Program, Ottawa: Indian Affairs and Northern Development. pp. 94–97. ISBN 0-662-29320-7.

Borgmann, U. and D.M. Whittle. 1991. Contaminant concentration trends in Lake Ontario lake trout. *J Great Lakes Res.* 17:368–381.

CACAR. 1997. Canadian Arctic Contaminants Assessment Report. Chapter 3. J. Jensen, K. Adare, and R. Shearer (eds.). Indian and Northern Affairs Canada, Ottawa. 460 pp.

Lockhart, W.L., D.A. Metner, D.A.J. Murray, R.W. Danell, B.N. Billeck, C.L. Baron, D.C.G. Muir, and K. Chang-Kue. 1989. Studies to determine whether the condition of fish from the lower Mackenzie River is related to hydrocarbon exposure. Environmental Studies No. 61, Northern Affairs Program. 84 pp.

Li, Y.F., T.F. Bidleman, and L.A. Barrie. 1997. Global HCHs usage trends and their impact on the Arctic. *Geophy Res Let.* 25:39–41.

Muir, D., T.F. Bidleman, and R. Norstrom. 2000. An assessment of sources of HCH isomers to wildlife and humans in the Canadian Arctic. In: Synopsis of Research Conducted under the 1990–2000 Northern Contaminants Program, Ottawa: Indian Affairs and Northern Development. pp. 119–131. ISBN 0-662-29320-7.

Oehme, M. 1991. Dispersion and transport paths of toxic persistent organochlorines to the Arctic-levels and consequences. *Sci Total Environ.* 106:43–53.

Stern, G.A., W.L. Lockhart, and M.G. Ikonomou. 2001. Temporal trends of organochlorine, organobromine and heavy metal contaminants in burbot from Fort Good Hope, Northwest Territories. In: Synopsis of Research Conducted under the 2000–2001 Northern Contaminants Program, Ottawa: Indian Affairs and Northern Development. pp. 230–236. ISBN 0-662-30872-7.

Stern, G.A., W.L. Lockhart, and M.G. Ikonomou. 2000. Temporal trends of organochlorine, organobromine and heavy metal contaminants in burbot from Fort Good Hope, NWT. In: Synopsis of Research Conducted under the 1999–2000 Northern Contaminants Program, Ottawa: Department of Indian Affairs and Northern Development. pp. 233–236. ISBN 0-662-29320-7.

Wagemann, R. 1985. Heavy metals in from the Mackenzie River at Fort Good Hope (April 1985 sampling). DFO report, Winnipeg, Canada. 10 pp.

New Persistent Chemicals of Concern in an Eastern Arctic Food Web

Project leaders

Gregg Tomy, Freshwater Institute, Fisheries and Oceans Canada, Winnipeg MB R3T 2N6; phone: (204) 983-5167; fax: (204) 984-2403; e-mail: tomyg@dfo-mpo.gc.ca; Paul Helm, Freshwater Institute, Fisheries and Oceans Canada, 501 University Crescent, Winnipeg, MB R3T 2N5; phone: (204) 983-7113; fax: (204) 984-2403; e-mail: helmpa@dfo-mpo.gc.ca

Project team

Wes Budakowski, Thor Halldorson, Gary Stern, Eric Braekevelt and Colin Fuchs, Fisheries and Oceans Canada, Winnipeg, Manitoba.

Abstract

Detecting and demonstrating bioaccumulation of current use or "new" chemicals in the Arctic environment is critical in the context of restricting such compounds under global agreements such as the Persistent Organic Pollutants protocol of the Convention on Long Range Transboundary Air Pollution and the Stockholm Convention on POPs. For this reason, and because of concerns about exposure of Arctic peoples to these chemicals through traditional diets, fluorinated surfactants such as PFOS and its precursors were studied in a food web from the Eastern Arctic including zooplankton, Arctic cod, deepwater redfish, shrimp, beluga, narwhal and walrus. The highest levels of PFOS were found in mammals illustrating that they do bioaccumulate. Metabolic differences were found between redfish and mammals in their ability to transform the PFOS precursor N-EtPFOSA. This transformation may also contribute to the higher levels of PFOS in narwhal and beluga.

Key Project Messages

1. Fluorinated compounds are accumulating in the Arctic food with highest concentrations observed in marine mammals.
2. Differences in abilities to transform fluorinated chemicals between species are apparent. Transformation of precursor compounds may contribute higher levels of PFOS in marine mammals in addition to bioaccumulation from lower trophic levels of the foodweb.

Objectives

1. To determine the levels of fluorinated organic compounds (FOCs) [perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA)], polychlorinated naphthalenes (PCNs), coplanar polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) in an archived marine food web from the Eastern Arctic.
2. To examine the extent of accumulation and transfer of FOCs, PBDEs and PCNs, and coplanar PCBs in the food web.

3. To establish baseline levels of these contaminants through a survey of the Eastern Arctic food web for comparison to future studies after possible addition of these compounds to international agreements (e.g. UN-ECE LRTAP — POPs Protocol; UNEP Global POPs Convention).

Introduction

The Arctic environment has become a sentinel for highlighting the persistence and accumulation potential of halogenated organic contaminants over the past few years. This has now been formalized in an international agreement, the United Nations — Economic Commission for Europe (UN-ECE) Convention on Long Range Transboundary Air Pollution — Protocol on Persistent Organic Pollutants (LRTAP-POPs protocol), in which the presence of compounds in "remote regions" in part fulfills the criteria for long range transport potential. This agreement and the recently negotiated Stockholm Convention on Persistent Organic Pollutants have mechanisms for adding new chemicals to the original list of banned or restricted compounds. Monitoring data and bioaccumulation information for new compounds are cited in documents assessing potential additions to these lists (e.g. Lerche et al., 2002).

In this study, three classes of compounds, perfluorinated acids, brominated diphenyl ethers, and chloronaphthalenes, are examined for their occurrence, accumulation and transfer in food web components from the Eastern Arctic. Perfluorinated acids are surfactants used in fabrics and other household products. PFOS has been detected in human blood (Hansen et al., 2001) and biota from around the globe including remote regions of the Canadian Arctic (Giesy and Kannan, 2001). Additionally, perfluorosulfonamide FOCs such as *n*-ethyl perfluorooctanesulfonamide [N-EtPFOSA], which is the insecticide Sulfuramid (used in the U.S), were included in this study. This compound can deethylate to form perfluorooctanesulfonamide (PFOSA), and both N-EtPFOSA and PFOSA can form PFOS (Tomy et al., unpublished data).

Polybrominated diphenyl ethers (PBDEs) are flame retardants used in a range of consumer products including textiles, furniture, and electronics. The estimated global consumption of these compounds indicates that their usage is on the rise (deWit, 2002). The usage patterns, persistence and hydrophobicity of PBDEs have resulted in startling increases in concentrations over the past two decades in ringed seal (Ikonomou et al., 2003) and beluga whales (Law et al., 2003) in the Canadian Arctic.

PCNs are a group of 75 compounds manufactured as complex technical mixtures for use as dielectrics for flame-resistance and insulating in capacitors, transformers, cable

Figure 1. Concentrations (arithmetic mean ± 1 standard error) of PFOS and PFOA (ng/g, wet wt.) in an Eastern Arctic food web

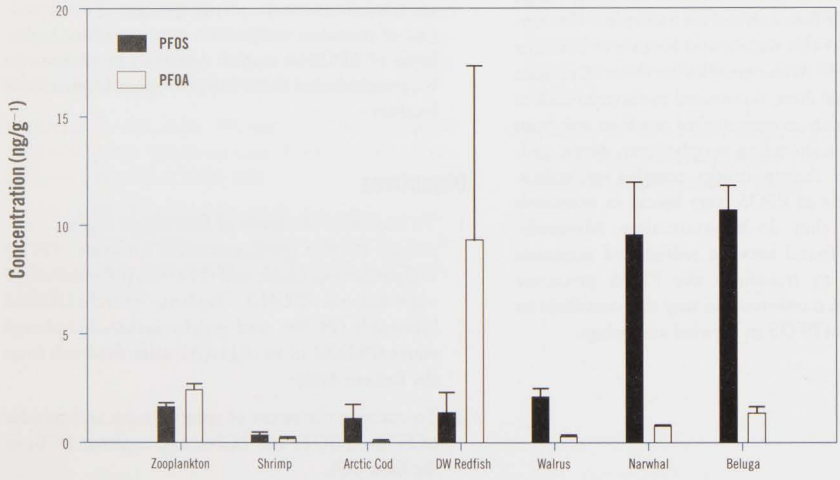
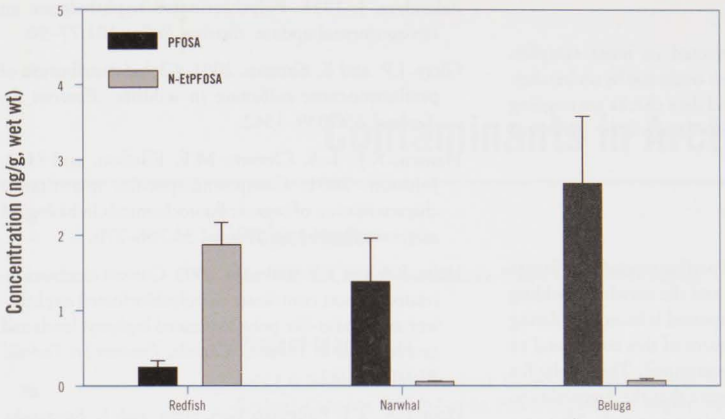


Figure 2. Concentrations (arithmetic mean ± 1 standard error) of N-EtPFOSA and PFOSA (ng/g, wet wt) in livers of redfish, narwhal and beluga from the Eastern Arctic



and wires, pre-dating the use of PCBs (Falandysz, 1998). In addition to evaporation from past-use materials, current sources of PCNs include PCB formulations (Yamashita et al., 2000) and emission from industrial and waste combustion processes (e.g. Abad et al., 1999; Helm and Bidleman, 2003). PCNs, proposed additions to the list of banned chemicals under the UN-ECE LTRAP-POPs protocol (Lerche et al., 2002), were found in beluga whales and ringed seals from the southern Baffin Island region of the Canadian Arctic (Helm et al., 2002).

Activities

In 2002–2003

Archived liver (FOCs) and blubber, zooplankton, and whole fish and shrimp (PBDEs and PCNs) were extracted and analyzed for the compounds of interest. Mammal samples were obtained through Fisheries and Oceans collection programs and sponsored by the NWMB. Fish and shrimp were obtained from trawls on Davis Strait in 2000 and 2001. Zooplankton were collected in Frobisher Bay in 2002. FOC and PBDE results were presented at the NCP Symposium in March 2003. FOC results were presented at Dioxin 2003 in Boston in August and a manuscript will be submitted on FOCs to the special issue of *Science of the Total Environment.* Currently, samples are being re-extracted and re-analyzed for PBDEs and PCNs.

Results

PFOS and PFOA

These compounds were detected in all animals. Figure 1 shows the levels of PFOS and PFOA in the food web from the Eastern Canadian Arctic. The highest concentrations of PFOS were found for beluga (PFOS: 8.7–14.3 ng/g, w/w) and narwhal (PFOS: 3.9–16.2 ng/g, w/w). PFOA levels were highest for the deepwater redfish (2.9–57 ng/g, w/w). PFOS (1.1–2.1 ng/g, w/w) and PFOA (1.7–3.4 ng/g, w/w) present in zooplankton are possibly due to uptake directly from the water.

The biomagnification factors (BMF = mean wet wt. concentration in predator/mean wet wt. concentration in prey) of PFOS and PFOA between beluga and cod were 9.4 and 5.4, respectively. Between narwhal and cod, respective PFOS and PFOA BMFs were 8.5 and 3.1.

Neutral sulfonamide precursors: N-EtPFOSA and PFOSA

Levels of N-EtPFOSA and PFOSA in the food web were also examined (Figure 2) since the biotransformation of N-EtPFOSA to PFOS in fish has been demonstrated (Tomy et al., 2003). One possible reaction pathway for the transformation of N-EtPFOSA to PFOS is via PFOSA. Deepwater redfish had the highest levels of N-EtPFOSA (1.3–2.9 ng/g) of all the animals. Concentrations in zooplankton, shrimp, cod, and walrus were below method detection limits. Relative to redfish, the higher

trophic level animals (beluga and narwhal) had much lower levels of N-EtPFOSA and higher levels of PFOSA.

PBDEs and PCNs

PBDEs and PCNs were detected in most samples. However, accurate quantification could not be undertaken due to an error. Re-analyses and data checks are ongoing for PBDEs and PCNs and this data will be presented when prepared.

Discussion

The highest concentrations of perfluorooctane sulfonate (PFOS) occurred in the beluga and the narwhal providing a clear indication that this compound is bioaccumulating in the Arctic. However, the source of this compound to these mammals is yet to be determined. The results for N-EtPFOSA and PFOSA indicate that the precursors to PFOS are present and accumulating as well. The predominance of PFOSA over N-EtPFOSA in the narwhal and beluga compared to the deepwater redfish suggest that metabolic capabilities differ between the species and that narwhal and beluga are more able to transform N-EtPFOSA. Such differences have been observed between marine species for other organochlorine contaminants (Boon et al., 1989). The higher concentrations of PFOS in these mammals may in part result from transformation of accumulated N-EtPFOSA in addition to the uptake of PFOS through the food web. This is an area for further study.

Acknowledgements

Arctic cod, redfish and shrimp were collected by scientists and crew aboard the *RV Paamiut* (Greenland Institute of Natural Resources) in Davis Strait. Tim Siferd and Paul Wilkinson (DFO) assisted in Frobisher Bay collections.

References

Abad, E., J. Caixach, and J. Rivera. 1999. Dioxin like compounds from municipal waste incinerator emissions: assessment of the presence of polychlorinated naphthalenes. *Chemosphere.* 38:109–120.

Boon, J.P., F. Eijgenraam, J.M. Everaarts, and J.C. Duinker. 1989. A structure-activity relationship (SAR) approach towards metabolism of PCBs in marine animals from different trophic levels. *Mar Environ Res.* 27:159–176.

DeWit, C.A. 2002. An overview of brominated flame retardants in the environment. *Chemosphere.* 46:583–624.

Falandysz, J. 1998. Polychlorinated naphthalenes: an environmental update. *Environ Pollut.* 101:77–90.

Giesy, J.P. and K. Kannan. 2001. Global distribution of perfluorooctane sulfonate in wildlife. *Environ Sci Technol.* 35:1339–1342.

Hansen, K.J., L.A. Clemen, M.E. Ellefson, and H.O. Johnson. 2001. Compound-specific, quantitative characterization of organic fluorochemicals in biological matrices. *Environ Sci Technol.* 35:766–770.

Helm, P.A. and T.F. Bidleman. 2003. Current combustion-related sources contribute to polychlorinated naphthalene and dioxin-like polychlorinated biphenyl levels and profiles in air in Toronto, Canada. *Environ Sci Technol.* 37:1075–1082.

Helm P.A., T.F. Bidleman, G.A. Stern, and K. Koczanski. 2002. Polychlorinated naphthalenes and coplanar polychlorinated biphenyls in beluga whale (*Delphinapterus leucas*) and ringed seal (*Phoca hispida*) from the Eastern Canadian Arctic. *Environ Pollut.* 19:69–78.

Ikonomou, M.G., R. Sierra, and R.F. Addison. 2002. Exponential increases of the brominated flame retardants, polybrominated diphenyl ethers, in the Canadian Arctic from 1981 to 2000. *Environ Sci Technol.* 36:1886–1892.

Lerche, D., E.J. van de Plassche, A. Schwegler, and F. Balk. 2002. Selecting chemical substances for the UN-ECE POP Protocol. *Chemosphere.* 47:617–630.

Law, R.J., M. Alaee, C. Allchin, J.P. Boon, M. LeBeuf, P. Lepom, and G.A. Stern. 2003. Levels and trends of polybrominated diphenylethers and other brominated flame retardants in wildlife. *Environ Inter.* 29:757–770.

Tomy, G.T., V.P. Palace, S.A. Tittlemier, W. Budakowski, E. Braekevelt, L. Brinkworth, and K. Friesen. 2003. Biotransformation of N-ethyl perfluorooctane sulfonamide (N-EtPFOSA) by rainbow trout liver microsomes. Aquatic Toxicity workshop, Ottawa, Sept 29–Oct 1.

Yamashita, N., K. Kannan, T. Imagawa, A. Miyazaki, and J.P. Giesy. 2000. Concentrations and profiles of polychloronaphthalene congeners in eighteen technical polychlorinated biphenyl preparations. *Environ Sci Technol.* 34:4236–4241.

Contaminants in Arctic Sea Ducks

Project leader

Mark Wayland, Environment Canada, Prairie and Northern Region.

Project team

Judit E.G. Smits and Tracy Marchant, University of Saskatchewan; H. Grant Gilchrist, Canadian Wildlife Service, Prairie and Northern Region; Jonathan Keating, Environment Canada, Prairie and Northern Region.

Abstract

Populations of many North American sea ducks are declining. Biomarkers may offer valuable insights regarding the health and fitness of sea ducks in relation to contaminant burdens. In this study we examined body condition, immune function, corticosterone stress response, liver glycogen levels and vitamin A status in relation to tissue concentrations of mercury, selenium and cadmium in female common eiders during the nesting period. The study was conducted in the eastern Canadian Arctic during July 2000. Hepatic mercury and selenium and renal cadmium concentrations ranged from 1.5–9.8, 6.5–47.5 and 74–389 $\mu g \cdot g^{-1}$, dry wt, respectively. Mercury concentrations were negatively related to dissection body mass, heart mass and fat mass. Cadmium concentrations were negatively related to mass at capture and dissection mass after controlling for the mercury concentration-dissection mass relationship. Cell-mediated immunity was assessed by the skin swelling reaction to an injection of phytohemagglutinin-P, and was unrelated to metal concentrations. After adjusting the corticosterone concentration to account for the time between capture and sampling, there was a negative relationship between the residual corticosterone concentration and selenium. Liver glycogen concentrations were not significantly related to metal concentrations. Mercury concentrations were positively related to those of hepatic retinol and retinyl palmitate and the ratio of the retinol to retinyl palmitate in liver. They were negatively related to the ratio of plasma to liver retinol. Our findings do not indicate that exposure to metals may have adversely affected the health of these birds. They do, however, suggest that more research is required to elucidate mechanisms by which exposure to these metals could impact body condition.

Key Project Messages

1. Populations of eider ducks and other sea ducks are declining. The reasons for the declines are not known but contaminants have been suggested as one of the possible causes.
2. Biomarkers can offer valuable insights about the health of animals. When linked to information about contaminant burdens, they can provide valuable information about whether contaminants are affecting the health of animals. If contaminants are negatively affecting the health of sea ducks, their reproductive success and survival, and therefore population levels, may ultimately be affected.
3. Our study was done at a common eider duck breeding colony on Southampton Island during July 2000.
4. The study linked levels of mercury, cadmium and selenium in tissues of eider ducks to various biomarkers that reflect the overall health of the animals.
5. In general we found that the health-related biomarkers that we examined were not negatively impacted by contaminants, although one biomarker, body condition, was negatively related to contaminant burdens. This

finding has been reported in other studies of wild sea ducks. However, the finding is not supported by experimental research in which captive birds have been fed large amounts of mercury, cadmium or selenium. Studies must be undertaken to determine why the findings of our and other studies of wild ducks differ so much from those of controlled, experimental studies.

Objectives

To examine the relationship between biomarker responses (immune function, stress response, glycogen levels, vitamin A status, and body condition) and tissue concentrations of mercury, selenium and cadmium in nesting common eider ducks.

Introduction

The northern common eider (*Somateria mollissima borealis*) is a subspecies of sea duck that breeds in Arctic and subArctic coastal areas of Canada and Greenland. Like other species of sea ducks in North America, its population has declined in recent decades (Canadian Wildlife Service et al., 1998; Gratto-Trevor et al., 1998; Robertson and Gilchrist, 1998; Suydam et al., 2000). Contaminants are believed to be one of several risk factors that may be contributing to these declines (Canadian Wildlife Service, 1998). Toxic trace elements have been found at elevated concentrations in North American sea ducks, including the northern common eider (Henny et al., 1991, 1995; Hoffman et al., 1998; Trust et al., 2000; Wayland et al., 2001). In contrast, organochlorine concentrations are usually very low in sea ducks (Elliott and Martin, 1998; Olafsdottir et al., 1998). Several factors combine to make the northern common eider a good bioindicator species for examining metal contamination in North American sea ducks. For example, trace metal concentrations and recent population trends are broadly comparable between the northern common eider and other species of North American sea ducks (Wayland et al., in press). Furthermore, its colonial nestling habits make it feasible to catch and sample large numbers of birds in the wild.

Population dynamics of sea ducks are strongly influenced by survival rates of adults, whereas reproductive success, at least in the short term, has little effect (Goudie et al., 1994). Therefore, if contaminants are contributing to population declines in sea ducks, they are most likely doing so by interacting with natural environmental stressors in such a way as to reduce adult survival rates. For example, contaminants, through their possible effects on energy and nutrient metabolism and the immune system (Lawrence, 1985; Hontela, 1997), may reduce the ability of adults to withstand severe winter weather conditions or the rigors of nesting. Such stressors may lead to mortality or a heightened susceptibility to disease (Korschgen, 1977; Fournier and Hines, 1994).

At present, logistical considerations limit the ability of researchers to conduct long-term studies that would directly link the survival of sea ducks to their contaminant burdens. However, the use of biomarkers may provide a reasonable alternative to such studies. Biomarkers are valuable tools because they can provide insight into the health status of individual animals (Depledge et al., 1993). Such insights may be improved by simultaneously examining a suite of biomarkers, chosen specifically to reflect animal health and fitness (Stegeman et al., 1993). When linked to information about contaminant levels, it may be possible to ascertain whether exposure to contaminants is affecting the health and fitness of a particular population of animals.

Body condition may be considered as a general biomarker of effect (Stegeman et al., 1993) in sea ducks because it has been related to exposure to metals (Debacker et al., 2000; Spalding et al., 2000; Yamamoto and Santolo, 2000; Takekawa et al., 2002) and is an important determinant of fitness and survival in ducks (Milne, 1976; Bergan and Smith, 1993). Similarly, changes in the immune system, which can affect susceptibility to disease, may provide sensitive, early warning signals of the toxic effects of metals (Lawrence, 1985; Weeks et al., 1992). Another potentially-useful biomarker that may be affected by exposure to toxic metals is the response to acute stress, as evaluated by measurements of corticosteroids (Hontela, 1997). Corticosteroid hormones are relevant to animal health and fitness because of their role in regulating energy metabolism, maintaining osmotic balance and suppressing immune responses (Hontela, 1997). When accompanied by measurements of glycogen reserves, it is possible to assess whether contaminant-induced changes in adrenal function are having an effect on the physiological status and fitness of the animal. Glycogen reserves are strongly influenced by corticosteroid activity and are an important source of energy in fasting animals (Hontela, 1997). Vitamin A is an essential micronutrient involved in growth, development, reproduction and immune function (Underwood, 1984; Dennert, 1984). It has been widely applied as a biomarker in studies examining the effects of chlorinated hydrocarbons on wildlife (Rolland, 2000). Vitamin A storage and metabolism are also known to be affected by exposure to certain metals such as cadmium (Sugawara and Sugawara, 1978; Massanyi et al., 1999).

In this study, we used a biomarker approach to assess whether exposure to cadmium, mercury and selenium is affecting the health and fitness of nesting, female common eiders at a location in the Canadian Arctic. We specifically examined relationships between tissue metal concentrations and body condition, immune function, the corticosteroid stress response, glycogen reserves and vitamin A concentrations.

Activities

In 2000–2001

This study was conducted at a common eider breeding colony located within the East Bay Migratory Bird Sanctuary in Nunavut, Canada (64°04'N, 82°00'W) between July 4–23, 2000.

Twenty-one female common eiders were captured on nests between the second and third week of incubation. A standardized field protocol was used to collect data or samples for assessment of (1) immune function (2) stress response (3) liver glycogen levels (4) vitamin A status, (5) body condition (6) body size (7) liver mercury and selenium concentrations and (8) kidney cadmium concentrations.

Immune function was assayed by the skin swelling response to an intradermal injection of the mitogen phytohemagglutinin-P. Stress response was defined as the residual of the corticosterone concentration after adjustment for time since capture. Vitamin A status was investigated by determining concentrations of retinol in plasma and liver and retinyl palmitate in liver and by calulating ratios of plasma to liver retinol and liver retinol to liver retinyl palmitate. Overall body size was estimated from various morphometric measurements that were integrated in a principal components analysis. Various indices of body condition were used including body mass at capture, body mass at dissection (birds were killed one day after capture), heart mass, liver mass, kidney mass and spleen mass and mass of abdominal and leg fat. Where necessary these masses were adjusted for body size.

Statistics

Data were checked for normality (W-statistic, PROC UNIVARIATE, SAS Institute, 1988). Where necessary, data were transformed using log, square-root or rank (Conover and Imam, 1981) transformations to normalize data. Principal component analysis was used to derive a principal component (PC1) from the combination of HL, BL, CL, NL, TL, WL and KL. PC1 explained 56% of the variability and was positively correlated with each morphometric variable. It was used an index of structural size. We regressed body/organ masses on PC1 and used residuals from those relationships with P-values < 0.1 in subsequent analyses (Kellett and Alisauskas, 2000).

We defined the stress response in two ways: (1) the residual corticosterone concentration in the first blood sample taken as soon as possible following capture (8 ± 5 min, mean ± 1SD, 4–23 min, range), and (2) the residual corticosterone concentration in the second sample taken 23–50 min after capture (37 ± 6 min, mean ± 1SD, 23–51 min, range). Residuals were calculated as differences between observed concentrations and those expected based on the linear relationship between corticosterone concentration and time since capture (corticosterone = $10.8 + 0.8\ \text{time}_{\text{minutes}}$, $P < 0.0001$, $R^2 = 0.45$) and capture mass.

We used residuals from relationships with P-values < 0.1 in subsequent analyses. In these preliminary analyses that examined relationships between biomarkers and potential covariates such as body size and weight and, in the case of corticosterone, time since capture, we used the more liberal significance value of 0.1 (than the traditional 0.05), because we believed it would be more appropriate to account for the possible influence of these covariates than it would be to ignore their possible influence.

Then, multiple regression (forward selection method, PROC REG, SAS Institute, 1988) was used to examine the relationship between tissue metal concentrations (independent variables) and biomarker responses (dependent variables). A significance level of 0.05 was used for these analyses. However, in keeping with the contention that statistical hypothesis testing has been overused in wildlife science and that more importance needs to be placed on describing the strength and direction of effects (Guthery et al., 2001), we also report trends in the data and use graphs to describe the relationships.

Results

Metal concentrations

The geometric mean hepatic selenium concentration in the eiders was 16.1 $\mu g \cdot g^{-1}$ (range: 6.5–47.5) (Table 1). Mercury concentrations in liver averaged 3.3 $\mu g \cdot g^{-1}$ (range: 1.5–9.8) while those of cadmium in kidneys averaged 164.6 $\mu g \cdot g^{-1}$ (range: 74.1–389.1). Metal concentrations were not correlated with one another (all P values ≥ 0.28). The selenium: mercury molar ratio averaged 15.1 ± 10.8 (mean ± 1SD) and ranged from 4.8–51.7.

Body condition and metals

Body and organ masses were not significantly correlated with our index of structural size (PC1) (all P values > 0.1). Therefore, it was not necessary to adjust for structural size before examining the relationships between metals and body and organ masses. Hepatic mercury concentrations were negatively related to dissection mass ($P = 0.016$, $R^2 = 0.27$), heart mass ($P = 0.007$, $R^2 = 0.32$) and fat mass ($P = 0.007$, $R^2 = 0.33$) (Table 2, Fig. 1). After controlling for its relationship to mercury concentration, dissection mass was negatively related to renal cadmium and the relationship was nearly significant ($P = 0.056$, $R^2 = 0.14$) (Table 2). Cadmium concentration was also negatively related to capture mass ($P = 0.02$, $R^2 = 0.25$) (Fig. 1). Kidney mass was positively related to hepatic selenium, the relationship approaching significance ($P = 0.07$, $R^2 = 0.16$) (Table 2). After controlling for selenium, kidney mass was negatively related to cadmium concentration ($P = 0.03$, $R^2 = 0.14$) (Table 2).

Table 1. Geometric means, 95% confidence limits and ranges of hepatic selenium and mercury and renal cadmium in 21 female, nesting common eiders. Units are in $\mu g \cdot g^{-1}$, dry wt

Metal	Mean	95% CL	Range
Selenium	16.2	12.8–20.4	6.5–47.5
Mercury	3.3	2.6–4.2	1.5–9.8
Cadmium	164.6	138.0–196.3	74.1–389.1

Immune function

Cell-mediated immunity as evaluated by the PHA skin test was not significantly related to metal concentrations ($P = 0.27$) (Table 2). The PHA skin response averaged 0.5 mm (1SE = 0.19, range = −0.05–3.60).

Stress response

The residual corticosterone concentration in the first blood sample, taken as soon as possible after capture, was

Table 2. Summary of results of multiple regressions of various response variables on tissue trace element concentrations in nesting, female common eider ducks

Variable	Model Step	Trace Element[a]	Slope	Partial R^2	Pr > F
Body mass at 1st capture	1	Cd	−486.6	0.25	0.021
Body mass at dissection	1	Hg	−382.8	0.26	0.016
	2	Cd	−370.8	0.14	0.056
Liver mass	–	–	–	–	–
Kidney mass	1	Se	3.6	0.16	0.071
	2	Cd	−5.2	0.19	0.03
Spleen mass	–	–	–	–	–
Heart mass	1	Hg	−5.5	0.33	0.007
Fat mass[b]	1	Hg	−4.1	0.33	0.007
CMI[c]	–	–	–	–	–
Stress response 1[d]	1	Se	−16.5	0.17	0.067
Stress response 2[e]	–	–	–	–	–
Plasma retinol	–	–	–	–	–
Liver retinol[f]	1	Hg	0.82	0.32	0.008
Liver retinyl palmitate	1	Hg	291.8	0.2	0.04
$retinol_{plasma}/retinol_{liver}$[g]	1	Hg	−16.9	0.37	0.004
retinol/retinyl palmitate[g]	1	Hg	4.0	0.23	0.029

NOTE: Variables in rows with dashed lines had P-values > 0.1

[a] concentrations of all trace elements were $\log_{10}$-transformed prior to analysis. Mercury and selenium were analyzed in livers and cadmium was analyzed in kidneys

[b] values were square root-transformed

[c] rank-transformed values for cell-mediated immunity based on PHA skin test as described in Methods

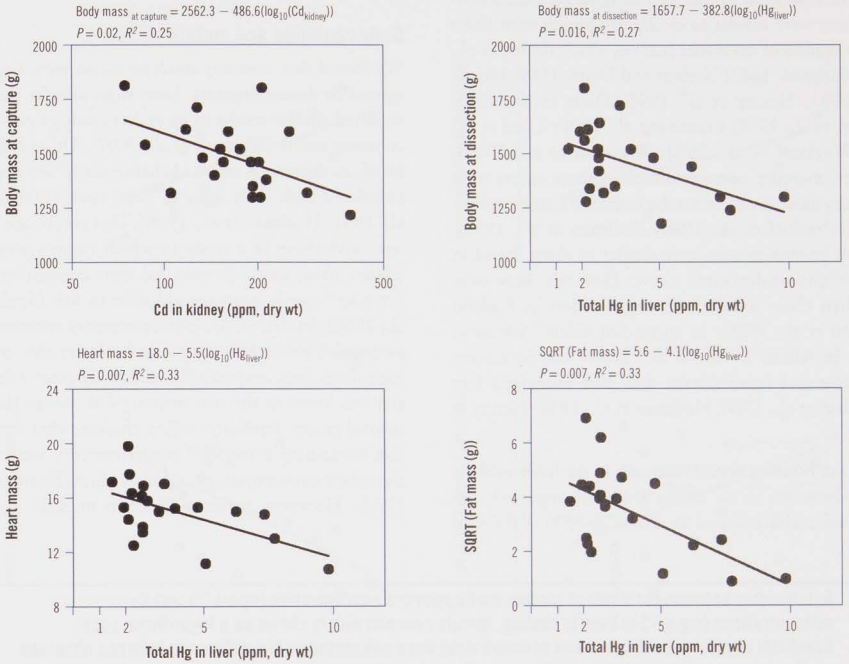
[d] measured as time-adjusted residual plasma corticosterone concentration determined in the first 20 min after capture

[e] measured as time-adjusted residual plasma corticosterone concentration determined between 25–50 min after capture

[f] values were $\log_{10}$-transformed prior to analysis

[g] values were rank-transformed prior to analysis

Figure 1. Relationship between the concentration of Cd in kidney and and body mass at capture (upper left), and the concentration of Hg in liver and body mass at dissection (upper right), heart mass (lower left) and fat mass (lower right) in nesting, female common eiders. Metal concentrations were $\log_{10}$-transformed and fat mass was square-root transformed prior to analysis



negatively related to hepatic selenium concentration, but the relationship was not quite significant (P = 0.061, R^2 = 0.17) (Table 2, Fig. 2). It was not significantly related to mercury or cadmium (P values > 0.05). After accounting for the amount of time since capture, the residual corticosterone concentration in the second set of blood samples, taken approximately 30 min following capture, was positively related to capture mass (P = 0.008). After accounting for time since capture and capture mass, there were no significant relationships between residual corticosterone concentrations in the second set of blood samples and tissue metal concentrations (P > 0.05). Corticosterone concentrations in the second series of blood sample averaged 42.2 ng·ml^{-1} (1SE = 3.3, range = 13.4–72.1).

Glycogen

Glycogen concentrations in liver were not significantly related to metal concentrations (P > 0.5). Glycogen concentrations averaged 3.6 mg·g^{-1} (1SE = 0.85, range = 0.6–17.1).

Vitamin A

Retinol, retinyl palmitate, the ratio of serum to liver retinol and the ratio of liver retinol to retinyl palmitate were not significantly related to capture mass or dissection mass (all P values ≥ 0.35).

Mercury concentration was positively related to retinol (P = 0.008, R^2 = 0.32) and retinyl palmitate concentrations in liver (P = 0.045, R^2 = 0.2) (Table 2, Fig. 3). The ratio of serum to liver retinol was negatively related (P = 0.004, R^2 = 0.37) and that of liver retinol to liver retinyl palmitate was positively related to mercury (P = 0.03, R^2 = 0.23) (Table 2, Fig. 3). Cadmium and selenium were not significantly related to the above measures of vitamin A status (P > 0.05) and serum retinol was not significantly related to any of the three metals (P = 0.05).

Discussion

Metal concentrations

In these nesting, female common eiders, hepatic mercury concentrations were similar to and renal cadmium concentrations were similar to or slightly higher than those in other studies of sea ducks (Lande, 1977; Karlog et al., 1983; Norheim, 1987; Nielsen and Dietz, 1989; Henny et al., 1991; Henny et al., 1995; Dietz et al., 1996; Hollmén et al., 1998; Franson et al., 2000; Trust et al., 2000; Wayland et al., 2001; Wayland et al., 2002). However, mercury concentrations in these eiders were lower than those found in sea ducks in San Francisco Bay, USA (Ohlendorf et al., 1986; Hoffman et al., 1998). Selenium concentrations were similar to those found in several of the studies cited above. However, they were lower than those found in common eiders in Finland (Hollmén et al., 1998), in spectacled eiders (*Somateria fischeri*) in Alaska (Trust et al., 2000) and in scoters (*Melanitta* sp.) from Alaska and San Francisco Bay (Ohlendorf et al., 1986; Hoffman et al., 1998; Henny et al., 1995).

We did not measure organic mercury in the livers of these eiders. However, in an earlier study we reported that organic mercury accounted for about 70–88% of the total mercury found in the livers of eiders (Wayland et al., 2001). This agrees with the findings of Scheuhammer et al. (1998) who found that organic mercury comprised the majority of the mercury in the livers of birds when total mercury levels were relatively low (< 10 $\mu g \cdot g^{-1}$ dry wt).

Body condition and metals

We found that mercury concentrations were negatively related to dissection mass, heart mass and fat mass. We reported similar results in an earlier study of pre-nesting common eiders (Wayland et al., 2002). Other field studies of sea ducks also reported that mercury was negatively correlated with body mass or heart mass (Ohlendorf et al., 1991; Hoffman et al., 1998). Our results are consistent with those of a study in which captive great egret (*Ardea albus*) nestlings were fed diets containing 0.5 or 5 $mg \cdot kg^{-1}$ methylmercury chloride in fish (Spalding et al., 2000). In that study, hepatic mercury concentrations averaged 15 and 140 $\mu g \cdot g^{-1}$ in birds on the low- and high-dose diets, respectively, and body mass relative to size was lower in the two mercury-fed groups than in a control group. Similarly, young chickens that were fed a diet containing 6 $mg \cdot kg^{-1}$ methylmercury weighed less than their counterparts on a control diet (Fimreite et al., 1970). However, mercury levels in mussels, the most

Figure 2. Relationship between residuals of plasma corticosterone concentration ($ng \cdot mL^{-1}$) and Se concentrations ($\mu g \cdot g^{-1}$) in liver in nesting, female common eiders shown on a logarithmic scale. Residuals of plasma corticosterone concentration were calculated as the difference between observed corticosterone concentrations and those predicted from the relationship between corticosterone concentrations and the amount of time from capture until blood samples were taken (corticosterone = 10.8 + 0.8time$_{minutes}$, $P < 0.001$, $R^2 = 0.45$). It was necessary to add 11.2 to all residual corticosterone concentrations in order to be able to log-transform them prior to analysis

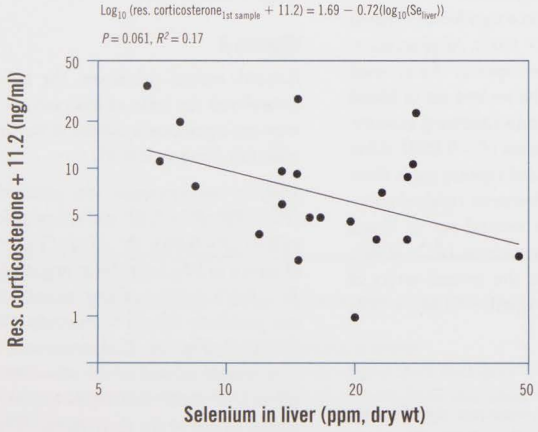
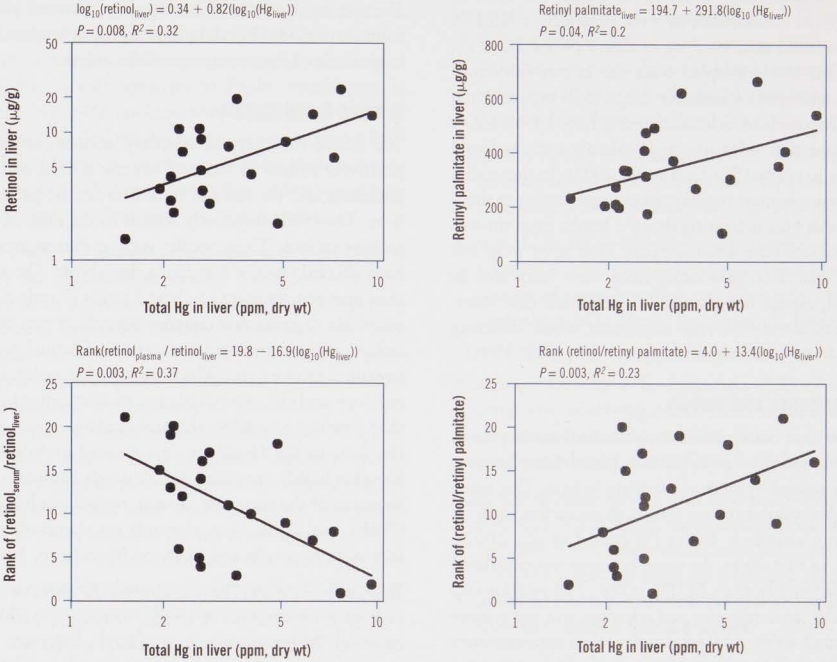


Figure 3. Relationships between log_{10}-transformed concentrations of Hg in liver and the following measurements of vitamin A status: log_{10}-transformed concentrations of retinol in liver (upper left), concentrations of retinyl palmitate in liver (upper right), the rank-transformed ratio of retinol in serum to retinol in liver (lower left) and the rank-transformed ratio of retinol in liver to retinyl palmitate in liver (lower right)



important food for eiders (Bustnes and Erikstad, 1988) are much lower than the dietary doses cited above, usually less than 0.1 $\mu g \cdot g^{-1}$ (Dietz et al., 1996; Rigert et al., 2000). Thus, their findings may not be directly applicable to eiders. Furthermore, several studies in which adult birds were fed relatively high concentrations of mercury in the diet did not show evidence of lower body weights in the mercury-dosed groups (Fimreite, 1971; Heinz, 1979; Heinz and Hoffman, 1998).

We found that cadmium concentrations were negatively related to capture mass, dissection mass and kidney mass. We reported similar findings in earlier studies, specifically that cadmium was negatively related to body mass and fat mass in pre-nesting, female common eiders (Wayland et al., 2001, 2002). Other field studies of sea ducks have reported negative correlations between cadmium concentrations and body mass (Henny et al., 1991; Franson et al., 2000). However, as was the case for mercury, there is little experimental evidence that cadmium has an effect on body mass of adult birds (White and Finley, 1978; DiGiulio and Scanlon, 1985; Bennett et al., 2000).

The lack of agreement between experimental feeding studies and field studies may indicate that cadmium and mercury can affect body condition of wild birds through indirect mechanisms that are not present among captive birds. An alternative explanation is that, in the wild, cadmium and mercury concentrations fluctuate seasonally, in response to normal patterns of weight gain and loss (Rattner and Jehl Jr., 1997). In our study, birds were incubating eggs, an activity that lasts for approximately 24 days during which time they do not eat (Parker and Holm, 1990; Bottita, 2001). Consequently, eiders lose about 25% of their body mass during incubation (Parker and Holm, 1990). During this period, it is likely that relatively immobile metals such as cadmium and mercury would become increasingly concentrated in the declining pool of tissue.

Immune function and metals

We did not find evidence that the cell-mediated immune response to an injection of PHA-P was affected by exposure to mercury, cadmium or selenium at the levels observed in this study. In an earlier study, we reported that selenium concentrations were positively related to PHA-P-induced skin swelling in eiders (Wayland et al., 2002). This result coupled with the known beneficial effects of selenium on immune function in experimental animals (Kiremidjian-Schumacker and Roy, 1998), led us to speculate that selenium may enhance cell-mediated immunity in eiders (Wayland et al., 2002). In our earlier study, tissue selenium concentrations were similar to those found in this one, indicating that the results from the two studies should have been similar. That they were not suggests that our previously-held view may not be warranted, especially when it is considered that inter-annual consistency is very important when inferring causality from contaminant exposure data (Fox, 1991).

Stress response and metals

We found that corticosterone concentrations in plasma in the first series of post-capture blood samples were negatively related to those of selenium in liver. This result is somewhat similar to our results in an earlier study of pre-nesting common eiders (Wayland et al., 2002). However, in that study, the stress response was calculated slightly differently than in this study. The relationship between the stress response and selenium was not evident in the second series of blood samples taken approximately 30 min following capture. In agreement with our findings based on the first blood sample, selenium reduced corticosterone synthesis in seal adrenal glands (Freeman and Sangalang, 1977) while relatively high plasma selenium concentrations were associated with low basal serum cortisol levels in humans (Erfurth et al., 1990). In contrast, acute exposure to selenium was associated with increased corticosterone concentrations in rats (Rasekh et al., 1991; Potmis et al., 1993) while selenium deficiency was associated with reduced corticosterone secretion *in-vitro* (Chanoine et al., 2001). The implications of varying levels of dietary intake of selenium over the long term need to be evaluated in order to understand whether selenium status of these sea ducks affects their corticosterone response to acute stress.

In an earlier study (Wayland et al., 2002), we found that cadmium levels were positively related to corticosterone stress responses of fasting, female eiders during the nesting period. The finding was supported by experimental evidence that mallards (*Anas platyrhynchos*) that were simultaneously food-restricted and exposed to cadmium had higher concentrations of corticosterone than their non-cadmium exposed and non-food-restricted counterparts (Di Giulio and Scanlon, 1985). In this study, we did not find evidence of a relationship between cadmium and the corticosterone stress response in nesting eiders. Because of the lack of consistency between years, we cannot conclude that cadmium exposure is related to the magnitude of the stress response in eiders.

Vitamin A and metals

We found that hepatic mercury concentrations were positively related to those of hepatic retinol and retinyl palmitate and the ratio of retinol to retinyl palmitate in liver. They were negatively related to the ratio of plasma to liver retinol. These results suggest that mercury may have affected vitamin A status in these birds. The relationship between mercury levels and ratios of retinol:retinyl palmitate suggests that mercury may affect processes that influence the enzymatic conversion of retinyl palmitate to retinol or vice versa. The negative relationship between mercury and the ratio of plasma to liver retinol suggests that mercury may affect the mobilization of retinol from the liver to the blood stream. Retinol mobilization to blood is highly regulated and depends primarily on the secretion of the transport protein, retinol-binding protein (RBP), which, in turn, depends on the availability of retinol in liver cells and in blood (Goodman, 1984).

Relatively few studies have examined the effect of mercury exposure on vitamin A status. Mercury, provided at extremely high concentrations in food to pigs and rabbits, was associated with a reduction in vitamin A in their livers (Abdelhamid, 1988; Raszyk et al., 1992). However, in those studies, the authors found evidence of damage to kidneys, livers and other organs. Such damage can affect the storage, metabolism and excretion of vitamin A (Goodman, 1984; Underwood, 1984). There was no histopathological evidence of damage to livers and kidneys of common eiders with tissue concentrations of mercury and other metals that were similar to those found in this study (Wayland et al., 2001). Thus, the results of those experimental studies are probably not applicable to our study. The relatively low levels of mercury in eider livers in this study coupled with the relatively high selenium to mercury molar ratios should have precluded any toxic effects of mercury (Scheuhammer, 1987). We are unaware of studies that have examined the relationship between vitamin A status and relatively low but chronic mercury exposure. Such studies are needed in order to properly interpret the results we obtained.

There is much evidence that halogenated aromatic hydrocarbons (HAHs), such as PCBs and dioxins, have affected

the vitamin A status of wildlife (Rolland, 2000). We cannot discount the possibility that variation in our vitamin A data may have been attributable to exposure to HAHs (which we did not measure). However, HAH concentrations in livers of eiders are normally very low (total PCBs < 0.1 $\mu g \cdot g^{-1}$ wet wt, Olafsdottir et al., 1998). In comparison, Murk et al. (1998) estimated that the vitamin A status of European otters (*Lutra lutra*), a species that is very sensitive to PCBs, would not be affected when PCB concentrations in their livers were ≤ 4 $mg \cdot kg^{-1}$ (based on the sum of seven common PCB congeners). Based on the results of these studies, we do not believe that HAH exposure in these eiders would have been sufficient to affect their vitamin A status.

In this study, 15 multiple regression tests were used to examine the relationships between metal concentrations and biomarker responses. This could lead to the reporting of spurious significant results. Therefore, we have interpreted the results conservatively in order to avoid placing too much emphasis on statistical significance. We have emphasized the similarity or dissimilarity of these results to those we reported in an earlier paper (Wayland et al., 2002) and to those described elsewhere in the literature. Further, we have questioned the validity of some significant results that either were inconsistent with results reported in earlier studies or did not conform with accepted theory. At most, we have contended that such significant results may provide a basis for further research. Only when our results were supported by theory and consistent with results reported elsewhere in the literature have we suggested that the relationships were likely to be 'real'.

Overall, most of the results of this study and our earlier studies (Wayland et al., 2001; Wayland et al., 2002) have failed to consistently show adverse health-related effects that could be attributed to exposure to mercury, selenium or cadmium. However, relatively high tissue concentrations of mercury and cadmium were consistently associated with relatively poor body condition, a finding that was supported by other field studies but not supported by experimental dosing studies using captive birds. Future research should determine whether exposure of free-living birds to metals can affect their body condition through mechanisms that are not operative in experimental studies using captive animals.

Expected Completion Date

Project has been completed.

References

Abdelhamid, A.M. (1988). Effect of dietary contamination with mercury on the performance of rabbits. *Archives of Tiernahr.* 38:207–214.

Bennett, D.C., M.R. Hughes, J.E. Elliott, A.M. Scheuhammer, and J.E. Smits. 2000. Effect of cadmium on pekin duck total body water, water flux, renal filtration, and salt gland function. *J Toxicol Environ Health.* Part A 59:43–56.

Bergan, J.F. and L.M. Smith. 1993. Survival rates of female mallards wintering in the Playa Lakes Region. *Journal of Wildlife Management.* 57:570–577.

Bottita, G.E. 2001. Effects of body condition and environmental variability on incubation behaviour and nest success of arctic-breeding common eiders (*Somateria mollissima*). MSc Thesis. Peterborough, Ontario: Trent University.

Bustnes, J.O. and K.E. Erikstad. 1988. The diet of sympatric wintering populations of common eider, *Somateria mollissima* and king eider, *S. spectabilis* in northern Norway. *Ornis Fennica.* 65:163–168.

Canadian Wildlife Service, U.S. Fish and Wildlife Service, and U.S. Geological Survey (Biological Resources Division). 1998. Conservation issues for North American Seaducks: a concept paper for a Seaduck Joint Venture under the North American Waterfowl Management Plan. Ottawa: Canadian Wildlife Service.

Chanoine, J.-P., N.A. Compagnone, A.C.K. Wong, and S.H. Mellon. 2001. Modulation of steroidogenesis by selenium in a novel adrenal cell line developed using targeted tumorigenesis. *Biofactors.* 14:229–238.

Conover, W.J. and R.L. Iman. 1981. Rank transformation as a bridge between parametric and non-parametric statistics. *The American Statistician.* 35:124–129.

Debacker, V., T. Jauniaux, F. Coignoul, and J.-M. Bouquegneau. 2000. Heavy metals contamination and body condition of wintering guillemots (*Uria aalge*) at the Belgian coast from 1993 to 1998. *Environ Res.* 84: 310–317.

Dennert, G. 1984. Retinoids and the immune system: immunostimulation by vitamin A. In: M.B. Sporn, A.B. Roberts and D.S. Goodman (eds.). *The retinoids. Vol.2*, pp. 373–390. Orlando: Academic Press.

Depledge, M.H., J.J. Amaral-Mendes, B. Daniel, R.S. Halbrook, P. Kloepper-Sams, M.N. Moore, and D.B. Peakall. 1993. The conceptual basis for the biomarker approach. In: D.B. Peakall and L.R. Shugart (eds.).

Biomarkers: research and application in the assessment of environmental health. NATO ASI Series H, Cell Biology, Vol. 68, pp. 15–29. Berlin: Springer-Verlag.

Di Giulio, R.T. and P.F. Scanlon. 1985. Effect of cadmium ingestion and food restriction on energy metabolism and tissue metal concentrations in mallard duck (*Anas platyrhynchos*). *Environ Res.* 37:433–444.

Dietz, R., F. Riget, and P. Johansen. 1996. Lead, cadmium, mercury and selenium in Greenland marine animals. *Sci Total Environ.* 186:67–93.

Elliott, J.E. and P.A. Martin. 1998. Chlorinated hydrocarbon contaminants in grebes and seaducks wintering on the coast of British Columbia, Canada, 1988–1993. *Environmental Monitoring and Assessment.* 53:337–363.

Erfurth, E.M., A. Schutz, A. Nilsson, L. Barregard, and S. Skerfving. 1990. Normal pituitary hormone response to thyrotropin and gonadotrophin releasing hormones in subjects exposed to elemental mercury vapour. *British Journal of Independent Medicine.* 47: 639–644.

Fairbrother, A. and J. Fowles. 1990. Subchronic effects of sodium selenite and selenomethionine on several immune functions in mallards. *Arch Environ Contam Toxicol.* 19:836–844.

Fimreite, N. 1970. Effects of methylmercury treated feed on the mortality and growth of leghorn cockerels. *Can J Ani Sci.* 50:387–389.

Fimreite, N. 1971. Effects of dietary methylmercury on ring-necked pheasants, with special reference to reproduction. Canadian Wildlife Service Occasional Paper 9, Ottawa: Canadian Wildlife Service.

Fournier, M. and J.E. Hines. 1994. Effects of starvation on muscle and organ mass of king eiders *Somateria spectabilis* and the ecological and management implications. *Wildfowl.* 45:188–197.

Fox, G.A. 1991. Practical causal inference for ecoepidemiologists. *J Toxicol Environ Health.* 33:359–373.

Franson, J.C., T. Hollmén, R.H. Poppenga, M. Hario, and M. Kilpi. 2000. Metals and trace elements in tissues of common eiders (*Somateria mollissima*) from the Finnish archipelago. *Ornis Fennica.* 77:57–63.

Freeman, H.C. and G.B. Sangalang. 1977. A study of the effects of methyl mercury, cadmium, arsenic, selenium, and PCB, (Aroclor 1254) on adrenal and testicular steriodogenesis in vitro, by the grey seal *Halichoerus grypus. Arc Environ Con Toxicol.* 5:369–383.

Goodman, D.S. 1984. Plasma retinol-binding protein. In: M. Sporn, A. Roberts and D.S. Goodman (eds.). *The retinoids, Vol. 2*, pp. 42–88. Orlando: Academic Press.

Goto, N., H. Kodama, K. Okada, and Y. Fujimoto. 1978. Suppression of the phytohemagglutinin skin response in thymectomized chickens. *Poul Sci.* 57:246–250.

Goudie, R.I., S. Brault, B. Conant, A.V. Kondratyev, M.R. Peterson, and K. Vermeer. 1994. The status of sea ducks in the north Pacific Rim: towards their conservation and management. *Transactions of the North American Wildlife and Natural Resources Conference.* 59:27–49.

Gratto-Trevor, C.L., V.H. Johnston and S.T. Pepper. 1998. Changes in shorebird and eider abundance in the Rasmussen lowlands, NWT. *Wilson Bulletin.* 110: 316–325.

Guthery, F.S., J.J. Lusk, and M.J. Peterson. 2001. The fall of the null hypothesis: liabilities and opportunities. *Journal of Wildlife Management.* 65:379–384.

Heinz, G.H. 1979. Methylmercury: reproductive and behavioural effects on three generations of mallard ducks. *Journal of Wildlife Management.* 43:394–401.

Heinz, G.H. and D.J. Hoffman. 1998. Methylmercury chloride and selenomethionine interactions on health and reproduction in mallards. *Environ Toxicol Chem.* 17:139–145.

Henny, C.J., L.J. Blus, R.A. Grove, and S.P. Thompson. 1991. Accumulation of trace elements and organochlorines by surf scoters wintering in the Pacific Northwest. *Northwest Naturalist.* 72:43–60.

Henny, C.J., D.D. Rudis, T.J. Roffe, and E. Robinson-Wilson. 1995. Contaminants and sea ducks in Alaska and the circumpolar region. In: R. Rolland, M. Gilbertson and T. Colborn (eds.). *Environmentally-induced alterations in development: a focus on wildlife*, pp. 41–49. *Environ Health Persp.* 103 Supplement 4.

Hoffman, D.J., H.M. Ohlendorf, C.M. Marn, and G.W. Pendleton. 1998. Association of mercury and selenium with altered glutathione metabolism and oxidative stress in diving ducks from the San Francisco Bay region, USA. *Environ Toxicol Chem.* 17:167–172.

Hollmén, T., J.C. Franson, R.H. Poppenga, M. Hario, and M. Kilpi. 1998. Lead poisoning and trace elements in common eiders *Somateria mollissima* from Finland. *Wildlife Biology.* 4:193–203.

Hontela, A. 1997. Endocrine and physiological responses of fish to xenobiotics: role of glucocorticoid hormones. *Reviews in Toxicology.* 1:1–46.

Karlog, O., K. Elvestad, and B. Clausen. 1983. Heavy metals, (cadmium, copper, lead and mercury) in common eiders (*Somateria mollissima*) from Denmark. *Nordic Veterinary Medicine.* 35:448–451.

Kellett, D.K. and R.T. Alisauskas. 2000. Body-mass dynamics of King Eiders during incubation. *The Auk.* 117:812–817.

Kiremidjian-Schumacher, L. and M. Roy. 1998. Selenium and immune function. *Z Ernahrungswiss.* 37:50–56.

Korschgen, K.E. 1977. Breeding stress of female eiders in Maine. *Journal of Wildlife Management.* 41:360–373.

Lande, E. 1977. Heavy metal pollution in Trondheimsfjorden, Norway, and the recorded effects on the fauna and flora. *Environ Pollut.* 12:187–198.

Lawrence, D.A. 1985. Immunotoxicity of heavy metals. In: J.H. Dean, M.L. Luster, A.E. Munson and H. Amos (eds.). *Immunotoxicology and immunopharmacology,* pp. 341–353. New York: Raven Press.

Massanyi, P., L. Bardos, K. Oppel, S. Hluchy, J. Kovacik, G. Csircsai, and R. Toman. 1999. Distribution of cadmium in selected organs of mice: effects of cadmium on organ contents of retinoids and beta-carotene. *Acta Physiologia Hungarica.* 86:99–104.

Milne, H. 1976. Body weights and carcass composition of the common eider. *Wildfowl.* 27:115–122.

Murk, A.J., P.E.G. Leonards, B. van Hattum, R. Luit, M.E.J. van der Weiden, and M. Smit. 1998. Application of biomarkers for exposure and effect of polyhalogenated aromatic hydrocarbons in naturally-exposed European otters. *Environ Toxicol Pharmacol.* 6:91–102.

Nielsen, C.O. and R. Dietz. 1989. Heavy metals in Greenland seabirds. *Meddelelser om Grønland, Bioscience.* 29:3–26.

Norheim, G. 1987. Levels and interactions of heavy metals in seabirds from Svalbard and the antarctic. *Environ Pollut.* 47:83–94.

Neugebauer, E.A., G.L. Sans Cartier, and B.J. Wakeford, 2000. *Methods for the determination of metals in wildlife tissues using various atomic absorption spectrophotometry techniques.* Tech Rept Ser. No. 337E, Canadian Wildlife Service, Headquarters, Hull, Québec, Canada.

Ohlendorf, H.M., R.W. Lowe, P.R. Kelly, and T.E. Harvey. 1986. Selenium and heavy metals in San Francisco Bay diving ducks. *Journal of Wildlife Management.* 50:64–71.

Ohlendorf, H.M., K.C. Marois, R.W. Lowe, T.E. Harvey, and P.R. Kelly. 1991. Trace elements and organochlorines in surf scoters from San Francisco Bay, 1985. *Environ Monitor Assess.* 18:105–122.

Olafsdottir, K., K. Skirnisson, G. Gylfadottir, and T. Johanneson. 1998. Seasonal fluctuations of organochlorine levels in the common eider (*Somateria mollissima*) in Iceland. *Environ Pollut.* 103:153–158.

Parker, H. and H. Holm. 1990. Patterns of nutrient and energy expenditure in female common eiders nesting in the high arctic. *The Auk.* 107:660–668.

Potmis, R.A., V.K. Nonavinakere, H.R. Rasekh, and J.L. Early. 1993. Effect of selenium (Se) on plasma ACTH, beta-endorphin, corticosterone and glucose in rat: influence of adrenal enucleation and metyrapone pretreatment. *Toxicol.* 79:1–9.

Rasekh, H.R., R.A. Potmis, V.K. Nonavinakere, J.L. Early, and M.B. Iszard. 1991. Effect of selenium on plasma glucose of rats: role of insulin and glucocorticoids. *Toxicol Let.* 58:199–207.

Raszyk, J., H. Docekalova, S. Navratil, J. Masek, and L. Rodak. 1992. Experimental chronic phenylmercuric chloride poisoning in pigs. *Veterinaria Medicina (Praha).* 37:379–391.

Rattner, B.A. and J.R., Jr. Jehl. 1997. Dramatic fluctuations in liver mass and metal content of eared grebes (*Podiceps nigricollis*) during autumnal migration. *Bul Environ Contam Toxicol.* 59:337–343.

Rigert, F., R. Dietz, P. Johansen, and G. Asmund. 2000. Lead, cadmium, mercury and selenium in Greenland marine biota and sediments during AMAP phase 1. *Sci Total Environ.* 245:3–14.

Robertson, G.J. and H.G. Gilchrist. 1998. Evidence for population declines among common eiders breeding in the Belcher Islands, Northwest Territories. *Arctic.* 51:378–385.

Rolland, R.M. 2000. A review of chemically-induced alterations in thyroid and vitamin A status from field studies of wildlife and fish. *Journal of Wildlife Diseases* 36:615–635.

SAS Institute. 1988. *SAS/STAT User's Guide Release 6.03.* Cary, NC: SAS Institute.

Scheuhammer, A.M. 1987. The chronic toxicity of aluminum, cadmium, mercury, and lead in birds: a review. *Environ Pollut.* 46:263–295.

Scheuhammer, A.M., A.H.K. Wong and D. Bond. 1998. Mercury and selenium accumulation in common loons (*Gavia immer*) and common mergansers (*Mergus merganser*) from eastern Canada. *Environ Toxicol Chem.* 17:197–201.

Spalding, M.G., P.C. Frederick, H.C. McGill, S.N. Bouton, and L.R. Mcdowell. 2000. Methylmercury accumulation in tissues and its effects on growth and appetite in captive great egrets. *Journal of Wildlife Diseases.* 36:411–422.

Spear, P.A. and T.W. Moon. 1986. Thyroid-vitamin A interaction in chicks exposed to 3,4,3', 4'-tetrachlorobiphenyl: influence of low vitamin A and iodine. *Environ Health.* 40:188–198.

Stegeman, J.J., B. Ballachey, J. Bickham, B. Hocker, S. Kennedy, H. Thompson, and A.D. Vethaak. 1993. Implementation of biomarker-based studies. In: D.B. Peakall and L.R. Shugart (eds.). Biomarkers: research and application in the assessment of environmental health: NATO ASI Series H: Cell Biology, Vol. 68, pp. 32–48. Berlin: Springer-Verlag.

Sugawara, C. and N. Sugawara. 1978. The effect of cadmium on vitamin A metabolism. *Toxicol Applied Pharmacol.* 46:19–27.

Suydam, R.S., D.L. Dickson, J.B. Fadely, and L.T. Quakenbush. 2000. Population declines of king and common eiders of the Beaufort Sea. *Condor.* 102: 219–222.

Takekawa, J.Y., S.E. Wainwright-De La Cruz, R.L. Hothem, and J. Yee. 2002. Relating body condition to inorganic contaminant concentrations of diving ducks wintering in coastal California. *Arc Environ Contam Toxicol.* 42:60–70.

Trust, K.A., K.T. Rummel, A.M. Scheuhammer, I.L. Brisbin, and M.J. Hooper. 2000. Contaminant exposure and biomarker responses in spectacled elders (*Somateria fischeri*) from St. Lawrence Island, Alaska. *Arch Environ Contam Toxicol.* 38:107–113.

Underwood, B. 1984. Vitamin A in animal and human nutrition. In: M.B. Sporn, A.B. Roberts and D.S. Goodman (eds.). *The retinoids. Vol.1*, pp. 282–392. Orlando: Academic Press.

Wayland, M., H.G. Gilchrist, D.L. Dickson, T. Bollinger, C. James, R. Carreno, and J. Keating. 2001. Trace elements in king and common eiders in the Canadian arctic. *Arch Environ Contam Toxicol.* 41:491–500.

Wayland, M., H.G. Gilchrist, T. Marchant, J. Keating, and J.E. Smits. 2002. Immune function, stress response and body condition in arctic-breeding common eiders in relation to cadmium, mercury and selenium concentrations. *Environ Res Section A.* 90:47–60

Weeks, B.A., D.P. Anderson, A.P. DuFour, A. Fairbrother, A.J. Goven, G.P. Lahvis, and G. Peters. 1992. Immunological biomarkers to assess environmental stress. In: R.J. Huggett, R.A. Kimerle, P.M. Mehrle, Jr. and H.L. Bergman (eds.). *Biomarkers: biochemical, physiological, and histological markers of anthropogenic stress*, pp. 211–234. Boca Raton: SETAC Spec. Publ. Ser., Lewis Publishers.

White, D.H. and M.T. Finley. 1978. Uptake and retention of dietary cadmium in mallard ducks. *Environ Res.* 17:53–59.

Yamamoto, J.T. and G.M. Santolo. 2000. Body condition effects in American kestrels fed selenomethionine. *Journal of Wildlife Diseases.* 36:646–652.

Monitoring the Health of Arctic Peoples and Ecosystems and the Effectiveness of International Controls

Part C: Local Contaminants Concerns

Yukon Local Contaminants Concerns Program

Project leader

Patrick Roach, Contaminants/Waste Programs, Renewable Resources, Indian & Northern Affairs, Whitehorse, Yukon.

Project team

Yukon Contaminants Committee, and various other stakeholders for the individual projects.

Abstract

The Yukon Contaminants Committee (YCC) provides direction to the Local Contaminants Concerns (LCC) program. The LCC is intended to address concerns raised by individuals and Yukon communities regarding potential local sources of contaminants, rather than the long-range transport issues. Many of these are unplanned or "walk-in" projects that occur through contact with the YCC. A number of these usually involve deformed fish, which people are concerned may have acquired the deformities through elevated levels of contaminants. In the 2001 field season there were four major investigations under LCC. The first was a project lead by a graduate student from the University of British Columbia, who was investigating the potential for mining to effect local vegetation. The second was a sampling trip to Itsi and Pelly Lakes to determine if the underlying geology was contributing to increased levels of mercury, as it may have in fish in the Northwest Terittory. The third study was an associated trip to two old mineral exploration sites. The fourth was a response to concerns raised by a Yukon First Nation regarding a large number of abandoned barrels or oil drums located on a creek.

Key Project Message

The Yukon Local Contaminants Concerns (LCC) program provides for timely responses to public concerns to specific issues. Discrete studies are conducted and the results are considered to determine if a larger study is warranted or if the issue requires a response from a regulatory authority. In this way the LCC either answers the local concern or feeds into other agencies or the regulatory process.

Objectives

1. To address local concerns related to contaminated sites in the Yukon in a timely manner;
2. To evaluate individual issues and respond back to the community and/or determine the responsible authority.

Introduction

The Yukon LCC program receives direction from the Yukon Contaminants Committee (YCC) and provides a format for responding promptly to local specific concerns regarding contaminants. The LCC process includes both planned projects and a number of unplanned or "walk-in" concerns annually.

Consequently, work under LCC varies yearly, but the focus remains in dealing with specific concerns through the use of a discrete study. LCC studies usually result in a small report to the person or community which originated the concern, but occasionally result in either a larger study being planned or turning the issue over to a regulatory authority. Often there is no contaminant

problem identified, but the LCC process provides for a great deal of "peace of mind" for the persons or communities involved.

Activities

In 2001–2002

A number of projects were conducted during the 2001 field season. As usual a number of small walk-in projects were covered and four larger studies were conducted. These four projects are covered here.

Metal contamination in berries and plants harvested by the Little Salmon Carmacks First Nation, Yukon Territory

This project addressed a concern expressed by the Little Salmon Carmacks First Nation (LSCFN), regarding the contamination of local vegetation by a mine. Members of the First Nation gather berries and hunt in the Mt. Nansen region near Carmacks, Yukon. Recent practices by the BYG Natural Resources Inc., a gold mining company, left the LSCFN strongly concerned about exposure to contaminants through their traditional foods, and consequent risks to their health. Other mine sites near Carcross, YT (the Venus Mine and the Arctic Gold and Silver Mine) have recently been reclaimed and their tailings capped. These sites occupy land traditionally used by the Carcross/Tagish First Nations, who are concerned about health risks associated with direct or indirect consumption of plants growing in the area. The study was designed to accommodate the concerns of both communities in one study.

With assistance from First Nation field assistants and Elders during the summer of 2001, medicinally- and culturally-significant plants were successfully identified and sampled. Soil and background samples were also collected to ensure proper methodology. Analysis of inorganic and organic arsenic in plants growing near gold mine tailings that are suspected or already identified as sources of arsenic contamination was conducted.

Following laboratory analyses for arsenic contents, results will be statistically analysed for spatial and temporal trends using data from this and previous studies, to identify any locations with high-health risks using national and international guidelines. Ultimately, the goal is to determine if the plants are safe to eat.

During fall 2002, final results will be presented to community members and other interested parties through oral and poster presentations and in non-technical reports. Technical and journal manuscripts based on the research will also be submitted after completion of the MSc dissertation by H. Nicholson.

Results

The sampling has been taken in both locations and the samples have been sent for analysis. While the analysis is completed, the data is currently under evaluation by Ms. Nicholson. A full presentation package is anticipated for the early fall of 2002.

Discussion and Conclusions

There are a large number of old mine sites in the Yukon and a significant amount of arsenic-bearing rock in the local geology. Knowing more about which species of traditionally harvested plants have a tendency to accumulate arsenic, from both natural and anthropogenic sources, will be a valuable tool for the YCC to have available. The Committee often has questions from concerned individuals, regarding the consumption of country foods. The more detailed the knowledge of these foods, by species, the more accurate the response the YCC can provide.

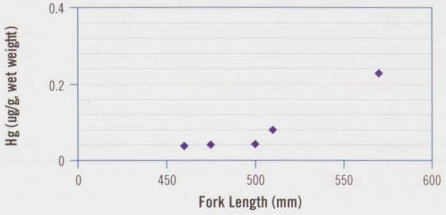
Expected Completion Date

This project is expected to end in the fall of 2002.

Itsi and Pelly Lakes

Studies in the Northwest Territories have indicated elevated levels of mercury in predatory fish, in Lakes west of the Nahanni Mountains (Lockhart et al., 2001; Evans and Lockhart, 2001). The underlying geology in this region has shown naturally high levels of Hg and while there is no indication as yet as to whether this is an influence on the levels in the fish, a similar region of geology exists in the Yukon (Painter et. al., 1994). This area on the Selwyn Basin shows Hg concentrations in stream sediments are 189 μg/g rather than the average of 56 μg/g in the rest of the Yukon. A proposal to extend the Northwest Territories work into this region of the Yukon, was submitted to NCP for research during the 2001 field season. While this work was subsequently not funded, the local Ross River Dena First Nation, in whose area the work was to have taken place, had been contacted as part of the on-going NCP consultation process. This led to concerns and an expectation of an evaluation of the fish from lakes identified in the proposal. The YCC was contacted and a small sampling study was developed to cover two lakes

Figure 1. Muscle mercury concentrations in trout of varying lengths collected from Itsi Lakes in 2000. The red line corresponds to the guideline level of 0.20 mg·g^{-1} recommended for subsistence fisheries



from the list on the proposal. Both of the lakes selected have a population of lake trout and a small but consistent traditional harvest of them. The two lake chains investigated were Itsi Lakes, on the North Canol Road, near Macmillan Pass, and Pelly Lakes located Northeast of Ross River, Yukon.

Water samples were collected from each lake system and five lake trout were collected from Itsi Lakes. The collection of trout from Pelly Lakes was initially unsuccessful and the sudden end of the 2001 field season eliminated the potential for acquiring fish until the 2002 field season.

Results

Water samples from Pelly and Itsi Lakes were well below the CCME guidelines for aquatic health; 0.1 µg/L. The largest Itsi Lakes trout contained fish tissue mercury concentrations slightly greater than the subsistence consumption levels of 0.2 µg/g, at 0.228 µg/g.

Discussion and Conclusions

The water sampling is consistent with results reported in the Northwest Territories (Evans and Lockhart, 2001), where the water chemistry indicated low levels for Hg, despite the elevated levels of Hg in the underlying geology. The fish tissue concentrations in the Itsi Lakes trout is consistent with other Yukon lakes and reported values from Northern lakes for Hg in predatory fish (Lockhart et al., 2001). This has left a number of questions regarding the cause of variations in Hg levels in predatory fish. There is no clear connection to natural or anthropogenic sources, and the variations may be due to subtle characteristics of the food web from individual lakes. The small n = 5 sample size is too limited to answer these larger questions and a much more extensive study of the food web of Itsi Lakes would be required to provide further clarification. Sampling at Pelly Lakes in 2002, will take place to meet the commitment made to the Ross River Dena people.

Expected Completion Date

This project is expected to end in the fall of 2002.

Howard's Pass and MacMillan Pass

This was a water quality study related to the work being conducted at Itsi and Pelly Lakes. The concerns about elevated levels of Hg in the native rock of the boundary area between the Yukon and Northwest Territories, led to concerns regarding the potential for Hg drainage from two known ore bodies located in this region. Both of theses ore bodies had exploratory drifts completed into them. The drift at Howard's Pass was opened by Placer Dome in the 1970s, and the Tom property at MacMillan Pass was explored underground by Hudsons Bay Mining in the same period. Both have open adits, which drain to the local watersheds. Sampling of these adit drainages for Hg has been limited and past sampling was suspect (Whitley, pers. comm., 2001), due to the sampling protocols employed at the time. Subsequently, grab sampling of both adits was conducted in the early summer of 2001, with the intention of supplementing the work being done at Itsi and Pelly Lakes.

The ores at both sites are composed of sphalerite (zinc sulphide), a mineral readily chemically weathered and known to contain substantial mercury in the deposits at Howard's Pass (Painter, 1994). While similar sulphide ores exist at the Tom Property (Burns and de Graff, 1999; Kwong and Whitley, 1992), the Hg levels are unreported by Hudsons Bay Mining. Natural acid rock drainage occurs in both of the Passes and acid mine drainage is substantial at both of the adits. As both sites are zinc ore bodies, the levels of zinc and associated metals are quite high in the adit discharges.

Results

Total mercury determined in the water samples taken from the drainages at the adits and upstream and downstream were below the detection limit of 0.002 mg/L.

Table 1. Comparison of water chemistry of metals that exceed CCME guidelines (2001) at Howard's and Macmillan Pass to the guidelines. Water samples were taken in June 2001

	Howard's Pass — Don Creek			MacMillan Pass — Tom Creek			CCME Guidelines	
Metal	u/s	Adit	d/s	u/s	Adit	d/s	Drinking Water	Protection of Aquatic Life
Aluminum	**1430**	40	**1240**	**5430**	**18,400**	**7720**		5 to 100
Cadmium	**3**	> 1	**3**	**6**	**97**	**18**	5	0.017
Copper	**14**	1	**25**	**121**	**104**	**156**	> 1000	2 to 4
Iron	**1980**	118	**2200**	**5800**	**82,900**	**10,300**	300	300
Lead	**90**	> 5	**75**	**40**	**104**	**86**	10	1 to 7
Zinc	**597**	**802**	**860**	**627**	**21,100**	**3140**	> 5000	30

Please Note: Concentrations are in μg/L. Bolded figures exceed guidelines. Guidelines are used for comparison only

Discussion and Conclusions

While the concentration of other metals in the adit drainages is high, Hg levels are below the detection limit. It appears that while the levels of Hg in both the reported ores and sediments are elevated, it is not mobilizing into the water column at measurable levels. Values obtained for the other metals have been passed to the appropriate regulatory authority for possible action.

Expected Completion Date

This project is completed.

Tizra Creek

Residents from Old Crow, Yukon reported a large number of barrels at the confluence of Tizra Creek and Porcupine River. Little was known about the location's previous land use and they had voiced concern over the potentially hazardous contents of the barrels. On June 13th, 2001, Contaminants staff completed a reconnaissance of the site. This visit consisted of identifying the contents of the barrels, the previous owners of these drums, and a general survey of the site to assess any potential environmental hazards.

Results

One hundred and eleven barrels were found at different sites. Only one barrel was found to have contents and was identified as a 45 gallon drum of stove oil (kerosene) in unopened condition. Of the other barrels, 75 had contained kerosene, 25 of jet fuel and 10 of hydraulic fluid. There was no sign of spillage or perforation of the drums. The contents had likely been consumed and the empty barrels were sorted by time in separate areas and placed in a pile. The heavy nature of the drum construction and the notation of jet fuel as JP4, indicated that the drums dated to before the 1970s. The type of organization of the drums for disposal is consistent with practices of the era.

A short report was generated and sent to the local Regional Management Officer and the Vun Tut Gwitchin First Nation. As the site is within the Vun Tut Gwitchin Self Government settlement lands, the ultimate fate of materials on the site rests with the First Nation.

Discussion and Conclusions

The drum of stove oil is likely still in usable condition and the heavy wall drums have long been used as wood stoves. The site is readily accessible from the river and the removal of these materials can be conducted by this route.

Expected Completion Date

This project is completed.

The LCC program is continuing to provide a cost effective response to local concerns that have no other ready avenue of approach, while meeting the requirements of the YCC. The YCC has allowed the LCC a significant degree of flexibility in responding to concerns as they are raised and it has continued to expand the range of issues it addresses.

The LCC continues to receive good support from the general public, First Nations, and other government agencies. To date, most of the projects undertaken have produced an identifiable conclusion and usually within an acceptable time frame. The challenge to LCC is the increasing demand as more stakeholders become aware of

the Program, and providing a comprehensive response in a timely manner.

References

Burns, B. and N. de Graff. 1999. Assessment and characterization of effluent originating from the Tom Mining Property (Sekie Creek #2) Mac Pass, Yukon. Report prepared for the Ross River Dena Council, 34 pp.

Evans, M and L. Lockhart. 2001. An investigation of factors affecting high mercury concentrations in predatory fish in the Mackenzie River Basin. In: Synopsis of Research Conducted Under the 2000/2001 Northern Contaminants Program. 174–184.

Kwong, J. and W.G. Whitley. 1992. Natural acid rock drainage at Macmillan Pass, Yukon. National Hydrology Research Institute Contribution, CS-92046, 41 pp.

Lockhart, L., G. Stern, G. Low, and M. Evans. Mercury in fish from stock surveys in the western Northwest Territories: investigations into the factors affecting mercury levels. In: Synopsis of Research Conducted Under the 2000/2001 Northern Contaminants Program. 194–201.

Painter, S., E.M.Cameron, R. Allan, and J. Rouse. 1994. Reconnaissance geochemistry and its environmental relevance. *J Geochem Explor.* 51:213–246.

Education and Communications

Inuvialuit Regional Corporation Contaminants Coordinator 2001–2003

Project leader

Barbara Armstrong, Regional Contaminants Coordinator, Box 1887, Inuvik, NT X0E 0T0; phone: (867) 777-2072; fax: (867) 777-2135; e-mail: recycle@nt.sympatico.ca

Project team

Nellie Cournoyea, Chair and Chief Executive Officer, Inuvialuit Regional Corporation, Inuvik, NT; Duane Smith, Chairman, Inuvialuit Game Council, Inuvik, NT; Eric Loring, Inuit Tapiriit Kanatami (ITK) , Ottawa, ON; Northwest Territories Environmental Contaminants Committee; Chairs: Aklavik, Holman, Inuvik, Paulatuk, Sachs Harbour and Tuktoyaktuk Community Corporations; Presidents: Aklavik, Holman, Inuvik, Paulatuk, Sachs Harbour and Tuktoyaktuk Hunters and Trappers Committees.

Abstract

The objective of the Inuvialuit Regional Corporation Regional Contaminants Coordinator (RCC) position is to provide the Inuvialuit and all community members with a better understanding about the presence of contaminants within the Inuvialuit Settlement Region (ISR), how they enter the food chain, and their possible effects on wildlife and the Inuvialuit population. The RCC communicates with community members and organizations, and works with scientists and researchers to determine what work is required for the future to better understand contaminants issues in the ISR, and to be able to answer questions and concerns raised by Inuvialuit on these issues. Through this network, stronger communication links among communities, schools, the Northern Contaminants Program, and industry have been built. With the introduction of the ISR RCC, apprehension, mistrust and alarm over contaminants information among community members have continued to be mitigated, because someone from their region can explain contaminants in plain language and in their own language. Opportunities also arise for the RCC to participate with the Northwest Territories Environmental Contaminants Committee (NWTECC) to develop Local Contaminant Concern (LCC) projects for the ISR region.

Key Project Messages

1. Communities within the Inuvialuit Settlement Region (ISR) have a broad range of concerns related to contaminants and their effects on wildlife and human health in the ISR. Ongoing, coordinated exchanges of information and research results among researchers, project managers and community members has been critical.

2. Several management plans related to wildlife and the environment have been developed through the efforts of the co-management boards established under the Inuvialuit Final Agreement. These plans provide guidance to the agencies responsible for the overall management of the region's wildlife and environment. The identification of contaminants within the ISR and their impact on the wildlife and human population of the region is required to help monitor the

impacts and was therefore added to these management plans as a result of NCP work in the region.

3. The current priority of the Inuvialuit RCC is to work with the different levels of government, various communities and industry to begin updating information on contaminated sites in the ISR and to assess specific sites about which communities are concerned.

Objectives

1. Achieve an appropriate level of understanding among the Inuvialuit about the presence of contaminants within the ISR, how they enter the food chain and their effects on wildlife and the health of the Inuvialuit population.
2. Understand the questions and concerns Inuvialuit have in relation to contaminant issues within the ISR and beyond.
3. Facilitate interactions within and among Inuvialuit communities with regard to contaminant issues and, in turn, to facilitate interactions among communities, the Northern Contaminants Program (NCP) and research program managers.
4. Build capacity and partnership at the community level to effectively communicate community concerns and priorities, with regard to contaminants, to decision-making bodies at regional, national and international levels.

Introduction

In the past within Inuvialuit communities, miscommunication regarding contaminant issues has led to unnecessary alarm, apprehension and mistrust. Language and cultural barriers have been major obstacles to effective communication. Promising communications strategies have now been developed at the community level and there has been increased communication at the regional and inter-regional levels.

Communication of contaminants information and data from technical components of the NCP is a major element of Phase II of the NCP. Inuvialuit who consume large amounts of traditional/country foods are continually requesting information on the levels of contaminants present in their area and their potential impact on people and the environment. Many of these requests have led to workshops dedicated to contaminants information, which are able to summarize and communicate information from past and present contaminants-related research, such as the Centre for Indigenous Peoples' Nutrition and Environment (CINE) dietary benefits/risks study, the Inuvik Regional Human Contaminants Monitoring Program and the status of contaminants in fish and marine mammals in the ISR.

Inuvialuit are concerned about local contamination issues related to water quality, solid and sewage waste practices as well as contaminated sites from past Distant Early Warning (DEW) Line sites and abandoned oil exploration sites, where past and present activities have left contaminants behind. Efforts have been made to deal with these concerns, such as the Department of National Defence's DEW Line clean-up projects; in addition, abandoned well sites are still an issue.

Reports on two major nutritional surveys were made available in 2000 (Kuhnlein et al. 2000; Usher, 2001). It is vital that this information continue to be communicated throughout the ISR in an effective and culturally appropriate manner. There also remains to be a need for broad community dissemination of information on sensitive and current issues, such as mercury levels in beluga muktuk, the clean-up of abandoned DEW Line sites, the increasing awareness of abnormalities in fish and wildlife, high cancer rates and safety of community drinking water.

Activities

In 2001–2002

In the summer of 2001, Regional Contaminants Coordinator, Mr. Billy Archie, resigned his position to devote his energies to his business interests within the region. The position was advertised throughout all Inuvialuit communities and I am pleased to advise that Ms. Barbara Armstrong of Inuvik was appointed as Regional Contaminants Coordinator for the period ending March 31, 2003.

Activities

Billy Archie

Billy Archie worked on three main activities during the April–August portion of his time as the Contaminants Coordinator. Mr. Archie was involved with ongoing communications that took place in all ISR communities through memos and quarterly reports. He initiated the Tuk Harbour fish study and Mr. Archie also assisted in hosting the ITK CINE workshop in Inuvik with Eric Loring in April 2001. At this time, two contaminants awareness posters were drafted during the CINE Dietary Results workshop, held April 4–5, 2001. Mr Archie also

participated in a number of teleconference meetings with the NWT Environmental Contaminants Committee.

The following is a list of general tasks completed by Billie Archie between April and August 2001:

- Attended NCP annual results workshop in Calgary (September 25–27).
- Initiated Tuk Harbour Study.
- ITK April CINE Dietary Benefit/Risk Workshop in Inuvik.
- Participated in two teleconference meetings with the NWT Environmental Contaminants Committee (October and November 2001).

Activities

Francine Ross

Francine Ross filled in for a few weeks in between Mr. Archie's resignation and Barbara Armstrong taking over the contaminants position. Ms. Ross took part in conference calls and received and responded to all e-mails and other communications.

Activities

Barbara Armstrong

As an introduction to this new combined position with the Inuvialuit Regional Corporation and the Northern Contaminants Program, she attended the Northern Contaminants Program 11th Annual Results Workshop held on September 25th to 27th, 2001 at the Calgary Marriott Hotel & Telus Convention Centre.

This initial opportunity to meet with the various researchers and scientists was a good introduction to the NCP program and an opportunity to meet with fellow contaminants coordinators, to learn from the research presentations, as well as to participate in small informative group discussions outside the conference rooms where a poster display of ongoing and past studies were set up. The following is a list of general tasks completed by Barbara Armstrong since September 22, 2001:

- Attended NCP annual results workshop in Calgary (September 25–27).
- Orientation meeting(s) with Roger Connelly, the Game Council, IRC board meetings with various introductions to members of the Hunters and Trappers committees.
- RCC training with DIAND in Yellowknife (November 2001).
- Conducted a site visit at Taiga lab in Yellowknife and met with Kathy Racher to explore the possibilities of sending future samples to a NWT facility.
- Meeting to review health issues with Erica Myles of GNWT Health and Social Services.
- Conducted research on a NCP Local Contaminants Concern project regarding the Assessment of Contaminant Levels in Traditionally Harvested Foods in Tuktoyaktuk Harbour Study. This involved a one-day research visit to Tuk, with the appointed fish harvester, Chris Felix and the collection of four different species of fish that were sent to the Taiga Lab in Yellowknife for contaminants testing.
- Assisted potential researchers that expressed interest in conducting NCP projects in preparation for submitting a proposal for the 2002–2003 term.
- Prepared and submitted the RCC position proposal to the NCP.
- Prepared and submitted a proposal to the NCP for an educational community tour in the ISR to deliver CINE Dietary Benefit Risk information.
- Provided input on a NCP proposal for a Pan-Inuit poster contest by ITC.
- Prepared reports of my activities to the IRC and Joint Secretariat, Game Council, board meetings providing an introduction for the new RCC position and then a summary of my activities.
- Ongoing communications took place in all ISR communities through memos and quarterly reports drafted by the RCC.
- Working relationships were established with research institutions, government departments/agencies, and Inuvialuit co-management boards.
- Participation in four Northwest Territories Environmental Contaminants Committee meetings.
- Informal discussions took place with researchers to consider the establishment of a comprehensive monitoring program for contaminants in various fish and wildlife species in the ISR. The expertise from the scientific community is needed to determine when to analyze for various contaminants and to help determine whether contaminants are increasing or decreasing in all species harvested by Inuvialuit.

- Attended and participated in meetings for the 2002 NCP proposal reviews.
- The RCC accompanied members of the Joint Secretariat and the Game Council on a week-long community tour to Holman, Sachs Harbour, Tuktoyuktuk, Aklavik and Paulatuk. We gave presentations to students in the upper grade levels at each school, to Hunters and Trappers meetings and finally to community members regarding the structure, responsibilities and role of the Game Council in the ISR. The environmental process for review and the status of various species of wildlife and marine mammals were also discussed. The RCC took along information posters that were distributed and introduced the new contaminants coordinator in both formal and informal meetings. I spoke to various community members about returning to the communities to deliver the CINE Dietary Benefit/Risk study and to the school staff regarding the potential of a future contaminants Poster Contest. These visits were generally a learning exercise for the new RCC and a way to introduce the new RCC in the role of their Contaminates Coordinator to the individual communities. I was available to answer questions regarding contaminants and contaminant issues and to explain the role of the NCP at the federal and community levels.
- The RCC was also able to assist Scot Nickels from ITK with a Climate Change project, which included a weekend training workshop offering instructions on conducting oral research seeking Tradition Knowledge within Inuit Communities. Participating with this project allowed the RCC a second opportunity to visit the other communities of the ISR to ask qualitative questions regarding climate change for a survey. These community visits and the valuable opportunity to be in the ISR, interacting with community members, provided an exercise to continue to introduce myself in the role of their Contaminates Coordinator. The RCC was available to answer questions regarding contaminants and contaminant issues and to explain the role of the NCP at the federal and community levels.
- Continue to assist Scot Nickels from ITK with the Climate Change project, in combination with a Snow Change project that has been organized with the Aurora Research Center, Mike Salomons and the Joint Secretariat staff. This included a second workshops in three communities, (The first community visits to Sachs, Holman and Paulatuk have still not been completed).
- RCC Workshop/Training with DIAND, NCP staff, in Inuvik May 6th–9th with John Edwards, the new RCC for the Gwitch'in board.
- It is also a plan for me to return to the communities to deliver the results of the CINE Dietary Benefits/ Risk research in combination with upcoming CACAR2 results. During the proposal review meeting the NCP Management Committee realized that the communication of CACAR2 (Canadian Arctic Contaminants Assessment Report 2 — a summary of the past 5 years of research currently being compiled), had not been properly addressed under the Education and Communications envelope. It was decided that the communication of CACAR2 results to both northern and southern audiences needs to be a focus for this last year of Phase 2. Thus extra criteria were considered when reviewing the proposals to ensure the projects supported CACAR2 or efforts to renew NCP for a Phase 3. This means that no other research proposals were approved for this coming year, and all the education and communications funds will be directed towards delivery of CACAR2.
- Continue with my objective to assist Eric Loring with a proposed Pan-Inuit Poster Contest to be offered in the IRS, although it will not be funded under the NCP program.
- The RCC is presently gathering information regarding the issue of old sites (drill sites, storage areas, camp sites, etc.) in the delta area that were used, cleaned up and abandoned during the last oil and gas boom (1970s and early 1980s). The RCC has taken the lead role in investigating the present status of these old sites and has just had a meeting with Carole Mills and the contaminants staff to work towards identifying what types of sites should be included in the study and the location of the sites through DIAND in the hopes of developing a site visit/testing program.

Activities

In 2002–2003

The Regional Contaminants Coordinator position was reassigned to Mrs. Barbara Armstrong of Inuvik for the period starting in April 2002 and ending on March 31, 2003. Mrs. Armstrong brings a broad experience in contaminants and related fields to this position and she continued the productive relationship with community organizations and their ad hoc committee members already established by her predecessor, Billy Archie 1999–2001.

Barbara continued her position with the Inuvialuit Regional Corporation and the Northern Contaminants Program. Barbara attended the Northern Contaminants Program Canadian Arctic Contaminants Assessment Symposium held

on March 4th to 8th, 2003 at the government conference centre in Ottawa. This final opportunity to meet with the various researchers and scientists was a welcome and useful aspect to the NCP program and an opportunity to meet with fellow contaminants coordinators, to learn from the research presentations, as well as to participate in small informative group discussions outside the conference rooms where a poster display of ongoing and past studies was set up. A poster and brief oral presentation were made to highlight the role of the RCC in the Inuvialuit Settlement Region.

The following are a list of tasks completed by the RCC since April, 2002

- Attended NCP Symposium March 4–8, 2003 in Ottawa.
- Participated in RCC training with DIAND in Inuvik (May 6th–9th, 2002).
- Conducted a meeting and second site visit at Taiga lab in Yellowknife, and met with Kathy Racher and DIAND staff to prepare to send future samples to a NWT facility.
- Participated in creating contaminants fact sheets.
- Created an RCC-ISR Poster.
- Meetings with Alisha Chauhan, JS-IGC to propose Key Message for community visits relating to CACAR II and the distribution of the new Country Foods Fact Sheets.
- Participated in the creation of the NWT-ECC Newsletter.
- Reviewed current research with Kelly Cott, DFO regarding ongoing Tuk Harbour and Aklavik Studies.
- Completed research on a NCP Local Contaminants Concern project on the Inuvik Landfill. This involved field work with DIAND staff, the Gwich'in Tribal Council. Analysis was conducted at Taiga lab.
- Created a Historical Map and database that records past ISR land use activities.
- Prepared reports of activities to the IRC and Joint Secretariat, Game Council, board meetings.
- Ongoing communications took place in all ISR communities through memos and quarterly reports drafted by the RCC.
- Working relationships were established with research institutions, government departments/agencies, and Inuvialuit co-management boards.
- Participation in two in-person and 10 teleconference meetings of the Northwest Territories Environmental Contaminants Committee.
- Drafted a letter for the NCP renewal support for the IRC.

Results

The RCC has been acting as a conduit for a two-way information exchange between communities and the NCP, and has brought contaminants issues to the attention of various individuals and agencies. A few proposals were drafted and submitted by the RCC, and some funding has been approved for these proposed projects as well as studies by other researchers conducting work in the ISR.

From NCP related projects conducted in the ISR, such as dietary studies, and the LCC Inuvik Landfill Project, Inuvialuit have been informed that contaminants are present in traditional/country foods but at low levels, monitoring contaminant levels should continue to ensure levels continue to be low.

Inuvialuit communities expressed health-related comments and concerns during the Inuvialuit Community Tour, which took place in January 2001 and then again during the community visits in 2002 and 2003. In general, all communities had questions about contaminants, global warming/climate change and the oil and gas industry/development. Specific concerns of the communities are listed below.

Tuktoyuktuk

- The ocean is flooding the landfill each year — What about contaminants getting into the fish?
- Concerns over the state of the Tuk Dump.
- Contaminant levels in geese and birds — There is no information on geese gizzards which are an important food source.

Paulatuk

- Brucellosis in caribou.
- Global warming and changes in caribou herd migration.
- Contaminant levels in migratory birds.

Holman

- Residents do not drink tap water, they drink water from melted ice blocks — Can that water be tested?

- Parasites and bacteria in food, including brucellosis.
- Contaminants in king eiders and geese.

Sachs Harbour

- Contaminant levels in geese and migratory birds.
- Climate change.

Inuvik

- Oil and gas development.
- Climate change.
- Landfills — regulating what is being dumped.
- The old Dump site on Navy Road.
- *Helicobacter pylori* in the drinking water.
- Making sure communication occurs with residents before the press.

Aklavik

- Exposure to asbestos — It was removed from the school and placed in the dump.
- Contaminants from DEW line sites.
- Oil and gas industry.
- Climate change.
- Landfill and sewage lagoon.
- More information on levels of concern and acceptable daily intakes for contaminants in food.

Conclusions

The role of the RCC in the ISR is to bridge the gap between community members and NCP scientists and management. Local concerns focus on local sources of contamination, but this does not fall within the NCP mandate. To build trust and respect, it is important to be able to address some of these non-NCP concerns. The RCC position remains that in order to communicate NCP information, we must first be aware of the big picture in our region, in particular, knowing who is responsible for specific local issues of water or waste management and what is being done about them. Therefore, in order to be effective, RCC's must be aware of issues both within and outside the NCP mandate.

One important thing that was learned from work conducted in the ISR was the results of work conducted by CINE, which was brought to the attention of the ISR. Examining the dietary study, it has shown that for the most part, the people in the ISR are exposed to relatively low levels of contaminants. This being the case, the RCC urges the NCP to keep up their monitoring efforts, especially for marine mammals and species which are at risk for heavy metals, particularly methylmercury.

Acknowledgments

Barbara Armstrong would like to offer a word of thanks and appreciation to Roger Connelly and the Inuvialuit Settlement Regions Project Team partners, all our community members, Eric Loring and also the ITK climate change crew as well as to Norm Snow and Alisha Chauhan and staff at the Joint Secretariat and the Game Council. An extra-special thank you to Michele Culhane, Lisa Dyer and Carole Mills from DIAND for all your past assistance and support. One final note, I had the pleasure of working with Mr. Francis Blackduck: he will be sadly missed.

References

Kuhnlein, H.V., O. Receveur, H.M. Chan, and E. Loring. 2000. Assessment of Dietary Benefit: Risk in Inuit Communities. Ste-Anne-de-Bellevue QC: Centre for Indigenous Peoples' Nutrition and Environment. ISBN# 0-7717-0558-1.

Tofflemire, K. 2000. Inuvik Regional Human Contaminants Monitoring Program: Regio nal Report. Inuvik Regional Health and Social Services Board. 38 pp.

Macdonald, C.R. 2000. The Status of Contaminants in Fish and Marine Mammals in the Inuvialuit Settlement Region. Prepared for The Fisheries Joint Management Committee, Inuvik, NWT. 52 pp.

Usher, P. 2000. Standard edible weights of harvested species in the Inuvialuit Settlement Region. In. S. Kalhok (ed.), Synopsis of Research of Research Conducted Under the 1999–2000 Northern Contaminants Program. Ottawa ON; Indian and Northern Affairs Canada: 77–79.

Assessing Awareness, Comprehension and Perception of Contaminants Issues in Two Regions of the Canadian North

Project leader

Christopher Furgal, PhD, Unité de recherche en santé publique, CHUQ-Pavillon, CHUL, Université Laval; Christopher.Furgal@crchul.ulaval.ca

Project team

Heather Myers, PhD, Department of International Studies, University of Northern British Columbia; myers@unbc.ca; Stephanie Powell, MA (in progress), Department of International Studies, University of Northern British Columbia.

Abstract

Through the development and application of a questionnaire, this project assessed the level of awareness and comprehension of basic contaminants concepts and messages that have been communicated to northern populations through efforts under the Northern Contaminants Program in the recent past. The questionnaire was implemented in two Baffin and two Labrador Inuit communities and was conducted face to face with Elders, hunters and women of childbearing age in these four communities. Participants reported a variety of concepts when asked what the term contaminants meant to them, potentially indicative of some important misconceptions regarding chemical contaminants, country foods and health. Less than 50% of participants in Baffin indicated awareness of basic contaminants information delivered through the Northern Contaminants Program in the past, while awareness appeared higher (approximately 65%) among participants in Labrador communities. Participants' responses to: a) questions relating to the sources of contaminants in their community and region; b) what they can do to avoid exposure to contaminants; and c) their perspectives on food safety, were all indications that there is a need for formal evaluations of communications in order to assess reception and comprehension of these important issues in northern regions.

Key Project Messages

1. The term "contaminants" means many things to northerners; some concepts are misconceptions of the chemical nature of contaminants as discussed within the NCP.
2. A low level of general awareness of contaminant issues exists.
3. Formal evaluation exercises are required to ensure reception and comprehension of communication efforts on these important issues and to improve messages and modes of delivery in the future.

Objectives

This project proposes to assess the level of awareness and comprehension of basic contaminants concepts and

messages that have been communicated to northern populations through efforts such as those under the Northern Contaminants Program in the recent past. Specifically the project will:

1. Develop, translate and apply a short questionnaire to assess the level of awareness and comprehension of basic contaminants concepts and messages in two northern regions (two communities in each) in the Canadian North;
2. Compare basic perception of environmental health risks among these populations;
3. Examine potential factors influencing differences in levels of awareness, comprehension and risk perception among these populations;
4. Identify needs and make recommendations for future communication efforts in these regions of the North based on results of this study.

Introduction

The management and communication of the risks posed by environmental contaminants in the food chain of northerners comprises a very challenging issue for health and environmental managers and health professionals. Traditional food is the anchor to cultural and personal well-being in the North. It is essential to the nutritional and social health of indigenous peoples (Van Oostdam et al., 1999; Condon et al., 1995). In many communities, and among some sub-groups of the population, there is a lack of available and accessible healthy alternatives to these food stuffs. However, despite the vital importance of traditional food sources, significant changes in their collection, use, consumption and valuation by individuals have occurred over the past two decades (Berkes and Farkas, 1978; Kuhnlein, 1992; Kinloch et al., 1992; Condon et al., 1995; Blanchet et al., 2001). Some of this change can be attributed to the presence of industrial pollutants in the Arctic ecosystem and the management and communication strategies utilized to address concerns related to human exposure to these contaminants through country food consumption (Kinloch et al., 1992; Jetté, 1994; Furgal, 1999). Risk management and communication strategies in the past have resulted in fear and confusion, distrust and anxiety; in some instances, among community residents they have had significant direct and indirect social, economic, and health impacts.

To date, great effort and significant resources have been invested in communication and education activities on topics related to contaminants and country foods in the Canadian North. However, limited attention has been given to formally assessing the reception, comprehension and awareness of this information and the effects that these communication and education activities have had (both positive and negative). As previously reported (Usher et al., 1995; Andersen et al., 1999), little to no formal review has been conducted on communications in the North to date, yet the need to conduct and document formal or informal processes of review and evaluation in order to assess whether activities have in fact achieved desired goals has been reported.

Activities

In 2002–2003

A questionnaire was developed based on the general messages developed and delivered through previous NCP communication activities (CACAR I, Contaminant Tours). The questionnaire was then verified and adapted in cooperation with Inuit field assistants in the participating communities. Using a method of non-probabilistic quota sampling from three target groups known to have been key audiences for these messages in the past (hunters, Elders, and women of childbearing age), 20% of each of these target groups were randomly selected from the populations of 2 communities in each of 2 regions and invited to participate in the survey (Table 1).

Table 1. Participants in the comprehension survey conducted in two Baffin and two Labrador communities

Community	Target Group	Participants
Pond Inlet, Nunavut	Elders	12
	Hunters	9
	Women of childbearing age	21
Clyde River, Nunavut	Elders	7
	Hunters	11
	Women of childbearing age	25
Nain, Labrador	Elders	17
	Hunters	17
	Women of childbearing age	26
Makkovik, Labrador	Elders	6
	Hunters	11
	Women of childbearing age	7

Results and Discussion

Participants to the surveys in the four communities responded with a variety of concepts when asked what "contaminants mean to you"? Issues such as wildlife abnormalities (zoonoses, under weight animals), oil drums left on the land, spoiled meats, food not fit to eat, and smoke were mentioned. The concept of "contaminants" includes a wide spectrum of related items (many of which are outside the definition of "chemical contaminants") as understood by northerners. There is a need to understand why these misconceptions exist and correct them in future communications as they influence the utility of much of the information delivered from research projects to accurately inform personal decision making.

Examples of responses to the question "What does the word 'contaminant' mean to you?"

"Animals with abnormalities" — "Walrus that have bugs in them" — "Old batteries and fossil fuels contaminate our waters" — "Animals that are too skinny, animals with white spots and bad joints" — "Something that affects the environment and animals" — "Contaminants mean bad food to me" — "Oil drums left around" — "Spoiled meats" — "Smoke" — "Air pollution" — "I think it never goes away" — "Not fit to eat" — "Chicken legs have contaminants in them, not country foods" — "It means poison, contaminants are dangerous".

Table 2 presents the raw results of recall of reception of contaminants communications in the region in the past.

In general, it appears that the level of reception and recall of any past communications regarding contaminants issues is relatively low (mean $< 50\%$) in Nunavut communities, while in Labrador communities the reception and recall of previous information is higher (mean $> 65\%$). Recall of reception of information on contaminants in Labrador was highest among hunters, followed by women of childbearing age and then Elders. In Nunavut, recall of hearing information about contaminants in the region previously, was highest among Elders in the two communities, and approximately the same among hunters and women of childbearing age.

When asked to identify the sources of contaminants for the region, almost all groups participating in the survey reported "development on the land (oil and gas development and mining)" as the most common source (Table 3). "Air pollution (sources from outside the region)", "local garbage dumps", and "motorized vehicles" were the most frequently reported sources following development. Noise pollution, tourists and then scientists were also reported to be a source of contaminants to the region by some participants.

The questionnaire was comprised of 31 questions and analysis is now complete to compare reports of knowledge and comprehension of contaminant related issues and to examine potential factors influencing differences in levels of awareness, comprehension and risk perception among these populations. These results are being discussed with the participating communities.

Table 2. Indication of awareness of contaminants in northern regions among Inuit residents of two Baffin and two Labrador communities

		Have you heard of contaminants in your region?		
Community	**Group**	**Yes (%)**	**No (%)**	**Don't know – no response (%)**
Pond Inlet, Nunavut	Elders	50	17	33
	WCBA*	33	5	62
	Hunters	44	22	33
Clyde River, Nunavut	Elders	86	14	0
	WCBA*	36	24	40
	Hunters	27	0	73
Nain, Labrador	Elders	29	59	12
	WCBA*	77	19	4
	Hunters	76	18	6
Makkovik, Labrador	Elders	67	33	0
	WCBA*	71	29	0
	Hunters	91	9	0

* WCBA – Women of childbearing age (18–40)

Table 3. Sources of contaminants — common responses reported in decreasing order of frequency by each group of participants

Community	Group	Most commonly reported sources of contaminants in the region
Pond Inlet, Nunavut	Elders	Development, air pollution, garbage dump, scientists
	WCBA	Development, air pollution, vehicles, garbage dump, noise, scientists
	Hunters	Development, air pollution, garbage dumps
Clyde River, Nunavut	Elders	Development, air pollution, vehicles, garbage dump, scientists, tourists
	WCBA	Development, vehicles, garbage dump, air pollution, scientists, cleansers
	Hunters	Development, air pollution, garbage dumps, noise
Nain, Labrador	Elders	Development, vehicles, noise, air pollution, garbage dump, tourists, scientists
	WCBA	Garbage dump, development, vehicles, air pollution, noise, tourists, scientists
	Hunters	Development, garbage dump, air pollution, vehicles, noise, tourists, scientists
Makkovik, Labrador	Elders	Development, vehicles, air pollution, garbage dump, noise
	WCBA	Development, vehicles, air pollution, garbage dump, noise
	Hunters	Development, vehicles, air pollution, garbage dump, noise, tourists, scientists

Definitions as presented in questionnaire ("Where do these contaminants come from?"):

*Development – development on the land (oil and gas development and mining)

*Vehicles – motorized vehicles (ATVs, skidoos, etc.)

*Air pollution – air pollution from outside the region

*Noise – airplane noise, etc.

Without some form of formal evaluation exercise, it is difficult to assess whether communication objectives have been attained. With limited empirical evidence it is premature to assume that we fully understand the dynamics of risk communication with such diverse communities or the most effective ways to engage them in decision making (Vaughan, 1995). The results of this project are being used to discuss with regional communicators and researchers to better understand what the current level of awareness and comprehension of basic contaminant concepts is among these population, why some differences in these variables exist, and how best to communicate these issues to northerners in the future.

Expected Completion Date

This project is complete and discussions are ongoing with regional organizations and communicators to develop future research and action initiatives based on these results.

References

Andersen, F., J. Lampe, F. Murphy, C.M. Furgal, and L. Craig. 1999. Country food, nutrition, and health: Developing effective communication strategies in Labrador. In: Kalhok, S. (ed.). Synopsis of Research Conducted Under the 1998/99 Northern Contaminants Program, Northern Affairs Program, Indian and Northern Affairs Canada. Ottawa, ON. ISBN 0-662-28151-9. pp. 291–294.

Berkes, F. and C.S. Farkas. 1978. Eastern James Bay Cree Indians: Changing patterns of wild food use and nutrition. *Ecology of Food and Nutrition.* 7:155–172.

Blanchet, C., É. Dewailly, P. Ayotte, et al. 2000. Contribution of selected traditional and market foods to the diet of Nunavik Inuit women. *Can J Diet Pract Res.* 61:50–9.

Condon, R.G., P. Collings, and G. Wenzel. 1995. The best part of life: subsistence hunting, and economic adaptation among young adult Inuit males. *Arctic.* 48(1):31–46.

Furgal, C.M. 1999. Addressing decision making capacity in northern communities: The case of health advisories and the Labrador Inuit. PhD Thesis, School of Planning, Faculty of Environmental Studies, University of Waterloo, Waterloo, ON.

Jetté, M. (ed.). 1995. Santé Québec. Report of the Santé Québec Health Survey among the Inuit of Nunavik: Diet, a Health Determining Factor. Ministère de la Santé et des Services Sociaux, Gouvernement du Québec, Montréal.

Kinloch, D., H. Kuhnlein, and D.C.G. Muir. 1992. Inuit foods and diet: a preliminary assessment of benefits and risks. *Sci Total Environ.* 122:247–278.

Kuhnlein, H.V. 1992. Change in the use of traditional foods by the Nuxalk native people of British Columbia. *Ecol Food nutrit.* 27:259–282.

Usher, P.J., M. Baikie, M. Demmer, D. Nakashima, M.G. Stevenson, and M. Stiles. 1995. Communicating about contaminants in country food: the experience in aboriginal communities. Research Department Inuit Tapirisat of Canada. Ottawa. May 1995.

Van Oostdam, J., A. Gilman, É. Dewailly, P. Usher, B. Wheatly, H. Kuhnlein et al. 1999. Human health implications of environmental contaminants in Arctic Canada: a review. *Sci Total Environ.* 230:1–82.

Vaughan, E. 1995. The significance of socioeconomic and ethnic diversity for the risk communication process. *Risk Analysis.* 15(2):169–180.

Gwich'in Tribal Council Regional Contaminants Coordinator

Program leader

Fred Carmichael, President, Gwich'in Tribal Council (GTC), Box 1509, Inuvik, NT XOE OTO; phone: (867) 777-4869; fax: (867) 777-4538

Abstract

The Gwich'in still rely heavily on traditional foods, comprising critical components of their diet. The Regional Contaminants Coordinator (RCC) position was developed in July 1999. The RCC position was developed so the Gwich'in would be able to participate in the Northern Contaminants Program (NCP). During the past year, a major component of the NCP in the Gwich'in Settlement Area (GSA) has been the development of programs to measure the level of contaminants in traditional foods. The RCC has developed programs that would address specific concerns under the Local Contaminants Concern blueprint. In this case, it was the collection and analysis of fish from Tsiigehtchic, NT and the collection and analysis of beaver and muskrat from the Mackenzie Delta. The RCC has attended local meetings in each of the communities to address further concerns and pass on information relative to contaminant concerns. Finally, the RCC participated in NCP activities including NCP Results/Training Workshop, Traditional Foods Monitoring Workshop, Emerging Wildlife Diseases Workshop and the Northwest Territories Environmental Contaminants Committee (NWTECC) meetings.

Key Project Messages

1. The Gwich'in Reginal Contaminants Coordinator has raised the awareness of the Gwich'in in regards to local, national and international contaminant issues.
2. Gwich'in continue to harvest and consume traditional/country foods.
3. The RCC has attended several workshops to enhance his capacity to carry out the duties of his position.

Objectives

1. To promote the role of the GTC as a partner in the NCP.
2. To assist Gwich'in communities to identify research and development.
3. To inform and educate the public about contaminants within the Inuvik region.
4. To present the results from studies that are relevant to the consumption of traditional foods in the GSA.
5. To increase capacity at the regional/local level.
6. To coordinate regional studies.
7. To identify complementary environment issues and funding sources.

Introduction

The RCC position has been identified as an integral part of the NCP. These frontline workers are important in the communications aspect of the NCP. Since the inception of the NCP the Gwich'in were not involved directly with the program. The Gwich'in still have strong ties to the

land and still consume traditional foods. In most cases, traditional food is the main staple of the Gwich'in diet. There has been concern expressed by the Gwich'in about contaminants from long range and local sources getting into the food chain. The GTC recognized the studies the NCP were doing in regards to how many contaminants were getting into the food chain and the need for further studies to be completed in order to address the concerns of the Gwich'in. There was also the requirement to communicate this information to the Gwich'in and the NCP. The GTC developed a position to participate in the NCP to address the concerns of the Gwich'in.

The activities carried out by the RCC in the second year were focused on participating in community initiated studies of contaminant levels in traditional foods. The RCC continued to attend community meetings to hear concerns and to pass on information relative to contaminant issues. Furthermore, the RCC participated in all local source contaminant issues in the GSA including the collection and testing of muskrat, beaver and fish species and the remediation of an abandoned Shell Oil Exploration site.

This year the focus of the RCC will be the development of programs to collect baseline data from the GSA, and consultation with the Gwich'in Renewable Resource Councils. The results of these consultations will be the development of proposals, which will be submitted to NCP.

Activities

In 2001–2002

Results Workshop in Calgary — Sept 25–27, 2001

NWTECC Meetings 2001–2002

NWTECC Proposal Review In Yellowknife — Feb 4–5, 2002

Tsiigehtchic Fish Study 2001–2002

Beaver/Muskrat Contaminant Uptake Study 2001–2002

Results

This year the RCC has raised the awareness of the Gwich'in to the activities of the NCP by presenting information at local Renewable Resource Council Meetings and acting as Co-chair of the NWTECC. The RCC has acquired information related to the consumption of traditional foods by collecting and testing fish, muskrats and beaver for contaminants. This has given the people of Gwich'in Settlement Area assurance that the fish are safe to eat. This analysis was brought on by concerns from people of Tsiigehtchic about possible contamination in local fish sources. There was also concern from the people of the GSA about contaminant levels in beaver and muskrat. The RCC position has continued to provide the Gwich'in coordination in Local Contaminant Issues. The RCC has also participated in and provided information to the Gwich'in on other federal environmental programs including Climate Change, Cumulative Effects Assessments, Cumulative Impact Monitoring and the Yukon Development Assessment.

Discussions and Conclusions

The NCP is very important to the Gwich'in because of the their continued reliance on traditional foods. The Gwich'in foresee many opportunities for future projects funded through the NCP. The RCC has brought to the Gwich'in, a position that is dedicated solely to environmental issues. Finally, because of continued use of traditional food the Gwich'in will always need information and reassurance regarding the consumption of those traditional foods.

First Nations Cancer Booklet

Project leader

Cindy Dickson, Council of Yukon First Nations (CYFN), 11 Nisutlin Drive, Whitehorse, Yukon Y1A 3S4; phone: (867) 393-9214; fax: (867) 668-6577; e-mail: cdickson@cyfn.net

Project team

Community Health Representatives, Yukon Contaminants Committee, Jody Walker, Norma Kassi, Yukon Territorial Government (YTG) Health & Social Services.

Abstract

Since the inception of the Northern Contaminants Program there have been numerous workshops and studies in the Yukon on environmental contaminants. People began asking questions about contaminants and their health effects, particularly about cancer. These questions include whether cancer rates are increasing, what types of cancers are most common, and what the relationship is between cancer and contaminants.

These and other ongoing questions have resulted in the need to synthesis available cancer data in the Yukon, and to produce a communications package to begin to answer some of these questions. A draft communications package has been developed, and this proposal is intended to finalize this package.

Key Project Messages

1. Smoking is the main cause of cancer.
2. Eat a healthy well-balanced diet that includes traditional foods.
3. Be physically active.

Objectives

1. To answer questions raised by Yukon First Nations about cancer in relation to environmental contaminants by completing a cancer information communications package.
2. To enhance the confidence of Yukon First Nations in making informed decisions about traditional food consumption and other health-related factors.

Introduction

For several years, there has been substantial information on contaminants and related issues disseminated to the Yukon communities, and the First Nations peoples through workshops, conferences and training. Communications and education continues to be the top priority as questions and related concerns continue to surface. Also within the past 10 years the YFN peoples have witnessed an increase in cancer and other chronic diseases. This has created concerns that needed to be addressed. Many were wondering if the increase in cancer incidence was related to contaminants of a local or long range nature. In an attempt to address these and other related concerns, a Yukon-wide dietary study was conducted which included an analysis of the risks and benefits of

traditional foods. While the results of this study showed that the benefits of consuming traditional foods far outweigh the risks, there continued to be concerns expressed about cancer even during the reporting of these results. Therefore, the Yukon Contaminants Committee proposed to develop a draft cancer information package in response to recommendations by health workers in the Yukon. A draft has now been completed, and this proposal is to complete a review of this draft and produce a final package. The completed cancer communications package will include a booklet and 2 posters, one aimed at children and the other at adults.

Activities

In 2001–2002

A steering committee was established to provide technical and culturally appropriate guidance to this project. Membership included the Yukon's Chief Medical Health Officer, Yukon Territorial Government (YTG) Health & Social Services representatives, Council of Yukon First Nations (Director of Health, Contaminants Program Manager), Canadian Cancer Society (Yukon representative), and a Yukon First Nations elder.

The steering committee assisted with the development of the cancer booklet, which was written up by Jody Walker and Norma Kassi. The booklets were distributed Yukon wide.

Results

The communications package included a booklet as well as colour poster, aimed at children and adults. The booklet contains colour images, both photos and illustrations, as well as plain language text.

Discussion and Conclusion

The posters were distributed to all Yukon First Nations communities (Schools, Health Centres, Chief & Council) in collaboration with territorial and community health workers and the Health Commissioners.

To date the booklet has been used to education individuals about cancers and distributed at General Assemblies and workshops.

Expected Completion Date

March 2002

Acknowledgements

There are many individuals to thank for this project — the steering committees, community members, elders, CHRs and First Nations, for their support and contributions. Mussi.

A Catalogue of Health and Contaminants Communication Materials

Program leader

Christopher Furgal, PhD, Unité de recherche en santé publique, CHUQ-Pavillon CHUL, Université Laval; e-mail: Christopher.Furgal@crchul.ulaval.ca

Project team members

Susie Bernier, Research Associate, CHUL Research Centre, Beauport, PQ; Sarah Kalhok, NCP Secretariat, DIAND, Ottawa, ON; Eric Loring, Inuit Tapirisat of Canada, Ottawa, ON; Stephanie Powell, University of Northern British Columbia.

Key resource organizations

Labrador Inuit Association, Nunavik Nutrition and Health Committee, Inuit Tapiriit Kanatami, Dene Nation, Council of Yukon First Nations, Department of Indian and Northern Affairs, Health Canada.

Abstract

A great deal of information has been developed and disseminated on the topics of country foods, contaminants and health in northern regions and have been met with both positive and negative reception. Specifically, this project has identified, collected and made available more than 250 pieces of communication material (print, audio, video, other) related to the issue of health, contaminants and food in 5 regions of the Canadian North (Labrador, Nunavik, Nunavut, Northwest Territories, Yukon). The focus of the material collected is on those materials produced in relation to the Northern Contaminants Program projects, however it has also included pertinent related material produced by organizations, agencies, and individuals in the last 15 years for their use in the North. The material has been catalogued and entered into a searchable inventory or database to be posted on the Inuit Tapiriit Kanatami, and Council of Yukon First Nations web sites so that it is available to health officials, wildlife representatives, aboriginal organization representatives, key communicators, educators, food distributors, etc. as well as community individuals in the North and elsewhere.

Key Project Messages

1. A great deal of material has been developed and delivered in the North on the issues of contaminants, health and country foods.
2. Much of this information has been developed outside of the North for a northern audience.
3. Little of this material underwent any formal evaluation in its development, or since its dissemination.
4. Regional communicators feel that they know what works best in their regions, but little evidence exists to support these beliefs.

Objectives

1. To identify and collect available communication materials related to the issues of health, contaminants and food in 5 regions of the Canadian North (Labrador, Nunavik, Nunavut, Northwest Territories, Yukon). Focus is on materials produced through the Northern Contaminants Program research projects but includes other pertinent material produced on these issues in the last 15 years (approx.) for their use in the Canadian North;
2. To develop a searchable catalogue or inventory of collected material;
3. To make available, the catalogue/inventory with critique through an existing organizational web-page and/or in electronic format.

Introduction

Challenges in communicating about contaminants, health and country foods have been noted in the North in the past (Usher et al., 1995; Furgal et al., 1995) and have resulted in perceptions and misconceptions of risks, and some changes in traditional cultural practices have been reported in Inuit populations in response to these misunderstandings or reactions to communication (Wheatley and Wheatley, 1981; Dewailly et al., 1994). Choices made by individuals can have significant impacts on aspects of traditional lifestyles resulting in negative impacts on personal health and social well-being (Wheatley and Wheatley, 1981; Dewailly et al., 1994). Usher et al. (1995), Furgal et al. (1995) and Furgal (1999) have documented the need to develop and evaluate culturally appropriate communication strategies to address the information needs of northern communities. To make best use of efforts and resources available, development of new materials should take into account methods, materials, and practices best suited for the northern region targeted, realizing their unique nature and the many differences between them.

A number of initiatives are currently underway by Aboriginal organizations and other regions of the Canadian North to develop easily understandable communication materials in a variety of forms to communicate the results of scientific studies on contaminants with northern communities. All of these activities attempt to base their efforts on the principles of "best practice", building upon past efforts, lessons learned, and methods and materials most appropriate for the region concerned. However, this is not always possible as numerous initiatives have produced a variety of materials in the past, often with limited distribution, and these materials are not easily accessible to communicators today for a number of reasons (accessibility, knowledge of their existence, out of print, etc.). Also, materials produced in one region are not often available, or known of in other regions where they might be helpful in developing material specific to that region, or may be easily applied in their existing form. As a result, a great deal of effort and finances are expended producing materials, and developing methods that already exist or perhaps have been delivered and met with limited success in the past.

By identifying and collecting available materials and messages produced under NCP projects in the past and other pertinent communication material relating to the issue of contaminants, health and food from the northern regions and cataloguing them in a central database accessible to all interested individuals and organizations, this project supports current and future communication efforts and helps develop a better understanding of what "best practice" is relating to these issues in the Canadian North. Additionally, it is argued that providing access to this form of information will directly support the roles and activities of the NCP Aboriginal partners, Regional Contaminant Coordinators, and Territorial and Regional Contaminants Committees.

Activities

2001–2002 / Results

All relevant local, regional, and national health, wildlife, and food distribution agencies (e.g. Northern Store) and organizations and Aboriginal organizations and territorial/regional contaminants committees were contacted and asked to forward known communication materials produced in the last 15 years (approx.) on the issue of food, contaminants and health to the research team. A researcher then visited each of the northern regional centres (Nain/Happy-Valley Goose-Bay, Iqaluit, Kuujjuaq, Yellowknife, Whitehorse) and Ottawa to follow up on these requests, identify and gather further materials and discuss the context of communications on these issues in the North. To ensure that all pertinent materials were collected and included in the database, researchers involved in the NCP during the past 10 years were contacted and similarly asked to forward any materials produced through their NCP funded research to the research team.

Northern organizations/agencies contacted and included in the review included:

- Regional Aboriginal Organizations
- National Aboriginal Organizations

- Regional Health Boards
- Regional and local radio and television stations/offices
- Regional Aboriginal Cultural Centres
- Regional Offices of wildlife, health and social services, and fisheries departments
- Regional and National Offices of northern food distributors (ie. Northern Store)
- National Health, Wildlife, Fisheries and Aboriginal Departments

All material was then sorted and catalogued according to the following topics:

- Type of material
- Year produced
- Title
- Author
- Distribution location and number (where applicable)
- Subject
- Availability
- Contact for materials

Table 1 summarizes the types and numbers of materials collected and included in the database.

A technical consultant was then hired and members of the research team worked with the consultant to develop an Internet-ready searchable database for the material. All material was then entered into the database, and visual material was scanned to link to its text description. The database, searchable by any of the previously described parameters as well as a series of key words linked to the material title and subject, allows the user to access and view (for visual materials) materials that have been previously used in the North. Arrangements are currently being made to post this database on the Inuit Tapiriit Kanatami website (http://www.itk.ca/) as well as the Council of Yukon First Nations contaminants web site (http://www.contaminants.ca) with pertinent links to other sites. A CD ROM version of this database is also being made available in limited numbers. The website will then be managed by the ITK technical staff and updated as more materials are produced and used in the North.

Discussion and Conclusions

From the collection of materials included in this project, it appears that a great deal of material has been produced outside of the North for northern audiences. According to other communications studies conducted in the North (e.g. Usher et al., 1995), the development and dissemination by northerners and in the North is critical to the successful reception and comprehension of messages intended for these communities. Further, although it was difficult to document for all pieces of communications materials collected, it was noted that few materials were reported to have been evaluated either prior to or following their release. Regional communicators and authorities report knowing the "best practice" for their communities, however little empirical evidence or formal evaluation exists to support these arguments. This finding is supported by previous work done by Usher et al. (1995) and Lampe et al. (1999).

Materials that are easy to use, have received positive informal feedback, and are easily adaptable to various regions and cultures have been transferred, and are widely disseminated across the North. Such materials as the GNWT fact sheets on country foods, and other that have been developed following the same format have received significant attention and use to date. The general nature of materials, and their simple adaptability appears to have made them more timeless, and flexible for northern audiences. Their simplicity in approach, but ability to provide some detail on the issues have proven very valuable thus far. Other similarly, simple, and short message oriented materials should continue to be developed based on what has been created in the past. Further, as Lampe et al. (1999) found in Labrador, the level of information synthesis required by the general public is often much greater than that assumed in many materials produced for northern audiences this far. Therefore, even if informal in nature, some form of pre and post evaluation of

Table 1. Summary of types of materials and numbers collected and included in the database on communication materials for health and contaminants in the North

Type of material	Number of pieces included in database
Workshop Proceedings and Presentations	37
Pamphlets/Handouts	27
Movies/Videos	14
Newsletters	18
Posters	12
Documents (research synthesis reports, etc.)	89
Health Fact Sheets	57
Health Advisories (actual advisory)	10

materials must be carried out and documented to ensure the effectiveness of communication material creation and dissemination and reporting of known "best practices" on a regional basis.

Expected Completion Date

This project is now complete, and arrangements are currently being made to post this database on one or more Web sites. It is expected that it will be Internet accessible by late September 2002.

Acknowledgements

We would like to thank all those organizations, agencies, and individuals who helped in the location and collection of communications materials both in the northern and southern locations. Your time and interest in this project is greatly appreciated.

References

Dewailly, É., P. Ayotte, H. Careau, S. Bruneau, and J. Grondin. 1994. Temporal and spatial trends of human exposure from foodchain contaminants in the Canadian Arctic. *Arctic Medical Research.* 53:359–363.

Furgal, C.M., J. Shortreed, R.F. Keith, L. Craig, and É. Dewailly. 1995. Inuit Perspectives on Environmental Contaminants: A report on Avativut/Ilusivut Risk Management Workshops in Nunavik and Labrador. Institute for Risk Research, University of Waterloo, Waterloo, ON. ISBN-0-9696747-6-7.

Furgal, C.M. 1999. Addressing Northern Decision Making Capacity: The case of health advisories and the Labrador Inuit. Ph.D. Thesis, Department of Urban and Regional Planning, University of Waterloo, Waterloo, Ontario, N2L 3G1.

Lampe, J., F. Murphy, C. Furgal, and L. Craig. 2000. Country food, nutrition and health: Developing effective communication strategies in Labrador (Year 2). In: Kalhok, S. (ed.). Synopsis of Research Conducted Under the 1999–2000 Northern Contaminants Program. Department of Indian Affairs and Northern Development, Ottawa, ON. ISBN: 0-662-29320-7. pp. 271–280.

Usher, P.J., M. Baikie, M. Demmer, D. Nakashima, M.G. Stevenson, and M. Stiles. 1995. Communicating About Contaminants in Country Foods: The experience in aboriginal communities. Research Department, Inuit Tapirisat of Canada: Ottawa, ON.

Wheatley, M.A. and B. Wheatley. 1981. The effect of eating habits on mercury levels among Inuit residents of Sugluk, P.Q. *Etudes Inuit Studies.* 5(1):27:43

Relationships Between Risk Perception of Food Chain Contaminants and Country Food Use, Contaminant Exposure and Determinants of Social and Mental Health Among Nunavimmiut

Project leaders

Carole Blanchet, M.Sc. and Christopher Furgal, Ph.D., Public Health Research Unit, Laval University Medical Research Centre, CHUQ, Québec (Carole.Blanchet@crchul.ulaval.ca; Christopher.Furgal@crchul.ulaval.ca)

Project team

Éric Dewailly, M.D., Ph.D., Gina Muckle, Ph.D., and Suzanne Gingras, M.Sc., Public Health Research Unit, Laval University Medical Research Centre, CHUQ, Québec.

Abstract

The consumption of country foods by northern residents represents both significant social, cultural and nutritional benefits but also risks related to the exposure of organic contaminants and heavy metals. The design of appropriate risk communication messages requires the understanding of how socio-demographic and cultural factors relate to differences in consumption patterns, perceptions of health risks and the potential impact this has on the social and mental well being of northern populations. This study conducted a more detailed analysis of the Santé Québec Health Survey database to determine the relationships between risk perception of food chain contaminants and country food use, contaminant exposure and some determinants of social and mental health among Inuit of Nunavik. More than 60% of Inuit surveyed had a favourable perception of country food safety and reported knowledge of contaminants while only 21% of participants had reported modifying their food related habits. Individual perceptions of country foods and knowledge of contaminants varied with some socio-demographic characteristics. However, the knowledge of contaminants did not appear to influence individual perceptions of country foods. Perception and/or knowledge of contaminants and country food were not associated with levels of country food consumption or contaminant intake. Yet, those individuals with a more favourable perception of country foods, knowledge of contaminants and who reported regularly participating in land based activities (hunting and fishing) had higher blood levels of some fatty acids. Finally, we found no association between the main study variables and indicators of psychological distress or social health.

Key Project Messages

1. Knowledge of contaminants and perception of country foods vary with some socio-demographic characteristics.
2. Knowledge of contaminants did not vary with perception of country food safety.
3. Perception of country foods and knowledge of contaminants were not associated with the level of country food consumption.
4. No association existed between the study variables and indicators of social or psychological health.

Objectives

The main objective of this project was to examine the relationships between perceptions and knowledge of the risks of food chain contamination and country food consumption, contaminant exposure and some determinants of social and mental health among the Inuit population of Nunavik.

The specific objectives were to:

1. Examine the relationship between the knowledge and perception of health risks versus actual country food intakes, and contaminant exposure to determine the influence of the perceptions of contaminants on actual consumption behaviours;
2. Examine the knowledge and perception of health risks related to contaminants in country foods according to socio-demographic factors and the level of participation in land based activities (hunting, fishing, etc.) by individuals;
3. Examine the relationship between country food use and some determinants of social and mental health status and thus indirectly the impacts of these perceptions on aspects of social and mental health among Nunavimiut.

Introduction

Country food is central to the values, economy, physical, social and mental health of Inuit communities and individuals and reflects the close relationship between Inuit and their environment. Moreover, the act of hunting, processing, sharing and consuming country foods adds to psychological and spiritual well-being (Usher, 1995). However, at the same time, country food is the primary source of exposure to most persistent environmental contaminants for Inuit. Strong evidence exists regarding a decrease in traditional food consumption by Inuit over past decades and that a fear of contaminants may play a role in influencing this reduction (Blanchet et al., 2000; Santé Québec, 1995; Dewailly et al., 1994). Because of the uncertainties inherent in risk assessments and thus risk management processes, ambiguous messages have been communicated to the Inuit population in the past (i.e., there are contaminants in country foods, but they are still the best foods to eat; the benefits outweigh the risks, but research is ongoing to better understand the risks posed to human health of country food consumption). Indeed, an examination of past experiences of health advisories has revealed potential impacts on the well-being of Inuit populations as they have resulted in confusion, fear, stress, anxiety, changes of consumption patterns, use of harvest areas, etc. (Grondin et al., 1994; Usher et al., 1995). A better understanding of the relationships between perceptions of contaminants and actual country food related behaviours, of the many factors influencing these perceptions; and the relationships between perceptions, participation in country food related activities (including consumption) and aspects of social and mental health in Inuit communities is required to help better manage and communicate to northern populations the risks and benefits of country foods and to support informed decision making on these issues. Currently, many of these relationships are hypothesized yet little or no quantitative data exists to support these arguments.

Risk determination for traditional food must simultaneously consider the potential risks from exposure to contaminants and the socio-cultural, nutritional, economic and spiritual benefits associated with traditional foods (Van Oostdam et al., 1999; Furgal et al., 2001). Indeed, designing an appropriate risk communication strategy requires understanding how socio-demographic and cultural factors relate to differences in consumption patterns, perceptions of health risks related to food contamination and the potential impacts these activities and perceptions have on the social and mental well-being of northern populations.

Activities

In 2002–2003

The work for this project consisted of a more detailed analysis of the existing data collected in 1992 during the Santé Québec Health Survey among Inuit of Nunavik, with an extension of our analysis to contaminant intakes by using contaminant databases previously developed at the Public Health Research Unit of CHUL (Québec).

Food contaminant data was drawn from database developed for the previously NCP funded project "Health risk assessment and elaboration of public health advices concerning contaminants in Nunavik", (Dewailly et al., 1996). Information for this study was also gathered from several of the questionnaires used in the Santé Québec Study including:

- 24-hour dietary recall (Completed by 433 Inuit ranging from 18 to 74 years of age — 197 men and 236 women),
- Household questionnaire gathering standard socio-demographic characteristics about the population and which included the following:
  - A perceptual index used to assess Inuit opinion regarding three country food statements ("commercial foods are less healthy and less nourishing than country foods"; "commercial foods are better and more modern than country foods"; and "commercial foods are better because country foods are contaminated by pollution"; Santé Québec, 1994).
  - Knowledge of country food contamination by PCBs and other contaminants.
  - Changes of food habits following the announcement of PCBs in the breast milk of Inuit women.
  - Frequency of country food consumption (marine mammals and associated food items).
  - Level of participation in traditional land activities (hunting and fishing).
  - Variables relating to determinants of social and mental health (such as psychological distress and social support).

Data analysis

Arithmetic means and 95% confidence intervals of contaminant and country food intakes and blood concentrations of contaminants were calculated according to various categories. Analysis of variance (ANOVA) was used to examine comparisons among groups and chi-square tests were also used to compare the proportions. All statistical analyses were conducted with the Statistical Analysis System (SAS, 1996) software and statistical significance was set at $p \leq 0.05$.

Partial non-response

Santé Québec reviewed and validated the data using intra- and inter-questionnaire techniques. When there was variation in the profiles of respondents and non-respondents, non-respondents were rejected. However, the partial non-response, which consists of the non-response on each question or variable, could have resulted in some biased estimates in the present study. Thus, caution should be used in interpreting the results. Moreover, in this study, we used data from the 24-hour dietary recall to assess country food and contaminant intakes according to the main study variables. The value of the 24-hour dietary recall method in assessing the intake of groups is well established (Willet, 1998). It can provide a fair estimate of a population's average

Table 1. Level of perception for country foods according to knowledge of contaminant health risk and attitudes

	Level of Perception		
	Less Favourable	No Opinion	Most Favourable
Knowledge of health risk associated to contaminants			
– Yes	18.8	13.5	67.7
– No	18.9	27.6	53.5
(p value)	(0.002)		
Changes in living habits			
– Yes	40.6	6.3	53.1
– No	12.7	15.2	72.2
(p value)	(< 0.001)		
Participation in land based activities			
– Yes	18.9	15.0	66.1
– No	16.4	30.9	52.7
(p value)	(0.01)		

intake. However, 24-hour dietary recalls are rarely representative of long-term intake and do not allow the identification of the proportion of individuals "at risk" for contaminant exposure. Hence, results obtained here do not permit us to infer a cause-effect relationship between socio-demographic factors and contaminant exposure.

Results

Statistical analysis revealed that in 1992, 61.8% of Inuit had a favourable perception of country foods whereas only 18.3% had a less favourable perception and 19.9% reported no opinion about country foods. Moreover, 69.4% of the adult population of Nunavik mentioned knowledge of PCB contamination in country foods, however, only 21.8% of Inuit declared having changed their living habits since first hearing about PCBs in breast milk of Inuit women.

The knowledge of food contamination did not appear to decrease the perception of country foods (Table 1). Among Inuit who knew of food chain contamination, a greater proportion had a very favourable perception of country foods than those who did not report knowing of contaminants in country foods. Among those reporting changing their living habits following the announcement of PCBs in breast milk of Inuit women in 1992, a greater proportion had a lower perception of country foods compared with those who did not report making any changes. In contrast, a greater proportion of Inuit who had a more favourable perception of country foods or no opinion did not change their living habits. A more positive perception of country foods was observed among Inuit who participated in land based activities (hunting and fishing). Changes in living habits and the practice of land based activities were not associated with the knowledge of food contamination.

A more positive perception of country foods was found among Inuit 30 years of age and older ($p < 0.001$), among those reporting having a wage earning job ($p = 0.014$), living in couples ($p = 0.003$), and living in households of 4 or more residents ($p = 0.031$). A greater number of people 30 years and older ($p < 0.001$), with no formal schooling ($p = 0.016$), married or living in common law ($p < 0.001$) reported knowledge of food chain contamination than those 18 to 29 years old, with some secondary school education, or who reported their marital status as single.

A greater proportion of Inuit women reported making changes in their living habits as compared with Inuit men. Among those women reporting changing their living habits ($n = 68$), 37% declared eating less marine mammals (in particular blubber), 15% ate less fish, 13% reported not eating marine mammals anymore, and 12% reduced the duration of breast feeding. Among the changes, only the consumption of marine mammals differed between the sexes with more men than women reducing this consumption.

A greater proportion of men than women ($p < 0.001$), and residents of Ungava coast communities ($p < 0.001$) reported regularly participating in land based activities. As well, more wage earning ($p = 0.01$), and married, divorced or widowed individuals ($p = 0.026$) reported participating regularly in land based activities than jobless and/or single individuals surveyed.

The perception of country foods and knowledge of contaminants did not vary significantly with the mean intakes of country foods and contaminants (Aroclor 1260, DDE, mercury and lead). However, Inuit who consumed seal fat two times or more per month had the most favourable perception of country foods as compared to those who ate this item less often ($p = 0.0002$). Moreover, a greater proportion of Inuit who participated in land based activities declared having eaten beluga and seal blubber at least two times per month as compared to those who reported not going out on the land (p values < 0.001) yet the consumption of seal and beluga meat, beluga blubber and muktuk did not vary with the levels of perception and knowledge of food contamination. The intake of country foods, Aroclor 1260, DDE and mercury were similar among all participants, however, mean lead intake was significantly higher ($p = 0.03$) among Inuit who had participated in land based activities. Mean concentrations of Aroclor 1260, mercury and lead varied significantly according to perception levels of country foods with Inuit having no opinion about country food safety and health showing the lowest concentrations for these 3 contaminants. Inuit who mentioned knowing of PCB country food contamination had higher concentrations of Aroclor 1260, DDE mercury and lead than Inuit who did not report knowing of the contamination. Finally, blood contaminant concentrations did not differ significantly between individuals reporting having changed (or not) their lifestyle since hearing of food chain contamination or according to their reported level of participating in land based activities.

When reviewing blood profiles of Inuit surveyed, mean concentrations of EPA + DHA were found to be significantly higher among Inuit who had a most favourable perception of country food ($p = 0.03$). Inuit who reported knowing of contaminants in country foods, and participated regularly in land-based activities had higher plasma concentrations of EPA + DHA than those who did not

know of the contamination ($p = 0.03$), or did not report being as active in land-based pursuits ($p = 0.05$). Finally, we verified whether main study variables were related to psychological distress and social health. No relationship was found between the variables.

Discussion

The results of our study support some of the previously assumed hypotheses regarding the relationship between perception of country foods and some socio-demographic factors and the consumption of certain country food items (Burger, 2000; Vaughan, 1995). Our results suggest that communication about environmental contamination had moderately affected the perception of food quality among Nunavimmiut. However, considering that 69.4% of the Inuit were aware of country food contamination and only 21.8% of Inuit declared to have changed their living habits following the announcement of contaminants, we believe that the knowledge of country food contamination did not decrease substantially the perception of country foods among Nunavimmiut (61.8% of Nunavimmiut had a very favourable perception of country foods at the time of the survey). Human conceptions, perceptions and reactions to risk are complex. Usher et al. (1995) concluded that political, economic, cultural and psychological factors shape perceptions of country foods in Aboriginal communities. Hence, the high social, economic, cultural and traditional value of country foods may explain why most Inuit had a very favourable perception of country foods even when aware of contaminant issues. More research is required in this area to assess the impact of social, economic and cultural influences on country food perception and the acceptance of health advice messages related to country foods and contaminants.

Our results showed that older Inuit had a better perception of country foods than younger Inuit, which may explain the higher consumption of country food by older Inuit. Borré (1991) reported certain comments of older Baffin Inuit revealing that Inuit who grew up eating traditional foods continue to do so regularly to survive. Furthermore, the Santé Québec Health Survey revealed that younger Inuit were less aware than Elders of the relationships between food and health. These observations may explain the most favourable perception of country foods that we found among Inuit of older ages. The most favourable perceptions of country foods were also reported by Inuit living in couples. Our recent project entitled "Socio-demographic factors influencing nutrition and contaminant exposure in Nunavik" revealed that Inuit living in couples were more likely to consume country foods as compared with others, suggesting that single, separated or widowed Inuit may have less access to traditional food resources or the resources to attain these foods (equipment, etc.). Recently, Duhaime et al. (2001) reported that the presence of a male as the head of a household and, to a lesser extent, access to a wage income raised the proportion of traditional/country foods in the total diet among Nunavik women. Wein et al. (1991, 1988) also reported that the availability of traditional/country foods depended greatly upon having a hunter in the family who was equipped with adequate resources (including means of transportation) and skills. We found that participation in land-based activities was greater among men, among Inuit having a wage-earning job and among those living in couples or divorced/widowed Inuit.

Results revealed also that among people who have changed their living habits following the announcement of PCBs in breast milk were, in general, evenly distributed according to socio-demographic factors. A greater proportion of Inuit women appeared to have made changes in their living habits. This observation appeared to be consistent with the type of communication released in Nunavik, e.g. the announcement of PCBs in the breast of Inuit women.

Finally, this study permitted the examination of contaminant exposure (intakes and blood concentrations) among the Inuit population of Nunavik according to perceptions and knowledge of country food contamination, subsequent modifications of food habits and the level of participation in land activities. Results do not permit us to establish causal relationships even though significant statistical associations were observed between the study variables. The combined results from several studies are needed to support causal relationships between such factors as socio-demographic elements and contaminant exposures. In this study, the main differences in contaminant intake observed according to the study variables may be explained by the quantity and items of country food consumed on the day before the survey. These factors depend on the availability and accessibility of traditional/country foods at this time, and the concentration of contaminants in specific country food items, which vary greatly between species.

Currently, there is very little literature concerning relationships between contaminant exposure and our main study variables. Our results showed that contaminant intake did not vary according to perception of country foods and knowledge of food chain contamination. In contrast, blood concentrations of contaminants varied significantly according to these variables (except for DDE). Concentrations of Aroclor 1260 and lead were higher among Inuit having a less favourable perception

of country foods whereas mercury concentration was higher among those having a very favourable perception. Moreover, Inuit having no opinion showed the lowest concentration of contaminants. These differences observed for the relationships between intakes and blood concentrations of contaminants may be explained by the source of contaminants consumed. Moreover, it is possible that the use of 24-hour dietary recall is not a valuable tool to compare intakes and blood concentrations of contaminants.

Expected Completion Date

This project has been completed and is being communicated to the Nunavik Nutrition and Health Committee during the fall of 2003.

References

Blanchet, C., É. Dewailly, P. Ayotte, S. Bruneau, O. Receveur, and B.J. Holub. 2000. Contribution of selected traditional and market food to Nunavik Inuit women diet. *Can J Diet Pract Res.* 61:50–59.

Borré, K. 1991. Seal blood, Inuit blood and diet: A biocultural model of physiology and cultural identity. *Medical Anthropology Quarterly.* 5(1):48–62.

Burger, J. 2000. Consumption advisories and compliance: the fishing public and the deamplification of risk. *Journal of Environmental Planning and Management.* 43(4):471–488.

Dewailly, É., S. Bruneau, C. Laliberté, G. Lebel, S. Gingras, J. Grondin, and P. Levallois. 1994. The contaminants. In: Santé Québec (ed.), Report of the Santé Québec Health Survey among the Inuit of Nunavik. Montréal, Ministère de la Santé et des Services Sociaux, Gouvernement du Québec. pp. 73–107.

Dewailly, É., C. Blanchet, S. Gingras, C. Furgal, and S. Bruneau. 2001. Sociodemographic factors influencing nutrition and contaminant exposure in Nunavik. In: Kalhok, S. (ed.), Synopsis of Research Conducted Under the 2000–2001 Northern Contaminants Program. Department of Indian Affairs and Northern Development, Canada. Ottawa, ON. ISBN: 0-662-30872-7.

Dewailly, É., P. Ayotte, C. Blanchet, G. Carrier, S. Bruneau, B.J. Holub, and M. Grey. 1996. Health risk assessment and elaboration of public health advices concerning food contaminants in Nunavik. Ottawa: Indian and Northern Affairs Canada, 55 pp.

Duhaime, G., M. Chabot, and M. Gaudreault. 2001. Food consumption patterns and socio-demographic factors among the Inuit of Nunavik. *Ecology of Food and Nutrition.* 40(2):91–118.

Furgal, C.M., S. Bernier, G. Godin, S. Gingras, J. Grondin, and É. Dewailly. 2001. Decision making and diet in the North: Balancing the physical, economic and social components. In: Kalhok, S. (ed.), Synopsis of Research Conducted Under the 2000–2001 Northern Contaminants Program. Department of Indian Affairs and Northern Development, Canada. Ottawa, ON. ISBN: 0-662-30872-7.

Grondin, J., J.-F. Proulx, S. Bruneau, and É. Dewailly. 1994. Public Health and Environment in Nunavik. *Inuit Studies.* 18(1–2):225–251.

Santé Québec. 1994. Report of the Santé Québec Health Survey among the Inuit of Nunavik. 1992. Ministère de la Santé et des Services Sociaux du Québec, Gouvernement du Québec, Montréal.

SAS Institute Inc. 1996. The SAS System for Windows. ed. 6.12. Edition. Vol. NC27513. Cary, USA. SAS Institute Inc.

Usher, P.J., M. Baikie, M. Demmer, D. Nakashima, M.G. Stevenson, and M. Stiles. 1995. Communicating about contaminants in country food: the experience in Aboriginal communities. Research Department of Inuit Tapirisat of Canada. Ottawa.

Van Oostdam, J., A. Gilman, É. Dewailly, P. Usher, B. Wheatly, H. Kuhnlein, S. Neve, J. Walker, B. Tracy, M. Feeley, V. Jerome, and B. Kwavnick. 1999. Human health implications of environmental contaminants in Arctic Canada: a review. *Sci Total Environ.* 230:1–82.

Vaughan, E. 1995. The significance of socioeconomic and ethnic diversity for the risk communication process. *Risk Analysis.* 15(2):169–180.

Wein E. and J.H. Sabry. 1988. Use of traditional/country foods by Native Canadians in the Taiga. *Arctic Medical Research.* 47(Suppl. 1):134–138.

Wein, E., J. Sabry, and F. Evers. 1991. Food consumption patterns and use of traditional/country foods by Native Canadians near Wood Buffalo Park, Canada. *Arctic.* 44(3):196–205.

Willet, W. 1998. Nutritional Epidemiology. In: Monographs in epidemiology and biostatistics. Second edition. New York, Oxford University Press, pp. 50–94.

Nunavik Nutrition and Health Committee Communications and Coordination Program: Regional Contaminants Coordinator

Program leader

Minnie Grey, Chairperson, Nunavik Nutrition and Health Committee, Nunavik Regional Board of Health and Social Services, Kuujjuaq, Nunavik; phone: 819-964-2222; fax: 819-964-2888; e-mail: Minnie.Grey@sympatico.ca; Serge Dery, Director of Public Health, Nunavik Regional Board of Health and Social Services, Kuujjuaq, Nunavik; phone: 819-964-2222; fax: 819-964-2888; Serge_Dery@ssss.gouv.qc.ca

Project team members

Nunavik Nutrition and Health Committee members: Nunavik Regional Board of Health and Social Services (4 representatives); Makivik Research Centre (2 representatives); Kativik Regional Government (1 representative); Inuulitsivik Health Centre (1 representative); Public Health Research Unit — CHUQ Research Centre (3 representatives); Inuit Tapiriit Kanatami (1 representative).

Abstract

The Nunavik Nutrition and Health Committee (originally named the PCB Resource Committee) was established in 1988 to deal with issues related to food, contaminants, the environment and health in Nunavik. Since its inception, the committee has broadened its perspective to take a more holistic approach to environment and health issues inclusive of both benefits and risks. Today, the committee acts as the authorized review and advisory body for health and nutrition issues in the region and includes representation from many of the organizations and agencies concerned with these issues, as well as those conducting research on them. The committee provides guidance and acts as a liaison for researchers and agencies, from both inside and outside the region, directs work on priority issues, communicates to and educates the public on health and environment topics and research projects, and represents Nunavik interests at the national and international levels. All activities are conducted with the goal to protect and promote public health in Nunavik, through more informed personal decision-making. The committee proposes to continue these activities through their involvement in the Northern Contaminants Program during the 2002–2003 research year.

Key Project Messages

1. The Nunavik Nutrition and Health Committee is the key regional committee for health and environment issues in Nunavik;
2. The committee originated in 1989 and supports the activities of the Public Health Director in advising and educating the public on food and health issues, including benefits and risks associated with contaminants and country foods;

3. The committee continues to be active within the NCP, reviewing and supporting research in the region, liaising with researchers, and helping in the communication of research results in a way that is appropriate and meaningful to Nunavimmiut.

Objectives

The general objective of this project is to address regional communication needs and provide information necessary for the public understanding of data relevant to environmental health and contaminants issues in Nunavik. Specifically, the objectives are:

1. To provide the population and health workers with background information to help them understand and contextualize environmental health, nutrition and contaminants research, objectives and results;
2. To compile elements of public concern that have not been addressed to date, and to steer and support research activities towards providing the data needed to address these concerns;
3. To undertake public communications of environmental health data, including results of Northern Contaminants Research Projects, and help develop regional communications and evaluations strategies for this information;
4. To prepare state of the knowledge summaries on these issues to assist in communication and intervention activities of local health and environment officials;
5. To facilitate research on environmental communications and risk perception issues;
6. To help researchers translate their data into meaningful information for the public;
7. To support partnerships in various research and intervention activities related to country foods, nutrition and health.

Introduction

In Nunavik, a group of individuals representing different organizations concerned with health, the environment, and nutrition issues formed to address these topics and communicate with/educate the public so that they may make more informed personal decisions. The group, the Nunavik Nutrition and Health Committee, evolved from the PCB Committee, created in 1989 and later renamed the Food, Contaminants and Health Committee. The name has changed over the years as the group has learned of the importance to not only focus on negative impacts of contaminants, but the need for a more holistic approach to nutrition, health and the environment including benefits as well. On an ongoing basis, the committee addresses a number of issues relating to food, contaminants, nutrition and health and the relationship to the environment. This report represents a synopsis of the committee's activities for the 2001–2002 year. The committee is the recognized and authorized body for the region on health and environment issues.

This evolution and recognition of the NNHC places it in an important role in addressing issues related to contaminants, food, health and the environment in the region. The committee is therefore well positioned, and has the necessary capacities to support research activities (through review, facilitation, and communication) related to these issues under the Northern Contaminants Program as a regional contaminants committee. This report represents a synopsis of the committee's coordination activities for the 2001–2002 year.

Activities

In 2001–2002

In 2001–2002, the coordinator of the committee:

- Participated in the ITK-RCC training activities;
- Supported the activities of the Public Health Director in regards to his role in the committee;
- Participated in the integration and communication of environmental health research findings for the general public as well as specific target groups;
- Participated in all regional community activities of the committee;
- Provided the link between committee members and between the committee and regional organizations on different topics related to country foods, nutrition and health;
- Participated in the organization of the committee meetings by preparing the agenda and by providing to committee members, documents, materials and correspondence related to topics discussed at the meetings;
- Prepared and distributed minutes of committee meetings;
- Acted as liaison between researchers, involved in the region and outside the region, and the committee;

- Represented Nunavik interests in the Inuit Diet and Health Study consultation meeting;
- Participated in adapting intervention strategies designed outside Nunavik for use in the region, and in mobilizing regional actors to define new or appropriate interventions.

Activities

In 2002–2003

The Regional Contaminants Coordinator (RCC) is working with the Nunavik Regional Board of Health and Social Services, under the Director of Public Health and chairperson of the committee. As a member of the NNHC, the RCC is working in an interdisciplinary environment of researchers, wildlife and health officials, health care professionals, and community representatives. The RCC has the responsibility of coordinating the activities and operation of the NNHC. The tasks of the RCC include: planning regular meetings, preparing the agenda, taking notes and preparing the minutes. Furthermore, the RCC fulfilled many other responsibilities:

1. Follow up the correspondence with other regional and national organizations.
2. Act as liaisons between researchers and specific communities to gain the proper authorization and conduct appropriate consultation with community councils, health officials, and potential participants.
3. Follow-up on researchers up-dates of their work to the NNHC and involvement in the planning and realisation of communication activities.
4. Inform researchers of committee's recommendations for communication/dissemination activities on their projects.
5. Organize all logistic aspects of regional communication tour.
6. Prepare mid-year and final reports for the NCP Program.

Conclusion

The Nunavik Nutrition and Health Committee is an active body supporting and enhancing the region's research and decision-making capacity related to environmental health issues including exposure to environmental contaminants. This is done through a variety of activities in which they represent the interests of Nunavik residents. Through these activities they cooperatively manage and disseminate information to the public to support informed decision making on issues of health and nutrition.

Expected Completion Date

This is an ongoing project as the committee coordinator is active on these issues in the region annually.

Acknowledgements

The committee coordinator would like to thank the Northern Contaminants Program and the Nunavik Regional Board of Health and Social Services for ongoing support and funding of their activities related to health, contaminants and nutrition in the region.

The GLOBE Program — New POPs in the Arctic, 2001–2002

Project leader(s)

Peter Hardy, GLOBE Arctic Coordinator, c/o Yellowknife Catholic Schools, P.O. Box 1830, Yellowknife, Northwest Territories X1A 2P4; phone: (867) 873-4888; fax: (867) 873-5732; e-mail: arctic_aussie@yahoo.com
Catherine McEwen, GLOBE Country Coordinator, c/o Northern Biomes Ltd, 220 Holmes Road, Salt Spring Island, BC V8K 1T6; phone: (250) 653-9148; fax: (250) 653-9602; e-mail: cmcewen@saltspring.com

Project team

Project team includes the teachers trained and conducting the GLOBE-NILU project with students. They are:
Donald Mearns, Vice Principal, Attagoyuk School, Pangnirtung, Nunavut; Stacy Applejohn, Science teacher, Samuel Hearne High School, Inuvik, NWT; Jeff Szeryk, Science teacher, Samuel Hearne High School, Inuvik, NWT; Andrew Applejohn, Research & Administration, Aurora Research Institute, Inuvik, NWT; Gary Morgan, Curriculum Initiatives Coordinator, Yukon Education, Whitehorse, Yukon; Bob Sharp, Experiential Science 11 teacher, Yukon Education, Whitehorse, Yukon; Mabel Tetlichi, Cultural/Education Liaison to Chief Zzeh Gittlit School, Old Crow, Yukon.
The Vuntut Gwitchin First Nation, Inuit Tapiriit Kanatami, Inuvialuit Regional Corporation, Council for Yukon First Nations, Dene Nation, and the Department of Education of Nunavut, NWT and Yukon, respectively, support the GLOBE-NILU Arctic POPs project in principal.

Abstract

The GLOBE Program — New Pops in the Arctic, 2001–2002 represents Canada's involvement in the GLOBE-NILU Arctic POPs project — a joint initiative of GLOBE Norway and The GLOBE Program. The project uses students and teachers to sample for the presence of PCBs and PBDEs in the Arctic food chain. The project involves at least two high schools from each of seven circumpolar countries participating. The international representation supports communication between the countries and encourages cooperation within the circumpolar world.

During the 2001–2002 funding period, teachers gathered at a workshop for training in Arctic POPs and in the specific protocol for field sampling for local fish, in addition to training in the many GLOBE protocols for monitoring the environment. Fish samples were sent to the Norwegian Air Research Institute (NILU) where they were analysed for PCB153, PBDE47, and PBDE99. The timing of receipt of the lab results exceeded the NCP funding period, precluding student analysis of the results during same period. Spring 2002 field sampling will repeat the Fall 2001 protocol, sampling local fish for PCBs and PBDEs.

An ongoing project for 4 years, each year the field sampling will include a different component of the food web or environment.

See www.nilu.no/niluweb/services/arcticpops/ for details on the Arctic POPs project. See www.globe.gov for details on The GLOBE Program.

Key Project Messages

1. Students and teachers learn about the important environmental issues surrounding Persistent Organic Pollutants (POPs) in the Arctic;
2. Students and teachers sample for known PCBs (polychlorinated biphenyls) and new PBDEs (polybrominated diphenyl ethers) in the Arctic food chain, offering new data to the scientific community;
3. Circumpolar in perspective, students gather comparative samples from around the Arctic;
4. Learning western scientific methodology, doing "hands-on" science, within the context of the local environment, offers an avenue for building capacity within the communities.

Objectives

1. To sample and evaluate the presence and distribution of Arctic POPs, namely PCBs and especially PBDEs in the Arctic food chain;
2. To increase the knowledge of Arctic POPs and environmental science in schools, and the greater community;
3. To invest in human resources through student training and development of research mentorship;
4. To make an example of the contribution of students to scientific knowledge.

Introduction

The GLOBE Program — New POPs in the Arctic, 2001–2002 project represents Canada's involvement in the GLOBE-NILU Arctic POPs project. The 4-year project has a circumpolar scope — involving Norway, Sweden, Finland, Russia, Iceland, Canada, and United States. Most countries have two high schools involved by virtue of GLOBE Norway offering to fund the cost of laboratory analysis of samples from two schools per country. Canada has chosen to have three schools participate, one each from Yukon, NWT and Nunauvt, respectively.

Modeled after The GLOBE Program, whereby students follow specific scientific protocol, as taught by pre-trained teachers, and gather data for use by scientists, GLOBE Norway developed a program for high school students to study Arctic POPs in their local environment and solicited the involvement of scientists at the Norwegian Air Research Institute (NILU). In keeping with the international aspect of The GLOBE Program, GLOBE Norway created a circumpolar project and invited all circumpolar countries involved with The GLOBE Program to participate.

In August 2001, participating teachers were trained in Fairbanks, Alaska — in the GLOBE-NILU protocol for sampling fish, in the GLOBE protocols, and in the characteristics and issues of persistent organic pollutants, especially in the Arctic. Scientists at NILU chose to have students investigate the presence of PCBs, already known to be in the Arctic food chain, and the presence of PBDEs, a "new" POP for parts of the Arctic.

The first round of sampling in Fall 2001 involved fish — sampling the muscle tissue of trout or salmon, or the liver of cod, dependent on what was locally available. Immature female fish were preferred. Odoliths were extracted for age determination. As per the sampling protocol, all precautions were taken to avoid contamination of the samples with plastics. See www.nilu.no/niluweb/services/arcticpops/ for further details on sampling methods and analysis.

Activities

In 2001–2002

Funding from NCP — Phase II for *The GLOBE Program — New POPs in the Arctic, 2001–2002* allowed for the training of Canadian teachers at the Fairbanks workshop and their participation with their students in the field sampling for PCBs and PBDEs.

Fairbanks, Alaska training workshop, August 2001

In August 2001, seven Canadian teachers (see above for names and schools) were trained in the GLOBE and Arctic POPs protocols in Fairbanks, alongside teachers from the six other participating circumpolar countries.

The newly appointed Country Coordinator for the GLOBE program in Canada, Cate McEwen, was also trained. Peter Hardy, acting as Arctic GLOBE Coordinator, organized the Canadian participation, participated as a GLOBE trainer at the workshop, and received training in the GLOBE-NILU Arctic POPs fish sampling protocol.

During this training workshop, a representative from each school gave a presentation on their school environment, their

Table 1. The GLOBE-NILU Arctic POPs Project — Arctic POPs results from Fall 2001 fish sampling – Raw data (see Table 2 for details on codes)

ng/g wet weight	NO1a	NO1b	NO2a	NO2b	NO3a	NO3b	IS1a
PCB 153	26.6787	26.3467	16.4312	97.0802	40.1798	71.3358	24.4956
PBD E47	7.7932	6.1845	2.997	12.4948	8.6673	19.7819	6.9919
PBD E99	1.8077	0	0	4.1575	1.741	4.2107	2.0369

ng/g lipid weight	NO1a	NO1b	NO2a	NO2b	NO3a	NO3b	IS1a
PCB 153	61.64943	65.294	35.20971	445.6864	92.32805	142.6716	66.84393
PBD E47	18.00861	8.425261	6.422143	57.36249	19.91635	39.5638	19.07959
PBD E99	4.177253	0	0	19.0867	4.000596	8.4214	5.55832

ng/g wet weight	IS1b	IS2b	SW1a	SW1b	SW2a	FI1a	RU1a
PCB 153	25.4449	48.7276	3.6209	3.8842	17.2569	5.0378	19.9181
PBD E47	10.0094	0	0.3798	0.5457	2.2891	0.4899	0
PBD E99	2.232	0	0	0.3319	0.7404	0	0

ng/g lipid weight	IS1b	IS2b	SW1a	SW1b	SW2a	FI1a	RU1a
PCB 153	63.12293	205.352	197.9425	285.2113	431.4225	866.5016	338.6077
PBD E47	24.83101	0	20.7624	40.06997	57.2275	84.2628	0
PBD E99	5.537077	0	0	24.37094	18.51	0	0

ng/g wet weight	RU1b	AL1a	AL1b	AL2a	AL2b	CA1a	CA1b
PCB 153	2.454	5.3	5.0972	0.2325	0.2256	9.0216	13.6753
PBD E47	0	0	0.9157	0	0	0	0.5686
PBD E99	0	0	0	0	0	0	0

ng/g lipid weight	RU1b	AL1a	AL1b	AL2a	AL2b	CA1a	CA1b
PCB 153	40.9	18.63548	23.04821	6.701471	7.53504	29.3202	40.43132
PBD E47	0	0	4.140557	0	0	0	1.681078
PBD E99	0	0	0	0	0	0	0

ng/g wet weight	CA2a	CA2b	CA3a	CA3b
PCB 153	4.3187	3.7492	2.739	0.9244
PBD E47	0	0	0	0.2307
PBD E99	0	0	0	0

ng/g lipid weight	CA2a	CA2b	CA3a	CA3b
PCB 153	33.55298	22.4952	34.57988	11.71623
PBD E47	0	0	0	2.923988
PBD E99	0	0	0	0

Table 2. Codes of samples detailing school origin, fish species, and whether muscle tissue or liver

Code	School
NO1a	Norway Vannraeid Cod liver1
NO1b	Norway Vannraeid Cod liver2
NO2a	Norway Vestvågøy Cod liver1
NO2b	Norway Vestvågøy Cod liver2
NO3a	Norway Kjøllefjord Cod liverA
NO3b	Norway Kjøllefjord Cod liverB
IS1a	Island VMA Cod liver1
IS1b	Island VMA Cod liver2
IS2b	Island Barnaskoli Haddock liver2
SW1a	Sweden Hjalmar Trout fillet1
SW1b	Sweden Hjalmar Trout fillet2
SW2a	Sweden Laestadius Salmon fillet1
FI1a	Finland Pudas Whitefish fillet1
RU1a	Russia Gymnasium Coregonus liver1.2
RU1b	Russia Gymnasium Coregonus liver3.2
AL1a	Alaska Kodiak Cod #1
AL1b	Alaska Kodiak Cod #2
AL2a	Alaska Polaris Salmon fish1
AL2b	Alaska Polaris Salmon fish2
CA1a	Canada Samuel HH Loche liver1
CA1b	Canada Samuel HH Loche liver2
CA2a	Canada Chief WF2-liver Lake whitefish
CA2b	Canada Chief WF3-liver Broad whitefish
CA3a	Canada Attagoyuk Char1 fillet
CA3b	Canada Attagoyuk Char2 fillet

students and community. These presentations alone initiated a circumpolar awareness among the participants.

Training at the workshop certified the teachers as GLOBE trainers, enabling them to train other teachers in GLOBE protocols and thereby spread the implementation of GLOBE in schools. The Arctic POPs training, provided by NILU, developed awareness about Arctic POPs and the impact of POPs on Arctic life.

Fall 2001 field sampling

Students sampled local fish — lingcod in Inuvik, Arctic char in Pangnirtung, and whitefish in Old Crow — by gill net or fishhook, during October 2001. Samples were then sent to Norway for analysis at the NILU facilities.

Results from NILU were received mid-April representing analysis for PCB 153, PBDE 47, and PBDE 99, as both wet weight and lipid weight (see below). Results await student interpretation, and at the close of the 4-year project, will be assessed and analysed by NILU scientists.

GLOBE team building through other training workshops

The Fairbanks training, in combination with a GLOBE training workshop held in Kananaskis, Alberta in August 2001 effectively creates GLOBE training teams across the Canadian North. In Yukon, there are now three GLOBE trainers, in NWT, the three participants represent a team for the Mackenzie Delta region, in addition to three others, and in Nunavut there are now two GLOBE trainers, one each in Baker Lake and Pangnirtung.

Results

(See Table 1 and 2)

Discussion and Conclusions

Laboratory analysis of the Fall 2001 field sampling was received from NILU in April 2002. The interpretation by students will be conducted largely in the 2002/03 school year.

The hands-on approach to scientific studies for student learning in a familiar and thus relevant environment is one of the many strengths of the GLOBE program. By sampling for PCBs and PBDEs, students are providing data about the presence and distribution of new Arctic POPs to the scientific community, as well as to their own communities. We are optimistic that the data collected by students through this project will add to the data bank of high-quality scientific research, which can be used to support international and global negotiations addressing Arctic concerns about POPs.

We are also optimistic that the GLOBE-NILU project will further the communications — encouraging cooperation in the circumpolar world.

Next phase of project: analysis of results, from Fall 2001 sampling.

In the first report of findings, students will be asked to focus on:

- the difference between wet weight and lipid weight;
- geographical differences; and
- comparing results with other reported measurements.

The interpretation of results by indigenous students introduces an important aspect of the project. The fieldwork and classroom lessons can serve to bring

together the two ways of knowing — western scientific and indigenous. In this vein, the GLOBE-NILU Arctic POPs project offers an opportunity for building capacity in Canada's northern communities, established on an understanding of POPs in the Arctic.

Scientific publication of the results will be done by NILU scientists with acknowledgement of and due credit to the students' efforts.

Work to be continued includes field sampling for local fish in Spring 2002. In August, a training workshop in Akureyri, Iceland, will prepare the teachers for the next sampling period — Fall 2002, when a higher trophic level will be sampled. The exact timing of the Fall 2002 field sampling will occur at the discretion of the respective schoolteachers, with samples to be sent to NILU for analysis, as in 2001. The project will include at least two further samplings (Spring 2003, Fall 2003) — with the trophic level to be sampled yet to be determined.

Expected Completion Date

Spring 2004

Communications of NCP Results in the Northwest Territories Using Various Media

Project leaders

Carol Mills, Manager, Contaminants Division, Indian and Northern Affairs Canada, P.O. Box 1500, Yellowknife, NT X1A 2R3; phone: (867) 669-2699; fax: (867) 669-2833; e-mail: phippens@inac.gc.ca; Chris Paci, Environment Manager, Dene Nation, P.O. Box 2338, Yellowknife, NT X1A 2P7; phone: (867) 873-4081; fax: (867) 920-2254; e-mail: denenationcp@ssimicro.com

Project team

Sub-committee within the NWTECC c/o Indian and Northern Affairs Canada, P.O. Box 1500, Yellowknife, NT X1A 2R3; phone: (867) 669-2699; fax: (867) 669-2833; e-mail: phippens@inac.gc.ca

Abstract

Communication of research results obtained from the Northern Contaminants Program focussed on a newspaper insert with short article, photos, key messages, questions and answers and kid's corner. Audio messaging focussed on the redevelopment of Inuit Tapiriit Kanatami (ITK) public service announcements for Dene audiences, translated into each of the Dene languages and distributed via CD to local radio and translated to effectively communicate them to the communities within the Northwest Territories.

Key Project Messages

Local radio translation (audio messaging) and newspaper inserts are effective for communicating NCP results to communities in the Northwest Territories.

Objectives

1. To effectively communicate results of research under the NCP to residents of the NWT (objective of blueprint).
2. To maintain and enhance understanding of issues related to contaminants among the general public in both the North and South, focusing particularly on the results of NCP Phases I and II.
3. Produce communication products on research to date, in particular, using local cable, web sites, radio, posters and workshops, as appropriate by region.
4. Produce region and species specific summaries of results.
5. To communicate results of NCP research, key messages, and general contaminants information to the audiences and/or messengers.
6. Develop and deliver communication packages and visual aids to communicate contaminants information specific to priority key audiences and regions.
7. Explore new and innovative media for communicating key messages.
8. To briefly communicate the goals, objectives and priorities of the NCP (Phases I and II).

9. To provide valuable information to contribute towards informed decision-making regarding the harvesting and consumption of traditional/country foods.
10. To undertake a bilateral transfer of knowledge by addressing questions from NWT residents posed throughout Phase II.

Introduction

This publication seeks to effectively communicate meaningful information on issues related to contaminants in the North; contribute to informed decision-making regarding the harvesting and consumption of traditional/country foods. By considering the different communication needs of NWT residents, materials presenting the results of the NCP will be developed and delivered in a culturally relevant format, thus fulfilling a key objective of the Education and Communications blueprint.

This work will focus on the overall considerations for the Education and Communications blueprint, but specifically it will satisfy the following criteria: "Concentrate on communication of research results in addition to general contaminants information". As Dene Nation and DIAND have had a great deal of experience (communicating the activities and findings of the NCP throughout both phases of the program), they will form an ideal team in providing results of Phase II in a culturally relevant manner. Lessons learned during community tours, workshops and retreats would be considered while developing and delivering results, which may sometimes be sensitive to residents.

Oral communications have always been a popular and effective means of communicating information in the Northwest Territories, particularly in smaller communities. For residents whose first language is not English, radio programming in local languages is often the most effective way to provide news and information. It is for this reason that audio recordings of NCP results and activities will be made in all eight official languages of the NWT, in addition to printed media. Thus all residents of the NWT were targeted.

Activities

In 2002–2003

- Production and distribution of a newspaper insert.
- Audio messaging translated into each of the Dene languages and distribution of CDs to local radio and community stations.
- Language translations for audio messaging included: English, French, Dogrib, Chipewyan, North Savey, South Slavey, Gwich'in and Inuvialuktun.
- Production of public service announcements (PSAs) on CD in various languages for all Denendeh regions.

Results

Feedback is still being received based on the newspaper inserts. People are contacting the Contaminants Division at Indian and Northern Affairs regarding the Territorial Contaminants Committee and the research they are involved with.

During community tours the residents tend to be more aware of NCP issues concluded by the number of questions being received.

Discussion and Conclusions

In 2002–2003, Dene Nation and Indian and Northern Affairs in Yellowknife co-operated to provide an effective way of communicating and educating local communities within NWT on the results obtained in NCP 2, which included local contaminants concerns. Based on community response via question and answer, the methods chosen seem to be effective.

Expected Completion Date

Completion of project by March 31, 2003.

Denendeh (Northwest Territories) Contaminants Communication Tour: The Deh Cho and Sahtu Regions

Project leader(s)

Contaminants Division, DIAND NT Region,(Yellowknife), PO Box 1500, Yellowknife, NT X1A 2H1; phone: (867) 669-2699; fax (867) 669-2833; e-mail: wardju@inac-ainc.gc.ca; Chris Paci, Dene Nation, Lands and Environment, Box 2338, Yellowknife, NT X1A 2P7; phone: (867) 873-4081; fax: (867) 920-2254; e-mail: cpaci@denenation.com

Project team

Sub-committee of the Northwest Territories Environment Contaminants Committee (NWTECC).

Abstract

Contaminants communication workshops in Denendeh (the Northwest Territories) in the past consisted of ad hoc regional meetings attended by community representatives. Regional contaminants meetings were held in Lac La Martre (March 1994), Inuvik (June 1995) and Yellowknife, for Akaitcho Territorial Government (March and April 1998).

To improve on these past efforts, a tour concept was developed, a new approach to communicating contaminants results and to gather community concerns through a workshop delivered to communities in a region determined to be of the highest need. The Denendeh tour of key communities in the Deh Cho and Sahtu regions was initiated and delivered in 2001 (October and November). These regions and communities were chosen based on their interest in recent mercury (Hg) work done on fish. In total, seven of 15 communities were visited during the tour.

Tour workshops consisted of visits by a team made up of a program representative, an Aboriginal partner, a health specialist, and a scientist. Sessions were held in the local schools and for the public. Discussions for the tour focussed on where Hg and other contaminants come from, their occurrence, measures of Hg and other contaminants in both ecosystems and traditional foods, Hg and other contaminants and human health, ongoing NCP activities, and community concerns related to Hg and other contaminants in traditional foods, waste, and health issues. This tour, like others in the Eastern Arctic (Nunavut 2000–2001), was an excellent opportunity for two-way discussions, which helps to establish a good understanding of the issues and concerns.

Key Project Message

1. The regional tour is an effective communication and education mechanism to present contaminants-related information to a variety of audiences, and provide an opportunity for two-way communication.

Objectives

1. Communicate the goals, objectives and priorities of the NCP Phase II to Dene communities in the Deh Cho and Sahtu regions of Denendeh.

2. Outline recent and current contaminants projects in the regions as well as to relay the findings of NCP Phase I.
3. Identify the issues and concerns of Dene communities regarding contaminants in the environment that could lead towards the development of monitoring plans.
4. To discuss the specific concern of Hg in fish and to assist individuals and communities in making informed decisions about their use of traditional foods.

Introduction

The classical workshop approach used to communicate and educate Aboriginal peoples on research results and program information has involved bringing selected community representatives to a major center, thus removing these individuals and distancing NCP researchers from the context of communities. In the past, community representatives would be given information regarding contaminants and the NCP and then sent home. The intention was to have these representatives return to each of their home communities to "spread the word" and disseminate what they learned to the rest of their communities. In reality, the burden placed on these individuals was significant. Many of the representatives were not in a position to talk with every person, interested or otherwise, and the person chosen to represent a community at a workshop was not necessarily hired on a full-time basis to convey the information when they got back home. Another shortfall was that community representatives attending a workshop had very little training in communications and education for fairly complex science on contaminants. Information overload and the potential for miscommunication of the results and information of the NCP was a real problem.

NCP territorial contaminants committees developed regional tours as an alternative mechanism for the education and communication of contaminants-related NCP information. The benefits of sending a small knowledgeable team to a region or a number of communities in a region for a variety of meetings was an improvement based on past experience. The teams generally consisted of a NCP representative, an Aboriginal partner, a health specialist, and a scientist. The primary means of communication was a public meeting; however, the team also took advantage of the time in the community to speak with school classes, radio, and other interested parties and organizations that were identified.

The advantage of having a team go into a community included reaching a broader community, raising the visibility of NCP and NCP research, communities having access to hear messages from sources and to access "expert knowledge" directly, easing the burden on limited community resources by providing a team in the community, and enabling teams to hear from communities to ensure that community concerns were and would continue to be addressed. The involvement of teams in more than one community in a region and more than one public meeting in each community, allowed individuals the opportunity to hear and comment about contaminants more than once. Because the information was being conveyed *in situ* it was felt that community members would be more comfortable, and being "at home" would encourage community members to express their opinions and concerns more freely about the program and contaminants in general.

While not a direct objective of the tour, the learning for team members was indispensable. A considerable value in the tour approach was the establishment of relationships while teams were in the communities. By having teams in the community, a wider audience has an opportunity to "put a face" to the voices and names of some of the individuals (scientists, Aboriginal organization representatives, regional contaminants coordinators, program representatives) who are working in their region. The benefits of improved relations between team and community members have been valuable. For example, in the proposals by participants in the tours, the area of communications is made much better. Also, proposals usually better address a concern that originated in the community. In addition, community members are usually more involved in the research, albeit typically in later stages research, for example in gathering data and samples.

A less lasting benefit is the economic spin-offs of the tour. While in the community the teams inject a small amount of money in terms of accommodations and meals, logistical support (meeting coordinator, translation, hall rental) and souvenir shopping. On a regional level teams often have to fly to communities without road access, or are able to drive to those with roads, again a small economic benefit to the region.

Activities

In 2001–2002

The Denendeh tour took place at the end of October and beginning of November 2001. The tour focused on mercury (Hg) in fish as the main theme. In the Deh Cho three (Deh Gah Got'ie Dene, Jean Marie River First Nation, and Liidlii Kue First Nation) of 10 communities were visited and in the Sahtu three (Tulita, K'asho Gotine Charter Community, Behdzi Ahda First Nation) of five were visited. A fourth community, Pehdzeh Ki Dene

Band, was contacted in the Deh Cho, but due to bad weather the visit was cancelled.

In each community visited this year, the team met with school students in the afternoon and hosted a public session in the evening at the community hall. During spare time, the team would divide up and visit the community, talking on the local radio station and to media, community organizations, and councils, communicating to these "frontline workers" the reason for the visit and to introduce themselves.

Results

Feedback from evaluations at the end of each public meeting indicates that the message is getting out there. The tours are most successful in providing a human face to contaminants research/results and the NCP. Due to the highly sensitive and personal nature of contaminants in traditional foods, the tours fill a particularly important role in education and communication.

The coverage of the Denendeh tour was less than complete and so there may need to be further consideration of these regions, in particular because 2002/2003 is the final year of Phase II of the NCP, thus there is a need to communicate CACAR II across these regions (in particular in communities not already visited). In the Deh Cho, 30% of the communities were visited and, in the Sahtu, 60% were visited and these visits were good opportunities to discuss Hg and fish. To get the CACAR II message across in 2002/2003 more tours are recommended.

While teams progressed through the tours in the communities, active participation of DIAND and Dene Nation managers in Yellowknife were essential to the success of the tours.

Problems could be minimized in subsequent years if managers visit communities ahead of time, and provide front-line training for coordinators, covering, in particular, the needs of the tours before the teams arrive, and communications. We learned the very important lesson that it was important to follow-up, often, with coordinators. Furthermore, community coordinators are often people who are already wearing a number of hats and so the tour is not always their top priority. In the future, it will continue to be important to keep these people informed of the tour needs, assist them in preparing communication strategies to advertise the meetings, and help them do the coordination in an effective and positive way.

Discussion and Conclusions

The Denendeh tour of the Deh Cho and Sahtu was encouraging and demonstrates that the tour is an evolving process. Each year we learn a little more about the best practices necessary to ensure the successful communication of the NCP, and environmental contaminants in general. This year's efforts will serve as the building block for future efforts. Meetings were well attended and audiences had opportunities to raise concerns about community health problems, noticeable changes in the quality of traditional foods, and local contaminants issues. During each meeting, there was good two-way dialogue which helped everyone understand the issues and concerns. Future tours will focus on other regions in Denendeh, in particular the Dogrib Treaty 11 region and Akaitcho Treaty 8. Teams and communities will continue to benefit from lessons learned on this and previous tours. We will continue to evaluate the effectiveness of each tour.

Expected Completion Date

Project was completed in April 2002.

Acknowledgments

We would like to thank the Sahtu Dene Chiefs Raymond Tutcho, Frank T'seleie, and Frank Andrew; the Deh Cho Dene Chiefs Rita Cli, Percy Hardisty, Stanley Sanguez, and Sam Gargan, in each community visited. The tours would not have come together so well without the help from community coordinators: Leann Yakeleya, Barry Gully, Alphonsine Mcneely, Tom Forbes, and Delphine Pierrot. Dene Nation would like to thank Sonny Lenoir and elder Andrew John Kenny for representing Lands and Environment on the tours. We appreciated the translation and the great meals provided for public meetings in each of the communities, "the moose stew and bannock were great." Contaminants Division, DIAND, would like to thank Denise Maxwell, Lisa Dyer and Michele Culhane for all their work.

The input from community members was indispensable and for this input and your hospitality, Mussi Cho. We would like to acknowledge the work and dedication of team members and work of planning and operating the tours by both Contaminants and Lands and Environment management. The support of NCP is a significant value in Denendeh.

Regional Contaminants Coordinator (RCC): Labrador Inuit Association

Project leaders

Jolynn Pijogge, Research Department, Labrador Inuit Association, P.O. Box 280, Nain, Labrador A0P 1L0; phone: (709) 922-2847/864; fax: (709) 922-1040; e-mail: natsiq@nunatsiavut.com; Mary Denniston, Research Department, Labrador Inuit Association, P.O. Box 280, Nain, Labrador A0P 1L0; phone: (709) 922-2847/864; fax: (709) 922-1040; e-mail: natsiq@nunatsiavut.com

Abstract

NCP's goal is to reduce and, wherever possible, eliminate contaminants in traditional foods. Supporting this goal are the NCP's priorities for providing people with the tools and information for making their own informed decisions through education, communication, and community participation in the program. Having a Regional Contaminants Coordinator in each of the northern regions ensures that this goal is being met by having a person in the region who is familiar with and sensitive to the culture and people.

In Labrador, the Regional Contaminants Coordinator's duties include acting as a liaison between five north coast communities and Upper Lake Melville, acting as a liaison between researchers and the community, communicating research results on risks and benefits of wild foods in plain language to the community residents in Labrador through various mediums, assisting in the delivery of workshops, open-houses, and information sessions, and carrying out projects funded by the NCP in the region.

Key Project Messages

1. This project continues to enhance the ability of the LIA Research Office to better deal with the issues related to man-made chemicals entering the environment, which are a concern among Labrador Inuit, and to provide information in a plain language, translated and accurate form in order to support Labrador Inuit in making informed decisions about their health and the environment;
2. The LIA Research Office strives to continue, in a culturally relevant manner, its communication efforts on contaminants, research and the environment, to conduct research and to promote mutually beneficial relationships between the communities of northern Labrador and outside scientists;
3. This project has enabled the Labrador Inuit Association Research Office to continue these communications, research and liaison activities, in order to effectively conduct research and communicate information on contaminants in the food chain and the environment, enabling Labrador Inuit to make informed decisions.

Objectives

An objective of the Northern Contaminants Program (NCP) is to reduce or, wherever possible, eliminate contaminants in traditionally harvested foods while providing information that assists informed decision making by individuals and communities related to their food use.

1. The Regional Contaminants Coordinator, under the Labrador Inuit Association Research Office, will continue to assist residents of Nain, Hopedale, Postville, Makkovik, Rigolet and Happy Valley-Goose Bay by providing information about risks, the means

to reduce risks, and information on the benefits of traditionally harvested foods to support residents in making informed decisions;

2. The Regional Contaminants Coordinator will assist communities of the north coast of Labrador and the Lake Melville area in becoming involved with contaminant issues and activities that affect the people and the region;

3. Additionally, this individual will act as a research liaison with outside researchers conducting work in the region on these issues, supporting their work and aiding them in conducting ethical, effective investigations and communications on these issues.

Introduction

Labrador Inuit are sustained by the animals, birds, fish and plants of the region. Research has shown that contaminants are present in these food sources due to the environment being contaminated by varying sources of short and long range pollution. Labrador Inuit are concerned about these contaminants in their food sources and in the environment. Key current concerns in Labrador include such things as PCB contamination at Saglek where the United States Air Force constructed a Polevault communications station in the 1950s, and the health of the George River caribou herd, a primary traditional food species in Labrador communities, among others. Following the objectives of the Northern Contaminants Program, the Regional Contaminants Coordinator acts as a key resource person and provides information to the population in a culturally relevant and plain language format on contaminant-related issues. This is done utilizing the guidelines developed through consultation with community individuals in the project *Country Food, Nutrition and Health: Developing Effective Communication Strategies in Labrador* conducted by LIA Research and consultants Chris Furgal, Ph.D, and Lorraine Craig. The relationship between Labrador Inuit and outside researchers has, in the past, lacked consultation, understanding of and recognition for Inuit culture and thus has not constituted "effective" and ongoing communications. Improvements have been made, however the need is ongoing for a Regional Contaminants Coordinator to aid in the establishment of mutually beneficial research relationships between individuals, communities and outside researchers. This is even more critical today as Labrador Inuit are in the final stages of negotiating a land claim agreement, and face many environmental health issues unique to this region in the Canadian North.

Activities

In 2001–2003: Communication

Community tour

As part of the communication responsibilities of an RCC, a community tour of all communities along the coast of Labrador, including Upper Lake Melville, was budgeted for under the Northern Contaminants Program call for proposals 2002/2003. The intent of this tour was to give the people of Labrador an overview of the Labrador RCC duties, objectives and goals, and provide information on the benefits and risks of traditional foods in the region. Further, the trips to communities were intended to gather new concerns and issues on the minds of the LIA membership related to health and the environment.

In February 2003, an open house was held in each community to give an overview of the different projects going on in the region, as well as to inform people about the activities of the LIA Research Office.

This gave community people a chance to view the work that is being conducted in the region this year, and learn about on-going duties and projects such as:

- Determinants of food choices in Labrador
- Climate change and health in Labrador
- The benefits of traditional foods
- Up-date on the Saglek Bay clean-up
- Contaminants: How they get into the North, the different types, and how they get into the food chain
- Posters on traditional foods developed by the LIA Research Office
- Avativut Newsletter — quarterly newsletter developed by the Research Office as a communication tool for the membership of the LIA

Many people suggested that this tour needs to be done more often and that the information on the benefits of traditional foods needs to be explored in greater depth. They reported that they would also like to see more information on the contaminants in their environment and the effects they are having on their traditional foods.

The comments which follow are quoted directly from the evaluation forms completed by participants in the open houses:

"I think it is very useful information, especially since wild foods are a big part of our diet"

"It was very clear & concise, with visual aids, was very well presented & presenter was very helpful"

"Need catchier headlines i.e. bring a focus on potential danger to our health from consumption of native foods"

"look forward to possible conclusive results"

"yes very important"

"I believe more community visits like this can be useful"

"This is the first display workshop I've seen and am very impressed"

"Yes, because I didn't know secondhand smoke has cadmium and we all know how dangerous secondhand smoke is"

"no, it's presented in the two main languages and well put together"

"The people hosting this exhibit were warm and friendly and very helpful. They are good choices to represent the people of Labrador"

"very, very important. There is a shortage of elders so it is good to see someone is putting this info on paper"

"well done job, Mary. Very interesting, great information"

"it is important for people to understand about the wild meat in our culture."

"if they would show a video on the PCB's in the north and in the food chain"

Avativut Newsletter

This newsletter is a quarterly publication that the LIA Research Office has developed and used to communicate to the Labrador Inuit population about such things as the benefits and risks of traditional foods, contaminants, health and environmental issues and to update people on current research activities in this region. The existence of a Regional Contaminants Coordinator and her involvement in this publication has enhanced the LIA Research Office's ability to communicate such information in a culturally-relevant manner. Without the RCC, it is likely that this newsletter would not be published. The main focus of the Avativut Newsletter is on the benefits of traditional foods to stress that traditional foods are still the most nutritious things to eat. Additional updates of new and ongoing research activities and relevant facts about health and environment issues in the region are also provided in this newsletter which is printed in English and Inuktitut (Labrador dialect) and distributed four times a year. A section of the Avativut Newsletter is also set aside for environmental news from each of the north coast communities, giving each community a chance to share their concerns and accomplishments with the coast regarding environment and health issues in their community.

PCB clean-up at Saglek, Labrador

The Regional Contaminants Coordinator (RCC) continues to assist with the communication about the presence of PCB contamination in the Saglek Bay area. The information being communicated to date on this topic includes results on the marine and terrestrial plants and animals that may have been contaminated by PCBs at the site, the effects this may have on people through their consumption of these species, and up-to-date information about the clean-up activities of the contaminated soil at the site.

Liaising/contact participation in research projects

Climate change and public health in Nunavik and Labrador

Dr. Chris Furgal of Quebec University Hospital Centre (CHUQ) is conducting research on observations and potential impacts that changes in the environment and climate in Northern Labrador and Nunavik have on individuals and communities. LIA Research staffer Mary Denniston continues to assist Chris in gathering knowledge from local elders, hunters, and women. This year, activities related to this project included bringing people together from each of the communities along the north coast, including the Upper Lake Melville area, to discuss their knowledge of the changes in the environment and weather and the impacts they have had on the people with regard to such things as the plants they gather and animals they eat, traveling conditions due to the changes in the temperature and weather conditions, etc.

Determinants of food choices in Labrador

Susie Bernier of Quebec University Hospital Centre (CHUQ) is conducting a research project called "Determinants of Food Choices in Labrador", funded under NCP this year. This project is now in its second and final year (2002–2003). The project will provide a better understanding of food preferences, attitudes and other factors influencing food choice behaviour to develop and apply a survey in order to determine what northern residents believe is necessary and possible to ensure food security for future generations.

Sixty-six residents of Nain (13 to 75 years old) participated in group discussions this past winter with Susie Bernier and Mary Denniston and a local translator. A total of 11 group discussions were conducted. Everyone provided valuable information that assisted in the development of the survey tool which was tested in the community this spring with 40 residents between 13–71 years old. The final survey is planned for the upcoming fall (2002).

Ongoing daily communications and research coordination

In addition to these specific activities, a number of ongoing communication responsibilities are fulfilled by the RCC. Daily activities of the Research Office include responding to community concerns, providing information to the Labrador Inuit Association, communities, and individuals on issues relating to contaminants, the environment and health, and acting as a liaison for the various people proposing to, and conducting work in the region. Additionally, the RCC acts as liaison for interactions between the region and ITK and the NCP. This involves regular daily interaction with various individuals and ongoing communications efforts.

Results

The existence of an RCC in Labrador has enabled and enhanced the abilities of the LIA Research Office to continue its mandate of providing information on contaminants, research and the environment, acting as a liaison between communities and outside researchers, conducting research and acting as a co-facilitator in delivering workshops and training for community representatives. The financial support provided through the NCP continues to enable the RCC to improve the way information is being presented and delivered to Inuit communities of northern Labrador by utilizing the latest project results for the region in developing effective communication strategies funded by NCP. In addition to facilitating communications on contaminants information, this project enables the RCC to anticipate and reduce the possibility of misunderstandings and mistrust among communities, organizations, researchers and scientists in communications in the region.

Discussion and Conclusions

The Regional Contaminants Coordinator continues to be a valuable addition to the LIA Research Office. The community tour conducted by the RCC in February 2002 gave the people of the Labrador region a chance to meet the RCC and to exchange any concerns they had with regards to environmental issues in their own community. The Community Tour also gave Labrador residents a forum in which to discuss their personal opinions and concerns about environmental issues in their community and the surrounding area and learn about the most recent activities and information related to these issues (this includes information about the NCP and funded projects in Labrador and other northern regions). The Labrador RCC continues to educate and empower the people of Labrador to better understand and deal with contaminants in their environment and traditional foods, and be aware of research and general environmental issues.

The Labrador Regional Contaminants Coordinator continues to:

- Enhance the activities undertaken by LIA Research Staff in providing information on research about contaminants and their effects on wildlife and humans through consumption of traditional foods which are based on the varied language and geographic needs of individuals and communities of Labrador;
- Enhance decision making abilities of Labrador Inuit through the delivery of information on risks and benefits of contaminants and traditional foods relevant to the region in an accurate, timely and accessible manner;
- Develop regionally relevant resource materials in consultation with the coastal communities and appropriate agencies (i.e. The Labrador Inuit Health Commission, DIAND, etc.). These materials include educational materials such as posters and a quarterly newsletter, with a mandatory requirement of publication in both Inuktitut and English;
- Use the research results from studies conducted in the region, such as the project *Country Food, Nutrition and Health: Developing Effective Communication Strategies in Labrador* to aid in effective delivery of information;
- Be responsible for interacting with and assisting outside researchers with community consultations. This assistance also includes negotiating research agreements between researchers and community organizations, and reporting project results to communities. The RCC will determine, in consultation with community representatives who are responsible for communication of contaminants, health and environment information, which medium(s) best suit the information needs of the community, etc. Those utilized often include presentations and workshops delivered in a plain language format. The RCC will continue to assist communities in identifying and prioritizing contaminants issues and assist in communicating community concerns and priorities to appropriate authorities;
- Take part in research projects and communication of research results when possible.

Date of Completion

The Regional Contaminants Coordinator is an ongoing project in Labrador.

Acknowledgements

The LIA Research Staff would like to thank Dr. Chris Furgal, CHUQ Research Centre, for his invaluable assistance and support in carrying out projects funded under the Northern Contaminants Program. Also, we thank Eric Loring, Inuit Tapiriit Kanatami, for his involvement and guidance with the Regional Contaminants Coordinator position. The support of the Labrador Inuit Association's Executive and its delegates ensures the continuation of the LIA Research Office mandate. We would also like to give special thanks to John Jararuse and Louisa Kojak, Interpreter/Translator, LIA, for the translation of communication materials, and Alice Pilgrim, K Naeme Tuglavina, Katie Harris and Sarah Obed for their assistance in translation activities related to the issues discussed in this report.

References

Lampe, J., F. Murphy, and C. Furgal. 2000. Country Food Nutrition and Health: Developing Effective Communication Strategies in Labrador.

Revision and Expansion of Yukon Contaminants Fact Sheets

Project leader

Pat Roach, Chair, Yukon Contaminants Committee, Department of Indian Affairs & Northern Development, Whitehorse, Yukon; phone: (867) 667-3283; fax: (867) 667-3341; e-mail: RoachP@inac.gc.ca

Project team

Yukon Contaminants Committee: DIAND; Council of Yukon First Nations; Environment Canada; Yukon Renewable Resources; Yukon Health and Social Services; Yukon Conservation Society; Yukon College.

Abstract

The Yukon Contaminants Committee (YCC) produced Fact Sheets on selected contaminants in 1992. The original sheets covered three organochlorine compounds (DDT, PCBs, and Toxaphene) and the metals arsenic, cadmium, copper, lead, mercury, and zinc. Our knowledge of the risk represented by the topics of the 1992 sheets has increased and new compounds have been identified. The YCC has produced a new run of Fact Sheets including updated information on DDT, PCBs, and Toxaphene, while adding polybrominated diphenyl ethers (PBDEs) and perfluoro-octane sulfonates (PFOS) to the list of organic compounds. The metals were also updated, and while copper and zinc were dropped, selenium was added. These new Fact Sheets were produced and distributed through workshops and libraries, to date.

Key Project Message

Our knowledge of the distribution, number, and risk of contaminants keeps increasing, and a good way for the public to remain informed is through a simplified information sheet.

Objectives

1. Ensure that the scientific research conducted under the Northern Contaminants Program (NCP) is communicated to Yukon peoples.
2. Keep updating the Yukon public on new issues and improved information on existing contaminants.

Introduction

In 1992, the YCC saw the need for the development of a simple method for communicating information on contaminants that were topical at that time in Yukon. It was decided that simply written "Fact Sheets" would provide an economical and easily distributed method of informing people with basic information on these selected contaminants. Since that time, our knowledge of these contaminants has increased and new compounds and metals have appeared in the Yukon food web. An updating and reassessment of the existing Fact Sheets was required if the Yukon public are going to remain informed on current issues. The newly identified contaminants of concern were added to the list of Sheets and two metals (Zn and Cu) were dropped from the list, as they are no longer a food-based concern.

Activities

In 2002–2003

The YCC reviewed and revised its list of contaminants covered by the 1992 Fact Sheets and produced an updated set. These have been distributed through Yukon libraries and at Workshops.

Discussion and Conclusions

The Yukon Contaminants Committee will continue to review and update the existing set of Fact Sheets as new information becomes available, and add to their number where required.

Expected Completion Date

March 2003.

Yukon Contaminants Studies 1991–2001: A Decade in Review

Project leader

Pat Roach, Chair, Yukon Contaminants Committee, Department of Indian Affairs & Northern Development, Whitehorse, Yukon; phone: (867) 667-3283; fax: (867) 667-3341; e-mail: RoachP@inac.gc.ca

Project team

Yukon Contaminants Committee: DIAND; Council of Yukon First Nations; Environment Canada; Yukon Renewable Resources; Yukon Health and Social Services; Yukon Conservation Society; Yukon College.

Abstract

An annotated bibliography was produced of the publications created during NCP funded research in Yukon from 1991–2001. The booklet is broken into subject areas and features an introduction to the Yukon Contaminants Committee and the Northern Contaminants Programs. A section in the back lists web sites and contact information.

Key Project Message

Ten years of NCP research has produced a large resource reference of contaminants studies in the Yukon.

Objective

Provide a reference summary of all publications, web sites, and databases created through NCP funded research work in Yukon.

Introduction

In the period from 1991 through 2001, a large number of contaminants studies have been conducted in Yukon. This work has produced refereed publications, reports, curriculum, fact sheets, databases and web sites. A single publication holding all of this information would be an asset to research scientists, students, and the public. An annotated bibliography, in the format of a booklet, was selected to list all of this material.

Activities

In 2002–2003

A booklet of 27 pages, containing an annotated bibliography, contact lists, and relevant background information was produced and distributed through Yukon libraries and at Workshops.

Discussion and Conclusions

As research continues on contaminants in Yukon, this booklet can be updated. Copies of the booklet can be obtained from the project leader.

Expected Completion Date

March 2003.

International Policy

ICC Core and Mercury and POPs Project

Project leader(s)

Stephanie Meakin, M.Sc., Technical Advisor, Inuit Circumpolar Conference (Canada), 170 Laurier Ave West, Suite 504, Ottawa, Ontario K1P5V5; phone: (613) 563-2642, direct (613) 258-9471; fax: (613) 565-3089; direct: (613) 258-7621; email: smeakin@attcanada.ca;
Terry Fenge, PhD, Strategic Counsel to the Chair, Inuit Circumpolar Conference, 170 Laurier Ave West, Suite 504, Ottawa, Ontario K1P5V5; phone: (613) 563-2642, direct: (613) 722-7006; fax: (613) 565-3089; email:tfenge7006@rogers.com

Project team

Sheila Watt-Cloutier, Chair, Inuit Circumpolar Conference, P.O Box 2099, Iqaluit, Nunavut X0A 0H0; phone: (867) 979-4661; fax: (867) 979-4662; e-mail: icccan@baffin.ca; Duane Smith, President, P.O. Box 2120, Inuvik, NT X0E 0T0; phone: (867) 777-2828; fax: (867) 777-2610; e-mail: inuvialuk@nt.sympatico.ca

Abstract

The Inuit Circumpolar Conference Canada in partnership with The Inuit Tapiriit Kanatami have taken pride in being managing partners in the highly acclaimed Northern Contaminants Program — a program of national and international importance. The results of the past five years of research were published in the Canadian Arctic Contaminants Assessment Report II (CACAR II). Our partnership with federal agencies, territorial governments, and other northern indigenous peoples continues to be fruitful and important.

ICC Canada continues to work toward the implementation of the Stockholm Convention and in March of this year published, "Northern Lights Against POPs: Combatting Toxic Threats at the Top of the World". This book will surely become the foremost authority on the international negotiations towards ridding the Arctic of these deadly contaminants.

By ensuring Inuit issues are reflected in the many working groups of the Arctic Council, we have contributed to the draft assessment of the Arctic Monitoring and Assessment Programme to be completed this fall. As well, ICC is an active participant in the Arctic Climate Impact Assessment which, when released next fall will be the most comprehensive climate change review globally.

Key Project Messages

1. The Arctic is a global indicator of environmental health — a global early warning system.
2. The linkages between global environmental change and health are an important area of research.
3. NCP Science informing national and international policy (NCP scientists as world leaders in their fields).
4. Data generated from the Northern Contaminants Program has supported the Circumpolar Arctic Monitoring and Assessment Programme. This is perhaps the most complete regional assessment of contaminant/environmental health globally.

5. NCP data supports hemispheric initiatives under the Commission for Environmental Cooperation, the North American Free Trade environmental side agreement.
6. The NCP data had a marked influence on the conclusion in 1998 and 2001, respectively, of international agreements to significantly reduce emission of key POPs into the environment.
7. That both international agreements single out the Arctic and Indigenous peoples is testament to this fact. In short, science conducted under the auspices of the NCP was successfully translated into international policy.
8. The utility of the research and data generated from the NCP should be fully explored as it has application to many environmental and health issues around the world including chronic disease epidemiology, environmental and human health effects from chronic low dose exposures to environmental contaminants, etc.
9. The NCP model has been seen to be an example of innovation and partnership throughout the world.
10. There continues to be a need for global action to maintain and improve the health of the Arctic ecosystem.
11. The NCP has provided capacity building to allow many northern aboriginal peoples to participate in international activities.

Objectives

The overarching objective of this work is to ensure Inuit are aware of the global, circumpolar and national activities and initiatives regarding contaminants and are in a position to participate where most effective.

Introduction

The adverse effects of contaminants on both the environment and human health is of great concern in the Arctic and, as such, the Arctic has a great interest in the success and effectiveness of the current international initiatives to reduce the presence of contaminants in the northern environment. For these reasons, it is crucial that the Arctic indigenous peoples understand the issues and continue to be full participants in the circumpolar and international efforts to reduce POPs and heavy metals in their homelands.

Contamination of the Arctic is a concern for all indigenous peoples who live in the circumpolar region, but also for all people in general, as the Arctic is an important indicator of the health of the global environment.

Activities

In 2002–2003

NCP core activities

- Participated as member of the NCP Science Managers Committee during 2002–2003.
- Participated in the drafting of the highlights Report and review of the technical chapters of the CACAR II.
- Actively Lobbied for NCP renewal during 2002–2003.
- Published POPs Book, March 2003.
- NCP Symposium, Ottawa, March 2003.
- SILAR, March 2003 edition.
- ICC has participated in numerous media communications events to publicize the research and results of NCP including northern, national and international radio and print interviews and specials (ie. USEPA's video on POPs).
- USEPA Tribal Population and Contaminants Review Committee.
- Arctic Parliamentarians.

Mercury/POPs activities

- Inuit representative on the CCME Hazardous Air Pollutants Working Group during 2002–2003.
- Monitored and reported on NAFTA CEC SMOC NARAP activities.
- Monitored the Great Lakes Binational Toxics Strategy with regards to mercury and POPs, and the EPA Mercury Action Plan activity and reported on the progress.
- Attended the INC 6 in Geneva, June 2002, as a member of the Canadian delegation. Participated in the meeting and working groups, reported back to the aboriginal partners.
- Participated in UNEP Global Mercury Assessment Review and Canadian consultations.
- General Assembly, Kuujjuaq, Nunavik, August 2002.
- Presented Case Study on POPs and Stockholm Convention at the World Summit, Johannesburg, September 2002.
- Participated in the Canadian consultations towards the UNEP Mercury Working Group Meeting in Geneva.

- Attended the Global Environment Facility Governing Council meeting to support POPs focal area and access by aboriginal persons to GEF funding.
- Lobbied for inclusion of contaminant issues and Inuit as a barometer of global environmental health at the UNEP GC Meeting, February 2003, Nairobi, Kenya.

Results

The Inuit voice was heard globally from Nairobi to Johannesburg, from Beijing to Moscow.

Discussion and Conclusions

ICC has worked hard over the last year to ensure that the Inuit voice is heard throughout the globe. We have continued our efforts to eliminate the incursion of persistent organic pollutants (POPs) into our food chain and into our bodies. We have renewed our efforts on the issue of climate change. While some may characterize these issues as 'environmental issues,' for Inuit they are so much more. They go to the root of who we are and how we live. They profoundly affect how we walk the land of our ancestors. (Sheila Watt-Cloutier)

The Inuit voice was heard — every member in every community should take pride in this achievement, as it is your voice the world is beginning to listen to, it is your issues the world is taking notice of, it is your knowledge the world so badly needs.

Acknowledgments

We would like to acknowledge the hard work at the national and community level by ITK (Scot Nickels and Eric Loring) and the dedication of Chris Furgal to Inuit issues. We would also like to thank David Stone and the NCP Secretariat for their support and tireless efforts.

Program Management

Public Management of Environmental Health Information: Nunavik Nutrition and Health Committee (NNHC)

Project leaders

Minnie Grey, Chairperson, Makivik corporation, Kuujjuaq, Nunavik; phone: (514) 745-8880; fax: (514) 745-8476; e-mail: mgrey@makivik.org; Suzanne Bruneau, coordinator; e-mail: Suzanne.Bruneau@crchul.ulaval.ca; Serge Dery, Director of Public Health, Nunavik Regional Board of Health and Social Services, Kuujjuaq, Nunavik; phone: (819) 964-2222; fax: (819) 964-2888; e-mail: Serge_Dery@ssss.gouv.qc.ca

Project team

Nunavik Nutrition and Health Committee Members: Nunavik Regional Board of Health and Social Services (4 representatives); Makivik Research Centre (2 representatives); Kativik Regional Government (1 representative); Inuulitsivik Health Centre (1 representative); Public Health Research Unit — CHUQ Research Centre (3 representatives); Inuit Tapirisat Kanatami (1 representative); Tullatavik Health Centre (1 representative).

Abstract

The Nunavik Nutrition and Health Committee (originally named the PCB Resource Committee) was established in 1988 to deal with issues related to food, contaminants, the environment and health in Nunavik. Since its inception, the committee has broadened its perspective to take a more holistic approach to environment and health issues inclusive of both benefits and risks. Today, the committee acts as the authorized review and advisory body for health and nutrition issues in the region and includes representation from many of the organizations and agencies concerned with these issues, as well as those conducting research on them. The committee provides guidance and acts as a liaison for researchers and agencies, from both inside and outside the region, directs work on priority issues, communicates to and educates the public on health and environment topics and research projects, and represents Nunavik interests at the national and international levels. All activities are conducted with the goal to protect and promote public health in Nunavik, through more informed personal decision-making. The committee proposes to continue these activities through their involvement in the Northern Contaminants Program during the 2002–2003 research year.

Key Project Messages

1. The Nunavik Nutrition and Health Committee is the key regional committee for health and environment issues in Nunavik;
2. The committee originated in 1989 and supports the activities of the Public Health Director in advising and educating the public on food and health issues, including benefits and risks associated with contaminants and country foods;

3. The committee continues to be active within the NCP, reviewing and supporting research in the region, liaising with researchers, and helping in the communication of research results in a way that is appropriate and meaningful to Nunavimmiut.

Objectives

1. To provide the population and health workers with background information to help them understand and contextualize environmental health, nutrition and contaminants research, objectives and results;
2. To compile elements of public concern that have not been addressed to date, and to steer and support research activities towards providing the data needed to address these concerns;
3. To undertake public communications of environmental health data, including results of Northern Contaminants Research Projects, and help develop regional communications and evaluations strategies for this information;
4. To prepare state of the knowledge summaries on these issues to assist in communication and intervention activities of local health and environment officials;
5. To facilitate research on environmental communications and risk perception issues;
6. To help researchers translate their data into meaningful information for the public;
7. To support partnerships in various research and intervention activities related to country foods, nutrition and health.

Introduction

In Nunavik, a group of representatives from different regional organizations concerned with health, the environment, and nutritional issues has formed to address these issues, and communicate to/educate the public so that they may make more informed decisions on these issues. The group, the Nunavik Nutrition and Health Committee, evolved from the PCB Committee, created in 1989 and later renamed the Food, Contaminants and Health Committee. The name has changed over the years as the group has learned of the importance to not only focus on negative impacts of contaminants, but the need for a more holistic approach to nutrition, health and the environment including benefits as well. On an ongoing basis, the committee addresses a number of issues relating to food, contaminants, nutrition and health and the relationship to the environment. The committee is the recognized and authorized body for the region on health and environment issues.

This evolution and recognition of the NNHC places it in an important role in addressing issues related to contaminants, food, health and the environment in the region. The committee is therefore well positioned, and has the necessary capacities to support research activities (through review, facilitation, and communication) related to these issues under the Northern Contaminants Program as a regional contaminants committee.

Activities in 2001–2002

Committee meetings

The committee met regularly through the year with special meetings being held (if needed) to respond to immediate issues. This past year the committee held three general meetings in Kuujjuaq (June and November 2001 and June 2002). At these meetings the committee addressed a number of issues. Past and current business was discussed, new issues were raised, and decisions were taken for action on many of these items. Furthermore, the committee held a special meeting in early February to evaluate projects submitted in 2002 to the NCP.

A summary of the issues discussed and addressed at meetings, and activities of the committee throughout the year is presented below.

Food security and sustainable development

The committee regularly reviewed updates of the botulism response and trichinellosis detection programs operated by Nunavik Public Health Department in partnership with the Kativik Regional Government (Hunters Support Program), and Makivik Research Centre (laboratory testing of samples), providing advice for communication of information and public education strategies during hunting seasons.

Trichinosis

Recent data shows that there were 11 trichinella outbreaks in Nunavik since 1982 and that 86 Inuit were affected and developed health problems. As 8 out of 11 outbreaks were positively linked with fermented or insufficiently cooked walrus, prevention and monitoring are still important. In 2002, Makivik and the NNHC updated the information pamphlet on this issue and distributed it to all communities and local organizations. Last fall, hunters participated actively in the program by sending samples for analysis. A total of 52 walrus samples were sent for analysis and

1 sample came back with a positive results. Hopefully, no one consumed that infected walrus.

Botulism

Prevention of botulism is always important for the committee. Since 1971, Nunavik represents nearly half of the Canadian cases with 62 outbreaks, 132 people affected and 12 deaths occurring. Almost all cases were caused by improper fermentation of seal, beluga and walrus. A prevention campaign is organized each fall. At this time, a Public Health representative does a regular radio show to remind people of the importance of aging food in a very cool place and storing it in containers (not plastic bags) which allow air to circulate. Furthermore, a prevention message is broadcast twice a week on the regional radio.

Toxoplasmosis

Makivik Research Centre has found that the prevalence of toxoplasmosis antibodies in caribou is very low. Furthermore, clinical data from both centres shows that toxoplasmosis infection is quite rare and that no conversions were observed among pregnant women in recent years. If many of the elders were exposed 30 years ago, it seems that teenagers are much less exposed now. However, since we still do not know a lot about vectors and cycles of the disease and why it is now decreasing, it is recommended that the monitoring program be continued. Antibodies will continue to be screened at the beginning of pregnancy. Since the clinical information given to pregnant women on toxoplasmosis is not accurate, it was suggested that the Clinical Prevention Committee update this information.

Research liaising

Additionally, committee members acted as liaisons between researchers and specific communities to gain the proper authorization and conduct appropriate consultation with community councils, health officials, and potential participants. Similar support is provided by the committee for projects funded within the region and conducted by various organizations on priority environmental health issues, including those related to contaminant exposure and human health. The committee also provided support in the form of results review and recommendations for communication/dissemination activities on many projects.

In some cases, the committee also worked with researchers to suggest needed research projects in order to address identified priority environmental health issues. A project monitoring the effectiveness of the ban on lead shot in the region was implemented as a result of these efforts.

Lead in Nunavik

Since two studies have identified lead shot used for gamebird hunting as a major source of population exposure to lead in Nunavik, this file was particularly active. In 2001–2002, an information campaign with the primary objective of achieving regional consensus on completely banning the use of lead shot in Nunavik was carried out. Furthermore, the hunters, retailers and the population were made aware of the problems of the high blood lead level in relation to the ammunition containing lead shots. For this purpose, various communications methods were used: local and regional radio, regional newspapers and newsletters and a phone-in radio show. Several activities to raise awareness were carried out: a poster on the importance of removing lead shot or fragments from meat before cooking and eating, meetings with the Hunters Support Program and the Hunters and Trappers Association coordinators to discuss this issue, etc. Moreover, the committee collaborated in the development of a clinical guide that deals with the investigation and follow-up of cases of elevated blood lead level. Finally, a student trainee is now working on a grid to monitor the presence of lead shot in Nunavik stores.

This intervention program seems to be quite successful in Nunavik. The public awareness campaign seems to have changed the practices of hunting in Nunavik. Recent data shows that the average blood lead level of the residents of Nunavik is decreasing and will probably continue to decrease in the future.

Research Projects

This year, the committee has been very active developing and implementing criteria for the conduct of research in the region. All researchers must now send regular updates of their work to the NNHC and must prove their involvement in the planning and realization of communication activities related to their project in order to gain support from the committee. Furthermore, all researchers are requested to comply with the demand that no national or international communications be made if the Nunavik population is not yet informed of the results of the study. The committee continues to review, provide advice and encourage valuable projects relating to environment and health issues in the region, such as the Food Security and Sustainable Development project, the Climate Change and Health project, and many of those conducted under NCP.

Communication Activities

The committee is active in communicating information relating to health and nutrition issues as well as preparing, reviewing and supporting communication activities of researchers conducting work on these issues in the region.

This past year, a tour of three communities, set up to communicate research results, had to be cancelled due to scheduling conflicts. Nevertheless, since 2002–2003 will be a big year in regard of communication activities, committee members were preoccupied and involved in the review, and delivery of new research results in innovative ways.

To increase its visibility in Nunavik, the committee has published an article explaining its philosophy and mandates in the *Makivik News* magazine. Additionally, committee members responded to requests to participate in radio phone-in shows and radio, newsletter and newspaper interviews (e.g. NRBHSS newsletter, *Makivik News, Nunatsiaq News*) in the region on issues related to health and the environment and specific community requests for information on these issues.

In regards to other public health issues, the committee was involved in the preparation and dissemination of a health advisory concerning mercury in the lake trout of Stewart Lake in Kuujjuaq. In June 2001, the Makivik Research Centre released information about mercury contamination of Stewart Lake fish species. Lake trout showed a level of contamination much higher than other species and created a situation of concerns particularly among non-Inuit residents of Kuujuaq. After consulting a panel of experts on the matter and considering the Health Canada guidelines for tolerable daily doses (TDI, which means the dose of a chemical that can be ingested daily during one's lifetime without any harm), the following guidelines for consumption of lake trout coming from Stewart Lake were communicated to the Kuujjuamiut: 1) For adults and children, it is safe to eat up to three meals a week, on a yearly basis; 2) For pregnant women, it is safe to limit ingestion to one meal a week, throughout the pregnancy.

Participation in workshops

The committee members are active in attending workshops to promote the activities of the committee, learn of other regional and international initiatives and communicate the results of regional research projects. This year, those conferences and workshops included:

- Food Security and Sustainable Development program review and scientific workshops — committee members provide regional "perspectives" and advice on projects being conducted in Nunavik.
- Northern Contaminants Program — participation at the Annual Results Workshop.
- Northern Contaminants Science Managers Meetings — review of NCP priorities, feedback on proposal review, and provide regional perspectives on NCP research.
- Social and Cultural Review Committee and Educations and Communications Review Committee meetings for NCP process.
- Participation in NCP CACAR II communication strategies.
- NCP Human Health and Country Food Monitoring workshops — presenting regional perspectives on communicating about benefits and risks of country food consumption, as well as monitoring and research on country foods in Nunavik and Labrador.
- Presentation by Minnie Grey at the International Society for the Study of Fatty Acids and Lipids (IASSFAL 2002).

Activities in 2002–2003

Committee meetings

Two meetings were held in Kuujjuaq (June and December) and one was held via telephone conference (October 10). As described further, at these meetings, past and current business is discussed but in 2002–2003 the committee was particularly active in preparing, reviewing and supporting communication activities of researchers conducting work on health and nutrition issues in the region.

In 2002–2003, the committee has been very active developing and implementing criteria for the conduct of research in the region. All researchers must now send regular up-dates of their work to the NNHC and must prove their involvement in the planning and realisation of communication activities related to their in order to gain support by the committee. Furthermore, all researchers are requested to comply with the demand that no national or international communication's be made if the Nunavik population is not yet informed of the results of the study. The committee continues to review, provide advice and encourage valuable projects relating to environment and health issues in the region.

Below is a summary of the issues discussed and addressed at meetings, and activities of the committee.

Regional communication tour

From November 11 to November 14, 2002, three communities were visited by two researchers of the CHUL-CHUQ research team: Kuujjuarapik, Inukjuak and Puvurnituq. The tour included the Nunavik Public Health Director, Dr. Serge Dery, the Nunavik Nutrition and

Health Committee chairperson and coordinator, Minnie Grey and Suzanne Bruneau; one representative for ITK, Soha Kneen; and two research assistants from Gina Muckle's team, Carole Vézina and Jocelyne Gagnon.

This regional communication tour has mobilized the committee's activities during the fall of 2002. After Dr. Muckle presented her results of studies on neurodevelopment impacts in infants related to contaminants exposure both before and during early school years to the Nunavik Nutrition and Health Committee, a work of simplification and adaptation was carried out to make sure that the data presented to the population of the three communities was appropriate and understandable. In order to have an integrated approach, it was decided that Gina's presentation would be combined with presentations of:

- The NNHC role, mandates and activities (Minnie Grey);
- The sources and pathways of food chain contamination in Nunavik (Dr. Éric Dewailly);
- Public health recommendations linked with study results (Dr. Serge Dery).

During the tour, communication activities included meetings with community councils, CLSC staff, and participants of Dr. Muckle's study, and a radio phone-in show. Afterwards, a report summarizing the trip activities was prepared. The document includes:

- discussions taking place during meetings, and
- concerns, issues and questions raised by partners, study participants and the general public in each community.

Input/questions/concerns raised in communities will be utilized to adapt current and future communication materials on the subject. All materials initially developed and delivered in communities will thus be a form of a "draft" and final materials distributed among the public will be sent afterwards and will incorporate these comments and concerns.

NCP — CACAR II

Communication activities related to wrapping up all data gathered in the last years by the Northern Contaminants Program were also elaborated. Two members of the NNHC participated in the NCP meeting, where a communication strategy framework was being developed. In collaboration with ITK's research department, key messages were then shaped and transformed into Public Service Announcements (PSAs). The PSAs are now available on compact disc and will soon be broadcast on all community local radios. In the continuum of communicating results of the CACAR II report, other activities will be elaborated and further disseminated to the Nunavik population.

Communication activities

The committee has collaborated on three articles published in the *Makivik News*. The first one, entitled: "Food Choices in Nunavik", was prepared by Susie Bernier of the Public Health Research Unit and was published in the summer of 2002. Michael Kwan, toxicologist at Makivik Research Centre and member of the NNHC, prepared two articles on the benefits of country foods vs. contaminants which were published in the fall of 2002. Additionally, committee members responded to requests to participate in radio phone-in shows and radio, newsletter and newspaper interviews (e.g. NRBHSS newsletter, *Makivik News*, *Nunatsiaq News*) in the region on issues related to health and the environment and specific community requests for information on these issues.

Trichinellosis

The NRBHSS Public Health Department, Makivik and the NNHC updated the information pamphlet on this issue and distributed it to all communities and local organizations. Last fall, hunters participated actively in the program by sending samples for analysis.

Botulism

A prevention campaign is organized each fall. At this time, a Public Health representative does a regular radio show to remind people of the importance of aging food in a very cool place and storing it in containers (not plastic bags) which allow air to circulate properly. Furthermore, a prevention message is broadcast twice a week on the regional radio.

A report entitled "*Clostridium botulinum* in the Arctic Environment" was submitted to the committee recently by Dr. Daniel Leclair of Makivik. The objective of this study was to determine the distribution and contamination levels of *Clostridium botulinum* in the coastline environment on which seals are commonly butchered. These results suggest that the environment could play a significant role in the epidemiology of the disease. Two other reports are presently in preparation and concern the contamination routes and growth factors of *C. botulinum* in seal meat, and the molecular sub-typing of environmental and food isolates.

Toxoplasmosis

The NNHC supported the decision of maintaining the Screening Program of antibodies in pregnant women. Since then, the Clinical Prevention Committee updated the clinical information to be given to pregnant women.

Participation in workshops

The committee members are active in attending workshops to promote the activities of the committee, learn of other regional and international initiatives and communicate the results of regional research projects.

This year, those conferences and workshops included:

- Northern Contaminants Science Managers Meetings — review of NCP priorities, feedback on proposal review, and providing regional perspectives on NCP research.
- Social and Cultural Review Committee and Educations and Communications Review Committee meetings for NCP process.
- Participation in NCP CACAR II communication strategies.
- The Santé-Québec Inuit Health Survey consultation meetings.
- Participation in the orientation committee of the 2004 Inuit Health Survey.
- The NAHO first annual Conference and Health Fair: "Health, get with it".

Research Projects

This year, the Committee has presented a research project that has the general objective of evaluating a risk reduction program for pregnant women exposed to food chain contaminants in Nunavik. This program is promoting the consumption of Arctic char among pregnant women living in three selected communities in Nunavik, and is evaluating to what extent pregnant women participate in the program and how efficient the program is in reducing contaminant intake (especially mercury) while maintaining or improving nutritional status during pregnancy. Results of this project will help regional public health authorities to assess and implement risk management actions including, but not limited to this one in Nunavik communities.

Conclusions

The Nunavik Nutrition and Health Committee is an active body supporting and enhancing the region's research and decision-making capacity related to environmental health issues including exposure to environmental contaminants. This is done through a variety of activities in which they represent the interests of Nunavik residents. Through these activities, they cooperatively manage and disseminate information to the public to support informed decision making on issues of health and nutrition.

Expected Completion Date

This is an ongoing project, as the committee is active on these issues in the region annually.

Acknowledgements

The committee would like to thank the Northern Contaminants Program and the Nunavik Regional Board of Health and Social Services for ongoing support and funding of their activities related to health, contaminants and nutrition in the region.

Northwest Territories Environmental Contaminants Committee (NWT ECC)

Project leader

Indian and Northern Affairs Canada, Chair, Northwest Territories Environmental Contaminants Committee (NWT ECC). Contaminants Division, Indian and Northern Affairs Canada, P.O. Box 1500, Yellowknife, NT X1A 2R3; phone: (867) 669-2699; fax: (867) 669-2833; e-mail: wardju@inac-ainc.gc.ca

Project team

Members of the NWT ECC, including representatives from: Dene Nation (Vice-Chair); Inuit Tapiriit Kanatami; Inuvialuit Regional Corporation/ Inuvialuit Game Council; Gwich'in Tribal Council; Sahtu Dene Council; Deh Cho First Nations; Dogrib Treaty 11 Council; Akaitcho Territory Government; North Slave Metis Alliance; Northwest Territory Metis Nation; Indian and Northern Affairs Canada (Chair); Environment Canada; Fisheries and Oceans Canada; Government of the Northwest Territories (GNWT) Resources, Wildlife and Economic Development; GNWT Health & Social Services; and Aurora Research Institute.

Abstract

The Northwest Territories Environmental Contaminants Committee (NWT ECC) membership is composed of representatives from various departments of the federal and territorial governments as well as national and regional Aboriginal partners. The Committee meets regularly throughout the year to facilitate scientific study and assessments as well as the communication of information to northerners on the presence and possible effects of contaminants in the environment. The NWT ECC also facilitates the communication of northern priorities to researchers. The NWT ECC met nine times in 2002–2003, with a focus in the later part of the year on discussing and implementing methods for communicating the second Canadian Arctic Contaminants Assessment Report.

Key Project Messages

1. The Northwest Territories Environmental Contaminants Committee (NWT ECC) enabled 16 different Aboriginal and government organizations in the NWT to coordinate their activities related to contaminants.
2. The NWT ECC provided a forum for discussion and two-way transfer of contaminants-related information among northerners of the Northwest Territories (NWT), researchers and programs such as the Northern Contaminants Program (NCP).

Objectives

1. To facilitate the efforts to address concerns arising from environmental contaminants in the NWT.
2. To provide a forum for the two-way transfer of contaminants information between Northwest Territories (NWT) northerners, researchers, the Northern Contaminants Program (NCP) and other contaminants-related programs.
3. To establish a communications network that ensures northerners are informed and involved in contaminants-related activities.
4. To identify priorities and information gaps related to environmental contaminants research in the NWT.
5. To act as a central repository for environmental contaminants information.
6. To provide advice on appropriate funding sources.
7. To review Local Contaminants Concerns proposals throughout the year.
8. To review NWT proposals for the NCP prior to full technical reviews (not applicable in 2002/2003).

Introduction

The NCP is now in the last year of the second phase with more than 11 years of research to date. The program has evolved to include NWT communities and regions extensively in research and communication efforts. This has increased the need to have a central body that can coordinate contaminants information and research initiatives. This group has an elected Chair and Vice-Chair to organize meetings, activities and distribute information, with the Chair location this year at the Contaminants Division, Indian and Northern Affairs Canada in Yellowknife. The Vice-Chair is Dene Nation. This year the Chair and Vice-Chair took on roles of Co-Chairs, and with each organization alternating the chairing of committee meetings. The Northwest Territories Environmental Contaminants Committee (NWT ECC) provides an opportunity for researchers and communities to provide input into contaminants activities and to express their concerns.

Membership is composed of representatives from various departments of the federal and territorial governments as well as national and regional Aboriginal partners, making it particularly suitable for addressing NWT research priorities and information gaps.

Activities

In 2001–2002

The NWT ECC met eight times to discuss various contaminants-related issues (Table 1). Frequent roundtable discussions and updates helped to keep contaminants workers in governments and regional and territorial Aboriginal organizations informed of study results, current activities, upcoming proposals or work and conferences. In addition, to provide an opportunity for committee members to become better informed of recent study results, the NWT ECC sent representatives to the annual NCP results workshop in Calgary, Alberta, in September 2001.

The NWT ECC held a two day in-person meeting in February 2002 to review the NCP proposals of immediate relevance to the NWT. Prior to the proposal review, the monitoring, health and communication blueprints were reviewed by the committee. Throughout the year the committee also considered Local Contaminants Concerns proposals from communities and approved six for funding.

Activities

In 2002–2003

The NWT ECC met nine times to discuss various contaminants-related issues (Table 1). Frequent roundtable discussions and updates helped to keep contaminants workers in governments and regional and territorial Aboriginal organizations informed of study results, current activities, upcoming proposals or work and conferences. Throughout the year, the committee also evaluated Local Contaminants Concerns proposals from communities and approved several for funding.

The NWT ECC held a two day in-person meeting in November 2002 to discuss communications strategies and action plans for the release of CACAR2. Discussions included the use of focus groups for key message testing for CACAR2, communications materials including fact sheets, newspaper inserts, public service announcements, and the NWT ECC newsletter. Action plans were developed for various communications approaches. In addition, to provide an opportunity for committee members to become better informed of recent study results, the NWT ECC sent several representatives to the NCP Symposium held March 4–7, 2003 in Ottawa, during which the second Canadian Arctic Contaminants Assessment Report was released and discussed.

Table 1. Meetings held by the NWT ECC during 2001–2002 fiscal year

NWT ECC Meeting #	Date	Key Agenda Items
24	April 19, 2001	Review of NWT ECC Terms of Reference Chair and Vice-chair nominations Update on approved project proposals Roundtable discussions
25	May 17, 2001	Local Contaminants Concerns and proposal review and update CACAR2 Highlights development Roundtable discussions
26	June 28, 2001	Greenhouse Gas Strategy presentation (Jim Sparling) Review of Education and Communications Blueprint meeting Roundtable discussions
27	August 28, 2001	Update on Results Workshop in Calgary (Sept. 25–27, 2001) Local Contaminants Concerns — proposal review Status update — Health Advisory Working Committee Roundtable discussions
28	October 1, 2001	Local Contaminants Concerns — proposal review Review of Results Workshop by members in attendance Participation in the NWT ECC Roundtable discussions
29	November 15, 2001	NCP Call for Proposals update Health Advisory Working Committee update November 2002 Symposium update NCP proposal review meeting Roundtable discussions
30	February 4 & 5, 2002	In-person review of NCP proposals Review of Local Contaminants Concerns proposals Updates on Local Contaminants Concerns projects Roundtable discussions
31	March 26, 2002	Review of Action items Election of Chair and Vice-chair for 2002–03 Update on Local Contaminants Concerns projects Summary of approved NCP projects for 2002–03 Next steps for NWT ECC newsletter Roundtable discussions

Results

In the 2001–2002 year, the NWT ECC provided detailed review and recommendations on 28 NCP research proposals pertaining to the NWT. These recommendations promoted research that is relevant and socio-culturally appropriate to northerners. The NWT ECC also provided funding for several smaller projects through the Local Contaminants Concerns Fund:

- Contaminants sampling of fish in the Tuktoyaktuk harbour;
- Arsenic in medicinal plants in the Yellowknife region;
- Contaminants sampling of beaver and muskrat in the Gwich'in Settlement Area;
- Contaminants sampling of soil and groundwater near the Jean-Marie River;
- Contaminant levels in the Bluenose-East caribou population; and
- Contaminants sampling of the West Channel at West Point First Nation.

The committee has been working on developing a number of information items including Contaminants Fact Sheets and an NWT ECC newsletter. These are still currently being reviewed by the committee. Minutes were produced to summarize the discussions, activities and decisions of the committee from each meeting. These are available from DIAND Contaminants Division in Yellowknife.

Table 2. Meetings held by the NWT ECC during 2002–2003 fiscal year

NWT ECC Meeting #	Date	Key Agenda Items
32	May 7, 2002	Honoring Francis Blackduck Update on newsletter and website Letter to GNWT Health re: elimination of contaminants position Annual review of NWT ECC Terms of Reference Roundtable discussions
33	June 13, 2002	Update on Metis representation Update from GNWT Health & Social Services — Andre Corriveau Update on CACAR2 key messages and newsletter/website Roundtable discussions
34	July 25, 2002	Local Contaminants Concerns proposal review Update from NCP Management Committee meeting Update on CACAR2 key message testing Roundtable discussions
35	September 5, 2002	Update on Regional Contaminants Coordinator positions Update on CACAR2 Update on newsletter and fact sheets Roundtable Discussions
36	October 25, 2002	Mirror Lake data — Next steps Update on CACAR2 and AMAP symposium Update on newsletter and fact sheets Roundtable discussions
37	November 21–22, 2002	Regional Contaminants Coordinator positions and training Status of Dene Nation/RWED monitoring project Communications/Focus groups for CACAR2 Key message testing for CACAR2 Taiga lab training program (Guest: Shane Harnish, Taiga lab) Summary of AMAP key results
38	January 15, 2003	Regional Contaminants Coordinator positions and training Update on newsletter, fact sheets and newspaper insert/PSAs Updates on Local Contaminants Concerns projects Roundtable discussions
39	February 20, 2003	Review of Local Contaminants Concerns proposals Updates from Regional Contaminants Coordinators Update on Dogrib and Akaitcho tours Discussion on mercury Roundtable discussions
40	March 31, 2003	Report on NCP CACAR2 symposium Next steps for the NWT ECC Updates on Local Contaminants Concerns projects Roundtable discussions

In the 2002–2003 year, the NWT ECC provided funding for small projects through the Local Contaminants Concerns Fund. These projects were:

- Contaminants sampling at the Inuvik Landfill (Inuvialuit Regional Corporation);
- Sampling for DDT in a pond near Colville Lake (Sahtu Dene Council); and
- Inventory of contaminated sites (Ft Smith Metis Council).

The committee worked on the development of several information items including Contaminants Fact Sheets, an NWT ECC newsletter and a newspaper insert to promote the release of CACAR2. They played an important role in reviewing these materials.

Minutes were produced to summarize the discussions, activities and decisions of the committee from each meeting. These are available from DIAND Contaminants Division in Yellowknife.

Discussion and Conclusions

The NWT ECC enabled 16 different Aboriginal and government organizations to coordinate their activities related to contaminants. Based on feedback from the organizations involved, the NWT ECC appears to have served well as a two-way communications conduit from community members to national and international programs. It continues to prove itself an effective and inclusive forum for discussing contaminants-related concerns and for providing northern input directly into the NCP.

Expected Completion Date

The NWT ECC will continue to meet despite uncertainty of future NCP funding, however the role and terms of reference for the committee may evolve based on funding decisions.

Yukon Contaminants Committee Communications

Project leader

Patrick Roach, Contaminants/Waste Programs, Renewable Resources, Indian & Northern Affairs, Whitehorse, Yukon.

Project team

Yukon Contaminants Committee.

Abstract

The Yukon Contaminants Committee (YCC) was established in 1992 and continues to coordinate research projects operated under the Northern Contaminants Program. It responds to inquiries by individuals, communities, research scientists, and others with an interest in the NCP or other environmental issues in the Yukon. The YCC consists of representatives from government, the Council of Yukon First Nations, individual First Nations, non-governmental organizations, Yukon College, and private industry. Membership has always been "open" and the active members vary over time, with a core group that has been involved since the inception of the Committee. The YCC reviews project submissions under the NCP, for scientific and socio-cultural relevance to Yukon communities. It then makes recommendations to the NCP Managers, on the suitability of these project proposals. The Committee often takes a leadership role in communicating the results of research through directed publications, the provision of guest speakers, representation at professional workshops and conferences, and in the development of materials for use in education. This year the Committee hosted an open house workshop in Whitehorse to communicate the results of the last five years of Yukon NCP research. In this role the YCC provides a link between the scientific community and the Yukon public. The Committee continues to grow with the NCP and remains a diverse and active organization in the North.

Key Project Message

The Yukon Contaminants Committee has been active since 1992, provides representation for all stakeholders to the NCP, direction for research professionals, and a Yukon perspective at the NCP Manager's meetings.

Objectives

Ensure that the scientific research conducted in the Yukon under the Northern Contaminants Program (NCP) meets the needs of the Yukon, while respecting the socio-cultural needs of its people.

Introduction

The establishment of the YCC came about in 1992, as a development of the committee studying the Lake Laberge toxaphene issue. It was created to provide the Yukon with an organization to review research projects planned for the Yukon, or which would effect the Yukon public. The Committee is composed of a diverse group of stakeholder representatives, who provide perspective from across the Yukon cultural and political landscape. While the principle role for the YCC is for project review, it has also taken a leadership role in communications designed to educate the Yukon public. It also provides an avenue for the public to express concerns regarding contaminants in the North.

Activities

In 2001–2002

The YCC continued to review project proposals for the 2002–2003 program year. Committee members travelled to the Manager's meetings, the NCP Workshop, and contributed to CACAR II, AMAP II, and the Education and Communications strategic planning for the final year of NCP II.

The Committee has begun the update and production of the original Contaminants Fact Sheets, and was busy in planning directed communications strategies for the 2002–2003 operating year. An open-house Workshop was held to communicate the results of the work-to-date in the Yukon, under the NCP, on metal contaminants in country foods.

Metal contamination in Yukon traditional foods

This workshop addressed the work, conducted to-date, in examining metal contaminants in the country foods of the Yukon and across the North (see Table 1). While the intention was to highlight the research conducted in the Yukon, the research results from other areas of the North was covered to provide a comparison. The health aspects of metals in food, where we are today and where research needs to go, were covered. The Grand Chief of the Council of Yukon First Nations offered his insight into the Yukon Contaminants Committee, the NCP, and where the future should take research in the Yukon. A poster session provided a review of specific work conducted in the Yukon, with respect to metal contamination in foods.

Table 1. Metal contamination in Yukon traditional foods, Workshop agenda, March 16, 2001

9:45–10:00	Coffee/tea	Meet & Greet
10:00–10:05	Welcome	Pat Roach, Chair Yukon Contaminants Committee
10:05–10:20	History of Yukon Contaminants Committee	Mark Palmer, Manager Environmental Services Public Works — Western Canada Region
10:20–10:40	First Nation Perspective on the NCP	Ed Schultz, Grand Chief Council of Yukon First Nations
10:40–11:00	Break	
11:00–11:10	Overview of the work of Yukon Inter Tribal Watershed Council	Vanita Sahni, Research Intern Yukon Inter Tribal Watershed Council
11:10–11:30	Overview of the Northern Contaminants Program	Sarah Kalhok, Environmental Scientist Northern Contaminants Program, DIAND
11:30–11:50	Terrestrial Contamination	Mary Gammberg Gamberg Consulting
11:50–11:55	Q & A	
12:00–1:00	Lunch break	
1:00–1:50	Mercury Trends in Northern Fish	Dr. Lyle Lockhart, Former Head Contaminants Research Section, Freshwater Institute, DFO
1:50–2:00	Q & A	
2:00–2:15	Break	
2:15–2:35	Methylmercury Risk Assessment in Health Canada	Dr. Mark Feeley Bureau of Chemical Safety Health Canada
2:35–2:40	Q & A	
2:40–3:00	Metal Contaminants in the North The Big Picture	Dr. Colin MacDonald Northern Environmental Consulting
3:00–3:05	Q & A	
Poster session open all day		

Results

Welcome and introduction — Pat Roach

Pat Roach, Chair of the Yukon Contaminants Committee, welcomed everyone to the workshop. The workshop summarizes and communicates what has been found in terms of metals in traditional foods in the Yukon in the last 10 years, i.e. what is there, how much is there and what is and is not an issue. Mr. Roach thanked all presenters for attending.

History of Yukon Contaminants Committee — Mark Palmer

The past Chair of the Yukon Contaminants Committee from about 1992 until 2000 was Mark Palmer. Mr. Palmer is now with Public Works and Government Services in Edmonton, involved in the environmental field.

- A lot of people have come up to the Yukon and talked about the history of the Yukon Contaminants Committee in the past.
- To put a perspective on it, Mr. Palmer has been here since the beginning, and a lot of people in attendance today have, as well.
- Back at the beginning, the history is that around 1989 or 1991, Environment Canada did a routine survey of Lake Laberge, not expecting to find anything at all. Environment Canada issued an advisory in 1991, saying, "Don't eat the fish in Lake Laberge, because there are PCBs in them."
- A few months later, they stated, "We're wrong, sorry about that. You can eat the fish again."
- A while later, they said, "Don't eat those fish. There are toxins in them now." So, it got really messy in 1991/1992.
- At the same time, a larger program, the Arctic Environmental Strategy, came out, which started throwing money into the program and sampling everything they could possibly sample, specifically fish in Lake Laberge.
- They took samples from an upstream, headwater lake, Atlin Lake, to show that it was a small, isolated problem in Lake Laberge, from the Whitehorse dump, which should go away.
- Atlin Lake, which has no industry on it, was sampled, and an advisory issued for toxic problems.
- The Lake Laberge Advisory Committee was formed, composed of 25–30 people, including representation from Health Canada and DIAND, with no funding to support it. The committee was too bureaucratic and was not going anywhere.
- Mark Palmer showed up on the scene in February of 1992, being brought over from Yellowknife where he was working on contaminant studies on the Slave River.
- The Lake Laberge Advisory Committee was replaced by a small, nine-person core group of government to government people. This group worked together to try and solve the Yukon contaminants problem. The second goal was to support the larger Northern Contaminants Program (NCP) and support any initiatives going on. There were no capabilities in their back yard, so they worked with researchers and consultants across the country and provided a link to the north.
- It was a partnership all the way through with CYFN, DIAND, YCS, Environment Canada and YTG, Health to work through the problems.
- The immediate goal was to restore faith in the fish in the Yukon.
- They went on a mad sampling spree, sampling every lake and ranking them on importance and on usage, putting confidence back in by proving to Yukoners it was okay to eat fish.
- They also relied on help from outside researchers to try and figure out why Lake Laberge and Atlin Lakes were high, where the stuff was coming from and what they could do about it.
- Mary Gamberg came along and raised the issue of terrestrial mammals and cadmium in the Finlayson caribou herd.
- This started another huge parallel process trying to figure out what the levels are in all terrestrial species with berries and plants and getting confidence back.
- The beginning of the program was very heavy on sampling, followed by communications.
- After a lot of data was collected, they got a handle on the fact that the Yukon is probably the cleanest place in the world, and they started putting their efforts into heavy communication, i.e. they went from 80 percent science and 20 percent communication to 80 percent communication and 20 percent science.
- Communication included a whole host of workshops, T.V., media and other means of getting the information out, road trips to every community. The whole committee volunteered.

- CYFN were key in providing cooperation and support.
- They supported the NCP, with representation to the larger group, and worked as a united front.
- There are still a couple of issues to talk about, i.e. metals and mercury.

The last message when Mark left the Yukon was that things are pretty good up here, keep eating the food and just watch it.

First Nation perspective on the Northern Contaminants Program — Grand Chief Ed Schultz

Chair Pat Roach noted that one of the key components to the success of the Yukon Contaminants Committee has been the support and direction of the Council of Yukon First Nations (CYFN), particularly in the area of the types of traditional foods and the regions of importance to look at first, and in designing effective communication strategies.

- Grand Chief Ed Schultz thanked the organizers and attendees for taking their Saturday morning to learn about this important topic.
- In the days Mark Palmer was referring to, the First Nations were represented by the Council for Yukon Indians (CYI).
- Importance of the Northern Contaminants Program for the First Nations — CYFN has been involved from relatively the beginning and brought their network to each and every community of the Yukon to the committee, particularly the end users of a lot of natural resources for fish and wildlife species.
- The Council provided linkages to hunters, trappers and fishers, who had some very long-term observations on the land, as well as the species that they were utilizing and the substantive changes they were seeing in them. Some coin this under the terminology of the day as "traditional knowledge" or a component of it where aboriginal people, through their observations, can bring information to a scientific or academic-type level of activity so that it can then be integrated or be part of the overall analysis of a particular issue.
- At the time, the First Nations were relatively inexperienced and not very knowledgeable about a lot of the scientific information that was being provided, i.e. terminology or basic understanding at a technical level or in relation to risk associated with human health.
- The program has a legacy of having a direct benefit to today in the sense that First Nations in large numbers were able to gain more insight and understanding into issues like heavy metals and persistent organic pollutants and what their possible effects might be, linkages and patterns within the food chain and possible associated risks.
- This legacy is very important particularly today when First Nations are moving into a system of self government where they are being directly involved in developing and designing independent programs and services for the environment or co-managing things with other governments.
- The practical experience was beneficial, for example, advisories issued on Lake Laberge regarding lowering of consumption of livers from burbot.
- As soon as one hears "contaminant" or "risk", a panic button causes everybody to stop eating traditional foods, and people are reluctant to even eat the flesh of the fish.
- The Northern Contaminants Program expanded the First Nations' knowledge, understanding and network of other processes and other institutions associated with contamination.
- Partnerships with other indigenous peoples, such as the Dene and the Métis, were developed through the program; and through the support of the Northern Arctic Environmental Strategy, by extension, a centre was created at McGill University, called "Nutrition and the Environment of Indigenous People". This centre was geared to take some of the test results derived from Northern Contaminants and other submissions elsewhere and get a fix on what the real meaning of the data is.
- There are chains of information, i.e. the people in the field collecting samples. Lab work is expensive.
- Test results did not extrapolate into tangible information for leaders of communities. They could pass numbers on, but they did not mean anything until there was a connection with the Health Branch people who had an understanding as to what levels might pose a risk to human health.
- With people panicking, it was important to ensure that they did not stop living in the way they always had.
- A lot of time had to be spent with the Northern Contaminants Program on assimilating information in a way that is understandable by their people and pertinent to their day-to-day lives.
- CYFN worked at length with a lot of government departments.

- McGill commissioned a traditional foods study in the Yukon and other northern communities on such issues as daily intakes.
- The centre also looked at the nutritional value of foods and the implications of quickly removing First Nations from having access to traditional foods.
- The nutritional content of the types of fish, ungulates and small wildlife that First Nations eat was looked at.
- Science substantiated what was always believed to be true, i.e. a good portion of the northern community peoples' dietary nutritional intake comes from their traditional foods.
- The study also looked at people who weren't consuming traditional foods but more western foods; and the findings suggested that for people who were not utilizing their own traditional foods but who had moved to a western-based diet, it had a more detrimental effect than if they had been eating western food all along. One's body tends to be more receptive to what you're used to.
- They were very concerned when they realized the worries and fears about kidneys of ungulates and livers of fish, and they spent a great deal of time getting people to understand the level of risk that they were being advised about.
- They did not want to have a bigger problem on their hands with a major shift in the diets of people to western-based foods.
- Fact sheets were produced, television and radio ads, workshops, visits to communities to get people to realize the type of contaminant and the correlation to the risk, e.g. the risk of smoking far exceeds any plausible risk of what is contemplated in some of the levels of intake in use of traditional foods.
- People needed to get a better understanding of the whole issue, because the media had sensationalized it far beyond what is necessary.
- Politicians may have misrepresented information for short-term political gain, and it was important to focus on the realities.
- A large First Nation summit was held at Lake Laberge. Participants from every community came in and spent a week with scientists and academics in the field, and many First Nations for the first time were directly exposed to an understanding of the whole issue.
- Some participants indicated it was the best workshop or conference they had ever attended, in that they got information out of it that they could apply directly in their communities. The Northern Contaminants Program has provided that invaluable legacy for this region. To be able to have First Nation people understand that level of information will be very beneficial in the future to everyone.
- There was also an understanding in discussions with the academics and scientists that some of the information that First Nations were filtering through the system was not necessarily being heeded at all times. In many cases that information was just being disregarded.
- The scientists and academics started to realize the value of information that the elders had to share, e.g. the flow of water in a certain area 50–60 years ago was quite a lot more significant on a more seasonal and annual basis than it is now, or the quality of the water has changed, or the number of species of certain wildlife in a certain range are not there, or the size of the animals has changed, or, in the process of field-dressing their game, they have seen certain abrasions or items within the species that were not there in the past.
- There was an attempt to feed this knowledge into the western scientific system that dictates that everything they do has to contain substantive, tangible data that they understand.
- CYFN has been advocating greater integration, i.e. that any people who derive their lifestyle and living out on the land are going to have keener observations on a day-to-day basis than a scientist or technician in the long term.
- The scientist or technician who is on the land for a week will pick up some raw, hard data, which can be utilized to show spatial and temporal trends.
- Scientists may be looking at an accumulative effect of certain contaminants or heavy metals over a longer haul by utilizing a small window of five- or ten-year-old data. An attempt should be made to try and capture as much traditional information or observations of people who have been in the area for a long time in order to arrive at a conclusion or final analysis as to where these things are accumulating from and/or the level or degree of increase.
- At the beginning, there was not that much acceptance of that process, but that's changed.
- Through the Northern Contaminants Program, there has been involvement in some of the international discussions and issues like biological diversity and global climate change.

- Indigenous partnerships have expanded to the Russian Association of Indigenous Peoples, Sami Councils in Scandinavian countries, and work has been done in the international arena looking at fundamental questions that are big problems for the world today.
- Canada is now one of the countries that supports the position of integrating traditional knowledge into the scientific information and actively encouraging the scientific community globally to not only solicit that information but to find the mechanism to process it and be included in the final analysis.
- Although there is an acceptance that traditional knowledge will be integrated today and there is no more debate about whether it should be, it is still being debated as to what it is ultimately and how it fits in.
- There is a recognition by many people, particularly in the medical sciences, that traditional knowledge has always lent itself to western products, such as aspirin. Medicines that are typically used on a day-to-day basis by the entire world were initially found with cooperation of the indigenous peoples, analyzing their traditional knowledge and trying to find what benefits there are.
- The traditional knowledge is useful, not only in the pure scientific and technical arenas of global climate management/environmental management; but also, the traditional knowledge and experience associated with a lifestyle.
- With agencies like the Fish and Wildlife Management Board, it's not so much trying to manage the fish and wildlife as trying to manage the people who access it, i.e. to ensure they are more in sync with the environment at a more sustainable level to have the enjoyment and use of the land but not to the degree that it's to the detriment of First Nation people in the long haul. The First Nations are advocating that this be done by people on a global context, thanks to the Northern Contaminants Program.
- Presently Grand Chief Shultz is the International Chair of the Northern Athabasca Council, which was formed three years ago, representing nearly 60 communities of indigenous peoples in Alaska, the Northwest Territories and the Yukon, doing work with some of the U.N. forums and the Arctic Council Forum particularly on environmental issues. The Council is an avant garde group of people, working with other indigenous partners to get all society to understand that the indigenous perspective is something that the rest of the world should pay heed to.
- The results of western philosophies and world views have not in all cases served the people well. Otherwise, we wouldn't be having problems with such things as global warming, species becoming extinct and polarized imbalances in society.
- Increasingly politicians, as well as scientists and academics, are saying, "Yes, we do need to start looking at how we can sustain ourselves better as the human race."
- Indigenous people globally seem to have common denominators in their societies which allow them to be more in sync and balanced with the environment and their surroundings, which have sustained them to today regardless of the external influences that have negatively impacted them.
- The Northern Contaminants Program still has tangible benefits for First Nations today in continuing to be involved in identifying and priorizing data collection and analysis.
- The long-term legacy goes much beyond the Yukon to the global communities.
- Grand Chief Shultz' ability to stand up in a room with ministers and leaders from eight countries, with scientific and academic leaders throughout the world asking for his opinion, is the achievement of the Northern Contaminants Program from its beginning. The Grand Chief has been proud that he and his organization have been involved with the program and what has been achieved and want to continue to be involved with it. He expressed gratitude to people in the room, particularly Mark Palmer, who was patient with him and helped guide him to a better understanding and fulfilled his fiduciary job on behalf of the Crown exceptionally well.

Yukon Inter Tribal Watershed Council — Vanita Sahni and Suchof Sunday

- The Yukon Inter Tribal Watershed Council is an organization that was put together and established by First Nations when First Nation groups around the Yukon River decided that the water quality was very important to them and that they wanted to all come together to learn more about the water quality and the scientific knowledge and integrate that with their traditional knowledge.
- They are a capacity-building group, attempting to transfer technical, scientific knowledge to regular English in a way that people can understand it;

teaching and guiding the First Nations who want to learn about it.

- A steering committee guides the Council, and the onus is up to the First Nations to take the initiatives to direct their learning.
- The Council is developing a website, which will be an important communications tool between the First Nations and the Tribes to provide up-to-date information, because the communities are so spread out. There will be restricted access to the Tribes and First Nations.
- They have been working with Environment Canada and creating a partnership between governments and First Nations.
- The Council assists communications and sharing of information between governments and First Nations.

Overview of Northern Contaminants Program — Sarah Kalhok

- The Northern Contaminants Program in the Yukon is part of a larger pan-northern program, called the "Northern Contaminants Program", which began in 1991 and includes Yukon, Northwest Territories, Nunavut and other northern regions of Quebec (Nunavik) and Labrador and covers the interests of all those regions.
- This all fits into a circumpolar program, called the "Arctic Monitoring and Assessment Program" (AMAP), which is made up of the eight circumpolar nations: Canada, U.S., Norway, Sweden, Finland, Denmark, Greenland and Russia.
- The objective of the program is to reduce and, wherever possible, eliminate contaminants in traditional or country foods while providing information that assists individuals and communities to make informed decisions about their food use.
- This includes gathering information about contaminants, reducing or eliminating them through international policy and getting that information across to northerners so they can use it to make decisions about consumption of traditional foods.
- The program looks at three groups of contaminants in general: heavy metals (mercury, lead and cadmium), persistent organic pollutants (POPs), which include DDT and PCBs, and radionuclides (Cesium 137). The focus of the program has been on POPs and heavy metals.
- Organizing the program to look at contaminants is done by subprograms, i.e. abiotic monitoring or looking at monitoring of the nonliving environment, i.e. the air, water and soil. The second subprogram looks at contaminants in the living environment, i.e. fish, caribou and marine mammals. The third subprogram is human health of those who are consuming the foods, i.e. benefits of traditional foods versus contaminants. The education and communications subprogram is led by the aboriginal partners to make the information understandable to northerners. The international policy subprogram is working at eliminating or reducing contaminants in the Arctic, because most of them are not generated there.
- The program is under the leadership of the Northern Contaminants Program, run out of DIAND and operates in partnership with aboriginal organizations such as CYFN and the Dene Nation.
- In addition to DIAND, there are three other Federal departments: Fisheries & Oceans, Health and Environment; and there is representation from Territorial and Regional Governments, which make up the management structure. The program also works closely with universities and research institutes, such as the Centre for Indigenous People's Nutrition and Environment.
- Abiotic monitoring has revealed where contaminants come from, which for the most part is not from the north but from agricultural and industrial areas in other parts of the world through ocean currents, air trajectories and rivers in a cold condensation or grasshopper effect of evaporation and condensation.
- One air monitoring site is at Tagish.
- The biotic monitoring looks at contaminant levels and trends in the environment and in wildlife.
- Contaminant levels in an animal build up over time (bioaccumulation). Younger animals usually have less contaminants in them than older ones.
- Marine animals illustrate why there is concern about biomagnification in the food chain, with contaminant concentrations increasing with each step of the prey/predator. Animals consuming other animals have higher contaminant levels than those that eat lower on the food chain. People in the north are at the top of this food chain, which is of particular concern.
- Temporal and spatial trends are being looked at in monitoring to determine how contaminant levels are

changing through time and how they differ in different parts of the circumpolar north.

- Northerners are concerned about levels of exposure through diet and resultant effects on people.
- There are contaminants in people in every region of the world based on the amount that is in their food and how much they're consuming. Dietary habits strongly influence contaminants levels in people.
- The big concern is the eastern Arctic where there is a very long food chain.
- At one point, the diets of northerners were made up entirely of traditional foods, but now market foods are also factoring in to total nutrition in the north.
- In addition to the nutritional benefits of a traditional diet, there are economic, cultural and social benefits. It is a way of life and involves the overall health, not just nutrition.
- Communications is a very important part of the program. The media likes to sensationalize this issue, i.e. how food is toxic and is poisoning people.
- The traditional foods in the Yukon are very healthy, and the benefits from consuming them far outweigh the risk at the contaminant levels found in the foods.
- Aboriginal organizations have taken the lead on communications, because they are closest to the people who are consuming the food, and they know how to convey that information. Balanced information, put into context with the benefits, is very important to get a full understanding.
- Education curriculum materials have experienced a lot of success.
- Some information about contaminants has caused people to alter their dietary habits and lifestyle, so it is important to get accurate information across. The program has a website, brochures and annual publications, letting people know in plain language what kind of studies are being done, plus an annual research synopsis.
- The second annual Canadian Arctic Assessment Report is being compiled, which summarizes and assesses information from the last five years of the Northern Contaminants Program. A plain-language highlights report, from the design through to the publication, led by the aboriginal organizations, is due to be released in the fall.
- The Northern Contaminants Program has had a lot of success in international policy negotiations, working toward protocols on POPs and heavy metals. Final negotiations with the United Nations Environment Program Convention on POPs took place in December 2000, in Johannesburg. Last May, more than 100 nations signed this convention. Canada was the first to ratify it. International negotiations are long and difficult. One aspect that has been successful and compelling to the international community is the aboriginal cooperation on the contaminants issue, particularly with respect to the POPs. The Canadian Arctic Indigenous Peoples Against POPs worked together with the Russian indigenous peoples of the north and the Sami Council at the negotiations to ensure that international agreements on POPs protected Arctic aboriginal people.
- Most POPs have already been restricted or banned from use in Canada.
- The focus of this workshop is on the heavy metals such as mercury. There are currently efforts under way to develop some international protocols on mercury.
- The NCP website: www.inac.gc.ca\ncp.

Terrestrial contamination — Mary Gamberg

- Mary has been involved in science by way of collecting hard data in the Yukon for ten years.
- Work had been done in Norway and Sweden, which raised concerns over an unexpected level of cadmium in caribou, which resulted in a health concern for people who were consuming the organs of the caribou.
- Cadmium is a nonessential element for people and is associated with zinc both biologically and geologically, e.g. lead-zinc mine.
- Contamination occurs through ingestion, i.e. eating food, and it localizes in the liver and kidney, which filter out toxins. It does not accumulate in the meat or muscle tissue. As it accumulates over time, older animals or people are expected to have more in their bodies. At a certain level, it becomes toxic and will result in kidney dysfunction.
- Samples in a freezer in Ottawa, plus samples taken from the Porcupine caribou herd, were examined.
- It was determined that across the Arctic, the levels were pretty much the same, i.e. the Porcupine Caribou Herd were pretty much the same as the NWT, northern Quebec and Norway, which resulted from a global transport of cadmium from the south blanketing the

north. The lichens, which are ingested by the caribou, absorb cadmium very well, as they have an anchor, rather than a root system like other plants, and absorb their nutrients through the air, which include contaminants.

- A study of 30 caribou from the Finlayson caribou herd was undertaken, and a huge difference was found in the animals, i.e. a lot more cadmium than expected and way more cadmium than any other caribou that had been measured anywhere. The Tay herd was also high in cadmium. This was rather a shock, and people started to panic over these results.
- One difference is the Finlayson is a woodland herd and feed a lot more on grass, willows and buds than the barren ground herds, which feed primarily on lichens.
- Three woodland herds were examined. The Tay and Finlayson herds are located near Ross River, where there is a large lead-zinc mine; ecologically a lot of lead, zinc and cadmium. The Bonnet Plume woodland herd was also looked at, which resides up in the Bonnet Plume mountains; rather than an area of industry or high geological cadmium.
- The Bonnet Plume herd had less cadmium than the Porcupine herd, which demonstrated that there is not a genetic difference between the woodland and barren ground caribou.
- The question was: Is it occurring naturally or because there is a mine in the area, i.e. from the tailings?
- Samples of lichen, soil, vegetation, berries, water and overflow on lakes were taken; and it was discovered that the source of the cadmium was not the mine but the land. Certain plants, such as willows, are very good at absorbing cadmium out of the soil, which gets in the buds, leaves and twigs; and when caribou eat it, they accumulate a lot of cadmium.
- The woodland caribou are not migratory. They live in one area all their lives.
- Health Canada did a health assessment. The amount of caribou kidney recommended that one can ingest safely differs among herds, because the amount of cadmium is different. The lowest number is the Tay herd, and one should limit intake to seven kidneys per year and four livers. It does not accumulate in the meat, so there is no advisory in that regard.
- People in the Yukon, both First Nations and otherwise, eat a lot of traditional foods.
- A huge study was undertaken in 1995, including large and small mammals, working with all First Nations and foods that were taken at traditional times from traditional places; as well as with samples submitted by hunters. Most of the studies centred on what was consumed, but included bear and short-tailed weasel; birds, mostly ducks, grouse and ptarmigan; plants; berries and anything people collected for use.
- The samples were analyzed for a suite of 26 metals and organic pesticides. No pesticides were found in anything.
- There was a little bit of mercury in the caribou kidneys, but that was less of a health concern than the cadmium. If intake was maintained to what was recommended for cadmium, it was safe for mercury, as well.
- The concentration of cadmium depends on the habits of the animal and where the animal lives, i.e. muskrat do not tend to eat anything that accumulates cadmium, so they will never show cadmium. Grouse eat a lot of willow buds, which can be very high in cadmium. Some showed low levels of cadmium, and others showed such high levels that if they were laboratory rats, they would have been dead a long time ago. Beaver and porcupine eat a lot of willow and tend to accumulate cadmium.
- One unexpected result was that the moose were also very high in cadmium, i.e. similar to the Finlayson and the Tay caribou, which is different from moose that have been measured in other places. The ecoregion is unique, in that it is very mineral-rich compared to moose that are living in a large ranging area. They are big animals, and they eat a lot of willows during the course of a day, thus taking in a lot of cadmium. Cadmium does not accumulate in the meat, only in the kidneys and a little in the liver. It is recommended people keep their intake to one kidney and a little over half a liver in a year. This is cumulated, so if a person doesn't eat any one year, they can eat twice as much next year. These health assessments are for non-smokers. For a smoker, the numbers will be lower.
- Most Yukon country foods have no contaminants concerns, and they are valued food sources.
- Hunter surveys of moose and caribou have been continued, i.e. they submit a kidney, some liver, muscle and a tooth from each animal. In some cases, there is actually 10 years of data.
- The most data available is for the Porcupine caribou herd. Arsenic and lead are barely measurable and are not changing. There is some measurable mercury, but it is

not very high, and it is very stable. Selenium and copper, necessary trace elements, are very stable. Cadmium is listed as stable, because although it is increasing a little bit, statistically, it is not significant.

- The data available for moose indicated lead, mercury and arsenic barely measurable; copper and selenium, stable; cadmium very stable but a much higher level than the Porcupine caribou herd.

The conclusion from the hunter survey after 10 years of research is that contaminant levels in moose and caribou appear to be stable.

Mercury trends in northern fish — Lyle Lockhart

- A sample of mercury was passed around. Places where mercury is rich in the rocks, one finds cinnabar, which is the ore that is often mined when industrial mercury is produced.
- Mercury is a natural element.
- Mercury concentrates in fish, and it is toxic to humans, and mercury can hurt humans if we get enough of it.
- Subjects to be discussed: how much mercury is in the fish analyzed from the Yukon and where the mercury comes from.
- There is natural mercury that occurs in the rocks, and some mercury is produced due to the fact that over the past 2,000 years or so, man has been moving mercury around in ways that nature doesn't very often do.
- There are varying opinions about whether mercury matters to the animals and fish.
- An understanding of mercury started with an incident in Japan where people were poisoned by mercury in the environment after an industrial corporation had discharged mercury into the environment. It got into the sea and got into the fish. People ate the fish, and they were poisoned. People noticed something was wrong with the cats, who were being fed parts of the fish that the people didn't use.
- There is the same amount of mercury on earth now as there was a million years ago, but we've moved it around in ways that nature has not done, especially by burning things.
- The larger the population, the more energy-intensive our lifestyle is and the more we burn, the more mercury gets into the air. The air distributes it throughout the planet, the Yukon being on the periphery. Some gets rained out into the ocean.
- There is mercury in petroleum fuels; burning coal, garbage and cremation (dental fillings) being big contributors.
- There is a lot of range in the numbers in studies, with the best estimates being that the air we are presently breathing in North America being about half natural and half coming from human activities, largely burning of fossil fuels.
- In Canada, the biggest source is probably smelting of sulphide ores, and in the U.S. it's burning fossil fuels.
- A lot of the reason for interest in mercury in the north stems from studies by Health Canada.
- Health Canada surveyed about 500 native communities across the north and measured the amount of mercury in the blood of the people, as well as sampling the hair.
- From a Yukon perspective, things look good.
- There is a biological cluster of coastal communities in the eastern Arctic which have high readings. It is believed a lot of that is due to their consumption of marine mammals.
- The Yukon is a place where one expects to find mercury geologically. It is unknown how much the driving force of the mercury in the fish is due to this and how much is something else.
- There are not good mercury maps for geological concentrations in Canada.
- One hot spot was identified in the Yukon.
- Fish samples were taken from the NWT/Yukon border where there is a high concentration of geological mercury.
- Toxicologists have figured out how much mercury we can take in without hurting ourselves, then backtrack it to determine if one is getting the mercury from food, how much food can be consumed without causing a person to go over the "too much" levels.
- Commercial fish are recommended to be under .5 parts per million (ppm) and even less for people who consume a lot of fish.
- The Canadian Food Inspection Agency will remove fish that test above the recommended level of mercury, however, they cannot control consumption from private fishing.
- The Northern Contaminants Program is oriented toward contaminants that move around by air and get into our settings but don't necessarily originate here.

- With mercury, some of the contamination could be coming from the locks that are in the lake, which adds a huge complication in trying to interpret the results. With PCBs, one knows they come from human activities somewhere, but with mercury in a lake, that is not the case.
- Mercury is not an essential element to humans like copper.
- Sarah Atkins-Baker wrote a report in 1979 where she described mercury in fish that she obtained from all over the Yukon in 1977. All the dots are green except for a couple of yellow ones; no red dots, which is good.
- Salmon, char and suckers were good news.
- Only a small number of inconnus and ciscos were sampled, and they tested quite high (Old Crow Flats).
- Northern pike had several yellow dots and even a red dot, i.e. fish that eat other fish have high levels. The Yukon seems to be a bit better with northern pike than parts of the western NWT.
- Grayling are almost all green.
- Mercury follows protein, so one does not expect to find it in the liver.
- The Yukon is not all that different from other northern territories.
- Arctic char are really clean fish, because they derive a lot of their calories from the marine food chain, which seems to be less problematic than the fresh water food chain.
- White fish are very good, Yukon has almost all green and three yellow dots.
- Lake trout has about the same number of red as green dots, with the largest category being yellow. There is a problem all across the north with lake trout.
- The highest problem species is walleye, which has a great tendency to pick up mercury.
- Average figures conceal all kinds of sins.
- The bigger the fish, the more mercury one will likely find in it. So, a person would not want to each as much of the larger size range of fish.
- A steep line on the graph means the fish are picking up mercury quickly, and a flat line means they are not picking it up very quickly at all.
- One lake where there appears to be a potential mercury problem shaping up is Kusawa. Practically all fish that have been analyzed from this lake are over .2 and many exceed .5. There are more fish from Kusawa in the lab now, so future analyses will be occurring.
- In the data for the Yukon, there are several lakes where the same kind of fish have been sampled more than once.
- Between 1977 and 1998, in white fish from Lake Laberge (all similar size) that were sampled the mercury appears to have gone down a bit.
- Levels in Mayo Lake stayed about the same with white fish; but lake trout went down a bit. Probably the fact that smaller fish were sampled could have a bearing on the results.
- Quiet Lake stayed about the same, and fish sizes were not recorded.
- Studies in birds and whales indicate that mercury seems to be increasing.
- Data is sent to Health Canada, and they advise how much is safe to eat of each species, i.e. evaluate how much fish from Kusawa would be safe to consume.
- In a summary published by USEPA in 1995, there were 1,300 advisories for mercury, some of them including all the water in an entire state. The advisories on mercury outweigh all the others combined, i.e. PCBs, chlordane, dioxin and DDT. Mercury will probably be a difficulty in the north for a long time.
- The controversy is it is recommended to eat foods from each group every day, while at the same time, consuming only 225 grams of lake trout per week, which is not enough.
- International negotiations to try and limit the sources works for things like PCBs; but because mercury is connected to our lifestyle and use of energy, it will be hard for us to get rid of.
- Studies are being done to determine whether it is mercury that is coming in the air that is the source of the problem.
- The Yukon does not catch very much of the atmospheric vector from Asia. It is unknown how much of the mercury coming in from this source is adding to the amount of mercury that is in fish.
- Northerners are in the position where they have to make the most rational balance and judgment they can between the nutritional good obtained from eating the

fish and other animals and the risk. It is generally agreed that the nutritional benefits from the traditional foods exceeds the risk of poisoning one would get, but it is an individual choice to be made.

- In some parts of the globe, there is really rich geological mercury. The southeastern Yukon has some.
- There may be local stuff such as old pulp mills or old mines that are a source of mercury.
- In some parts of the world, there is a big loading into the atmosphere. The Yukon has only a small atmospheric component.
- The Yukon does not have the same sort of problem as northern Quebec or some of the eastern islands.
- Lakes have a remarkable history, which is different from the oceans, in that lakes gradually fill up over time. There are lakes that have a mile or more of sediment. As layers form in the bottom, they gradually fill up, and the lake becomes like a bog. A core put through the layers cuts back through the history of the lake. The core can be sliced and radionuclides utilized to get an idea when each of the slices was deposited in the lake.
- Nature has given us a wonderful clock, which is due to the radium in the soils. Radium decays through a series of steps to a gas, called "radon". This gas does not stay radon for very long but decays through another series of steps to form lead-210, which will attach to any particle it meets.
- The lead-210 can be used to date the layers, i.e. each time you have the counts of lead-210, it takes about 22 years. Radionuclides decay at a very constant rate, and nothing changes the tendency to decay at all. The results of the dating can be plotted onto a graph.
- One other phenomena that is used to assist with plotting is the fallout from the testing of nuclear bombs, the peak time being the early 1960s.
- Noah in the U.S. produced graphs to illustrate a typical world pattern for things such as metals. A lot of the decline is from a worldwide switch away from coal towards oil and natural gas. Coal is a much dirtier fuel than the other fossil hydrocarbons.
- Some people believe that the cores are just artifacts and imagination.
- In the Kusawa Lake core, the mercury points are high and then drop off and form a stable base. Lead is far more variable than it ought to be. Normally lead is not like that. There is something going on in Kusawa Lake that is difficult to understand. Copper and zinc are pretty flat, and iron and manganese bounce around all over the place, because they depend on how much oxygen is in the system. There is no indication of cadmium in the lake. Aluminum and titanium are usually indicators of inputs of terrestrial soils, no change there. Mercury stands out as the only metal that may have changed and probably in the absence of much change in lead.
- The other lake in the Yukon that seems to have something going on in the sediments is Fox Lake. The mercury is very much like Kusawa, a long flat period, and then, it spikes up; a huge effect on lead. Something other than gasoline lead has caused a big change in Fox Lake.

Methylmercury risk assessment in Health Canada — Mark Feeley

- Outlined the health risk assessment process (also known as "the health hazard assessment process"), how it has evolved and what is involved; the "regulations" Health Canada utilizes and an example of a more traditional food health hazard assessment the department has recently been involved in; an idea where Health Canada might be moving and how this will affect the health hazard assessment process for country foods in the future.
- Health Canada is responsible for "monitoring" the health and safety risk related to the sale and use specifically of foods and pesticides.
- Health Canada's current motto is: Helping the people of Canada maintain and improve their health, and their code of practice is maximizing the safety of the food supply; and they are supposed to be promoting good nutrition and informed use of food.
- The *Food and Drug Act* is Health Canada's principal piece of legislation that gives it the legal authority to monitor and maintain the safety of the food supply.
- The Act is approximately 80 years old. The preliminary phase was called the *Food Adulteration Act.* The Act applies to all foods sold in Canada, whether manufactured in Canada or out of Canada.
- The Act not only specifies the safety of the food, but also what can actually be in the food product, i.e. nutritional aspects and labelling have to conform to the *Food and Drug Act*, and this is primarily where Health Canada is involved in terms of the safety and potential hazardous products or contaminants or

pollutants that might show up in the food supply in terms of prohibiting the **sale** of food.

- When the *Food and Drug Act* was initially enforced, they didn't have to deal with the chemicals and pollutants that came in with industrialization and similar processes.
- Food includes any article manufactured and sold or even something that someone may try to represent as food, i.e. drinks like bottled water, chewing gum or any ingredient that is mixed with food for any purpose whatsoever. Health Canada is in the process of setting what can be in water. The Act specifies the maximum residue limits or contaminant substances, food additives such as caffeine, packaging material. Anything that could be in or on food is regulated by the *Food and Drug Act.*
- The *Food and Drug Act* gives Health Canada the right to inspect anything associated with food, including the food itself and the premise of producing the food. It also gives Health Canada the right to seize food as they did with the potentially dangerous chocolates on the market. By trying to sell food, one runs the risk that you will forfeit the food and Health Canada will do whatever it wants with the food.
- Anyone who contravenes the Act or commits an offence related to food is subject to a fine not exceeding $50,000 and imprisonment for a term not exceeding six months (summary conviction). If Health Canada has to take someone to court and they are indicted, they can increase the fine to $250,000 and the term of imprisonment to three years. This is scare mongering, because Health Canada doesn't like taking people to court. The worst scenario has been a $500 fine and a term of three months, which rarely happens. However, this illustrates that the *Food and Drug Act* gives Health Canada the authority to inspect, seize, forfeit or destroy food.
- "Hazard" is the potential for a chemical or other pollutant to cause human injury or illness. This basically involves the inherent toxicity of a chemical which could deal with radiation, with germs or anything. From Health Canada's perspective, everything is potentially hazardous, i.e. a certain concentration of salt could potentially cause damage, and they look at whether or not there is a risk associated with a hazard.
- "Risk" is a measure of the probability that damage to health or environment will occur as a result of the given hazard; and "risk assessment" is taking the inherent hazard in a particular substance and trying to figure out whether for a specific population or specific circumstance or situation it is likely that there is a definable risk.
- Risk assessment processes are comprised of three principal entities: trying to determine the estimated daily ingestion or intake of the substance, the average daily intake, how much an individual is being exposed to on a daily, weekly, monthly or yearly basis.
- Total exposure assessment means people take into account what might be in the air, the soil, the water or food. Hazard identification is the easiest to determine, because it relates to any potential for the chemical or compound one is dealing with to have any sort of toxic properties; and the answer to that is usually "Yes".
- The hazard characterization, which is generally referred to as some form of dose-response relationship, i.e. taking into consideration some sort of exposure assessment with the intrinsic property of the chemical to be hazardous, is used in trying to figure out how much one has to be exposed to before it will eventually constitute some sort of risk. The statement would be that they don't want anybody to be exposed to more than an acceptable quantity of a particular substance or another term that is used in relation to contaminants is "a tolerable amount" that one can ingest on a daily or weekly basis and still be reasonably assured over the course of one's lifespan that it would not result in any sort of risk based on the hazard.
- Managing an identified risk complicates matters.
- Health Canada has been criticized for not giving enough information on the overall risk assessment process for people to understand why suggested maximum levels are set for consumption of fish and substances such as livers. Risk management is a very confusing area and the process tends to change with identification of a product being a stronger hazard than it used to be or more exposure from one commodity.
- The cycle of mercury is complex. In the case of Quebec where there have been massive floodings for hydroelectric dams, this is probably one of the prominent sources of mercury getting into the watershed or the atrophic environment. Methalation of the mercury in an inorganic form is then more susceptible to bioconcentration and biomagnification. As the higher levels of mercury move up to the higher atrophic levels, somebody fly fishing will have a definable concentration of mercury in his catch.
- The food intake is the primary route of exposure for methylmercury, with fish being the primary commodity

for the majority of the population. Gold mining and dental amalgams are other sources of mercury exposure to humans.

- It is estimated that in general, the maximum intake a person might have if they are only eating retail commodities on the market is 2–15 micrograms per person per day.
- Estimates for intake of methylmercury for people who are also consuming traditional country foods can be up to almost 100 micrograms per day in a variety of sources such as marine mammals and organ meats, which are contributing significantly to the mercury intake.
- Usually one can determine how much mercury a person has been exposed to by how much they have in their body by taking a blood or hair measurement.
- For the vast majority of the general population who have been exposed to mercury in retail fish and seafood, usually the hair mercury level is less than 1 ppm.
- In the 1980s after some of the hydroelectric dams and the resulting flooding of the property in Quebec, some of the James Bay Cree had 60–120 ppm of mercury in their hair, demonstrating that populations with an extensive subsistence lifestyle who may be eating a larger quantity of fish than the average southern Canadian, will be reflected in having quite highly elevated concentrations of mercury in their body.
- Every 5–10 years, Stats Canada, in conjunction with health departments, conduct consumer surveys, and for those living a nonsubsistence lifestyle, the average is about 6–45 grams/day, which is about half a pound of fish consumed per week. Ninety percent of the population would be defined as consuming less than 225 grams a day, which is about half a pound.
- If the food-based surveys are expanded as to how much fish Great Lakes subsistence populations eat, the average value suddenly exceeds the 90 percentile, i.e. on average some of the Great Lakes First Nation populations are up to over a half a pound of fish a day; and in certain cases, an individual will say that they eat 1426 grams of fish a day, which is a little over four pounds of fish, extrapolated over the course of a year is about half a ton, illustrating the vast range of possible exposures.
- Complicated formulas are used to extrapolate detailed information on the standard exposure assessment.
- Health Canada come up with advisories, based on the average weight of Canadians, the commodity, consumption patterns, food preparation techniques and the protein content of foods consumed.
- In the case of the Great Lakes, it is recommended that visible sources of fat be removed before the flesh is consumed.
- For the general population, some of the surveys which have been recently completed, 90 percent of the population, especially for reproductive-aged women, which tend to be the most sensitive, can be defined as having less than 1.4 ppm of mercury in their hair, which is considered near baseline. Children are even lower, i.e. about .4 ppm mercury in hair.
- In 2000, New Jersey did a survey, looking specifically at pregnant women, not particularly high fish consumer, and 97 percent of the population were less than 2 ppm in their hair. Out of the 199 pregnant women, only one fell at a level that would be considered high.
- Some of the NCP-generated data indicates the general population is about 1 ppm in blood samples (which contains less than hair), which is considered standard.
- The World Health Organization considers that anything less than 5 is where the general population is at.
- NCP studies which looked at the level of mercury in Nunavik Inuit were finding considerably elevated levels of mercury, i.e. up to 14.2 ppm.
- When the study was extended to the Baffin Inuit, where there is a lot of marine mammal consumption, they were still clearly elevated for the general population.
- Studies of Northwest Territories Dene Métis showed only slightly higher elevated results than the general population.
- There is a formula that allows a back-calculation from levels of mercury in hair or blood to estimate average daily intake of micrograms of mercury, i.e. number of fish meals someone may have in a week.
- Statistics show that one can definitely influence your body in terms of what you eat.
- Mercury hazards assessments: Organic forms of mercury are usually considered to be more toxic because it's almost completely absorbed in diet.
- Methylmercury is toxic, but di-methylmercury is even more toxic.

- Unlike some contaminants such as cadmium, the placenta offers no barrier to mercury, and it can, therefore, accumulate in the developing foetus. This was seen on work done on elective abortions in Germany and Sweden, where levels of mercury could be determined in the foetus and in the mother relative to the mother's consumption pattern. Mercury was also found in breast milk at about five percent of the level that was in the blood, illustrating that it is a source of exposure for developing infants.
- A lot of the neurotoxicity is associated back to neural damage, which is unfortunately, irreversible, and is one reason why Health Canada tends to be relatively concerned about giving advice about levels of mercury.
- Specific brain damage or neurological areas which are affected can not be regenerated like a liver.
- Some of the earliest signs seen in human populations affected by mercury involve vision, hearing, speech and muscle coordination.
- In severe cases of methylmercury poisoning, there will be blindness, cerebral palsy and mental retardation.
- Historical background: About 12,000 people were affected by the Minamata poisoning episode. Around the time data was being analyzed from this, the World Health Organization became very concerned and suggested that mercury residue limits should be applied to every food item on the market, initially as low as .02 ppm.
- In 1969, Sweden was one of the first countries to illustrate that there probably was some atmospheric transport of mercury taking place, that the lakes were a good sync for this source, plus there was probably mercury getting into the fish from the soil itself; and certain fish species in Swedish lakes, primarily pike, were coming up with very high levels. Sweden was recommending that pregnant women should not consume any fish between 0.2 and 1 ppm of mercury.
- Based on the previous Minamata poisoning episode, Health and Welfare Canada suggested .5 ppm for commercially-sold fish.
- In 1969, some of the major monitoring activities started taking place, and certain commercial fisheries were closed due to high levels of mercury in fish.
- Industrial activities can have a major impact on the level of mercury in fish.
- In 1972, after a variety of human poisonings or expansion of the study results in Minamata, the World Health Organization suggested that on a weekly basis, humans should not ingest more than .2 milligrams of mercury or 0.47 micrograms/kilogram of body weight/day (tolerable daily intake = the amount one can ingest on a daily basis where the organization responsible for giving that advice can state with reasonable certainty that methylmercury is not going to have an adverse effect on you over the course of your lifetime).
- A review of more recent information of a poisoning in Iraq, where they used a methylated form of mercury as a fungicide on seeds, there was a definitive poisoning with some of the same symptoms they saw in Japan being evident. People were supposed to use the seeds for planting the crop but instead ingested bread made with the seeds.
- In 1976, the World Health Organization applied some of the chronic intakes associated to the human body, i.e. if a human starts to get up to .2 ppm in the blood or 50 ppm in the hair, there was about a five percent risk for adults that they might be starting to show some symptoms of mercury intoxication, reiterating what they previously stated that on a weekly basis, a human should be consuming no more than .2 milligrams of methylmercury.
- The World Health Organization last took a look at methylmercury and confirmed the 1976 values from Japan and Iraq poisonings. There was additional data from Canada, New Zealand and Iraq, which confirmed that the .2 ppm in the blood and the 50 ppm in the hair levels is probably where you start to see effects in adult; but because some of the studies started to look at children, they decided to come up with more conservative advice, stating that pregnant women may start to show signs of mercury intoxication at levels lower than 50 ppm in hair and that the developing infant and the foetus is more sensitive to mercury neurotoxicity than adults would be and suggested that if a mother had levels around 10–20 ppm in the hair, that might be where you start to pick up on a delay in motor skills in the development of an infant.
- Health Canada has conducted more recent studies in the Seychelles, a south pacific island chain, with a heavy fish-consuming population but at relatively low levels. A Rochester, New York, group has done a very detailed analysis of the population of the Seychelles.
- With the adults from Minamata, the people who have been chronically poisoned over a long period of time are starting to show the effects of less than the 50 ppm, probably down around 35 ppm.

- Some of the Canadian studies have been controversial, because it is very hard to define whether the results were specifically a lifestyle-related effect or associated with other factors relating to mercury. There is an indication there may be mild symptoms associated with the level of 10–16 ppm in the hair.
- Tests conducted in clinical conditions on infants of native mothers in New Zealand showed subtle psychological behavioural deficits in the area of hand-eye coordination, visual acuity tests and language skills associated with a maternal hair level of between 10–15 ppm.
- Infants from mothers who had greater than 12 ppm in their hair had poorer child developmental test scores in the area of language skills, perception of surroundings and cognitive abilities to be able to recognize pictures.
- However, with the Seychelles cohort testing, reanalysis of the infants did not support the initial observations (now about 12 years of age). The consensus is that the children with the higher levels of mercury are actually showing better test scores in these areas, which has led researchers to confirm that fish are such a good source of protein and fatty acid content that the mercury is an indices of the consumption of the fish, but fish is "brain food".
- Another cohort is being looked at on the Faeroe Islands where there are high consumers of fish, as well as pilot oil. When the infants were tested at seven years of age, they started to show some of the attention, language and memory lower test scores that were common in the Seychelles. Thirteen percent of the population was at a level that the World Health Organization thought one might start to see the effects, indicating a consistency around the 10 ppm of mercury in the maternal hair. The same subtle effects were seen in the infants where the maternal hair was about 12–13 ppm.
- In 1997/1998, Health Canada synthesized the information and suggested that based on the evidence to date, it might be prudent to state that mercury hair concentrations around 10–11 ppm is roughly equivalent to where one might start to see the effects on infants with very sophisticated neuro-psychological testing procedures. The 10–11 ppm level in the maternal hair results from a dietary intake of about 60 micrograms per day.
- For the general population, Health Canada wanted to reduce this amount five-fold. They suggest that for reproductive-aged women or women who might be pregnant or be thinking of becoming pregnant and young infants, they should ingest no more than 12 micrograms of mercury on a daily basis.
- The guideline Health Canada sets for commercial fish is a limit of .5 ppm, and the Canadian Food Inspection Agency has the authority to sample the fish.
- Shark, swordfish and fresh and frozen tuna fish in the commercial market are known to consistently exceed the .5 ppm guideline.
- Under risk management, Health Canada has decided that because the consumption of these particular species is so limited, they exempted them from the .5 ppm guideline.
- There are currently no restrictions on canned tuna and salmon. These are routinely sampled. Canned salmon is very low; and because the tuna used in canning are usually the young species, it routinely tests well below the .5 ppm. In southern Canada, canned tuna is the most commonly consumed fish product. Health Canada has not found it necessary to provide any sort of consumption advice for these products, and they are reasonably assured that if women and children consume no more than .2 micrograms/kilograms of body weight and for the general population .47 micrograms/kilograms of body weight there should not be a risk of suffering adverse health results.
- Health Canada has assisted organizations that have come to them for advice regarding non-commercial or non-retail commodities on the market. Anybody can submit an evaluation request to Health Canada. After a detailed assessment, a condensed, lay-person's summary, including recommendations, is provided. The Northern Contaminants Program, DIAND, YTG, Department of Health or other contacts may be utilized to synthesize and convey information.
- The Canadian Wildlife Service, Environment Canada, requested assistance on some metals when they had performed an analysis on waterfowl. Health Canada has no data base to suggest what the average waterfowl liver consumption rate might be for the general population. Almost 100 percent of the population that consumes waterfowl does not consume liver. In this particular assessment, the average mercury concentration of the liver was approximately .55 ppm, and applying the formula, the recommended intake for adults was they could eat a little less than a pound of liver a week (355 grams), and for women a little less than half of that

value, for children less. The Northern Contaminants Program was used to communicate the fact that they know the population isn't eating that much waterfowl liver per week, so they would tell the community there is no problem.

- Only a small percentage of the mercury toxicity is found in the organs.
- There can be something in the commodity that would be of benefit and counteract the risk and hazards associated with the exposure.
- Cohort studies are still ongoing, i.e. children are being continually assessed.
- The original study when the children were four-to-six years of age showed subtle effects; the latest studies showed no effects. However, the Faeroe Islands study have shown effects on children at both the lower and higher ages. Whether these will be consistent or transient effects is unknown. There are also some reports out of the Faeroe Island studies that are more puzzling, which is the idea that there may be cardiovascular effects, i.e. increases in blood pressure and heart rate variability, in children from mercury exposure. This is totally against the norm, because usually mercury in fish consumption is thought to be good for the cardiovascular system.
- There is a great deal of interest in Nunavik, as the highest levels were evident in the NCP monitoring done on cord blood for mercury.
- The Nunavik cohort was substituted with children from Greenland, and all the children will be subject to the same type of testing. This will hopefully be able to define whether the risk level that Health Canada has taken to set its guideline is a valid number.
- In the next couple of weeks, there will be a Health Canada workshop on Human Contaminant Guidelines, at which the at-risk level, increasing risk-level and no-risk level will be looked at.

Metal contaminants in the north, the big picture — Colin MacDonald

- When the Northern Contaminants Program goes into the communities and talks about concerns, they can be broken down into: will the contaminants in the food make people sick, will the contaminants make the animals sick, i.e. environmental toxicology, how much animals have in them and how much the fish are taking up and can we safely eat the food.
- The objectives of this discussion: review the levels of cadmium and mercury in caribou in the north, examine the global sources of metal, whether there are any obvious temporal trends in biota (utilize Cesium 137) and priorities for monitoring and further studies.
- Local sources, including incinerators, land fills and fuel drums, need to be understood and controlled if possible.
- The State of the Environment Report for the Yukon has maps of known problems, i.e. sites of specific contaminants.
- Material can come from a distant source via long-range transport, move through the atmosphere and be deposited in the north. Although the model refers to organic chlorines, it also applies to some metals.
- In a paper by Pacyna and Pacyna, 2001, they went through country-by-country, added up the sources in 1995, e.g. tonnes produced by continent by items like number of cars, number of chimneys. China is a big producer of mercury and cadmium.
- In 1983, they estimated about 3,500 metric tonnes/year of mercury, with a decrease in 1995. The United States has put controls on mercury, which has cut down their sources.
- With the exception of lead (removed from gasoline), all other metals are correlated. Coal is being burned less, and modern technology is being used in industrial operations (e.g. more scrubbers).
- Nickel and vanadium are correlated. Vanadium is not very toxic, and did not show up in recent caribou studies.
- A 1997 study out of China indicates that because of all the industrial activity going on to increase production and with the burning of coal, the estimate of mercury output to the atmosphere is 4.8 percent per year, and is something to keep an eye on as to a source of mercury.
- Anthropogenic and natural mercury in the atmosphere is about 50/50; cadmium is higher. Lead, vanadium (due to burning of oil) and nickel have increased.
- It is expected that those metals which are increasing will start to show up in the Arctic.
- When caribou consume metals through the lichen, they are distributed in the animal, some to the liver, some to the kidney; organochlorines stay in the fat.
- Analyzing tissues from hunts to come up with patterns.

- Tay and Finlayson herds are miles above everything; examined raw data for patterns.
- The Bathurst and Beverly are mainland caribou herds out of Yellowknife, move over to Baffin Island.
- Cadmium is highest in the kidney and some in the liver.
- Levels of cadmium and mercury are similar in males and females in most herds.
- The liver acts as a reservoir for copper. Differences between males and females may have been due to the fact that the females were lactating or a big change in their body condition.
- The kidney is like the filter of a car.
- There are relatively low levels of mercury in the Yukon. Higher levels are found in northern Quebec and Hudson Bay.
- Data agrees with Mary Gamberg's data.
- Looks like there was a decrease for mercury, but could be due to analytical changes by labs.
- Cesium 137 has been a concern in the north. It is a manmade radionuclide that accumulates in caribou muscle. The amount of time that it is actually in an animal is only about 30–60 days. The source is from nuclear weapons testing, and in the mid-50s to mid-60s a lot was released into the atmosphere, deposited on lichen, consumed by caribou and levels built up in the caribou. Chernobyl was the other big source back in 1986. The reindeer in Europe were probably the best example of this process.
- There was a very small amount of Cesium 134 produced from weapons testing, a lot from Chernobyl, and this is used as a marker of how much residue from Chernobyl is actually showing up in the north.
- After a three-year moratorium, people started testing again. This changed to underground testing. Some of the underground tests leaked and ended up as a source to the atmosphere anyway. Levels in reindeer and herders in Finland peaked in the mid-60s for Cesium 137, decreased; and after Chernobyl there was a bump, i.e. a direct correlation between what is in the animals and the people ingesting the animals.
- Ingenious ways of measurement were undertaken, e.g. with a test that occurred in the north of China, an aircraft flew from India to Australia, and when it landed, they wiped down the inside of the aircraft and tested the wipings, found all kinds of isotopes; conclusion that there was a pretty good distribution of nuclides from the blast down to the southern hemisphere.
- In 1997, where it was actually deposited was looked at.
- Most of northern Canada escaped most of the deposition because there was not much precipitation; with the higher levels of precipitation in the Yukon, that's where most of the material came out.
- Health Canada data from southern Yukon was grouped together.
- There were a bunch of papers from the mid-60s and the mid-90s for the western Arctic and several reindeer herds in Alaska.
- Cesium is extremely variable in the animals; as soon as the animals change their diet, levels decline.
- The highest levels back in the mid-60s were about 2,400 becquerels per kilogram; after Chernobyl some of the European herds were up to about 30–40,000, the highest levels being mid-latitude.
- By the mid-80s the levels in the original four or five herds had declined quite a lot, although there were higher levels in Quebec.
- The levels are so low on the readings from the western Arctic herds, that they are almost below detection.
- With the Bathurst herd, it was up around 2,000 in the mid-60s, and it is now down around 100 or so. The source has declined a lot every 10 years.
- The cadmium remains high in the kidneys of some caribou herds in the Yukon. This is from a natural source, and has probably been like this for 10,000 years. However, the levels in the meat are low.
- Mercury appears to be low in Yukon caribou relative to other northern herds.
- Sources to the atmosphere for some metals are declining and increasing for others, which means monitoring should continue in the atmosphere and receptor species on the ground.
- Cesium 137 has declined about 10 times in the Yukon herds since the 1960s.
- Metals should be monitored every five years for evidence of temporal trends and to ensure they fit the general predictions.

Discussion and Conclusions

The Workshop presented a broad spectrum of investigations into metals contaminants in country foods and the insight provided by the Grand Chief, as to the positive effect of the NCP for Yukon First Nations, provides direction for the future.

Expected Completion Date

This project is on-going.

Acknowledgements

The Yukon Contaminants Committee would like to thank all of the presenters who generously volunteered their time for the Workshop.