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Environmental Studies No. 72

Synopsis of Research Conducted Under the 1993/94 Northern Contaminants Program

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Northern Affairs Program

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

FOREWORD

This report summarizes the results of research and monitoring studies on contaminants in northern Canada. These studies were conducted under the auspices of Canada's Green Plan Arctic Environmental Strategy/Action on Contaminants Program.

The projects cover all aspects of the northern contaminants issue, including sources and transport; contamination of marine, freshwater and terrestrial ecosystems; human exposure through diet and related health implications; communication and education of northern residents; and international initiatives addressing the global aspect of the problem.

These projects were evaluated by the Technical and Science Managers Committees on Contaminants in Northern Ecosystems and Native Diets to ensure that they supported the overall Northern Contaminants Program objectives.

An address list of the project leaders is given in Appendix 1.

PRÉFACE

Ce rapport résume les résultats de recherches sur les contaminants et d'études sur la surveillance des contaminants dans le Nord canadien. Ces études ont été menées dans le cadre du programme Action sur les contaminants de la Stratégie pour l'environnement arctique du Plan vert du Canada.

Ces projets représentent tous les aspects du problème des contaminants, incluant les sources et le transport, la contamination des écosystèmes aquatiques (eaux douces et eaux salées) et terrestres, l'exposition de l'organisme humain en raison de son régime alimentaire et ses effets sur la santé, la communication avec les résidants du Nord et leur éducation et les initiatives internationales abordant l'aspect global du problème.

Les comités de gestionnaires techniques et scientifiques sur les contaminants dans les écosystèmes du Nord et dans les régimes alimentaires des Autochtones ont examiné ces projets afin de s'assurer qu'ils répondent à l'ensemble des objectifs du programme Action sur les contaminants.

Vous trouverez à l'appendice 1 une liste d'envoi des gestionnaires de projet.

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INTRODUCTION

The Arctic Environmental Strategy's Northern Contaminants Program (AES-NCP) was initiated in 1991 in response to results of cooperative studies undertaken in the mid to late 1980s by a number of federal departments on the issue of contaminants in the Arctic. The studies indicated that there was a wide distribution in the Arctic ecosystem of a spectrum of substances, many of which had no Arctic sources, but which were, nevertheless, reaching unexpectedly high levels in Arctic biota. These findings were of concern because of the potential human health implications arising from the dependence of many northern native peoples on country foods and their position as high trophic level consumers. The Program's key objective is therefore "to reduce and, wherever possible, eliminate contaminants in country foods." The three main contaminant groups of concern are heavy metals, radionuclides and persistent organic pollutants, particularly organochlorines.

The NCP is directed by a management committee and a technical committee, both of which include representatives from the five northern aboriginal organizations (Council for Yukon Indians, Dene Nation, Metis Nation, Inuit Tapirisat Canada and the Inuit Circumpolar Conference), the Yukon and Northwest Territorial governments, and four federal departments (Environment Canada, Fisheries and Oceans Canada, Health Canada and Indian and Northern Affairs Canada). Development of the strategic research plan and priorities for the NCP were based on an ecosystem approach, focusing on three main categories i) Sources, pathways and fate, ii) Ecosystem uptake and effects, and iii) human health. The priority work areas which complement and/or are supported by the scientific research are a) communications and education and b) initiatives to promote international control of contaminants

Since 1991, the AES-NCP has contributed approximately $14.7 million to some 80 research projects, in addition to supporting the McGill Centre for Nutrition and the Environment of Indigenous Peoples (CINE), and participation of native organizations in the AES. To date, progress of research funded by the Program has enabled us to firmly establish a number of important points: 1) the majority of contaminants detected in the biotic and abiotic environment of the Arctic are derived from sources outside the Arctic and outside Canada, 2) the atmosphere plays a major role in the transport of contaminants to the north, and 3) measurable and often significant levels of a number of contaminants occur in a wide range of important country food species, as well as in other ecosystem compartments. Ongoing monitoring programs contribute to the knowledge base on spatial and temporal trends of contaminants in the biotic and abiotic environment.

The implications of contamination to Arctic ecosystem and human health are being examined, and while obvious effects on Arctic wildlife populations have not been documented, there are preliminary indications of possible associations with subtle effects on humans. Levels of contaminants and exposure in certain Arctic human populations are similar to those in Great Lakes populations where effects have been reported. It is well known that it is difficult to establish clear cause and effect relationships between chronic environmental contamination (i.e. not occupational or accident related exposure) and changes in human and/or wildlife populations. Effects from low-level chronic exposure are often very subtle, exposure is usually to a mixture of compounds, effects may be transgenerational or have delayed onset, and in humans confounding factors related to lifestyle often play a major role. These factors limit our ability to definitively quantify exposure-effects relationships.

Effects, exposure and nutrition data, as well as health risk assessments, are required in order to provide northerners with information for decisions regarding country food consumption. The information generated by the Program is only useful to communities if it is available to them in a format which is relevant to their interests and needs. This holds true at every stage of the research process, from project planning and implementation to reporting of results and follow-up.

In tandem with the Program's shift toward human health research, efforts to develop effective "community dialogue" processes and tools are increasing, as is recognition of the importance of community participation. A requirement for researchers to involve communities in their work has been advanced through development of the Guidelines for Responsible Research, and initiatives such as the Metis Nation's contaminants curriculum development and the Government of Northwest Territories' video on contaminants will be extended to enable sharing of resources among Program participants. A strategic plan for coordination of Contaminants Program communication is evolving and will form an important basis for much of the work to be undertaken in the coming years.

Finally, due to the transboundary nature of the issue of contaminants in the arctic food chain, Canada must pursue international initiatives for control of these substances, with the scientific evidence generated by the program providing substantiation for our concerns and calls for action. The two main fora in which Canada plays a leadership role, and to which data generated by the AES-NCP provide a strong contribution are the Arctic Environmental Protection Strategy's (AEPS) Arctic Monitoring and Assessment Programme (AMAP), and the United Nations Economic Commission for Europe's (UN ECE) Task Force on Persistent Organic Pollutants (POPs) under the Convention on Long-range Transboundary Air Pollution (LRTAP).

The AEPS is a declaration signed in 1991 by the eight Arctic nations, under which programs for cooperation and for protection of the Arctic environment will be undertaken. One such program is AMAP, the objective of which is to monitor the levels and assess the effects of pollution in the Arctic environment. Using information from current Arctic monitoring projects and from the published literature, AMAP is drafting an assessment report of contaminants (POPs, heavy metals, radionuclides, acidification) in the circumpolar Arctic. This report will be presented to Ministers of the eight Arctic nations in 1997. The UN ECE Task Force on POPs is working toward a legally binding international agreement for control of POPs under the LRTAP Convention. To date, the Task Force has completed its substantiation report, containing basic elements of a draft protocol, and a State of Knowledge report on POPs. The Executive Body decision on whether to go ahead with a protocol on POPs will be made in late November 1994.

This report provides a summary of the research and activities which were undertaken in the 1993/94 fiscal year and funded by the Arctic Environmental Strategy's Northern Contaminants Program. A workshop will be held in late January 1995 at which researchers will present their results from 1993/94 as well as any available preliminary results from projects funded in the 1994/95 fiscal year.

SOURCES, PATHWAYS AND FATE OF NORTHERN CONTAMINANTS

SOURCES, PATHWAYS AND FATE
NEW FINDINGS

Organochlorines

1) A review of HCH concentrations in air at stations in Canada and Norway and from cruises in the Bering-Chukchi Seas has revealed that α- and γ-HCHs in arctic air during the summer have decreased, from 880 pg/m^3 in 1979 to approximately 100 pg/m^3 in 1992. The changes appear to have occurred in steps, with a drop after 1982 and another between 1990 and 1992. An HCH decline is also evident in winter, although less strongly than summer. The record of HCHs in water of the Bering-Chukchi Seas shows a 3% decline per year between 1979 and 1993, from approximately 4 to 2.6 ng/L, while little or no loss has occurred in the Beaufort Sea. Limited data from Resolute Bay suggests that chlorinated bornane (CHB) concentrations in air and water have also declined since the mid-1980s.

2) In a sampling of snow from ice caps and sea-ice surfaces in the Canadian and Russian Arctics, several chlorinated pesticides were found, including α-, β- and γ-HCH, heptachlor epoxide, α-endosulfan, α-chlordane and dieldrin. Results confirm Eurasia as the source of most of the anthropogenic pollutants in the Canadian High Arctic.

3) Deposition of ΣPCB to the Agassiz Ice Cap on north-central Ellesmere Island, NWT was generally higher in the early 1960s with a maximum of 930 $ng \cdot m^{-2} \cdot a^{-1}$ in 1967/68. In 1968/69 there was a significant decrease in deposition which increased slowly and consistently until 1979/80 when a further decrease in deposition occurred with the period of record minimum of 91 $ng \cdot m^{-2} \cdot a^{-1}$ in 1980/81. Subsequently, ΣPCB deposition has again risen with a local maximum of 848 $ng \cdot m^{-2} \cdot a^{-1}$ in 1989/90 and a mean flux for the last three years of 465 $ng \cdot m^{-2} \cdot a^{-1}$. In contrast, PAHs show a distinct decline over the last thirty years which more or less corresponds to reductions in fossil fuel combustion.

4) In a study of Amituk Lake on Cornwallis Island, NWT, concentrations of total HCH ranged from about 300 pg/L in shallow snow on lake ice to greater than 4000 pg/L in deep (5 m) valley snow. Total HCH levels in a small influent stream averaged 765 pg/L over the study period, although an initial stream concentration of 2008 pg/L was measured at the onset of snowmelt. Lake concentrations of total HCH were similar at depths of 3.0 and 20.0 m — 1422 and 1351 pg/L, respectively. The relative proportions of α- and γ-HCH were quite variable in the different sampling media at Amituk Lake. α/γ-HCH ratios ranged from 1.6 - 3.1 in shallow to deep snow to 5 - 6 in Rock Creek and Amituk Lake and to 9 in the lake outflow.

5) Atmospheric deposition rates of organic contaminants to the Yukon are quite variable and apparently depend on the amount of precipitation which in turn determines the degree of scavenging that occurs. Relatively few organochlorine (OC) pesticides and related compounds were detected in snow samples from the Yukon, including pentachlorobenzene, *p,p*-DDE, α-HCH, γ-HCH, γ-chlordane and α-endosulfan.

6) The predominant OCs in water samples from the Yukon River system are HCHs, particularly α-HCH (0.9-1.8 ng/L) and γ-HCH (0.2-0.4 ng/L). Atmospheric deposition appears to be the major source of contaminants to this basin.

7) Earlier studies, revealing high levels of toxaphene in fish from Lake Laberge and Atlin Lake in the Yukon, raised the question of whether there were local sources for direct input to these lakes. However, similar concentrations of toxaphene in various lakes indicates that there is no point source in this system.

Metals

1) Sediment samples collected from Kusawa Lake, Yukon, Amituk Lake, NWT and Hudson Bay (Grande Baleine Delta) show increasing levels of mercury in recent years, up to 24 ng/g in Hudson Bay and 72 ng/g in Amituk Lake.

2) Cadmium measurements in a peat sample in the Yukon (64°3' N and 139°4'30" W) indicate a reduction of atmospheric deposition of cadmium in recent years.

Radionuclides

1) Snow sampling from ice caps and sea-ice surfaces in the Canadian and Russian Arctics has shown that concentrations of radionuclides are greater in the Russian than the Canadian Arctic.

2) Analyses of ^{137}Cs and ^{239,240}Pu in surface sediments collected in 1992 from a broad region of the Barents Sea, from the Kola Peninsula to Franz Joseph Land, have revealed little evidence for major sources of radioactive contamination, other than those associated with fallout and inputs from European Reprocessing Plants. The exception to this is in the fjord of Chernaya Bay on the southwestern coast of the island of Novaya Zemlya, the site of three underwater nuclear weapons tests between 1955 and 1961. Plutonium concentrations in surface sediments from this fjord are among the highest recorded anywhere in the marine environment.

3) Preliminary results indicate that the submerged ship containing radioactive wastes in the Novaya Zemlya Trough is not leaking significant quantities of radioactivity.

4) Levels of ^{137}Cs in the water column of the Canada Basin are far greater than any previous values reported for this region, and are apparently due to inputs of radioactivity from European reprocessing plants.

5) Analyses of sediment cores collected at a 1968 nuclear weapons accident site in Thule, Greenland have indicated that plutonium has undergone only minimal radial dispersion from the crash site. The site does not represent a significant, current source of contamination to proximal environments. The implication is that plutonium contained in nuclear weapons which have been deposited on the seabed will probably remain relatively immobile and be retained by, and incorporated into sediments.

ATMOSPHERIC EMISSIONS OF TOXIC SUBSTANCES

PROJECT LEADER: E.C. Voldner, Atmospheric Environment Service, Environment Canada

PROJECT TEAM: Y.F. Li and E.C. Voldner

OBJECTIVE

To determine the sources and to estimate the emissions of organochlorines on a global scale as a basis for: 1) modelling activities, 2) interpretation of measurements, 3) assessment, and 4) international action.

RATIONALE

The estimation of contaminant source data on a global scale is required for input to atmospheric and ecosystems models (eg. Pudykiewicz 1989, Wania and Mackay 1994 - modelling projects supported under the Northern Contaminants Program), in order to determine which source regions may have a significant impact on sensitive areas such as the Arctic and the Great Lakes region. The establishment of source/receptor relationships and the determination of the relative contributions of sources in other countries to receptors in Canada will enable the assessment of control strategy scenarios, and hence aid Canada in the development of international control policies. The evaluation of both the historical and future trends in source strength is important for understanding and predicting the response time of the various components of the ecosystem to changes in releases of contaminants to the environment. Knowledge of sources can also serve as an "early warning system" for emerging problems and provide guidance on measurement strategies.

PROJECT DESCRIPTION

Phase I

Acidifying Species and Metals

The initial effort focuses on sulphur oxides (SOx), nitrogen oxides (NOx), volatile organic compounds (VOCs), and lead. Information on anthropogenic emissions has been sought from organizations and programs throughout the world, and where not available, estimated through surrogate methods such as emissions factors and statistical information on fuel use, production capacity, population, etc. A computerized database will be created, and emissions will be gridded for input to models. The emissions inventories will be updated as the information base improves.

Pesticides

The initial effort involves the compilation of information and the creation of a computerized database of historical, present and predicted global usage, the production or sale of the highly toxic, persistent pesticides: aldrin, dieldrin, chlordane, DDT, endosulphan, endrin, heptachlor, HCH, lindane and toxaphene. As these pesticides are banned or severely restricted in many countries, information is being sought on: the registration status; the amount of production/use/emission; the region of use/emission; the mode and time of application; the physical and chemical properties of the active ingredients and of the technical mixture; and representative concentrations in soils. This information is being obtained through literature surveys, contracts, contacts with international agencies and researchers.

Phase II

Phase II will consist of the estimation of emissions in representative regions for input to hemispherical/global models. Based on information obtained in Phase I (regionally representative crop and soil data, as well as climatological and meteorological data), a time-dependent numerical model will be executed to estimate the emissions (Scholtz and Voldner 1993). Development of the model will continue, as well as the assessment of its performance.

Phase III

Phase III calls for the extension of a North American study of sources and emissions of current use pesticides to the northern hemisphere. An attempt will be made to identify compounds, not presently considered under the Northern Contaminants Program, which either already have, or potentially will impact the Arctic ecosystem.

ACTIVITIES IN 1993/94

SOx, NOx, VOCs, Pb

Although the Northern Contaminants Program withdrew its support for the development of inventories of SOx, NOx, VOCs and lead, support from other programs allowed the continuation of this effort. These inventories are near completion and will be finalized in the first quarter of 1994/95.

Pesticides

The activities in 1993/94 centred on the analysis and interpretation of compiled data; the acquisition of additional pesticide information (to facilitate the latter task, the project was incorporated under the Global Emissions Inventory Activity of the International Geosphere/Biosphere Program); the expansion of the capabilities within the Canadian Global Emissions Inventory Centre; the further development of the canopy module of the air/surface exchange model; the "evaluation" of the model against pesticide fluxes and other measured parameters; the compilation of data required for Phase II; the initiation of the estimation of emissions; and the allocation of data to climate zones for input to ecosystems models.

RESULTS

SOx, NOx, VOCs and Pb

Results are described in proceedings of the fourth Workshop of the Global Emissions Inventory Activity of the International Geosphere/Biosphere program (GEIA 1994).

Pesticides

Results are described in Voldner and Li (1993, 1994a and b), and Scholtz *et al.* (1994) and only a summary is provided here.

Figure 1, which displays information on DDT, provides an example of the status of pesticide registration globally. The figure indicates where the use of the pesticide is banned, where it is not registered, where it is severely restricted, as well as the regions for which no information was found. The year a pesticide was banned or de-registered is also noted for the larger countries. It is important to note that the information can be misleading. Even though a pesticide was "banned" it may still have been allowed for special applications; the use of old stock may have been permitted; or illegal use may have occurred after the ban (PAN; Larsson and Okla 1989, Kundiev and Kagan 1993a).

The cumulative global use, accounted for in the search, of the ten "classical" pesticides and the largest consumer countries are shown in Table 1. Accumulated interpolated total use between 1970 and the present for toxaphene and DDT were 670,000 and 990,000 metric tonnes, respectively, while the amounts between 1950 to present were 1,330,000 and 2,600,000 tonnes, respectively.

The above estimates do not include the amounts of pesticides which have been placed in storage, or disposed of as waste. The export of pesticide waste from industrialized nations to developing countries has been documented (eg. Jain 1992, Global Pesticide Campaigner 1992).

Change-over from technical HCH to lindane has occurred at different times in various countries. The type of application also varies. HCH was used as a fog inducer by the military in the former East Germany (Beitz 1993). In China, lindane was used to prevent infestation of locusts (Sun *et al.* 1992). In the former East Germany, the carrier isomer was discarded as waste in the production of lindane. Waste sites included open pits (Heinish 1994). Such information is valuable when interpreting environmental measurements such as isomer ratios and concentrations in air.

Figures 2 and 3 show the cumulative losses of triallate and trifluraline as predicted by the "emissions model" used in this project, and measured by the relaxed eddy accumulation technique, which is still in the development stage. This limited comparison, described in Scholtz *et al.* (1994) provides some confidence in both the performance of the model and the measurement system.

Since the final allocations of funds for 1993/94 were received only in November 1994, the estimation of emissions was limited to a few regions in North America. Most of the required global scale supplementary data bases have been compiled and/or developed along with the necessary software in order to be able to extend the work to representative regions around the globe during 1994/95. Data on the usage of toxaphene and DDT, allocated to climatological regions, were provided as input to an ecosystem model (Wania and Mackay). For contribution to international activities, see the project entitled "International Emissions Inventory Activities" in this volume.

CONCLUSION

Data on the present and historical use of persistent organochlorines are both difficult to obtain and uncertain. The reported information, which does not include pesticides placed in storage or disposed of as waste, should therefore be viewed with caution.

It appears that many countries do not keep records on pesticides, while in other countries such as Canada, information is confidential. Only a limited number of countries report to the Food and Agriculture Organization (FAO). Commercial data bases are proprietary and costly to access. But through direct contracts or contracts arranged by the International Registry of Potentially Toxic Chemicals (IRPTC) of the United Nations Environment Programme (UNEP), information for key regions has been obtained.

Unfortunately, the word "banned", when used in connection with pesticides, often carries little weight. The pesticide can still be authorized for special application; the use of old stock may be allowed; and illegal use may also occur after the ban. The banning of HCH and its subsequent replacement with lindane has resulted in the disposal of the "inactive isomers" directly into the environment. The export of pesticide waste from industrial nations has also been documented.

Although emissions estimates have not yet been finalized, the study provides support as to the need for national and international actions aimed at the enforcement of existing regulations; for full disclosure of the figures for the production and the use of organochlorines and other pesticides into a central repository; and for the introduction of new international initiatives to limit the input of these and other toxic chemicals to the environment.

Expected project completion date: 1996/97

REFERENCES

Beitz, H.A. 1993. Use of pesticides in the former GDR. Report prepared for Environment Canada, Downsview, Ontario. (E.C. Voldner).

GEIA. 1994. Fourth International Workshop on Global Emissions Inventories, Boulder, Colorado, November 30 - December 2, 1993. Summary Report, IGAC, International Geosphere Biosphere Program, P. Middleton and H. Lansford (eds.), Boulder, Colorado.

Global Pesticide Campaigner. 1992. Transylvanian pesticide dumpsite uncovered. 2: 16.

Heinisch, E. 1994. Production of chloroorganic pesticides and PCB in East-Central Europe and the resulting hygienic-toxicological problems. Report prepared under contract for Environment Canada, Downsview, Ontario, (E.C. Voldner), 37 pp.

Jain, V. 1992. Disposing of pesticides in the third world. Environ. Sci. Technol. 26: 226-228.

Kundiev, Y.I. and Y.S. Kagan. 1993a. Pesticide usage in the U.S.S.R. Report prepared for Environment Canada, Downsview, Ontario, (E.C. Voldner).

Kundiev, Y.I. and Y.S. Kagan. 1993b. Pesticide usage in the Russian Federation. Report prepared for Environment Canada, Downsview, Ontario, (E.C. Voldner).

Larsson, P. and L. Okla. 1989. Atmospheric transport of chlorinated hydrocarbons to Sweden in 1985 compared to 1973. Atmos. Environ. 23: 1699-1711.

PAN. 1992. "Demise of the dirty dozen", chart background information and source material, compiled by the Pesticide Action Network North American Regional Center for Pan International, San Francisco, CA., 30 pp.

Pudykiewicz, J. 1989. Simulation of the Chernobyl dispersion with a 3-D hemispheric tracer model. Tellus 41B: 392-412.

Scholtz, M.T. and E.C. Voldner. 1993. Modelling air-surface exchange of pesticides with application to the estimation of emissions. Proc. First Workshop on Emissions and Modelling of Atmospheric Transport of Persistent Organic Pollutants and Heavy Metals, Durham, North Carolina, U.S.A., J.M. Pacyna, E. Voldner, G.J. Keeler and G. Evans (eds.). EMEP/CCC-Report: 7/93: 189-206.

Scholtz, M.T., E.C. Voldner and E. Pattey. 1994. Pesticide volatilization model comparison with field data. 87th Annual Meeting of the Air and Waste Management Association, Cincinnati, June 19-24, 1994. Paper 94-MP5.03, 12 pp.

Sun, L., J. Ke, D. Cai and G. Tang. 1992. Pesticide usage in China. Report prepared for Environment Canada, Downsview, Ontario, (E.C. Voldner).

Voldner, E.C. and Y.F. Li. 1993. Global usage of toxaphene. Chemosphere 27: 2073-2078.

Voldner, E.C. and Y.F. Li. Global usage of selected persistent organochlorines, Sci. Total. Environ. in press.

Wania, F. and D. Mackay. Global distribution model for persistent organic chemicals. Sci. Total Environ. in press.

Table 1: Accumulated global pesticide use (tonnes) accounted for in the sources with leading consumer countries.

PESTICIDE	TOTAL (ACCOUNT)	LEADING CONSUMING COUNTRY
ALDRIN	505,400	USA
CHLORDANE	7,800	India
DDT	1,495,100	USA
DIELDRIN	33,700	USA
ENDOSULFAN	57,000	India
ENDRIN	408,000	USA
HCH	550,000	China
LINDANE	721,200	USA
TOXAPHENE	455,000	USA

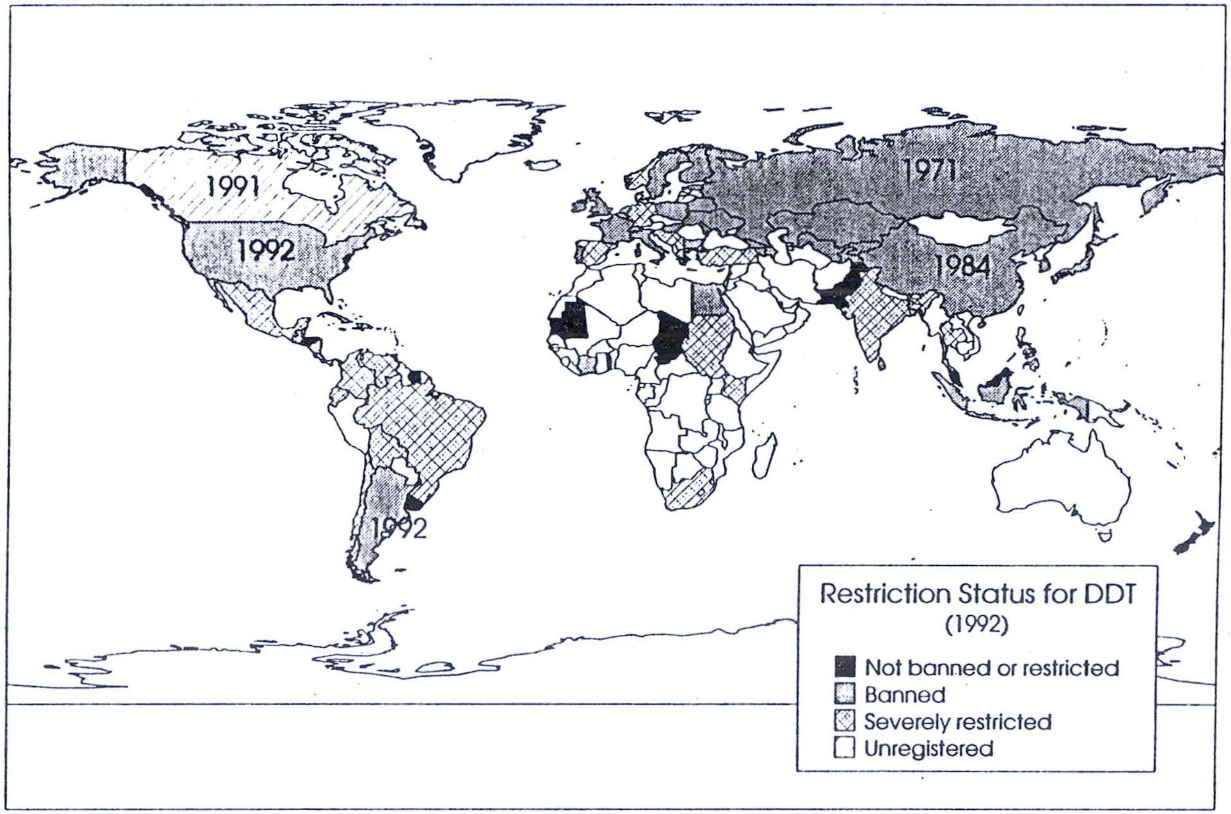


Figure 1. Registration status of DDT surveyed in 1992.

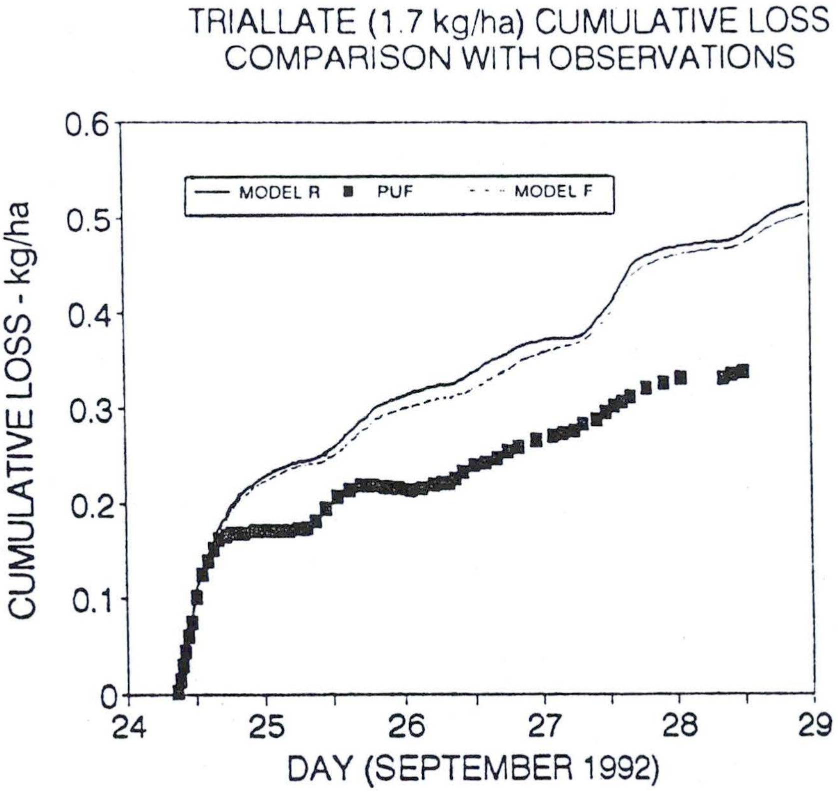


Figure 2. Comparison between modelled and measured cumulative triallate loss from the soil. Model R uses a radiation model while Model F uses net radiation as an input.

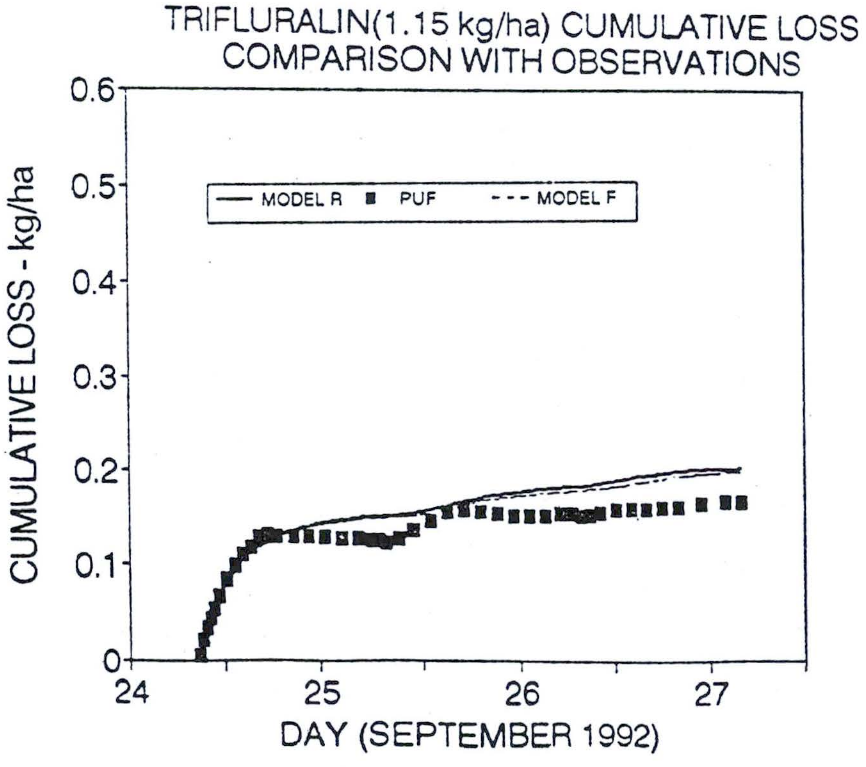


Figure 3. Comparison between modelled and measured cumulative trifluralin loss from the soil. Model R uses a radiation model while Model F uses net radiation as an input.

INTERNATIONAL EMISSIONS INVENTORY ACTIVITIES

PROJECT LEADER: E.C. Voldner, Atmospheric Environment Service, Environment Canada

PROJECT TEAM: E.C. Voldner and Y.F. Li

OBJECTIVES

1. To increase the effectiveness of Canada's efforts to develop contaminant source and emissions inventories by integrating and coordinating work with the international community.

2. To contribute to the United Nations Economic Commission for Europe's Task Force on Persistent Organic Pollutants and Heavy Metals (UN ECE TF POP HM); the UN ECE Expert Panel on Emissions; the Global Emissions Inventory Activity (GEIA) of the International Geosphere Biosphere Program (IGBP); and the International Joint Commission (IJC).

RATIONALE

It has been established that there is long-range atmospheric transport of heavy metals and persistent organic pollutants to the Arctic. Identifying the sources of these pollutants and determining how much they contribute to the contamination of the Arctic ecosystem will enhance the possibility of obtaining international action to either lessen or solve this problem.

Canada is taking a leadership role in a number of these international activities, which are aimed at controlling the releases of toxic contaminants to the environment, and thus reducing their impact on the Arctic. Resources are required to ensure that Canada can meet commitments made in support of these international activities.

ACTIVITIES IN 1993/94

Activities included: further developing the Canadian Global Emissions Inventory Centre (CGEIC) in a joint effort with ORTECH International; taking a leadership role on projects under GEIA (for further information, refer to the project entitled "Atmospheric Emissions of Toxic Substances" in this volume); preparing reports and conducting workshops in support of UN ECE; contributing to the formulation of the IJC's Virtual Elimination Strategy and conducting case studies in order to illustrate its feasibility; and developing schemes for the prioritization of contaminants to be sun-setted and controlled.

RESULTS

The first phase of the Canadian Global Emissions Inventory Centre, linking operating nodes at the Atmospheric Environment Service and ORTECH, has been completed. The Centre has processed and is now archiving data bases of significance to the Northern Contaminants Program.

The need for information on the global use and emission of organochlorines is now recognized under the GEIA/IGBP, and a project to gather this information has been established under the leadership of E.C. Voldner.

The Virtual Elimination Strategy, which is aimed at eliminating contaminants of concern to the Great Lakes and Arctic ecosystems, is global in scope. Information from the case studies to demonstrate the feasibility of the strategy, and from the reports on the workshops conducted for the UN ECE TF HM POP has all been incorporated into the Task Force's documents for the substantiation of protocols to eliminate and/or reduce the release of contaminants. The results are highlighted in the key publications listed in the references.

CONCLUSIONS

The establishment of the first phase of the CGEIC has given Canada the capability to address the issue of global sources of contaminants. In addition, active participation in international efforts has facilitated both the preparation of scientific background material and the formulation of strategies in order to provide the framework for international action to reduce and/or eliminate the release of contaminants to the environment.

Project completion date: 1997/98

REFERENCES

EMEP Co-operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe. EMEP/CCC-Report: 7/93.

GEIA. 1994. Fourth International Workshop on Global Emissions Inventories, Boulder, Colorado, November 30 - December 2, 1993. Summary Report, IGAC, International Geosphere/Biosphere Program, P. Middleton and H. Lansford (eds.), Boulder, Colorado.

International Air Quality Advisory Board: Progress report 15, 1993; Progress report 16, 1993; and Progress report 17, 1994, prepared for the Commissioners of the International Joint Commission.

Pacyna, J.M., E.C. Voldner, T. Bidleman, G. Evans and G.J. Keeler. 1993. Proceedings of the first workshop on emissions and modelling of atmospheric transport of persistent organic pollutants and heavy metals, under the UN ECE Convention on LRTAP, Durham, North Carolina, May 6-7, 1993.

Voldner, E.C. and Y.F. Li. 1993. Global usage of toxaphene. Chemosphere 27: 2073-2078.

Voldner, E.C and Y. Li. Global usage of selected organochlorine pesticides. Sci. Total Environ. In press.

STUDY OF THE TRANSPORT OF PERSISTENT ORGANIC POLLUTANTS WITH SPECIAL EMPHASIS ON ARCTIC REGIONS

PROJECT LEADER: J. Pudykiewicz, Atmospheric Environment Service (AES), Environment Canada

PROJECT TEAM: A. Dastoor, A. Sirois, E. Voldner, T. Bidleman, L. Barrie

OBJECTIVE

To apply a 3-Dimensional tracer model, developed by the AES during 1993/94, to study the movement of atmospheric contaminants on hemispheric and global scales. Special emphasis is given to studying the exchange of contaminants between the atmosphere and the Earth's surface in Arctic regions.

ACTIVITIES

During 1993/94, the model was run in both hemispheric and global modes using forecasted and objectively analyzed meteorological fields. The model runs were performed for sulfur chemistry with emission fields obtained from global emission inventory developed by Lawrence Livermore Laboratory. The sulfur chemistry was chosen for initial model runs for two reasons: a) the system is relatively simple and demonstrates sufficiently well the occurrence of ultra-long range transport of contaminants to the Arctic, and b) the existing experimental data base permits the model evaluation with better accuracy than for other chemicals.

In the case of HCH the problem must be studied from at least a hemispheric perspective. Because the substances involved in this research project have a lifetime in the atmosphere longer than 5 days, a substantial portion of material released at any particular time travels beyond continental boundaries. Their pathways are not only governed by transport processes but by chemical transformation and interaction with the Earth's surface.

In our study of pathways of HCH, models that simulate these complex processes serve to:

(i) organize the available information in a quantitative way,
(ii) assist in experimental design, and
(iii) assess the origin of a substance found in a receptor.

The present version of the model is a sophisticated computer system consisting of the 3-Dimensional eulerian dispersion model simulating transport processes and numerical weather prediction models providing information about the state of the atmosphere. The dispersion model is based on a system of the advection-diffusion equation transformed to the terrain-following coordinate system in order to incorporate the effects of topography.

The model is capable of moving substances on a global scale using observed wind fields while allowing them to interact with the Earth's surface and with model generated clouds and precipitation, and to chemically transform. This model can be run quite economically with simple parameterization of the processes and prescribed emission scenarios.

During 1993/94, attention was mainly focused on implementation of the recent results in the area of new numerical methods and providing a more realistic description of the emission field. The model is now equipped with accurate and efficient numerical methods. The modelling framework was also generalized to include both global and hemispheric grids. The initial runs were performed for sulfur chemistry.

The objective for 1994/95 is to continue the model application for the sulfur system and extend it to other species, including persistent organic pollutants, using the emission inventories assembled at the AES.

The model runs performed with sulfur chemistry will be used as an important tool in evaluation of the results.

The specific tasks being accomplished currently are:

(i) preparing the emission fields in a format compatible with the requirement of the modelling system. (The emission data provided are of a relatively coarse resolution);
(ii) maintaining the model libraries and data bases;
(iii) performing production runs with the tracer model;
(iv) processing the model results (graphics, time series analysis, budget calculations);
(v) evaluating the model results using observed data; and
(vi) preparing a scientific paper describing major conclusions of research performed during 1993/94 and 1994/95.

NORTHERN CONTAMINANTS AIR MONITORING

PROJECT LEADER: L.A. Barrie, Atmospheric Environment Service, Environment Canada

PROJECT TEAM: P. Fellin, D. Muir, B. Grift, L. Lockhart, B. Billeck, T. Bidleman, R. Bailey, G. Stern, D. Toom

OBJECTIVE

To measure the occurrence of selected organochlorines and polycyclic aromatic hydrocarbons in the Arctic atmosphere for a period of several years, thereby providing insight into sources, transport, transformation and surface exchange processes as well as data for validation of models of toxics pathways in the northern environment.

PROJECT DESCRIPTION

Since January 1992, measurements of persistent organic pollutants including herbicides, pesticides, synthetic industrial compounds and polycyclic aromatic hydrocarbons(PAHs) have been made on a weekly basis in the Canadian and Russian Arctic (Figure 1). This research was supported by the Arctic Environmental Strategy's Northern Contaminants Program and the Department of Foreign Affairs and International Trade.

In 1993, hi-volume air samplers placed at Alert (NWT), Tagish (Yukon), Cape Dorset (Baffin Island) and at the mouth of the Lena River on Dunay Island in Russia were used to collect particulate and gaseous fractions of these airborne pollutants on filters. The filters were subsequently extracted in organic solvents and analyzed for more than 80 organochlorines (OCs) and for 20 PAHs by gas chromatographic techniques. The sampling schedule is shown in the following table (the past, light arrows, and the future, bold arrows).

Site	1992	1993	1994	1995	1996	1997
Alert	<test> | <------------->|		<---------------------------------------> |			
Tagish	|<------------->|		<----|			
Dunay Island		|<-------|	<----------> |			
Cape Dorset		|<->|	<----------------> |			
W. Russia (proposed)				|<-------------------------> |		

RESULTS

At Alert in 1992, 18 PAHs and 29 OCs plus many PCB congeners were measured. A principal component analysis of the PAH and OC data (not including PCB) showed 9 components that explained 90% of the variance in the data set. The groupings are shown in the following table.

Component	Major Constituents	Minor Constituents
1.	*pp*DDT, *op*DDT, *pp*DDE, *pp*DDD, Mirex	*op*DDE, *op*DDD, Toxaphene
2.	Dieldrin, Endosulfan Heptachlor epoxide	Oxychlordane, Toxaphene, PCB118
3.	α-HCH	γ-HCH, PCA
4.	Methoxychlor	Trichloroveratrole, PCB187, Toxaphene
5.	TOT-PAH Plus Constituents*	Heptachlor, Penta-Chlorobenzene
6.	Octachlorostyrene	
7.	4-Cl-Ver	
8.	Trifluralin	
9.	Endrin	

*Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Retene, BaAnthracene, Chrysene, BkFluorene, BaP, BeP, Iso-Pyrene, Dibenzoanthracene, Benzoperylene

These components actually indicate groups of substances that have similar seasonal cycles in the Arctic troposphere. The seasonal cycle is affected by seasonal variations in sources, in transport to the Arctic, in removal from the atmosphere and in atmosphere-Earth surface exchange. In Figure 2, the seasonal cycle of the first six components is illustrated using representative constituents at Alert, namely, total DDT (*op* and *pp*), dieldrin, total HCH (α plus γ), methoxychlor (MeOCl), Total PAH and Octachlorostyrene.

The chlordanes had anomalously high field blanks until June of 1992. Therefore only results for the last half of 1992 can be shown (Figure 3). The *cis*-chlordane peaks in summer over *trans*-chlordane. This observation is consistent with shorter term observations made previously in the Arctic and likely reflects a relatively greater rate of degradation of *trans*-over *cis*- in the summer.

Toxaphene is a problem pesticide in the Canadian Arctic, being responsible for the closure of commercial fisheries in some large lakes in the Yukon. At Alert (Figure 3) it has a peak early in the year between March and early July and a minimum in late summer fall and winter. Preliminary data from Tagish and Alert (Bailey *et al.* 1994) from January to May 1994 (Figure 4) show that Alert and Tagish are not very different and that the Alert observations in 1993 are reproducible in 1994.

Finally, Figure 5 shows that the seasonal variation of the ratio of γ-HCH/α-HCH peaks in May and June. Lindane (γ-HCH) is the active pesticide while α-HCH is its degradation product as well as a contaminant in technical lindane ($\sim$55-70% α and 10-18% γ-HCH) which in former times was widely used when awareness of the deleterious effects of persistent organic substances in the environment was poor. Today, lindane rich mixtures are used. The spring peak likely reflects fresher mixtures of HCH as a result of spring time applications and tilling.

Publications, Presentations and Reports

Barrie, L.A., T. Bidleman, D. Dougherty, P. Fellin, N. Grift, D. Muir, B. Rosenberg, G. Stern and D. Toom. 1993. Atmospheric toxaphene in the high Arctic. Chemosphere 27: 2037-2046.

Bailey, R., L. Barrie, D. Dougherty, P. Fellin, B. Grift, D. Muir and D. Toom. 1994. Preliminary measurements of PCCs in air at Tagish Yukon. Proceedings of the Yukon Contaminants Committee Workshop, Feb. 1994, Whitehorse, Yukon.

Fellin, P., L. Barrie, D. Dougherty, D. Muir, N. Grift, L. Lockhart and B. Billeck. 1993. Air monitoring at Alert: results for 1992 for organochlorines and PAH's. *In*: Proceedings of the Symposium on "Ecological Effects of Arctic Airborne Contaminants", October 4-8, 1993, Reykjavik, Iceland, Christie and Martin (eds.). USA CRREL Rep. 93-23.

Fellin, P., D. Friel and D. Dougherty. Technical and Operating Manual for The Canadian Arctic Air Toxics Network, Concord Environment Report, J3034.

Figure 1. Location of ground level sampling in the Northern Contaminants Monitoring Network.

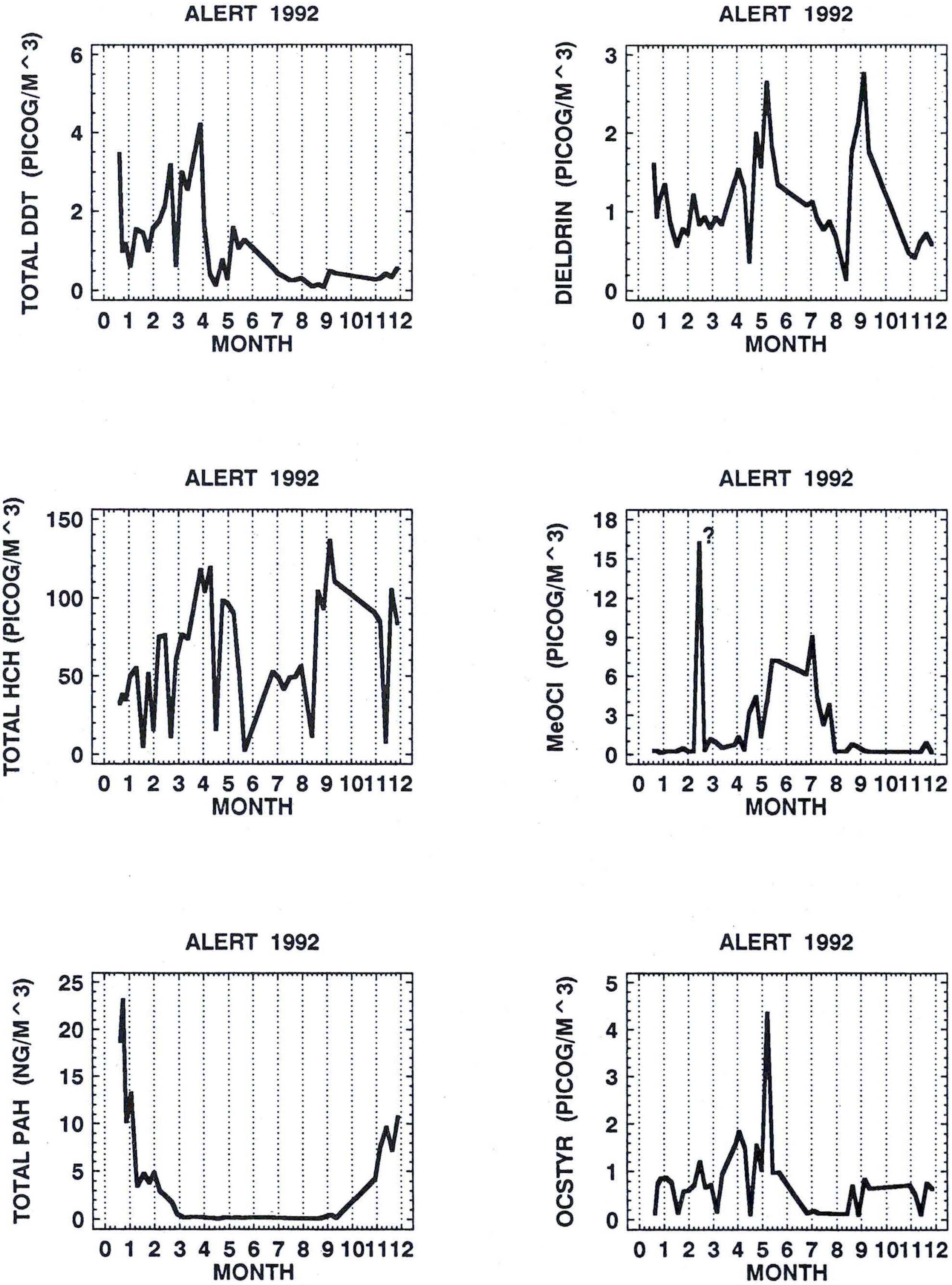
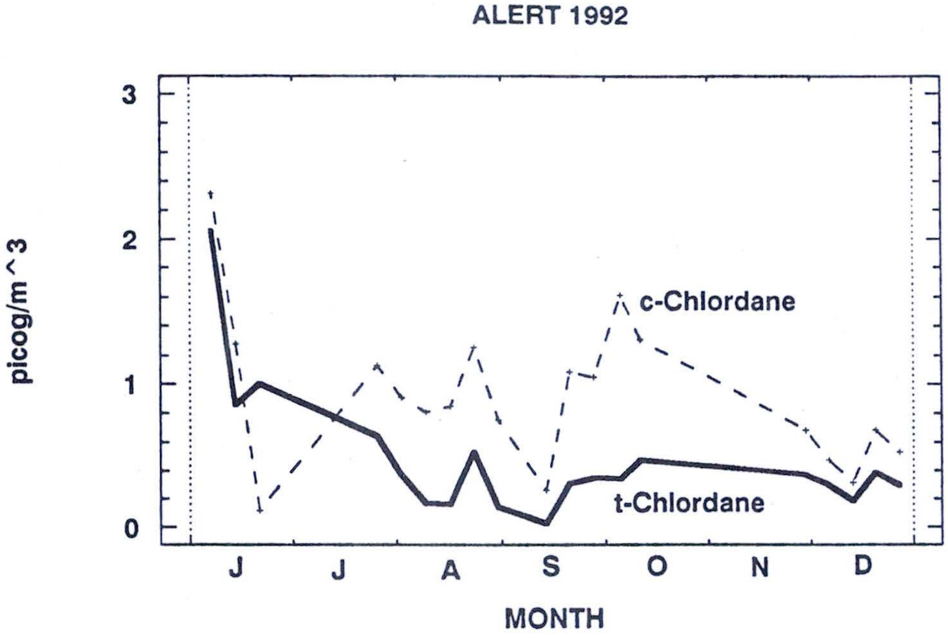


Figure 2. Seasonal cycles of six main components of arctic air contaminants as represented by total DDT (*op* and *pp*), dieldrin, total HCH (*α* and *γ*), methoxychlor (MeOCl), total PAH and octachlorostyrene. Based on observations at Alert, NWT in 1992.



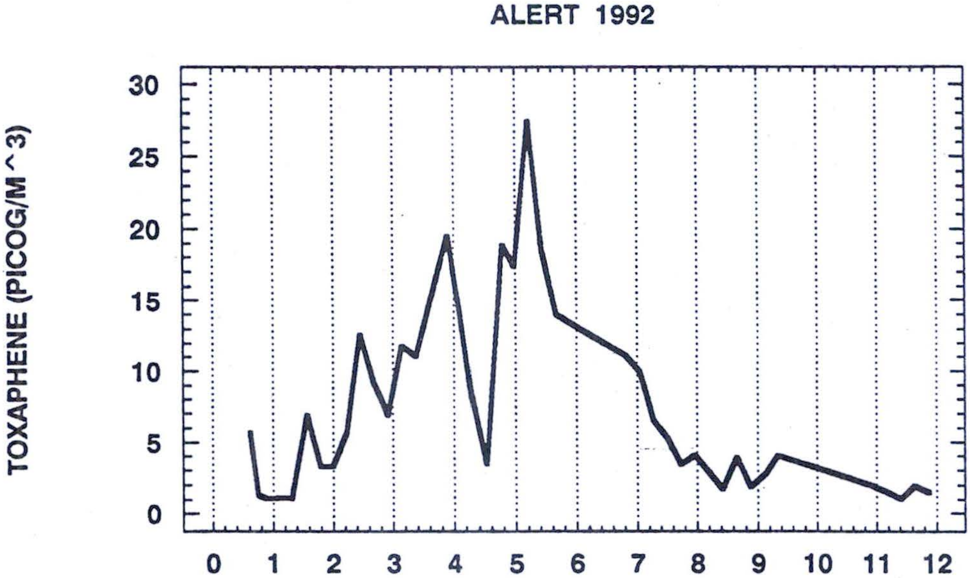


Figure 3. Seasonal variation of the isomers of chlordane and of toxaphene at Alert in 1992. Note that only the last half of 1992 data are shown for chlordane.

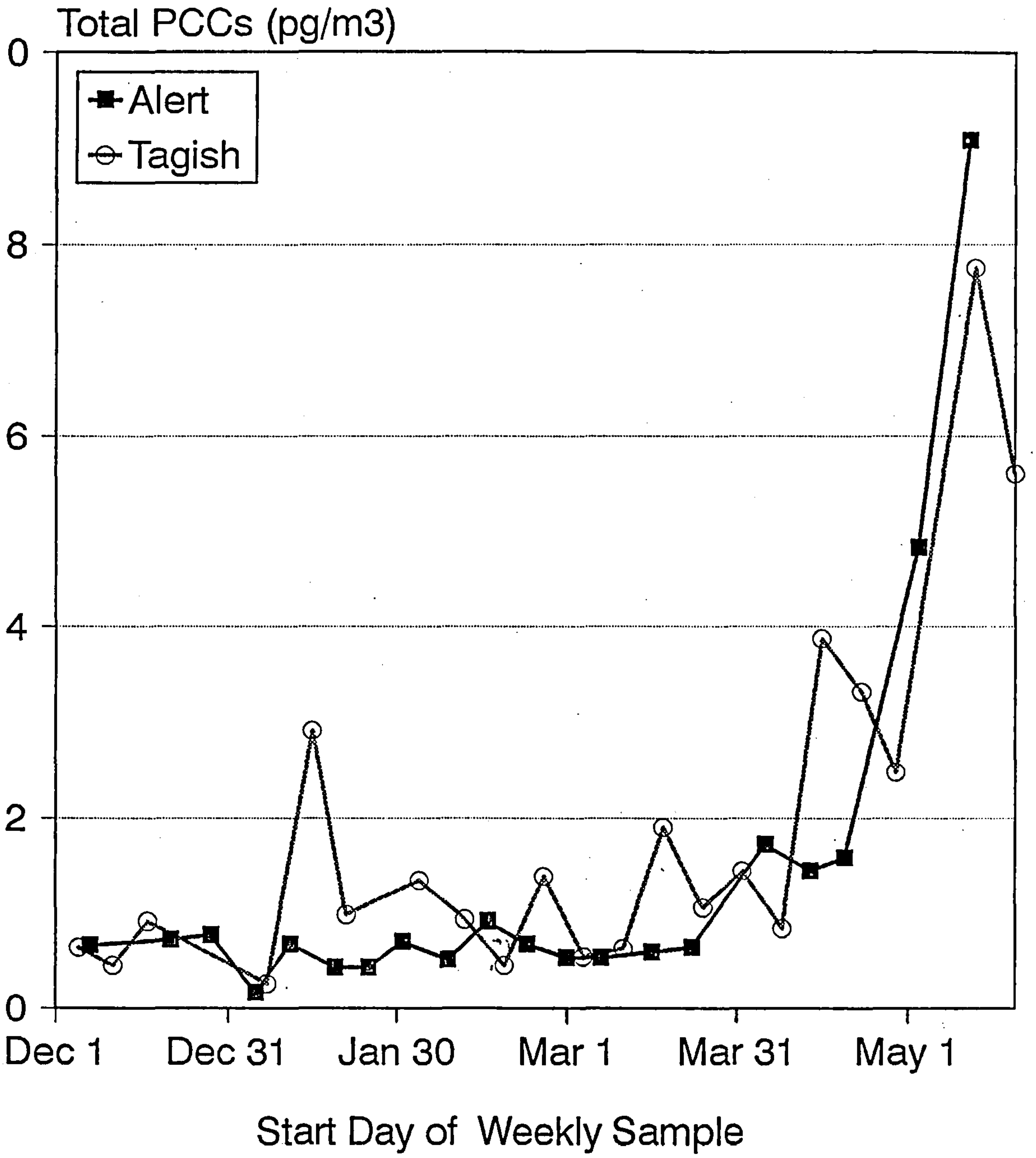


Figure 4. Air Concentrations of Total PCCs at Tagish, Yukon and Alert, NWT (December 1992 - May 1993).

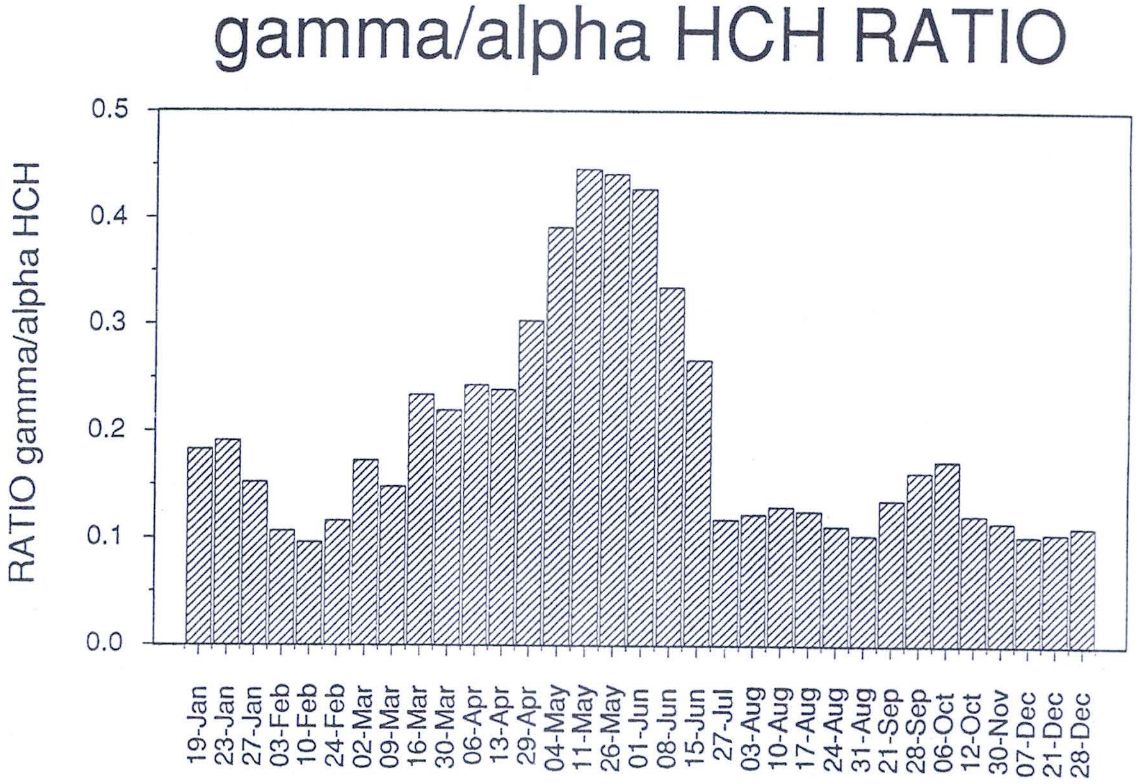


Figure 5. Seasonal variation of the ratio of the active pesticide isomer (*γ*) of hexachlorocyclohexane (HCH) to the inactive isomer (*α*) in air at Alert in 1992. HCH is released to the environment mostly as *γ*-HCH which is converted to *α*-HCH by chemical transformation. The ratio shown is an indicator of the freshness of the atmospheric mixture. A spring peak coincides with soil tilling and applications at mid-latitudes that release *γ*-rich HCH to the atmosphere.

ATMOSPHERIC MERCURY MEASUREMENTS AT ALERT

PROJECT LEADER: W.H. Schroeder, Atmospheric Environment Service, Environment Canada

PROJECT TEAM: W. Schroeder, A. Tham and T. Sandilands (Co-op Student, Jan.-Apr. 1994)

OBJECTIVES

To obtain air concentration data for total vapour-phase mercury (at Alert or an alternate site) for an initial assessment of:

a) ambient air (baseline) concentrations in the Canadian Arctic; and
b) the significance of atmospheric transport and deposition of this priority heavy metal to the remote Arctic environment.

PROJECT DESCRIPTION

The Arctic ecosystem is exhibiting increasingly disturbing evidence of contamination by persistent toxic substances, including heavy metals such as mercury. A major component of the Northern Contaminants Program of the Arctic Environmental Strategy focuses on the long-range atmospheric transport of persistent contaminants through investigations of their emission sources, environmental pathways, and sinks. The Arctic Monitoring and Assessment Programme (AMAP) identifies mercury as one of the 3 top priority metals. So far there is a dearth of definitive data on typical, ambient air levels of mercury in the Canadian North during various times of the year. This project is intended to provide such information for the first time.

Reliable measurements of atmospheric mercury (at background levels) still present a significant technical/scientific challenge. Until this year, there was no instrumentation commercially available for automated monitoring of mercury vapour in air. However, Tekran Inc. (of Toronto) has recently started to build an automated, "virtually real-time" mercury analyzer potentially applicable to background ambient air measurements.

ACTIVITIES IN 1993/94

This is a new project which was approved and was initiated with contingency funding from the Northern Contaminants Program at the 1993/94 Mid-Year Program Review Meeting at which new research proposals were considered. Funds were used to acquire an automated mercury vapour analyzer (from Tekran Inc.) on a "lease-to-own" basis as recommended by the Technical Committee. This new instrument is to be evaluated with respect to its suitability, ruggedness and reliability for making atmospheric mercury measurements in the Canadian Arctic.

Immediately upon arrival of the allocated funds at the Atmospheric Environment Service in Downsview in January 1994, a requisition for the lease of a Tekran mercury vapour analyzer was submitted (to Supply & Services Canada, Ontario Region). This instrument was delivered to Atmospheric Environment Service headquarters in Downsview during the last week of the fiscal year ending March 31, 1994.

Following its arrival and completion of the familiarization phase, a variety of diagnostic procedures, exploratory tests and carefully designed QA/QC experiments were scheduled to begin with this instrument, initially under controlled (laboratory) conditions. Subsequently, 'reality-check' tests will also be performed to challenge this analyzer with ambient (outdoor) air at our Downsview location (and possibly (an)other site(s) as well, should suitable opportunities for inter-laboratory testing and comparison arise).

RESULTS

The results from the tests/experiments to be performed with this instrument, as described above, will form the basis of an objective and thorough evaluation concerning the usefulness and applicability of this monitor for possible deployment in the Canadian North.

CONCLUSIONS

Not yet applicable during 1993/94 (new project).

Expected project completion date: March 31, 1996 (Objective a).

REFERENCES

Bloom, N.S., C.J. Watras and J.P. Hurley. 1991. Impact of acidification on the methylmercury cycling of remote seepage lakes. Water, Air, Soil Pollut. 56: 477-491.

Schroeder, W.H. 1994. Atmospheric mercury measurements at a rural site in southern Ontario, Canada. *In*: Mercury Pollution: Integration and Synthesis, Lewis Publishers, Boca Raton, Florida (in press).

Schroeder, W.H., J. Munthe and O. Lindqvist. 1989. Cycling of mercury between water, air, and soil compartments of the environment. Water, Air, Soil Pollut. 48: 337-347.

Slemr, F. and E. Langer. 1992. Increase in global atmospheric concentrations of mercury inferred from measurements over the Atlantic Ocean. Nature 355: 434-437.

Swain, E.B., D.R. Engstrom, M.E. Brigham, T.A. Henning and P.L. Brezonik. 1992. Increasing rates of atmospheric deposition in midcontinental North America. Science 257: 784-787.

Watras, C.J., N.S. Bloom, R.J.M. Hudson, S.A. Gherini, J.G. Wiener, W.F. Fitzgerald and D.B. Porcella. 1994. Sources and fates of mercury and methyl-mercury in Wisconsin Lakes. *In*: Mercury Pollution: Integration and Synthesis, Lewis Publishers, Boca Raton, Florida (in press).

MODELLING GLOBAL-SCALE TRANSPORT OF HEXACHLOROCYCLOHEXANES: REVIEW AND PREPARATION OF SUPPORTING DATA

PROJECT LEADER: T.F. Bidleman, Atmospheric Environment Service, Environment Canada

PROJECT TEAM: E.C. Voldner, A. Li, A. Sirois, J. Pudykiewicz, L.A. Barrie

OBJECTIVE

To compile and review physicochemical properties and environmental measurements of hexachlorocyclohexanes (HCHs) and assemble these data in a form suitable for input to global-scale modelling programs.

PROJECT DESCRIPTION

Due to their large-scale usage as insecticides and ease of environmental transport, HCHs have become the most abundant organochlorine (OC) pesticides in the world's atmosphere and ocean (Barrie *et al.* 1992, Iwata *et al.* 1993). The main transport pathways of HCHs to the Arctic Ocean are advection from oceans lying to the south (e.g. through the Bering Strait) and atmospheric deposition, especially air-sea gas exchange (Barrie *et al.* 1992). High concentrations of HCHs are found in the surface water of the Arctic Ocean (Hargrave *et al.* 1988, Patton *et al.* 1989, Macdonald and McLaughlin 1993, Falconer *et al.* 1994) as a consequence of enhanced gas-phase deposition into cold water and inefficient vertical mixing.

Most of the HCH in the Northern Hemisphere is applied as a technical mixture containing about 60-70% α-HCH, 5-12% β-HCH, 10-15% γ-HCH, and minor percentages of other isomers (Iwata *et al.* 1993). Technical HCH is heavily used in Asia. India accounted for 20 - 47 kilotonnes (kt) per year in the 1980s (Hinckley *et al.* 1991, Iwata *et al.* 1993), and tonnages reported for 1990/91 and 1991/92 were 29 and 24 kt (B.S. Parmar, Indian Agricultural Research Institute, personal communication). Cumulative world consumption of HCHs from 1960 to 1989 has been estimated at 404 kt technical HCH and 147 kt lindane (Ottar and Semb 1989, Semb and Pacyna 1989). Only γ-HCH has insecticidal activity, and this isomer is manufactured in >99% purity as the pesticide lindane. Lindane is the only HCH product now used in Canada, the United States, and western Europe. Technical HCH has not been permitted in Canada since 1971 nor the United States since 1978 (Barrie *et al.* 1992). All of the HCH isomers are toxic to non-target organisms in varying degrees. The order of acute toxicity is $\gamma > \alpha > \delta > \beta$, whereas for chronic toxicity the order is $\beta > \alpha > \gamma > \delta$ (U.S. Public Health Service 1992).

Because of the greatly differing composition of HCH formulations used throughout the world, the ratio of γ-HCH/α-HCH in atmospheric samples is an indicator of source region. In the Northern Hemisphere α-HCH predominates in air, precipitation, and seawater, suggesting long-range transport of technical HCH from Asia. The isomeric composition of HCHs in air is thus characterized by a global background of technical HCH, modified by episodes of lindane transport. Excursions of air from south-central Europe into the Norwegian Arctic can be followed by the increase in γ-HCH/α-HCH ratios due to lindane transport (Oehme 1991). Seasonal usage of lindane in the Great Lakes region is evident from a springtime rise in atmospheric γ-HCH/α-HCH (Hoff *et al.* 1992, Lane *et al.* 1992, McConnell *et al.* 1993).

The rationale for this project is to support an effort, led by J. Pudykiewicz, to adapt a three-dimensional model developed by Atmospheric Environment Service for the movement of airborne contaminants on a hemispheric scale and their exchange between the atmosphere and the earth's surface. More information is available on environmental concentrations of HCHs than for other OCs, and several physicochemical properties of HCHs are known as functions of temperature. These qualities make HCHs good candidates for global-scale modelling (Strand and Hov 1994). As HCHs are transported through the atmosphere, they continually exchange with land and water surfaces. One task of this project is to review literature reports of HCH concentrations in air, surface water, and soil, and compile this information for use in the transport model. Properties of HCHs necessary for describing environmental partitioning and fate are also reviewed.

ACTIVITIES IN 1993/94

I. Physicochemical Properties of HCHs

Xu and Lee-Ruff (1992) surveyed the physicochemical properties of HCHs and provided a discussion of their determination methods. Those of most use in environmental modelling are vapour pressure, water solubility, Henry's law constant, octanol-water partition coefficient, and hydrolysis rate constant. These properties were compiled from the review of Xu and Lee-Ruff (1992) and our own literature searches, taking care to include only primary references and not quotes from handbooks, etc. The data base for γ-HCH is relatively good, but much poorer for the other isomers. Only two values for the solid-phase vapour pressure of α- and β-HCH were retrieved. The Henry's law constant of α-HCH was determined in two studies, with results differing by a factor of three for seawater. "Selected" values of the above properties are listed in Table 1. In some cases these were literature averages, excluding outliers, but when only two disparate values were reported, the choice was subjective.

Many properties (P = vapour pressure, Henry's law constant, etc.) are related to temperature by a form of the Clausius-Clapeyron equation:

$$\text{Log } P = m/T + b \qquad (1)$$

The slope (m) is a function of a thermodynamic quantity. Thus, for the heat of vaporization of a liquid (ΔH_v, J/mol), $m = -\Delta H_v/2.303R$. Most of the properties in Table 1 have been reported as functions of temperature in at least one study. The exception is the octanol-water partition coefficient. Parameters of equation (1) are given in Table 1, along with values of properties at 25 °C.

II. Distribution of HCHs in Air and Water

Concentrations of HCHs in air, surface seawater, and large lakes were obtained from published reports and personal contacts with scientists who have new, unpublished results. Our recent measurements from Resolute Bay and the Bering - Chukchi (B-C) Seas are included. These data have been compiled on Lotus spreadsheets, along with the location (latitude, longitude), collection date, and citation. Thus far, the information in Table 2 has been compiled for 1976 to 1993.

Examination of the air data shows that high concentrations of HCHs occur in Asian source regions, particularly India. This is consistent with the heavy usage of technical HCH. Releases of lindane in Europe and certain areas of the U.S.A. are shown by an increased proportion of γ-HCH compared to α-HCH. Some long term trends are also revealed by the survey. Over 300 measurements of HCHs in arctic air have been made from Canadian and Norwegian stations and from cruises in the B-C Seas. These data are summarized in Figure 1a, where average concentrations are plotted for all stations reporting for a particular year. Concentrations of HCHs (sum of α- and γ-HCH) in arctic air during the summer have decreased, from 880 pg/m^3 in 1979 to ~100 pg/m^3 in 1992/93, or about 7% per year of the 1979 value. The changes appear to have occurred in steps rather than linearly, with a drop after 1982 and another between 1990 and 1992. The winter record also shows a decline in HCHs, although less strongly than summer.

Fewer HCH measurements have been made in northern waters, especially in the early 1980s. The record of HCHs in the Bering - Chukchi Seas from 1979 to 1993 (Figure 1b) suggests a decline of about 3% per year of the 1979 value. Little or no loss has occurred in the Beaufort Sea. HCHs in surface water from the Ice Island were 5100 - 8100 pg/L in 1986/87 (Hargrave *et al.* 1988, Patton *et al.* 1989), and 5500 pg/L in 1992 (Macdonald and McLaughlin 1993). HCHs in surface water at Resolute Bay averaged 4900 pg/L in 1992 (Falconer *et al.* 1994).

The rapid loss of HCHs from the Arctic atmosphere has profound effects on the saturation state of the surface ocean. In the 1980s, concentrations of α-HCH in the Beaufort Sea and the B-C Seas were about 80% of Henry's law saturation values (water/air fugacity ratio = 0.80), indicating a net air-to-water flux (Cotham and Bidleman 1991). Recent measurements of α-HCH at Resolute Bay (Falconer *et al.* 1994) and the B-C Seas (Jantunen and Bidleman 1994) show an oversaturation, implying water-to-air transfer (volatilization). Thus, surface waters in some arctic regions now appear to be outgassing α-HCH - the same process responsible for clearing tonnes of PCBs from Lake Superior over the last decade (Jeremiason *et al.* 1994).

CONCLUSIONS

Understanding air-surface exchange processes is a critical factor in modelling the transport and deposition of newly released HCHs. An up-to-date database on levels of HCHs in air, water, and soils is required for these efforts. There is also a need for more determinations of HCH physicochemical properties, especially for α- and β-HCH.

Work in 1994/95 will include updating the database on HCH concentrations to include Southern Hemisphere waters, and expanding it to include soil residues. Soil residue data are used to estimate releases to the atmosphere through a soil emissions model. Following a review of the spatial distribution of HCHs, representative regional concentrations in air, water, and soil will be selected. In the transport model, newly released HCHs will partition against the fugacity (back pressure) exerted by these HCH residues. We will also estimate the removal of HCHs from the atmosphere by wet deposition, and compare these estimates to measured levels of HCHs in precipitation from around the world.

Expected project completion date: March 1995

REFERENCES

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. 122: 1-74.

Cotham, W.E. and T.F. Bidleman. 1991. Estimating the atmospheric deposition of organochlorine contaminants to the Arctic. Chemosphere 22: 165-188.

Falconer, R.L., T.F. Bidleman and D.J. Gregor. 1994. Air-water gas exchange and evidence for metabolism of hexachlorocyclohexanes in Resolute Bay, N.W.T., Canada. Sci. Total Environ. (in press).

Hargrave, B.T., W.P. Vass, P.E. Erickson and B.T. Fowler. 1988. Atmospheric transport of organochlorines to the Canadian Arctic. Tellus 40B: 480-493.

Hinckley, D.A., T.F. Bidleman and C.P. Rice. 1991. Atmospheric organochlorine pollutants and air-sea exchange of hexachlorocyclohexanes in the Bering and Chukchi Seas. J. Geophys. Res. 96: 7201-7213.

Hoff, R.M., D.C.G. Muir and N.P. Grift. 1992. The annual cycle of polychlorinated biphenyls and organochlorine pesticides in air in southern Ontario. 1. Air concentration data. Environ. Sci. Technol 26: 266-275.

Iwata, H., S. Tanabe, N. Sakai and R. Tatsukawa. 1993. Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of the ocean on their global transport and fate. Environ. Sci. Technol. 27: 1080-1098.

Jantunen, L.J. and T.F. Bidleman. 1994. Reversal of the air-water gas exchange direction of α-hexachlorocyclohexane in the Bering and Chukchi Seas. In preparation.

Jeremiason, J.D., K.C. Hornbuckle and S.J. Eisenreich. 1994. PCBs in Lake Superior, 1978-92: decreases in water concentration reflect losses by volatilization. Environ. Sci. Technol. 28:

Lane, D.A., W.H. Schroeder and N.D. Johnson. 1992. On the spatial and temporal variations in atmospheric concentrations of hexachlorobenzene and hexachlorocyclohexane isomers at several locations in the province of Ontario, Canada. Atmos. Environ. 26A: 31-42.

Macdonald, R.W. and F. A. McLaughlin. 1993. Long-range transport of contaminants to the Canadian Basin. Pp. 15-20 *in*: Synopsis of Research Conducted Under the 1992/93 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 70. Indian and Northern Affairs Canada, Ottawa. 285 pp. QS-8490-000-EF-A!, Catalogue No. R71-19/70-1993E, ISBN 0-662-21037-9.

McConnell, L.L., W.E. Cotham and T.F. Bidleman. 1993. Gas exchange of hexachlorocyclohexanes in the Great Lakes. Environ. Sci. Technol. 27: 1304-1311.

Oehme, M. 1991. Further evidence for long range air transport of polychlorinated aromates and pesticides. North America and Eurasia to the Arctic. Ambio 20: 293-297.

Oehme, M., J.-E. Haugen and M. Schlabach. 1994. Ambient levels of persistent organochlorines in spring 1992 at Spitzbergen and the Norwegian mainland, comparison with 1984 results and quality control measures. Sci. Total Environ, this issue.

Ottar, B. and A. Semb. 1989. Emissions, atmospheric transport, deposition, and mass flows of chlorinated hydrocarbons. 8th International Conference of Comité Arctique International (CAI), Oslo, Norway, September.

Patton, G.W., D.A. Hinckley, M.D. Walla, T.F. Bidleman and B.T. Hargrave. 1989. Airborne organochlorines in the Canadian High Arctic. Tellus 41B: 243-255.

Semb, A. and J.M. Pacyna. 1988. Toxic trace elements and chlorinated hydrocarbons: sources, atmospheric transport, and deposition. Nordic Council of Ministers, Copenhagen, NORD 1988:74.

Strand, A. and Ø. Hov. 1994. A model strategy for the simulation of chlorinated hydrocarbon distributions in the global environment. Water, Air, Soil Pollut. (in press).

U.S. Public Health Service. 1992. Toxicological Profile for Alpha- Beta, Gamma, and Delta-Hexachlorocyclohexanes. Draft for public comment. Agency for Toxic Substances and Disease Registry, Atlanta, Georgia, p. 6.

Xu, G. and E. Lee-Ruff. 1992. Transport Properties and Chemical Processes of HCH Isomers. Research report prepared for Environment Canada, 90 pp.

Table 1. Physicochemical Properties of Hexachlorocyclohexanes, Selected Values.

	α-HCH	β-HCH	γ-HCH
Melt. point, °C	159	315	112
ΔS_f , J/deg-mol	72.0		59.2
Fugacity ratio liquid/solid. 25°C	49.1	2136[a]	8.0

Parameters of Equation (1) and Values of Properties at 25°C

	α-HCH			β-HCH			γ-HCH		
	m	b	25 °C	m	b	25°C	m	b	25 °C
Vapour pressure (solid), Pa	-4850	13.97	0.0050	-5357	13.91	0.000088	-5288	15.58	0.0070
Vapour pressure (liquid), Pa	-3575	11.38	0.24	-3344	10.49	0.19	-3680	11.09	0.056
Water solubility (solid), mol/m^3			0.0069			0.00083	-1433	3.25	0.027
Water solubility (liquid), mol/m^3			0.34			1.8	-243	0.16	0.22
Henry's law	-2969	9.88	0.836 (SW)[b]				-2703	8.68	0.412
const., Pa-m^3/mol	-2810	9.31	0.768 (FW)[b]			0.09	-2383	7.54	0.353
Base hydrolysis rate const., L/mol-min	-4091	14.15	2.69				-4417	15.11	1.98
Octanol-water part. coeff.			6170			6600			4370

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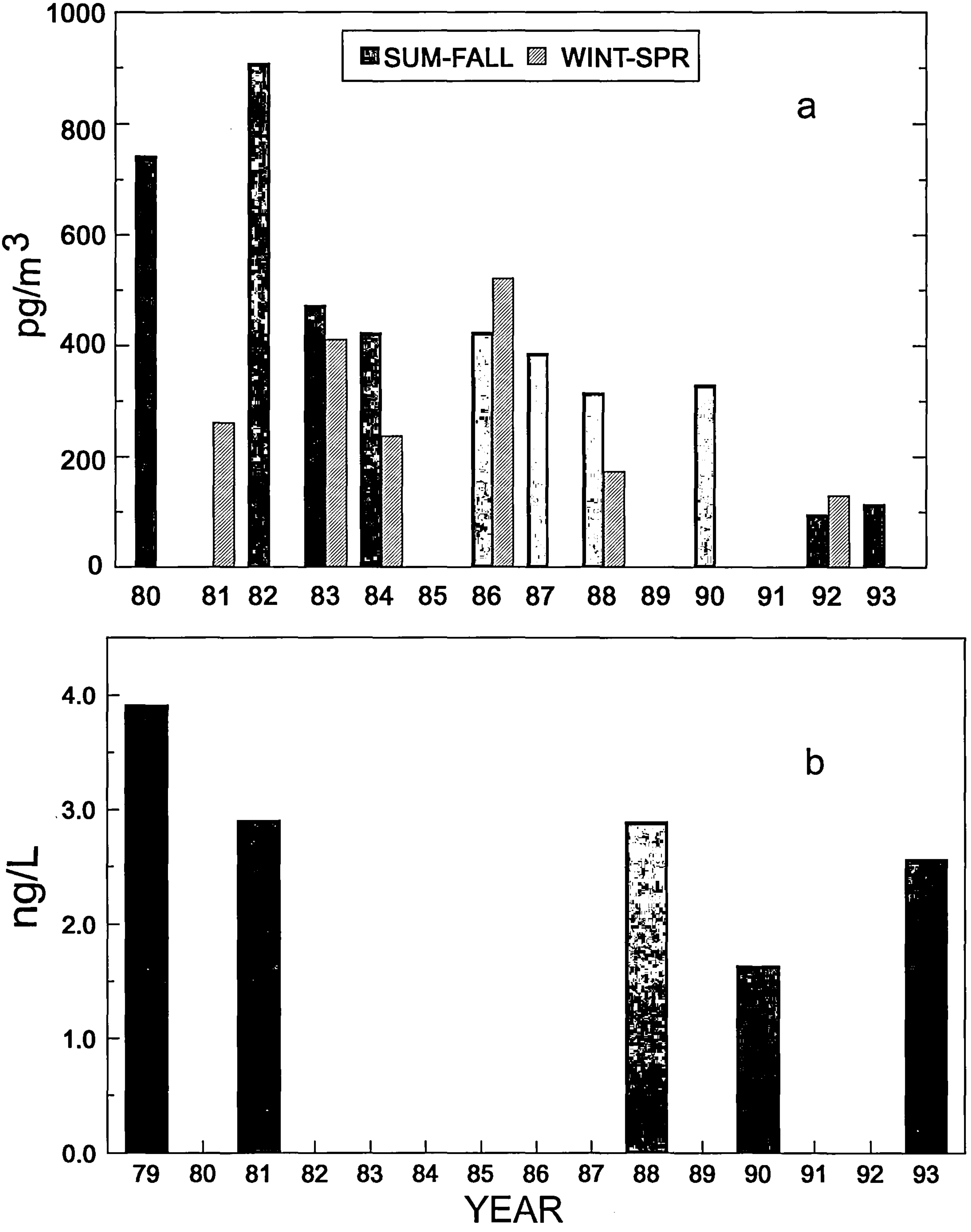
a) Assuming ΔS_f = 65.5 J/deg-mol, the average for α- and γ-HCH.
b) SW = seawater, salinity = 35; FW = freshwater

Table 2. HCH Concentration Data Available on Spreadsheets.

	Number of Measurements	Literature Citations
Air, Northern Hemisphere	1600	43
Air, Southern Hemisphere	125	11
Water, Northern Hemisphere	600	23

Figure 1a. Concentrations of total HCHs in arctic air from Canadian and Norwegian Stations and the Bering-Chukchi (B-C) seas. 1b. Trend of HCHs in B-C surface water, summer.



TOXAPHENE IN THE ARCTIC: ATMOSPHERIC DELIVERY AND TRANSFORMATION IN THE LOWER FOOD CHAIN

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OBJECTIVES

1. To determine concentrations and compare the gas exchange rates of toxaphene and hexachlorocyclohexanes (HCHs) in arctic waters.
2. To determine the physicochemical properties of toxaphene that affect its atmospheric transport and deposition.
3. To characterize the changes in the toxaphene complex mixture that accompany its transfer from air to water to the lower food chain.

PROJECT DESCRIPTION

Toxaphene is a complex mixture of chlorinated bornanes (CHBs) and related compounds with a theoretical number of congeners over 30 000 (Vetter *et al.* 1993). Global usage of toxaphene and other CHB products as insecticides from 1970-93 has been estimated at 670 000 tonnes (Voldner and Li 1993). CHBs are abundant in arctic invertebrates, fish, marine mammals, and polar bear (Muir *et al.* 1992, Hargrave *et al.* 1993, Kidd *et al.* 1993, Zhu *et al.* 1993), and in human milk from northern Quebec (Stern *et al.* 1992, Muir *et al.* 1994). Concentrations of CHBs often exceed those of other organochlorine (OC) pesticides, yet CHBs remain the most poorly characterized OCs with respect to physicochemical properties, transport pathways, and toxicology of individual congeners (Lockhart *et al.* 1993, Swackhamer *et al.* 1993).

Chromatographic patterns of CHB residues in biota are strikingly different from the toxaphene standard. Only a few CHBs are strongly accumulated in narwhal blubber, burbot liver, and human milk (Muir *et al.* 1992, 1994, Stern *et al.* 1992, Bidleman *et al.* 1993), whereas a greater number are found in fish and seal (Andrews *et al.* 1993, Hargrave *et al.* 1993, Kucklick *et al.* 1994). Changes in the CHB profile relative to a toxaphene standard result from selective volatility and water solubility of CHB congeners, and their different rates of uptake and metabolism by organisms.

Atmospheric deposition impacts the biologically active surface layer of the ocean and provides a direct link to the food chain. Aerial loadings of CHBs to the Arctic are estimated to take place largely through adsorption of gaseous CHBs to haze aerosols in winter followed by particle dry deposition, and by air-water gas exchange in summer. For hexachlorocyclohexanes (HCHs), the dominating mechanisms are gas exchange and precipitation scavenging (Cotham and Bidleman 1991). The initial transfer of CHBs from air to water to the lower food chain is governed by vapour pressure (adsorption to aerosols), Henry's law constant (gas exchange), and octanol-water partition coefficient (bioconcentration). These properties have been determined only for the entire toxaphene mixture, not for individual congeners, making it impossible to predict changes in the CHB profile that result from physical fractionation.

Once in the ocean, OCs are removed by photolysis, volatilization, sedimentation on particles, abiotic reactions (e.g. hydrolysis), and metabolism. Like amino acids, certain OC pesticides (including α-HCH, chlordanes, and some CHBs) exist in two chiral configurations (left and right handed). The ratio of these mirror-image molecules (enantiomers) in commercial pesticides is 1:1. Enantiomers have the same physicochemical properties, and thus behave identically in the environment in every respect except toxicology and metabolic breakdown. Because enzymes are themselves chiral molecules, they frequently react selectively with one of the enantiomers. Evidence for chiral breakdown of α-HCH was found in the North Sea (Faller *et al.* 1991, Pfaffenberger *et al.* 1992) and in laboratory cultures of marine bacteria (Ludwig *et al.* 1992). Differential metabolism of the enantiomers of α-HCH (Müller *et al.* 1991, Mössner *et al.* 1992), chlordanes (Buser and Müller 1993) and CHBs (Buser and Müller 1994) has been found in marine mammals.

This work is being carried out to increase the database for CHBs in arctic air and water, determine physicochemical properties of CHBs that affect atmospheric processes, compare air-water gas exchange of CHBs and HCHs, and determine the changes in the CHB profile that take place in the transfer from air to water to the lower food chain. The possibility of metabolic transformations occurring in seawater and arctic lakes is being investigated by examining the enantiomers of α-HCH.

ACTIVITIES IN 1993/94

I. CHBs and Other Organochlorines in Air and Water at Resolute Bay, NWT

Methods and Quality Control

Air and water samples collected August - September, 1992 at Resolute Bay were analysed for CHBs, HCHs, chlordanes, and DDTs. A description of these samples is given in Table 1. Details of the collection and analytical methods are given in two publications from this study (Bidleman *et al.* 1994, Falconer *et al.* 1994) and also by Kucklick *et al.* (1994), McConnell *et al.* (1993), and Patton *et al.* (1989). Air volumes of ~700 m^3 for HCHs and ~3000 m^3 for other OCs were pulled through a glass fibre filter (GFF) to collect particulate species followed by two polyurethane foam (PUF) plugs as a vapour trap. Back PUFs were used to check breakthrough losses from the front PUF. Breakthrough was low, 2% of front PUF quantities for α-HCH and less for other OCs, and the back PUFs were therefore used as air blanks. Water was collected in 20-L stainless steel cans, and 200 L was passed through a GFF followed by an XAD-2 resin trap for particulate and dissolved CHBs, chlordanes, and DDTs. HCHs in 4 L water were isolated on C_8 solid phase extraction (SPE) cartridges. CHBs, chlordanes, and DDTs were determined by capillary GC - negative ion mass spectrometry (GC-NIMS) at the University of South Carolina. HCHs were determined by capillary GC with electron capture detection (GC-ECD).

Water and snow samples from the Amituk Lake watershed on Cornwallis Island, obtained from D. Gregor (University of Waterloo), were examined for metabolic breakdown of α-HCH by GC-ECD on permethylated cyclodextrin capillary columns. The two enantiomers of α-HCH coelute on DB-5 and similar stationary phases, but are resolved on the chiral-phase columns GAMMADEX-120 and BETADEX-120 (Supelco). These two columns reverse the elution order of the enantiomers: (+)α-HCH followed by (-)α-HCH on BETADEX, and (-)α-HCH followed by (+)α-HCH on GAMMADEX, providing good confirmation of identity. Enantiomeric ratios (ERs) were also confirmed by GC-MS using the GAMMADEX column (Falconer and Bidleman 1994).

Blanks for air and water were obtained from filters and sorbents taken to Resolute Bay. Limits of detection (LOD) were defined as the mean blank + 3 x s.d. Water volumes of 4 L (HCHs) or 200 L (other OCs) and PUF plugs were spiked with OC standards at Resolute Bay for recovery checks. A summary of quality control experiments is given in Table 2. Results for samples have been corrected for blanks and recovery factors.

Results and Discussion

a) Concentrations of Organochlorine Compounds in Air and Water

OCs in air at Resolute Bay (Table 3) were lower than those found at the Canadian Ice Island in spring-summer 1986/87 (Patton *et al.* 1989). The decrease, expressed as the Resolute/Ice Island ratio, was greatest for CHBs (0.17), then HCHs (0.26) and chlordanes + nonachlors (0.34). HCHs and chlordanes at stations in the Norwegian Arctic were also lower in 1992 than 1984 (Oehme *et al.* 1994). CHBs in six air samples at Resolute Bay averaged 6.9 ± 3.3 pg/m^3. CHBs at the Alert air monitoring station ranged from <1.6 - 27 pg/m^3 during January - June, 1992 (Barrie *et al.* 1993). Two Resolute air samples were analysed for endosulfan, an OC insecticide still widely used in North America and Europe. Levels of the most volatile isomer (endosulfan I, or α-endosulfan) at Resolute Bay (3.7 - 4.1 pg/m^3) were within the range found at the Ice Island in 1986/87 (1.8 - 9.7 pg/m^3, Patton *et al.* 1989). By comparison, endosulfan I in two investigations from the Great Lakes region averaged 89 - 350 pg/m^3 (Hoff *et al.* 1992, Burgoyne and Hites 1993).

Concentrations of OCs in surface water from Resolute Bay and Resolute Passage are given in Table 3. Dissolved CHBs ranged from 26 - 65 (mean = 48) pg/L. Two surface samples from the Ice Island in 1986/87 gave values of 175 and 360 pg/L. Average α- + γ-HCH concentrations in this study (4900 pg/L) were at the lower end of the range for surface water at the Ice Island (5100 - 8100 pg/L, Hargrave *et al.* 1988, Patton *et al.* 1989), but higher than in the Bering and Chukchi seas (1600 - 3400 pg/L, Hinckley *et al.* 1991, Iwata *et al.* 1993, Jantunen and Bidleman 1994). Chlordanes + nonachlors in Resolute Bay water were 14 pg/L, compared to 5 pg/L at the Ice Island (Hargrave *et al.* 1988) and 10 pg/L in the Bering Sea (Kawano *et al.* 1988).

Although only two Amituk Lake water samples were quantitatively analysed for HCHs, and one for other OCs (Table 3), results indicate far different proportions of OCs than found in seawater. Relative to Resolute Bay, concentrations of HCHs in Amituk Lake were three times lower, chlordanes and nonachlors were about the same, and CHBs were three times higher. The level of CHBs in Amituk Lake (145 pg/L) falls within the range found for northern Ontario lakes (70 - 220 pg/L, Muir *et al.* 1994).

GC-NIMS profiles of the CHB homolog groups in air and water were similar, both being dominated by the early eluting components of toxaphene (Figure 1). This suggests air-water exchange of congeners having similar Henry's law constants. CHBs eluting at the retention times of 2-exo,3-endo,5-exo,6-endo,8,8,10,10-octachlorobornane (T2) and 2-exo,3-endo,5-exo, 6-endo,8,8,9,10,10-nonachlorobornane (T12) were found in air and water samples. T2 and T12 are abundant CHBs in marine mammals and fish (Muir *et al.* 1992, 1994, Bidleman *et al.* 1993), and in human milk from northern Quebec (Stern *et al.* 1992, Muir *et al.* 1994). Pure standards of T2 and T12, gifts from D. Hainzl and H. Parlar, University of Kassel, were used to establish the retention times of these CHBs in chromatograms of toxaphene and Resolute Bay samples. Other octa- and nonachlorobornanes coelute with T2 and T12 however (Vetter *et al.* 1993), so we cannot be sure that the corresponding peaks in the samples are single compounds.

b) Air-Water Gas Exchange

The net direction of gas exchange was determined from the water/air fugacity ratio ($f_w/f_a = C_wH/C_aRT$). C_w and C_a are the dissolved and gaseous concentrations of OCs in water and air (ng/m^3), H is the Henry's law constant (Pa m^3/mol) at the water temperature, T is the air temperature, and R = 8.314 Pa m^3/deg mol. OCs in air and water are at equilibrium when $f_w/f_a = 1.0$. Values of $f_w/f_a < 1.0$ and > 1.0 imply net deposition and volatilization, respectively. Henry's law constants of the HCHs as functions of temperature and at the salinity of seawater were taken from Kucklick *et al.* (1991). Henry's law constants of individual CHB congeners are not known, the only value is for the toxaphene technical mixture at 20 °C (Murphy *et al.* 1987). The temperature dependence of PCB Henry's law constants (Tateya *et al.* 1988) was used to extrapolate those of toxaphene (Murphy *et al.* 1987) and chlordane (Fendinger and Glotfelty 1989) from 20-23 °C to the temperature of Resolute Bay surface water (-1.4 °C).

Results of these calculations (Table 4) show that CHBs in Resolute Bay were undersaturated ($f_w/f_a = 0.26$), to the same extent as in Lake Baikal, Siberia ($f_w/f_a = 0.24$; McConnell *et al.* 1993). The net transfer direction of CHBs was thus air-to-sea. *Cis*-chlordane and γ-HCH were close to equilibrium. *Trans*-chlordane and α-HCH were oversaturated ($f_w/f_a = 4.15$ and 1.57, respectively), a condition leading to volatilization. During the 1980s the net exchange direction of both HCH isomers was depositional (Cotham and Bidleman 1991, Hinckley *et al.* 1991). Reversal in the exchange direction of α-HCH appears to be due to a three-fold drop in its atmospheric concentration since the mid-1980s. The large oversaturation of *trans*-chlordane may be an artifact of the seasonal cycle of chlordane isomers in the Arctic atmosphere, which is documented in several investigations (Hoff and Chan 1986, Patton *et al.* 1989, 1991, Oehme 1991, Fellin *et al.* 1993, Oehme *et al.* 1994). In winter the ratio of *trans-/cis*-chlordane in arctic air is close to unity. Gregor and Gummer (1989) found equal concentrations of *trans*- and *cis*-chlordane in a large-scale survey of the Canadian Arctic snowpack in 1986, thus snowmelt probably delivers equal quantities of the two isomers to the surface ocean. In summer, *trans*-chlordane is depleted in air relative to *cis*-chlordane, and the reduction in its atmospheric concentration raises $f_w/f_a > 1.0$.

c) Chiral Breakdown of α-Hexachlorocyclohexane in the Arctic Environment

The enantiomeric ratios of α-HCH (ER = +/-) in air samples from Resolute Bay, and snow from the Amituk Lake watershed were 1.00 ± 0.04 and 0.98 ± 0.03, respectively. A racemic α-HCH standard showed an ER = 1.00 ± 0.01 on the chiral columns. Seawater from Resolute Bay showed a slight depletion of (+)α-HCH (ER = 0.93 ± 0.06) which was significantly different from the standard ($p < 0.01$). Pfaffenberger *et al.* (1992) found a mean ER = 0.84 in the North Sea, whereas Faller *et al.* (1991b) found 0.80 - 1.19 in different regions of the North Sea.

More extensive breakdown of α-HCH was found in the Amituk Lake watershed. ERs in the deep lake at 20 m were essentially constant (0.77-0.78) from May - August, 1992. ERs for three streams feeding the lake were 0.88-0.99 in late June, and fell to 0.65-0.86 in mid-July, showing that changes in the ER begin even before HCHs enter the lake. These results suggest that microbial activity is an important degradation pathway for HCHs and possibly other OCs in arctic waters.

II. Organochlorine Compounds in Air and Water, Bering and Chukchi (B-C) Seas

This study was not funded by the AES-Northern Contaminants Program, however, the findings will be useful in meeting the objectives of the project on toxaphene in the Arctic.

Methods and Quality Control

In July - September 1993, we collected air and water samples in the B-C seas from the Russian ship OKEAH ("Ocean"). The cruise (BERPAC-93) was a sequel to a similar expedition in 1988 organized by U.S. and Russian scientists (Hinckley *et al.* 1991). Air samples were taken by the methods used at Resolute Bay. Surface and deep water was collected in 12-L Teflon-lined Go-Flo bottles and transferred to stainless steel cans. HCHs were preconcentrated using SPE cartridges. Water samples of ~1000 L were taken by W.M.J. Strachan (NWRI) using a continuous flow centrifuge to separate particulate matter. Approximately 80 L of the particle-free water was extracted on board ship with dichloromethane in a Goulden apparatus. These samples will be analysed for CHBs and chlordanes by GC-NIMS in our laboratory, and for other OCs by NWRI. Recovery experiments were carried out as for Resolute Bay; a summary of the QC data for HCHs is given in Table 2. The 21 air and 88 water samples taken for HCHs have been analysed, and are discussed in this report. CHBs and chlordanes are too low to be determined reliably in 700 m^3 air, and air samples are being combined in sets of 3-4 for future GC-NIMS analysis.

Results and Discussion

a) Concentrations of HCHs in B-C Seas Air and Water

Mean atmospheric levels (± s.d.) of α-HCH and γ-HCH were: 93 ± 23 and 23 ± 10 pg/m^3, respectively. This α-HCH result from 1993 agrees remarkably well with 114 pg/m^3 measured at Resolute Bay in 1992, and confirms the drop in this isomer since 1988-90, when average concentrations over the B-C seas were 270-290 pg/m^3 (Hinckley *et al.* 1991, Iwata *et al.* 1993). Levels of γ-HCH were twice those at Resolute Bay (10 pg/m^3). The ratio of average α- and γ-HCH concentrations on BERPAC-93 was 4.0, compared to 11.6 at Resolute Bay. Lower α-/γ-HCH ratios in summer have been previously found in air from the B-C seas (Hinckley *et al.* 1988, Iwata *et al.* 1993) compared to the Canadian Arctic (Patton *et al.* 1989).

A summary of HCHs in B-C water at different depths is given in Table 5. Surface concentrations averaged 2.0 and 0.45 ng/L for α- and γ-HCH, respectively, and varied little over the cruise track. For comparison, concentrations of α- and γ-HCH at Resolute Bay were 4.5 and 0.42 ng/L. In both locations, ratios of the two isomers in water closely paralleled those in the atmosphere. In the B-C seas, α-HCH decreased slowly with depth; concentrations at 120-350 m were about 75% of surface values. Much lower, but detectable, concentrations were found at 1500-3000 m.

b) Air-Sea Gas Exchange

Fugacity ratios (f_w/f_a) were determined from air and water concentrations as described in the Resolute Bay section. Values of f_w/f_a were (α-HCH, γ-HCH): South Bering Sea 1.95, 1.38; Chirikov Basin 1.37, 0.65; Chukchi Sea 1.45, 0.66. Thus both HCH isomers were oversaturated in the South Bering and the net transfer direction was sea-to-air (volatilization). In other regions, α-HCH was oversaturated and γ-HCH was undersaturated. On previous cruises both HCHs were undersaturated, to a greater extent than found on BERPAC-93 (Hinckley *et al.* 1991, Iwata *et al.* 1993). As at Resolute Bay, volatilization of α-HCH in the B-C seas further indicates that a reversal in the net flux direction is taking place as a consequence of its declining atmospheric concentration since 1988-90.

CONCLUSIONS

Gas exchange is a two-way street that allows both deposition and volatilization. Differences in the net direction of gas exchange are evident for OCs at Resolute Bay, in part due to short and long term changes in the atmospheric concentrations of these contaminants. A downward trend in airborne α-HCH since 1988-90 has led to a reversal of the net gas exchange direction, and some oceanic areas such as Resolute Bay and the Bering Sea are now acting as sources rather than sinks. Limited data from Resolute Bay suggests that CHB concentrations in air and water have declined since the mid-1980s, but that the ocean is still a sink for gaseous CHBs. A better assessment of the CHB situation requires additional air and water concentration data, and physicochemical properties for individual CHB congeners. The fate of OCs in the Arctic is poorly understood, but our preliminary examination of α-HCH enantiomers in Amituk Lake and Resolute Bay suggests that microbial breakdown may be an important loss pathway.

Future work in 1994/95 and 1995/96 will include: a) determining the vapour pressures and Henry's law constants of some CHB congeners, b) completing the analysis of B-C seas samples for CHBs and chlordanes, c) collecting air and water samples for CHBs and other OCs from the central Arctic Ocean on a joint Canadian/U.S. icebreaker cruise, July - September 1994, and d) examining the CHB congener profile in plankton and amphipods relative to air and water. The biota samples are being supplied by Barry Hargrave, Fisheries and Oceans Canada.

Expected project completion date: March 1996

REFERENCES

Andrews, P., W.H. Newsome, M. Boyle and P. Collins. 1993. High resolution selective ion monitoring GC-MS determination of toxaphene in Great Lakes fish. Chemosphere 27: 1865-1872.

Barrie, L.A., T. Bidleman, D. Dougherty, P. Fellin, N. Grift, D. Muir, B. Rosenberg, G. Stern and D. Toom. 1993. Atmospheric toxaphene in the High Arctic. Chemosphere 27: 2037-2046.

Bidleman, T.F., M.D. Walla, D.C.G. Muir and G.A. Stern. 1993. Selective accumulation of polychlorocamphenes in aquatic biota from the Canadian Arctic. Environ. Toxicol. Chem. 12: 701-709.

Bidleman, T.F., R.L. Falconer and M.D. Walla. 1994. Toxaphene and other organochlorine compounds in air and water at Resolute Bay, N.W.T. Sci. Total Environ. in press.

Burgoyne, T.W. and R.A. Hites. 1993. Effects of temperature and wind direction on the atmospheric concentrations of α-endosulfan. Environ. Sci. Technol. 27: 910-914.

Buser, H.R. and M.D. Müller. 1993. Enantioselective determination of chlordane components, metabolites, and photoconversion products in environmental samples using chiral high resolution gas chromatography and mass spectrometry. Environ. Sci. Technol. 27: 1211-1220.

Buser, H.R. and M.D. Müller. 1994. Isomer and enantiomer selective analysis of toxaphene components using chiral high resolution gas chromatography and detection by mass spectrometry/mass spectrometry. Environ. Sci. Technol. 28: 119-128.

Cotham, W.E. and T.F. Bidleman. 1991. Estimating the atmospheric deposition of organochlorine contaminants to the Arctic. Chemosphere 22: 165-188.

Falconer, R.L., T.F. Bidleman and D.J. Gregor. 1994. Air-water gas exchange and evidence for metabolism of hexachlorocyclohexanes in Resolute Bay, N.W.T., Canada Sci. Total Environ. in press.

Faller, J., H. Hühnerfuss, W.A. König and P. Ludwig. 1991. Gas chromatographic separation of the enantiomers of marine organic pollutants. Distribution of α-HCH enantiomers in the North Sea. Mar. Pollut. Bull. 22: 82-86.

Fellin, P., L.A. Barrie, D.M. Dougherty, D. Muir, B. Grift, L. Lockhart and B. Billeck. 1993. Air monitoring at Alert: results for 1992 for organochlorine and PAH compounds. Internat. Symp. on Ecological Effects of Arctic Airborne Contaminants, Reykjavik, Iceland, October.

Fendinger, N.J. and D.E. Glotfelty. 1989. Comparison of two experimental techniques for determining air-water Henry's law constants. Environ. Sci. Technol. 23: 1528-1531.

Gregor, D.J. and W.D. Gummer. 1989. Evidence of atmospheric transport and deposition of organochlorine pesticides and polychlorinated biphenyls in Canadian Arctic snow. Environ. Sci. Technol. 23: 561-565.

Hargrave, B.T., W.P. Vass, P.E. Erickson and B.T. Fowler. 1988. Atmospheric transport of organochlorines to the Canadian Arctic. Tellus 40B: 480-493.

Hargrave, B.T., D.C.G. Muir and T.F. Bidleman. 1993. Toxaphene in amphipods and zooplankton from the Arctic Ocean. Chemosphere 27: 1949-1963.

Hinckley, D.A., T.F. Bidleman and C.P. Rice. 1991. Atmospheric organochlorine pollutants and air-sea exchange of hexachlorocyclohexanes in the Bering and Chukchi seas. J. Geophys. Res. 96: 7201-7213.

Hoff, R.M. and K.-Y. Chan. 1986. Atmospheric concentrations of chlordane at Mould Bay, N.W.T. Chemosphere 15: 449-452.

Hoff, R.M., D.C.G. Muir and N.P. Grift. 1992. The annual cycle of polychlorinated biphenyls and organochlorine pesticides in air in southern Ontario. 1. Air concentration data. Environ. Sci. Technol 26: 266-275.

Iwata, H., S. Tanabe, N. Sakai and R. Tatsukawa. 1993. Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of the ocean on their global transport and fate. Environ. Sci. Technol. 27: 1080-1098.

Jantunen, L.J. and T.F. Bidleman. 1994. Reversal of the air-water gas exchange direction of α-hexachlorocyclohexane in the Bering and Chukchi seas. In preparation.

Kawano, M., T. Inoue, T. Wada, H. Hidaka and R. Tatsukawa. 1988. Bioconcentration and residue patterns of chlordane compounds in marine animals: invertebrates, fish, mammals, and seabirds. Environ. Sci. Technol. 22: 792-797.

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: 1975-1986.

Kucklick, J.R., D.A. Hinckley and T.F. Bidleman. 1991. Determination of Henry's law constants for hexachlorocyclohexanes as a function of temperature and salinity. Marine Chem. 34: 197-209.

Kucklick, J.R., T.F. Bidleman, L.L. McConnell, M.D. Walla and G.P. Ivanov. 1994. Organochlorines in the water and biota of Lake Baikal, Siberia. Environ. Sci. Technol. 28: 31-37.

Lockhart, W.L., M.A. Saleh, A.H. El Sabae, N. Doubleday, M. Evans, B. Jansson, V. Jerome, J.B. Walker and J. Witteman. Report of the working group on toxicology of chlorinated bornane compounds. Chemosphere 27: 1841-1848.

Ludwig, P., H. Hühnerfuss, W.A. König and W. Gunkel. 1992. Gas chromatographic separation of the enantiomers of marine pollutants. Part 3. Enantioselective degradation of α-hexachlorocyclohexane and γ-hexachlorocyclohexane by marine microorganisms. Marine Chem. 38: 13-23.

McConnell, L.L., J.R. Kucklick, T.F. Bidleman and M.D. Walla. 1993. Long range atmospheric transport of toxaphene to Lake Baikal. Chemosphere 27: 2027-2036.

Mössner, S., T.R. Spraker, P.R. Becker and K.A. Ballschmiter. 1992. Ratios of enantiomers of α-HCH and determination of α- β-, and γ-HCH isomers in brain and other tissues of neonatal northern fur seals (*Callorhinus ursinus*). Chemosphere 24: 1171-1180.

Muir, D.C.G., C.A. Ford, N.P. Grift, R.E.A. Stewart and T.F. Bidleman. 1992. Organochlorine contaminants in narwhal (*Monodon monoceros*) from the Canadian Arctic. Environ. Pollut. 75: 309-316.

Muir, D.C.G., B. Rosenberg, N.P. Grift and G.A. Stern. 1994. Biomagnification of specific octa- and nonachlorobornanes (toxaphene) in aquatic food webs. 24th International Symposium on Environmental Analytical Chemistry, Ottawa, Ontario, May.

Müller, M.D., M. Schlabach and M. Oehme. 1992. Fast and precise determination of α-hexachlorocyclohexane enantiomers in environmental samples using chiral high resolution gas chromatography. Environ. Sci. Technol. 26: 566-569.

Murphy, T.J., M.D. Mullin and J.A. Meyer. 1987. Equilibration of polychlorinated biphenyls and toxaphene with air and water. Environ. Sci. Technol. 21: 155-162.

Oehme, M. 1991. Further evidence for long range air transport of polychlorinated aromates and pesticides. North America and Eurasia to the Arctic. Ambio 20: 293-297.

Oehme, M., J.-E. Haugen and M. Schlabach. 1994. Ambient levels of persistent organochlorines in spring 1992 at Spitzbergen and the Norwegian mainland, comparison with 1984 results and quality control measures. Sci. Total Environ. in press.

Patton, G.W., D.A. Hinckley, M.D. Walla, T.F. Bidleman and B.T. Hargrave. 1989. Airborne organochlorines in the Canadian High Arctic. Tellus 41B: 243-255.

Patton, G.W., 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: 10867-10877.

Pfaffenberger, B., H. Hühnerfuss, R. Kallenborn, A. Köhler-Günther, W. König and G. Krüner. 1992. Chromatographic separation of the enantiomers of marine pollutants. Part 6. Comparison of the enantioselective degradation of α-hexachlorocyclohexane in marine biota and water. Chemosphere 25: 719-725.

Stern, G.A., D.C.G. Muir, C.A. Ford, N.P. Grift, E. Dewailly, T.F. Bidleman and M.D. Walla. 1992. Isolation and identification of two major recalcitrant toxaphene congeners in aquatic biota. Environ. Sci. Technol. 26: 1838-1840.

Swackhamer, D.L., L.L. McConnell and D.J. Gregor. 1993. Workgroup report on environmental transport and fate of chlorobornanes. Chemosphere 27: 1835-1840.

Tateya, S., S. Tanabe and R. Tatsukawa. 1988. PCBs on the globe: possible trend of future levels in the open-ocean environment. Pp. 237-281 *in*: Toxic Contamination in Large Lakes, N.W. Schmidtke (ed.). Vol. 3, Lewis Publishers, Chelsea, Michigan.

Vetter, W. 1993. Toxaphene: theoretical aspects of the distribution of chlorinated bornanes, including symmetry aspects. Chemosphere 26: 1079-1084.

Vetter, W., B. Luckas and M. Oehme. 1993. Mass spectrometric and gas chromato graphic identification of the two main toxaphene congeners present in marine mammals as minor constituents in the technical product. Chemosphere 27: 597-605.

Voldner, E.C. and Y.F. Li. 1993. Global usage of toxaphene. Chemosphere 27: 2073-2078.

Zhu, J. and R.J. Norstrom. 1993. Identification of polychlorocamphenes (PCCs) in the polar bear (*Ursus maritimus*) food chain. Chemosphere 27: 1923-1936.

Table 1. Air and Water Samples Collected at Resolute Bay, NWT, August - September 1992[a].

	Resolute Bay	Amituk Lake
Air (HCHs)	5	
Air (Other OCs)	6	
Water (HCHs)	15	2[b]
Water (other OCs)	8	1

a) See Falconer *et al.*, 1994 and Bidleman *et al.*, 1994 for details.
b) Quantitative analysis of HCHs. Additional samples from Dennis Gregor were examined for α-HCH enantiomers.

Table 2. Summary of Quality Control Experiments for Organochlorine Compounds[a].

		Mean Recovery of Spikes (%)[b]			
		Air	Air	Water	Water
Compound	LOD, ng[c]	Resolute Bay	B-C Seas	Resolute Bay	B-C Seas
α-HCH	6.4	87	104	74	71
γ-HCH	0.7	93	81	74	73
Chlordane & nonachlor	0.04-0.15	76		56	
p,p'-DDT	0.7	102		74	
CHBs	2.0	103		102	

a) See Falconer *et al.*, 1994 and Bidleman *et al.*, 1994 for details.
b) Numbers of spikes were: Resolute Bay air (3) water (2), B-C Seas air (3) water (23)
c) LOD = mean blank + 3 x s.d.

Table 3. Organochlorine Compounds in Air and Water at Resolute Bay[a], August 1992.

	Air (pg m^{-3})		Seawater (pg L^{-1})		Amituk Lake (pg L^{-1})
α-HCH	114 ± 16	(5)	4500 ± 900	(15)	1300
γ-HCH	9.8 ± 1.3	(5)	420 ± 90	(15)	280
CHBs	6.9 ± 3.3	(6)	48 ± 12	(8)	145
trans-chlordane	0.51 ± 0.34	(6)	7.3 ± 4.2	(8)	3.3
cis-chlordane	1.4 ± 0.8	(6)	4.5 ± 2.5	(8)	4.1
trans-nonachlor	0.77 ± 0.28	(6)	1.5 ± 1.3	(8)	1.9
cis-nonachlor	0.12 ± 0.06	(6)	0.4 ± 0.2	(8)	0.8
Endosulfan I	3.7 - 4.1	(2)	NA		NA
p,p-DDE	NA		1.0 ± 0.3	(4)	NA
p,p-DDT	<0.3	(5)	<4	(4)	<4

a) Gaseous and dissolved components in air and water, respectively. Given are the mean, standard deviation, and number of samples (in parentheses). Two samples from Amituk Lake were quantified for HCHs, and one for other OCs. NA = not analysed.

Table 4. Fugacity Ratios (f_w/f_a) of Organochlorines, Resolute Bay - Resolute Passage.

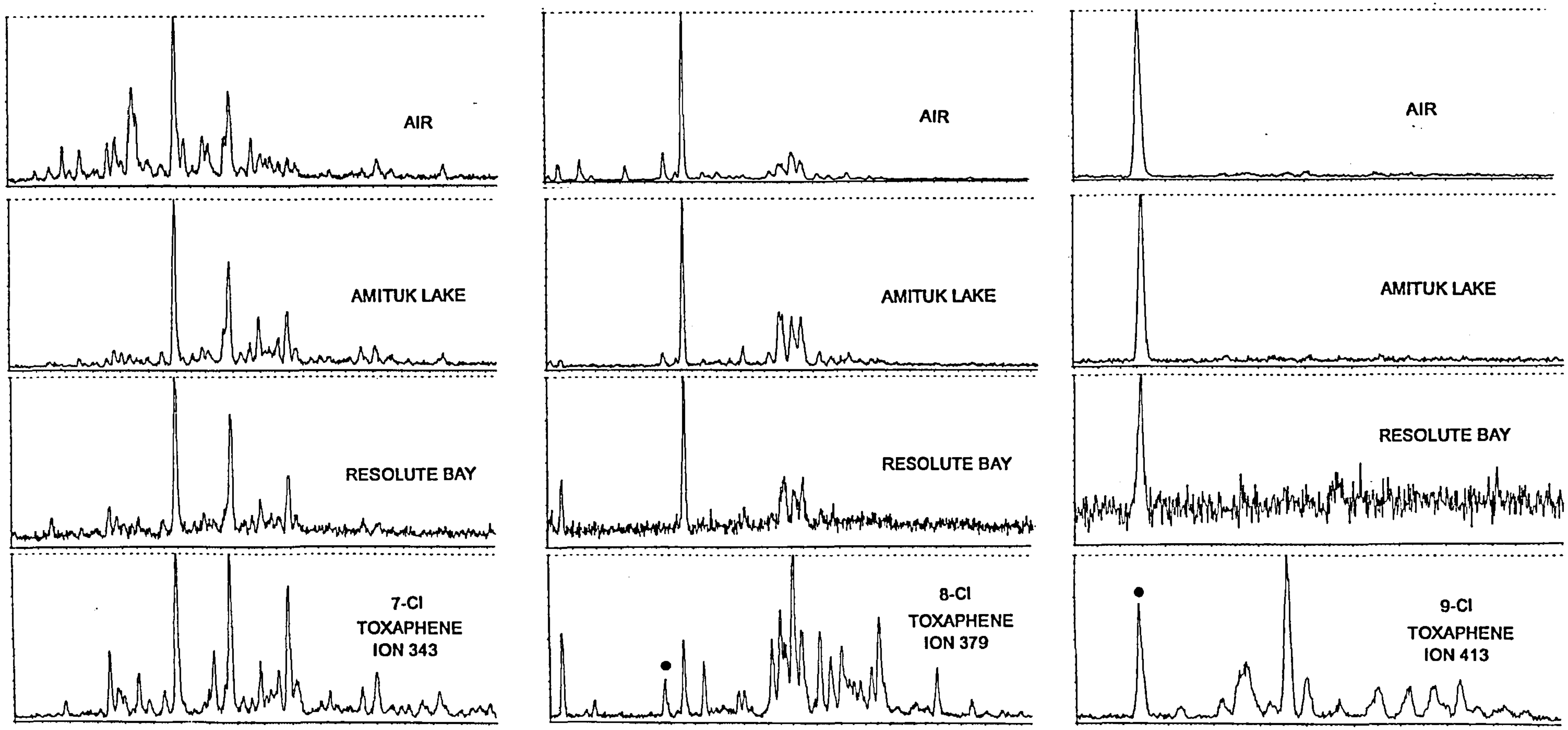
	H (Pa m^3 mol^{-1}) at -1.4 °C	Fugacity Ratio
α-HCH	0.090	1.57
γ-HCH	0.054	1.03
trans-chlordane	0.66	4.15
cis-chlordane	0.66[a]	0.94
CHBs	0.081	0.26

a) Assumed the same as for *trans*-chlordane.

Table 5. Hexachlorocyclohexanes in Water from the Bering and Chukchi Seas (ng/L).

		α-HCH		γ-HCH		
Location	Depth (m)	Mean	S.D.	Mean	S.D.	Number
Bering Sea	1-30	1.91	0.48	0.43	0.13	15
	50-75	1.87	0.52	0.45	0.09	9
	120-350	1.49	0.38	0.34	0.11	10
	1500-3000	0.07	0.01	0.04	0.04	3
Gulf of Anadyr	1-35	1.94	0.41	0.47	0.09	11
	54-84	1.69	0.50	0.41	0.12	5
	126	1.79	0.33	0.42	0.26	3
Chirikov Basin	1-37	1.95	0.44	0.46	0.07	10
Alaskan Chukchi Sea	1-40	2.16	0.63	0.45	0.08	12
	106-298	1.45	0.44	0.45	0.16	4
	1586	0.66		0.17		1
Siberian Chukchi Sea	1-40	2.06	0.36	0.43	0.01	7

Figure 1. GC-NIMS profiles of CHBs in air, Resolute Bay and Amituk Lake water, and a toxaphene standard. Dotted peaks on the standard chromatogram mark the retention times of T2 (8-Cl) and T12 (9-Cl). See text for discussion.



DEVELOPMENT OF MODELS DESCRIBING THE DISTRIBUTION OF ORGANIC CHEMICALS INTO COLD ECOSYSTEMS

PROJECT LEADER: D. Mackay, Institute for Environmental Studies, University of Toronto

PROJECT TEAM: F. Wania and W.Y. Shiu

OBJECTIVES

Short-term:

1. To develop, improve, and publish in the international refereed scientific literature, conceptual multimedia mass balance models describing the global transport and distribution of organic contaminants, with a particular emphasis on their transport to the Canadian North.
2. To provide a framework to compile, interpret and explain the spatial distribution and temporal trends of contaminant concentrations which are currently being measured in a variety of media in the Arctic environment. The aim is also to provide a scientific basis for assertions that some contaminants require international control because of their propensity to migrate to cold regions.

Long-term:

1. To provide tools to identify, understand and quantify the sources, pathways and sinks of organic contaminants in the Arctic.
2. To assist in the design of future research and monitoring programs by identifying major gaps in the available data.
3. To identify the environmental and chemical-related factors, which control the long term distribution of organic contaminants on a global scale and their accumulation in remote, cold areas.
4. To estimate future trends of contaminant concentrations in environmental media in the Arctic and elsewhere based on various prospective emission scenarios, thereby assessing the need for, effectiveness of, and urgency of implementation of control measures.

DESCRIPTION

Arctic regions are characterized by cold temperatures, reduced biological activity, low light incidence, extreme seasonality and the presence of permanently and seasonally frozen water in terrestrial, aquatic and marine ecosystems. All these factors are likely to influence the behaviour of persistent organic contaminants in the Arctic environment. It is often difficult to identify the effect of these factors and to quantify their magnitude. Similarly, the interpretation of measured concentrations of persistent organic contaminants in a variety of Arctic environmental compartments such as air, snow, water, sediment and biota is difficult, incomplete and possibly misleading if the discussion is restricted to one sampling medium. Comprehensive mass balance models of contaminant fate in multimedia environments can improve this understanding and interpretation.

ACTIVITIES AND RESULTS IN 1993/94

Depending on the type of information sought, chemical mass balance models vary in structure and complexity. Several approaches to modelling contaminant dispersion into high latitudes and behaviour within Arctic settings were pursued in 1993/94 and will be discussed in the following section:

1. Contaminant behaviour in generic environments of different temperatures

The physical-chemical properties of a chemical control, to a large extent, its behaviour in the environment. Since temperature affects these properties strongly, it is clear that the cold temperatures prevalent in Arctic regions will have a profound effect on chemical fate. This effect can be understood and illustrated with simple multimedia partitioning calculations in generic environments at different temperatures (Berger *et al.* 1994, Mackay and Wania 1994).

Figure 1 shows the results of such a calculation for hexachlorobenzene (HCB) in a generic six-compartment environment at 25 and 0 °C (Mackay and Wania 1994). Amounts and rates shown are those established after a prolonged period of steady emission of 10 kg/h of HCB into the atmosphere. The overall picture is that at the lower temperature the amount in air is decreased while the amounts in the other compartments increase as a result of greater net depositional fluxes. The net advection out of the modelled region is smaller at 0 than at 25 °C. This shift of distribution from the atmosphere to the condensed phases is caused both by (1) a shift in the equilibrium distribution reflected in higher partition coefficients between air and condensed phases at lower temperatures, and (2) an increase in the rate of depositional processes at lower temperatures. These phenomena have been summarized under the term "cold condensation" effect. It should be pointed out that organic contaminant concentrations in cold regions have the potential to be further increased due to the retardation of biological and photolytic degradation processes under Arctic conditions. This effect was not considered in the above calculation.

2. Contaminant transport: A conceptual framework

According to this simple model a contaminant emitted to the atmosphere is subject to three competing processes: it can be degraded in the atmosphere, it can be deposited to the Earth's surface or it can be advected out of the particular region of interest. This can be expressed in simple form by the steady state mass balance over an atmospheric source region:

$$E=M_A(k_R + K_DF + k_A)$$

where E is the steady emission rate, M_A is the amount in air, k_R, k_D and k_A are rate constants for reaction, deposition and net advection and F is a retention factor expressing how much of the deposited chemical is retained by the receiving surface (soil, vegetation, water). Whether or not an organic chemical has the potential to be transported to Arctic regions far from source areas is dependent on the particular combination of the values of the rate constants and the retention factor. An atmospheric contaminant which is stable (small k_R) and is neither deposited rapidly (small k_D) nor retained strongly in source areas (small F) tends to be advected readily (large k_A) and has the potential for long range transport. Indeed, it will become a global atmospheric contaminant and is likely to appear in Arctic ecosystems. It is important that we gain an improved appreciation of how existing (and new) chemicals fit into this conceptual framework.

3. Contaminant transport and deposition in cold regions

The drop of concentration in a parcel of air moving with a velocity of U from a source region into a remote area with no emissions can be described by:

$$\frac{dC_A}{dL} = \frac{-(k_R + k_D F)}{U} C_A \qquad \text{and integrated to give} \qquad \ln C_A = \ln C_{A_0} - \frac{k_R + k_D F}{U} L$$

where L is the distance from the source and C_{A0} is the concentration at the source.

C_A will decrease with increasing distance L. The rate of decrease will be high for highly reactive (k_R large), rapidly deposited (k_D large) and strongly retained (F large) compounds. Stable compounds which have a high potential for advection will have a more uniform air concentration profile.

The concentration in condensed media C_C can be approximated at least in principle by

$$C_C = C_A \cdot K_{CA}$$

where K_{CA} is a steady-state condensed phase-to-air partition coefficient. K_{CA} increases at lower temperatures both for thermodynamic reasons related to a shift in equilibrium partitioning and for kinetic reasons related to faster deposition (k_D increases) and retarded re-evaporation (F increases). Depending on the rate of decrease of the air concentration, the concentrations in the condensed media will thus increase or decrease with increasing distance from the source as is illustrated in Figure 2. This simple approach described in more detail in Mackay and Wania (1994) thus gives a possible explanation for the startling observation that some chemicals actually show higher concentrations in remote cold regions than they do in regions close to their points of release.

Properties that make a chemical susceptible to this kind of "global distillation" and the accumulation in polar regions are persistence and a relatively high K_{CA}, which derives from a combination of relatively high hydrophobicity and relatively low vapour pressure. Compounds with extremely low vapour pressure and very high hydrophobicity tend to be deposited and retained closer to the source. Compounds with high vapour pressure and low hydrophobicity (such as freons) may be transported to Arctic regions in the atmosphere, but have little tendency to accumulate in condensed media.

4. Global distribution model

In addition to the simple conceptual models, which describe chemical fate in generic environmental settings, a more complex global distribution model developed and described earlier (Wania and Mackay 1993) has been revised and improved during the period 1993/94. This one-dimensional model divides the global environment into nine zonal bands, each of which is represented by six compartments as shown in Figure 1. Meridional transport between the zones occurs in the atmosphere and the surface ocean. The model is more complex than the models described above in that it is non-steady state, the environmental parameters are as far as possible climate specific rather than generic, a number of environmental parameters such as temperature are allowed to vary seasonally and it is possible to specify different temperatures in various phases of one climate zone. A detailed description of the model is given in Wania and Mackay (1994).

A series of illustrative calculations was performed to investigate the importance of the major factors which govern the global dispersion of persistent organic chemicals (Wania and Mackay 1994). These calculations indicate that temperature and its influence on the partition behaviour is crucial to the understanding of global dispersion and accumulation processes of persistent organic chemicals. The location, medium and amount of chemical discharge into the global environment is of primary importance for the model results. Due to the long time scales of global dispersion processes, such information has to be known for the entire period during which a chemical has been released into the global environment. Finally, some environmental parameters such as soil depth and organic carbon contents have the potential to modify environmental contamination patterns substantially.

In a first attempt to simulate the long term fate of a persistent organic chemical on a global scale, we estimated an emission scenario for the hexachlorocyclohexanes (α- and γ-HCH) for the time period from 1945 to the present based on limited information available in the literature and calculated rates, distributions and concentrations as a function of time. Figure 3 shows the global compartmental distribution of α-HCH calculated for the summer 1985. The model results suggest that the bulk of the α-HCH emitted into the environment still resides in the soils which received this pesticide during application. The other major global reservoir is the world oceans holding about 20 percent of the total global inventory of the α-HCH. The major processes controlling the global mass balance are degradation in the cultivated soils, leaching into fresh water, evaporation from soils and receiving waters, and atmosphere-ocean exchange.

Figure 4 shows the zonal distribution of emissions and accumulated inventory for 1985. The model suggests that in the Tropics the share of the global emissions (more than half) is higher than the share of the total inventory of α-HCH (approximately a third), while the higher latitudes receive less of the current emissions, but store more of the accumulated amount of α-HCH. This indicates a net poleward transport of these chemicals in atmosphere and oceans.

To test the reliability of the results, the concentrations calculated for the year 1985 were compared with a database of measured HCH concentrations in air and ocean water compiled by T. Bidleman of the Atmospheric Environment Service. Figure 5 shows latitudinal profiles of total HCH concentrations in water and air. A comparison is difficult because the measured data show a very high variability even on a logarithmic scale. Some of the major features displayed by the measured concentrations are, however, reflected in the model results, namely the relatively uniform air concentrations of HCHs in the Northern hemisphere combined with a significant drop across the equator and the elevated water concentrations at high latitudes of the Northern hemisphere. In general, the calculated concentrations are somewhat higher than the measured ones. An interesting feature revealed in these calculations is that although the bulk of the HCHs does not leave the compartment of initial discharge, concentrations in Arctic and Subarctic ocean water can be higher than in the oceans closer to the current use areas.

With more accurate emission information becoming available through cooperation with Drs. E. Voldner and A. Li from the Atmospheric Environment Service, these simulations of global dispersion behaviour should be improved and extended to other chemicals.

CONCLUSION

The project is proceeding according to plan and we believe that progress has been satisfactory. We have been successful in publishing the results and we are now in contact with the principle scientific groups active in this area. We are increasingly convinced that in addition to the experimental and monitoring programs which identify contaminants and their levels in Arctic ecosystems there is need for a parallel modelling effort to explain and interpret these results. The focus of our continuing work is to improve the models and assure their credibility and usefulness in the context of the Northern Contaminants Program.

Expected project completion date: 1996

REFERENCES

Berger, D., F. Wania and D. Mackay. 1994. Pathways of toxic substances in the Canadian environment. Proceedings of the 6th Conference on Toxic Substances, Montreal, May 10-12, 1994, pp. 279-293.

Mackay, D. and F. Wania. 1994. Transport of contaminants to the Arctic: Partitioning, processes and models. Science of the Total Environment, in press.

Wania, F. and D. Mackay. 1994a. A global distribution model for persistent organic chemicals. Science of the Total Environment, in press.

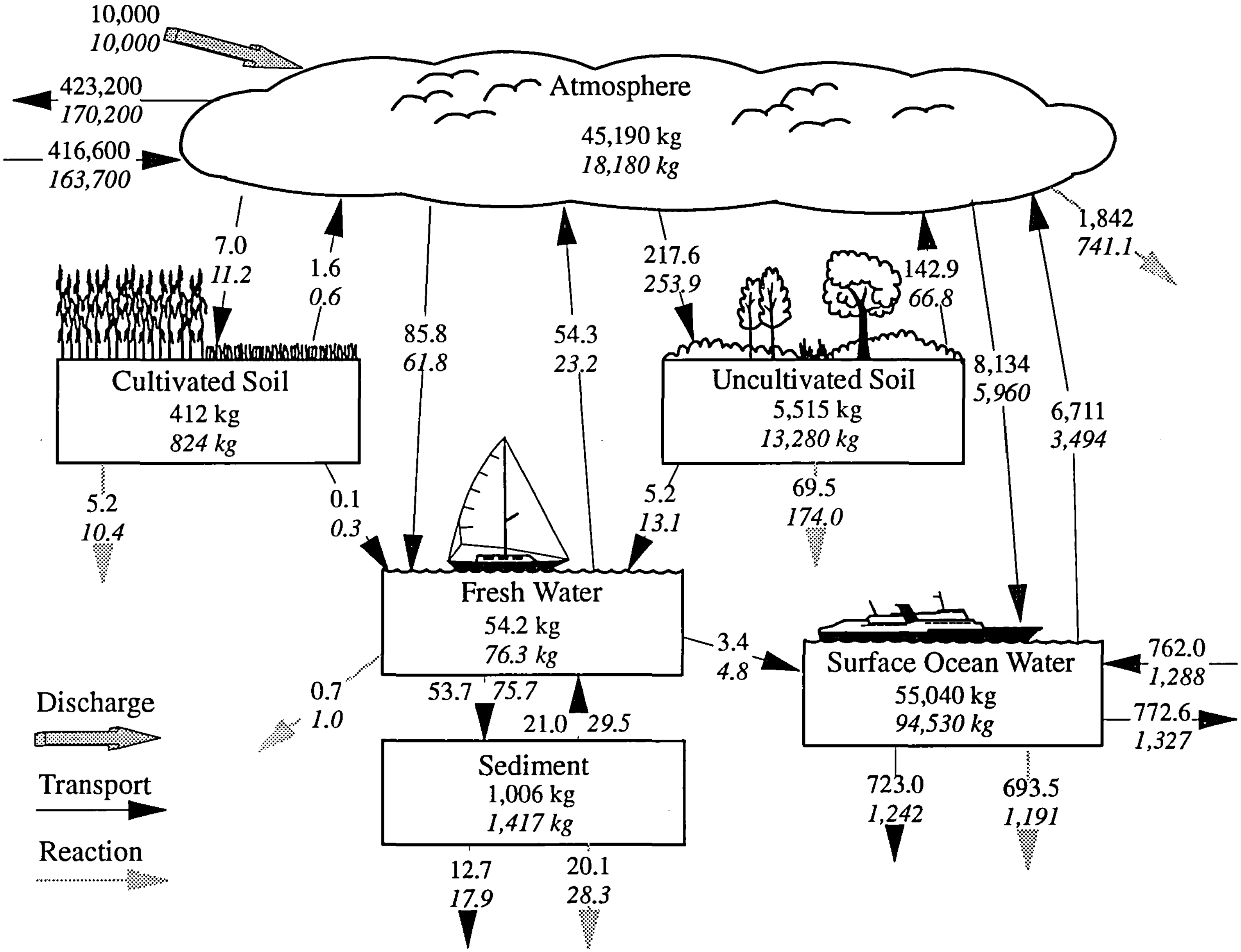


Figure 1: Masses (kg) and mass fluxes (g/h) of HCB in a generic environment at 25 °C and O °C (italics) after prolonged discharge of 10 kg/h into the air compartment. Figure taken from Mackay and Wania, 1994.

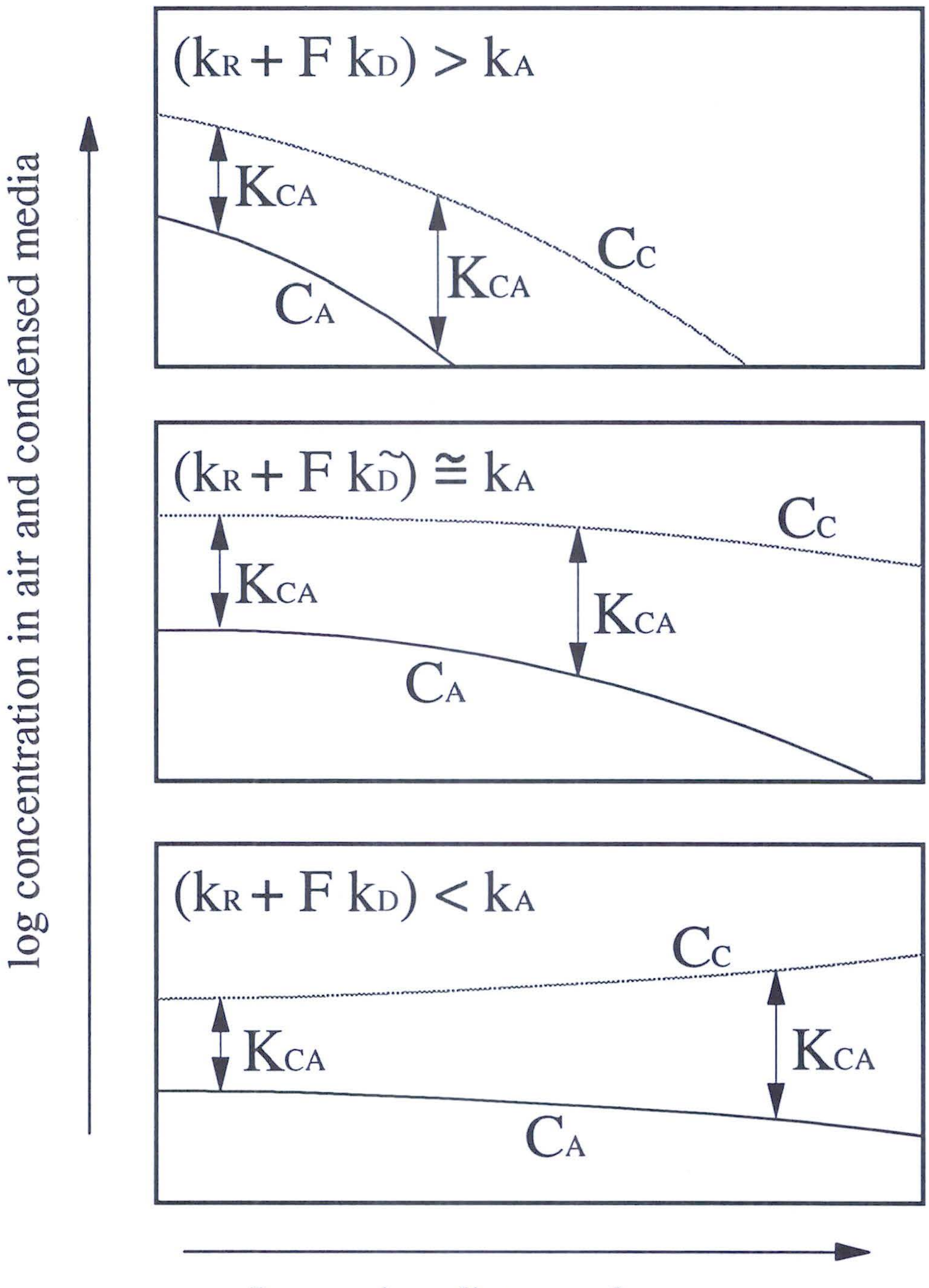


Figure 2: Suggested concentration in air (C_A) and in condensed media (C_C) such as soil as a function of distance from source with lower temperatures at greater distances. Depending on chemical characteristics C_A decreases with different slopes and C_C decreases or increases with distance from source. Figure taken from Mackay and Wania, 1994.

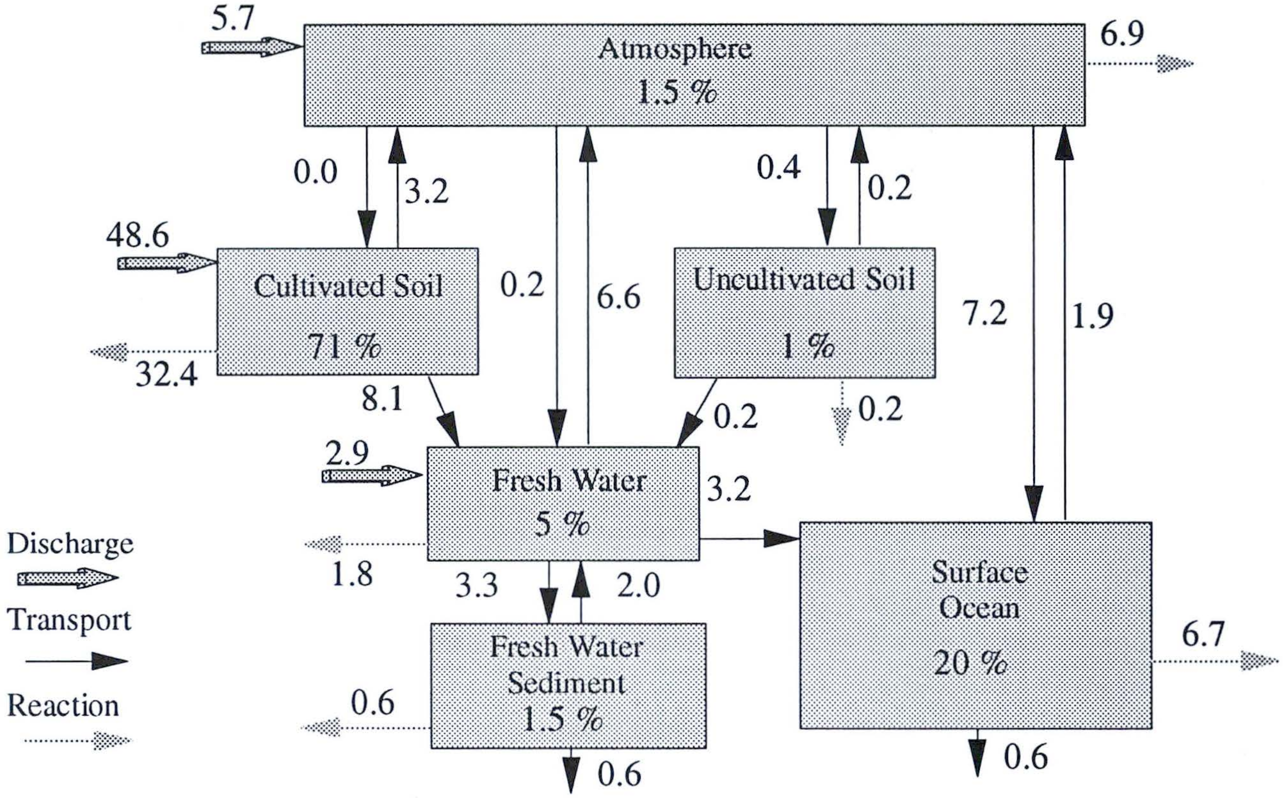


Figure 3: Global mass balance for α-HCH in kt/a calculated for summer 1985 by the global distribution model.

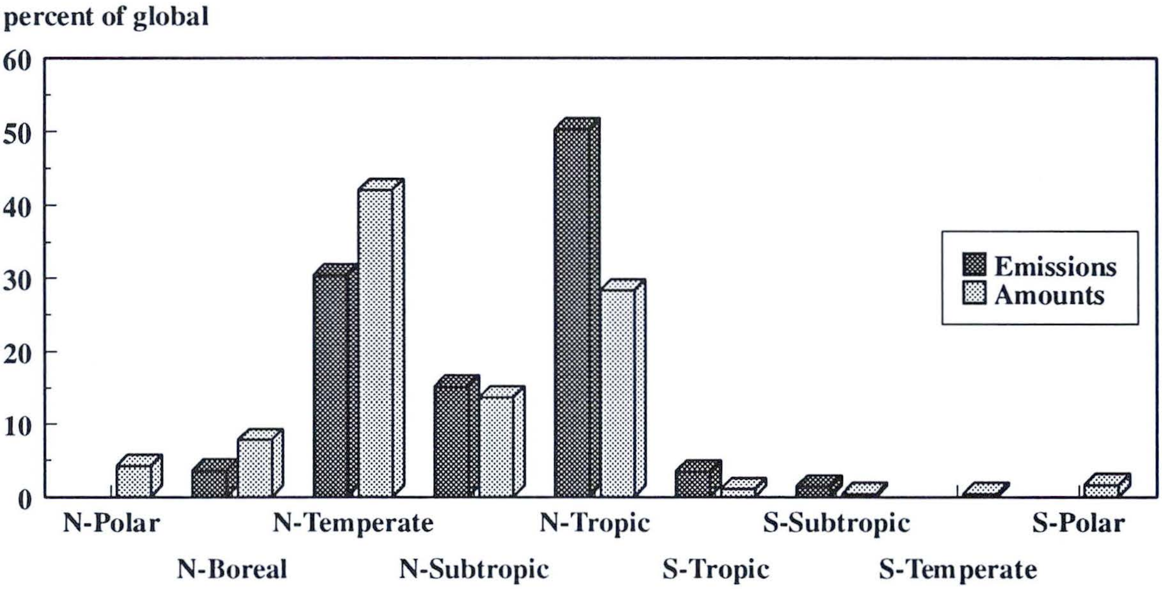


Figure 4: Latitudinal distribution of emissions and total accumulated amounts of α-HCH calculated by the global distribution model for 1985.

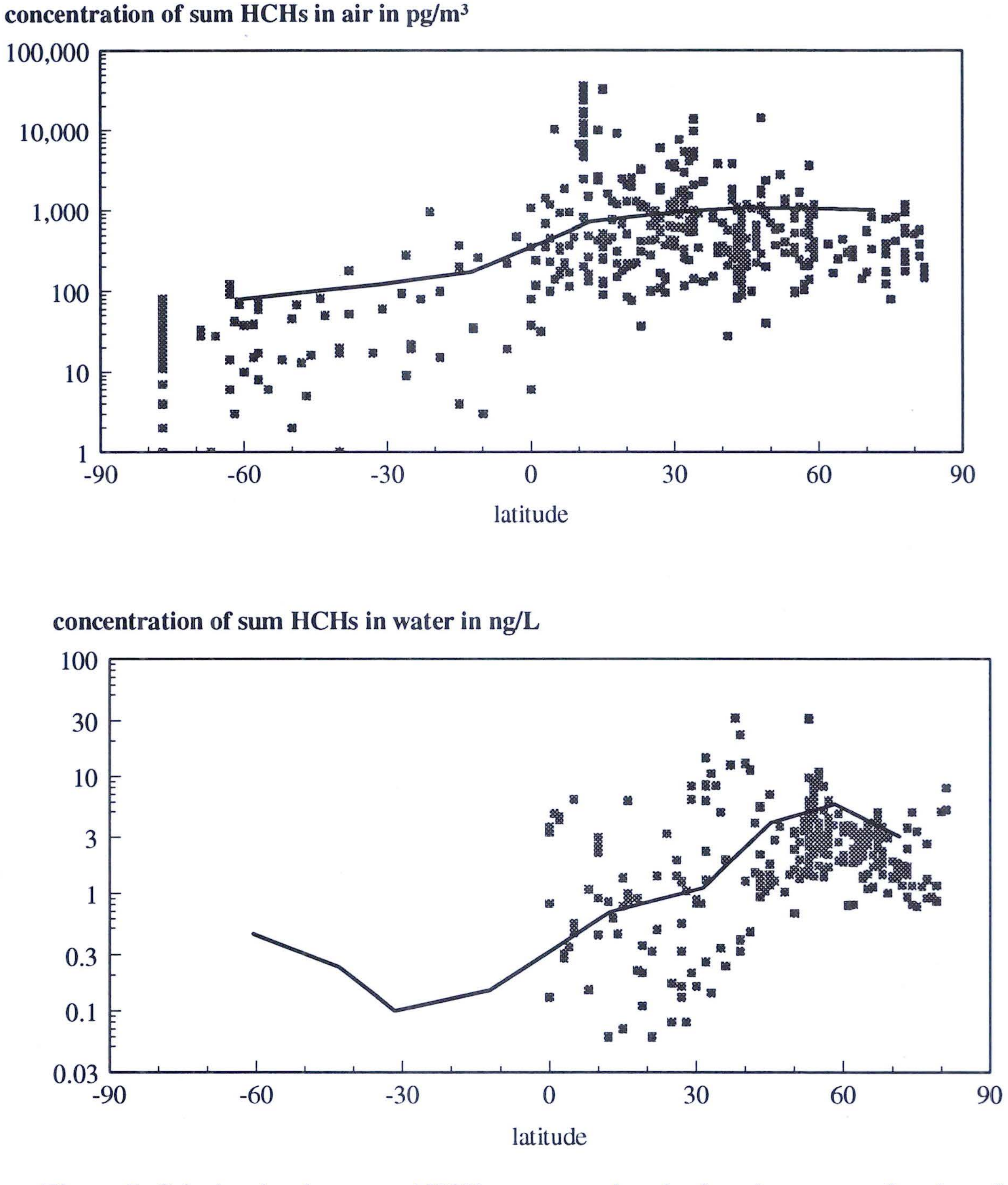


Figure 5: Calculated and measured HCHs concentrations in air and water as a function of latitude. Squares reflect measured data from different time periods compiled from various publications by Dr. T. Bidleman. Calculated profiles reflect the annual average for 1985.

PAST AND PRESENT CONCENTRATION OF CONTAMINANTS IN THE RUSSIAN AND CANADIAN HIGH ARCTIC

PROJECT LEADER: R.M. Koerner, Terrain Sciences Division, Geological Survey of Canada

PROJECT TEAM: J.C. Bourgeois, L. Barrie, V. Cheam, N. Doubleday, D.A. Fisher, D. Gregor, F. Hopper, A. Kudo, G. Lawson, J. Lechner, V. Potapenko, L. Savatyugin, J. Zheng

OBJECTIVES

1. To determine the spatial distribution of various contaminants in the circumpolar High Arctic by analysis of snow samples collected from ice caps in the Russian and Canadian Arctic and from the sea-ice surface of the Arctic Ocean.

2. To determine the temporal variations of the same contaminants between the industrial revolution and the present by the study of ice cores from one Russian and two Canadian ice caps.

DESCRIPTION

It has been known for some time that the Arctic atmosphere carries anthropogenic pollutants 'over the top' from industries based in Europe and the Russian part of Arctic Asia. Direct sampling of the atmosphere has been, and is used to measure the level of the pollutants. The number of Arctic sites is necessarily limited so that this project aims to fill in the gaps by measuring the concentrations of pollutants in the Arctic snow cover (representing the August to May winter period), thereby defining the pollutant pathways and sinks more precisely. Pollutant trends have already been developed by ice core analysis from an ice cap in northern Ellesmere Island. This work showed the dramatic increase of acid pollutants that occurred in the 1950s (Koerner and Fisher 1982, Barrie *et al.* 1985). Our knowledge of air mass trajectories in the Canadian Arctic has also been improved as a result of studies of pollen grain concentrations in snow from various sites (Bourgeois *et al.* 1985). The specific objectives for 1993/94 were to collect snow samples to measure the concentrations of major ions (Koerner), organochlorines (Gregor), black carbon particles (Hopper, Doubleday), pollen grains (Bourgeois), radionuclides (Kudo), stable isotopes (Fisher) and trace metals (Lawson, Cheam, Lechner, Zheng).

ACTIVITIES IN 1993/94

Sample collection

In March, April and May 1993, in conjunction with other field programs of the glaciology section of Terrain Sciences Division (Geological Survey of Canada), snow/ice samples were collected from four ice caps in the Queen Elizabeth Islands of the NWT, from one ice cap (Academii Nauk) in the Russian Arctic, and from the Arctic Ocean sea-ice snowcover between Russia and Canada.

Equipment and containers used for major ion and microparticle sample collection were pre-cleaned in the laboratory using 41 MegOhm, filtered water. The scoop used in sample collection was cleaned in the same manner and was additionally thrust into clean snow pit walls several times immediately before being used in the field. Laboratory tests of blanks showed that commercially available plastic bags ('whirlpaks') are sufficiently clean for sample collection without our pre-treatment. Containers for black carbon particle analysis (Hopper) were precleaned at the Atmospheric Environment Service (AES) laboratories and those for trace metal analysis (Lawson, Cheam, Lechner, Zheng) were specially prepared with ultra-clean nitric acids in the clean room at Natural Resources Canada (NRCan). Containers for organochlorines were prepared according to protocols described elsewhere (Gregor, this volume).

Trace metals were analysed at Canada Centre for Inland Waters - cadmium and zinc in a graphite furnace atomic absorption spectrophotometer (GFAAS), and lead in a graphite furnace laser excited atomic fluorescence spectrophotometer. Major ions were analysed at the Geological Survey of Canada (GSC), negative ions on a Dionex ion chromatograph and positive ions on a GFAAS. Methodology for organochlorine analysis appears in Gregor (this volume). Pollen grain analysis is described in Bourgeois *et al.* (1985). Other analyses still not completed at time of writing are not described here.

Most samples were collected by scooping snow into containers from several levels in the current annual snow layer. The sequence allowed identification of the spring layer where concentrations are highest. Trace metal samples were collected in two different ways. Firstly, surface samples were collected by scraping away the top 2-3 mm of snow, possibly contaminated by the helicopter/fixed wing aircraft delivering us to the site, and then pushing an opened container into the surface snow and walking it just below the surface, into the direction of the wind. Secondly, a sample was collected at most sites from the autumn to mid-winter snow using the same scoop used for major ion sample collection. Pollen and radionuclide samples were collected by shovelling snow into clean plastic bags. In the case of sample collection for organochlorines, both shovel and metal container were pre-cleaned with acetone and hexane. Pit dimensions were measured to determine the flux of organochlorines, radionuclides and pollen. In all other cases fluxes will be based on snow depth and density measurements made at each site.

Large volume snow samples were collected at each of the 6 sites comprising the transect from Dixon Island, Russia, through the North Pole and then south into Canadian territory at 86° N. Also compared here are triplicate large volume snow samples from the surface snow layer of the Agassiz Ice Cap as collected in May 1993. All samples were collected in pre-cleaned snow cases and returned to Resolute Bay for extraction. Subsequent analyses were performed at the National Water Research Institute (NWRI) laboratories with procedures and quality assurance protocols as per other sampling programs such as the Agassiz Ice Cap study.

Logistics

All samples at the Canadian sites were collected while on glacier mass balance traverses using snowmobile transport from tent camps. Polar Continental Shelf Project (GSC, NRCan) provided Twin Otter support. For the Russian/Arctic Ocean collection, logistics were arranged with a tourist organisation 'CenterPol', that runs North Pole tourist ventures. A charter aircraft was used between Ryazan (just south of Moscow) and Dikson. Beyond that all air transport was by helicopter. The GSC party camped on Academii Nauk ice cap for 5 days with two scientists from the Arctic and Antarctic Institute (St. Petersburg, Russia). During this time, surface snow samples and ice core samples covering 4 years of accumulation were collected. Sites to the North Pole were sampled during the one hour that the helicopters took to transfer fuel. A tent camp was made for 3 days at the North Pole when further sampling was done. Evacuation to Canada was effected by a PCSP Twin Otter stopping at one sampling site en route. A total of six sites were sampled outside of Canada.

RESULTS

Major ions

Analyses have been completed for the Agassiz, Melville, Meighen, Devon and Academii Nauk sites. A preliminary look at the results show fluxes up to 4 times higher on the Russian side. Sulphate and nitrate concentrations are consistently higher down through the snow pack on the Russian ice cap (Fig. 1). However, sulphate concentrations in the surface snow are very high on both ice caps and may be due to fallout of stratospheric volcanic acid aerosols from the Pinatubo eruption the previous year.

A suite of samples from a 2.5 m core, representing 4 years of accumulation, was taken from the Academii Nauk ice cap (the first site north of the Russian mainland, Figs. 2-4). Concentrations of both marine- and industrial-source aerosols are high but a seasonal resolution is not evident due to the high degree of melting each summer. While melting does not alter the overall concentration it can eliminate the chance of deriving a year by year record of pollutant influx from Russian sources. Further work in 1994 will define the resolution that may be achieved at this location.

Pollen

Snow samples (30 kg) were collected at each site. On Academii Nauk, samples were collected from 4 separate layers in the annual snow component. All of these samples have been reduced to slides and the pollen and types, counted. A remarkably high influx of pine pollen to the 86°N 95°E site (Fig. 2) indicates that episodic influxes along very narrow transport paths may play an important role in the transport of both natural and industrial pollutants.

Radionuclides

Snow samples (10 kg) were collected at each site and have been partly analysed at NRCan. Concentrations (Fig. 3) are higher on the Russian side of the Arctic Ocean (the highest concentration is from tap water at the Siberian coastal town of Dikson). However, the measurements show a drop to very low concentrations by the North Pole.

Organochlorines

PCB concentrations are comparable at all seven sites except for the very high concentrations of 8, 9 and 10 chlorinated homologs at the 84 and 86° N position on the Russian side (Fig. 4). We have no explanation for this phenomenon at this time without further sampling. The presence of these relatively heavy PCBs would normally suggest a proximity to a source as these are generally scavenged from the atmosphere close to the source.

Several chlorinated pesticides are detected in these samples. Three hexachlorocyclohexanes are consistently detected. Generally, the concentrations of lindane (γ-HCH) and β-HCH in the transect sites exceed those measured at the Agassiz Ice Cap (Fig. 5a) perhaps suggesting closer proximity to use areas and less opportunity for degradation of lindane to α-HCH within the atmosphere. Concentrations at all sites for heptachlor epoxide, α-endosulfan, α-chlordane and dieldrin are compared in Figure 5b with no clear spatial pattern evident. As illustrated in Figure 5c, heptachlor, the parent compound of heptachlor epoxide, was detected only at the Dixon Island site, suggesting a source vector for this compound. The concentrations of *trans*-nonachlor are all low and the pattern of increasing concentrations along the transect are therefore ambiguous. Both hexachlorobenzene and pentachlorobenzene are similar at all sites.

Trace metals

Concentrations vary between 25.7 and 0.4 pg/g for cadmium, 392.2 and 15.3 pg/g for lead, and 766 and 69 pg/g for zinc. The concentrations are significantly higher in the surface samples, sometimes by a factor of > 10, although the surface sampling technique is probably the cleaner of the two methods used (see above). The higher surface concentrations indicate that, like the major ions, deposition rates reach a maximum in spring. The results for cadmium are shown in Figure 6. They show higher concentrations on the Russian side of the Arctic Ocean with the surprising exception of Dikson. The lead and zinc results (not illustrated here) do not show such a clear pattern which may indicate sample contamination or different sources. High concentrations of all three metals are evident in samples from the Melville South ice cap (Fig. 4). Whether these concentrations are high due to methodological contamination or to an Arctic North American source is not yet known.

DISCUSSION

The results confirm Eurasia as the source of most of the anthropogenic pollutants in the Canadian High Arctic. However, the concentration gradient of the contaminants (e.g. radionuclides) show that some are reduced to very low levels by the time they reach the Canadian side of the Arctic Ocean.

The exceptionally high pine pollen concentrations at one of the sites on the Arctic Ocean (Fig. 2) indicate the importance of high injections of pollutants along narrow pathways. Low concentrations of radionuclides at this site excludes the Dikson/Novaya Zemlya area as a source (and possibly any locations south of this). Analysis of the other pollutant components at this site might allow for a better indication of the source. This site, hopefully, will provide a good example of the value of complete component analysis for source and pathway identification.

Future work will extend the sampling network to include ice caps in the New Siberian Islands and also the Franz Josef Island group. Such a distribution will incorporate the complete pollutant 'gateway' from Eurasia into the sampling net and allow further determination of the main sources.

Additionally, a record of pollutant influx covering the entire pre-industrial to present period should be gathered from ice cores from Agassiz (N. Ellesmere Island), Penny (S. Baffin Island) and Academii Nauk (Russia) ice caps. Together with results already published from Greenland, these cores will give a clear picture of how pollutants have changed from 'normal' background levels to present-day 'polluted' levels.

Further definition of source trajectories for PCBs and chlorinated pesticides across the pole would require more intensive sampling and these preliminary data indicate that efforts in this direction would be worthwhile.

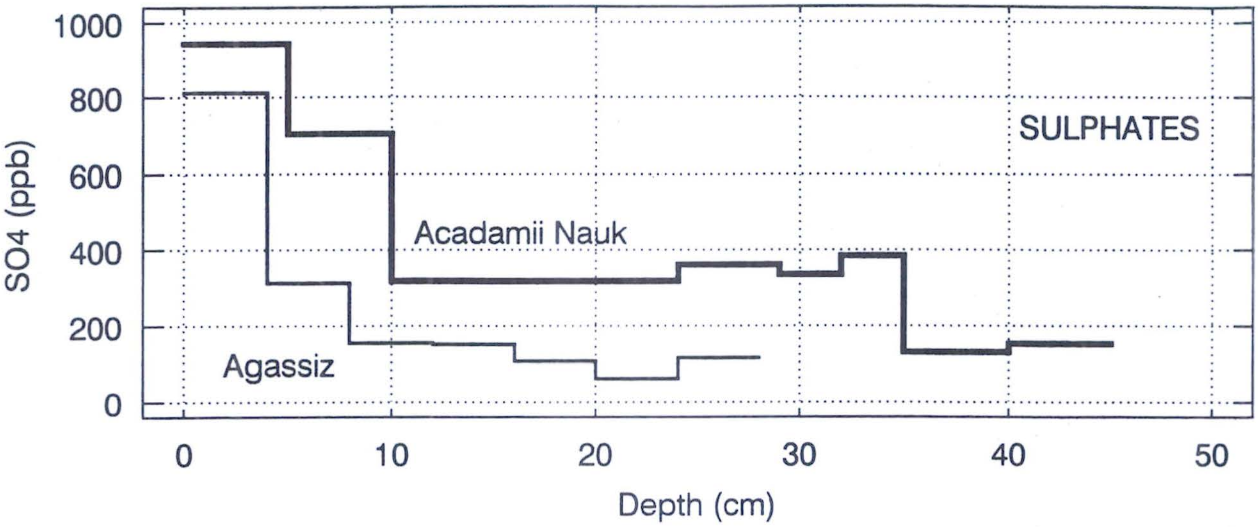
Expected project completion date: August 1997

REFERENCES

Barrie, L.A., D.A. Fisher, and R.M. Koerner. 1985. Twentieth Century trends in Arctic air pollution revealed by conductivity and acidity observations in snow and ice in the Canadian High Arctic. Atmospheric Environment 19(12): 2055-2063.

Bourgeois, J.C., R.M. Koerner and B.T. Alt. 1985. Airborne pollen: a unique air mass tracer, its influx to the High Arctic. Annals of Glaciology 7: 109-116.

Koerner, R.M. and D.A. Fisher. 1982. Acid snow in the Canadian High Arctic. Nature 295: (5845): 137-140.



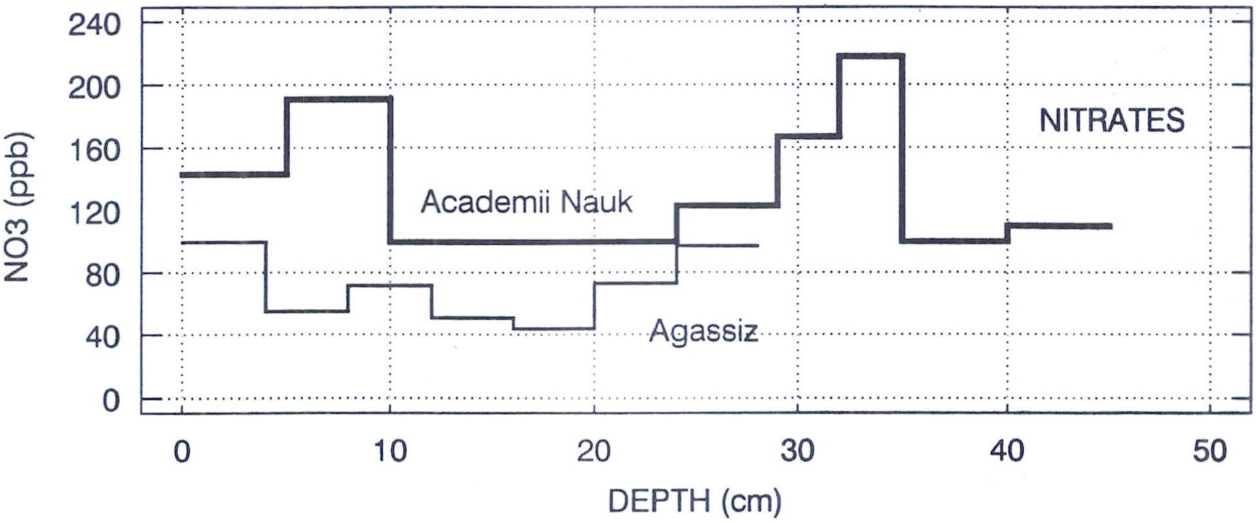


Figure 1. Concentration of sulphates and nitrates in the surface annual snow layer of Agassiz and Academii Nauk ice caps, April 1993.

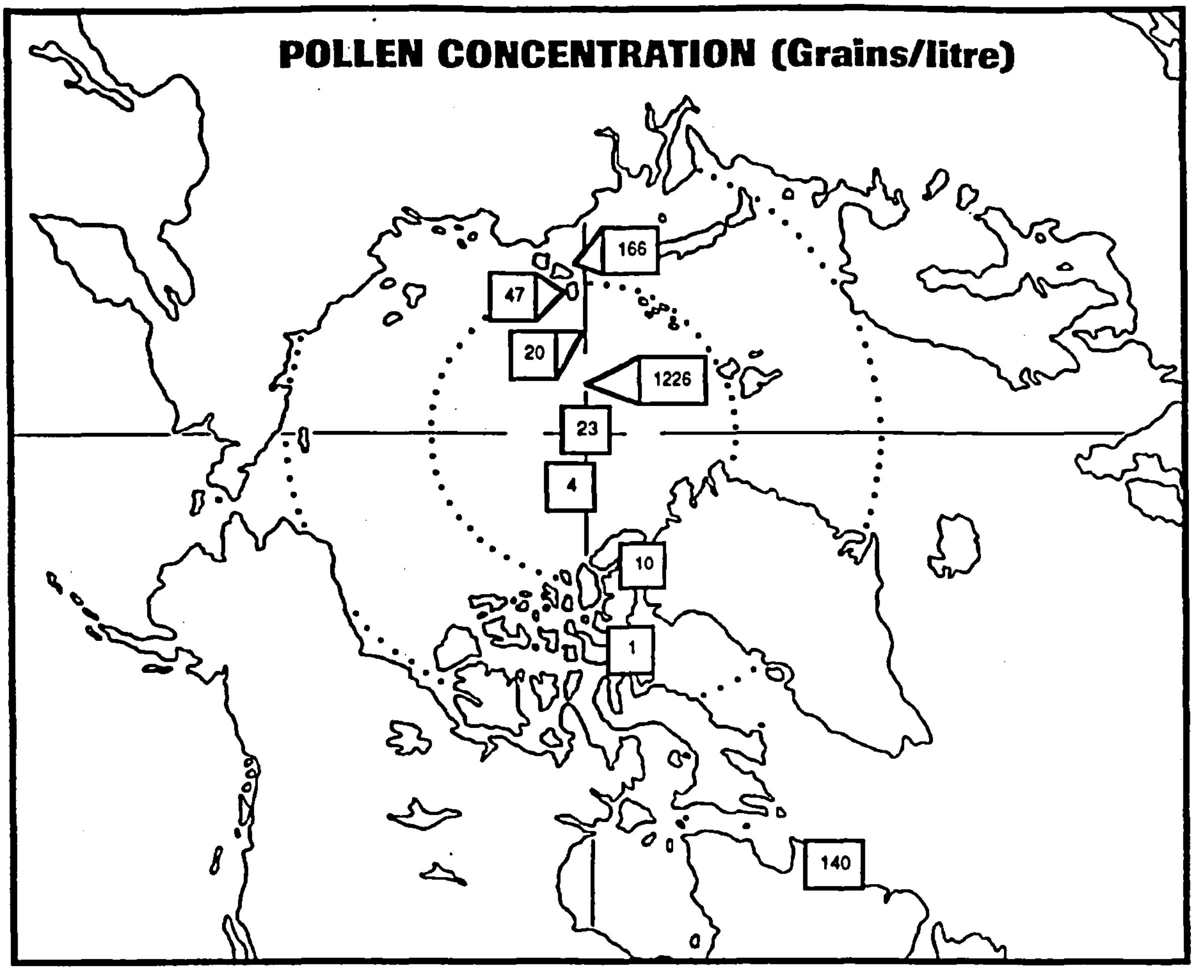


Figure 2. Pollen concentrations in the surface snow layer, April/May 1993.

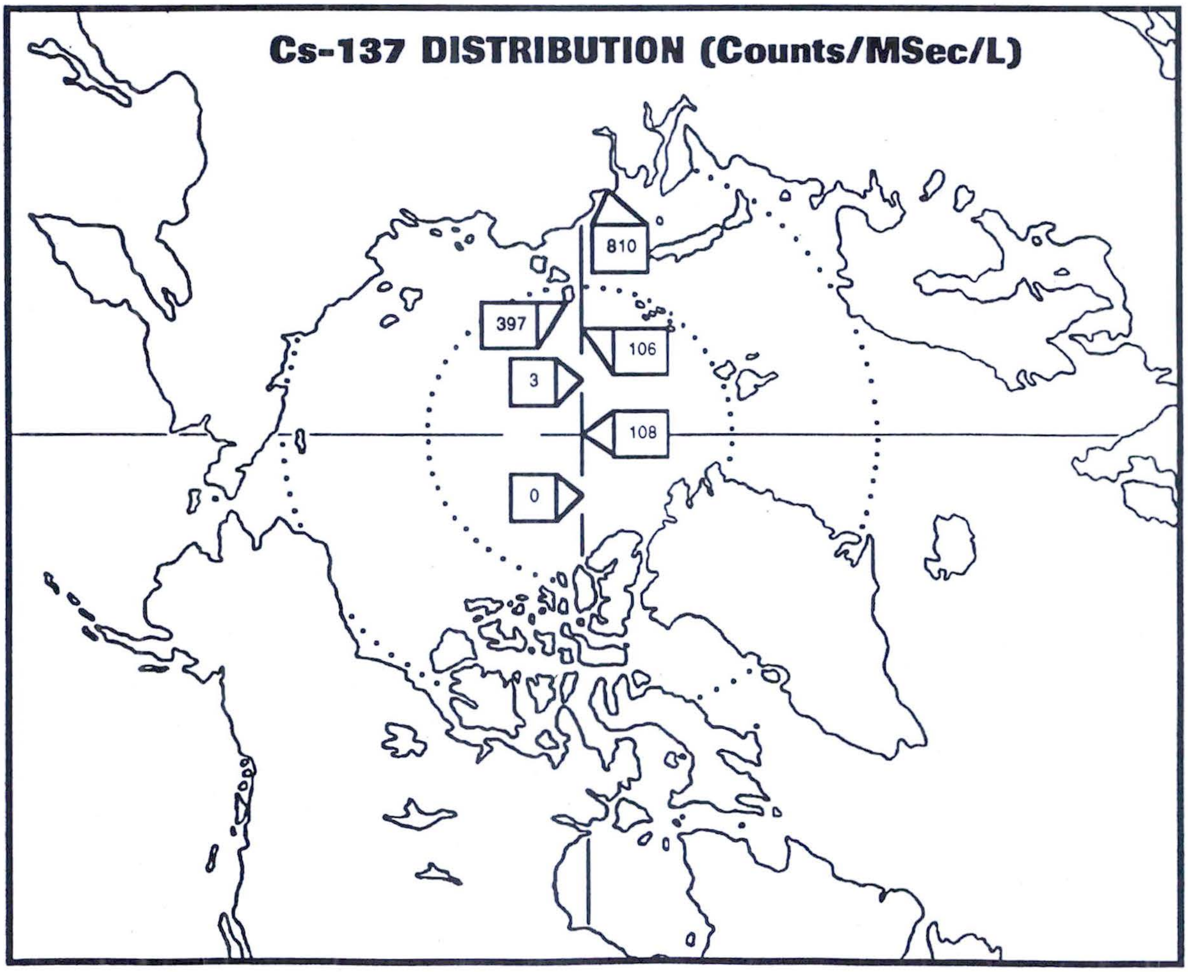


Figure 3. ^{137}Cs distribution in the surface annual layer, April/May 1993. These are preliminary values.

Figure 4. Comparison of PCB homolog concentrations in large volume snow samples collected during the polar transect from Dixon Island, Russia to 86°N plus the Agassiz Ice Cap at 80°N, April/May 1993.

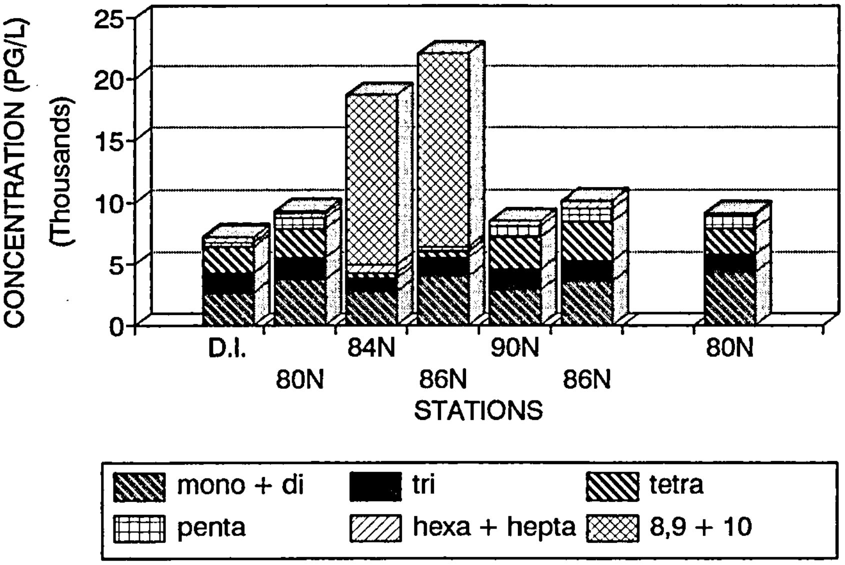


Figure 5a. Comparison of hexachlorocyclohexane concentrations in large volume snow samples collected during the polar transect from Dixon Island, Russia to 86°N plus the Agassiz Ice Cap at 80°N, April/May 1993.

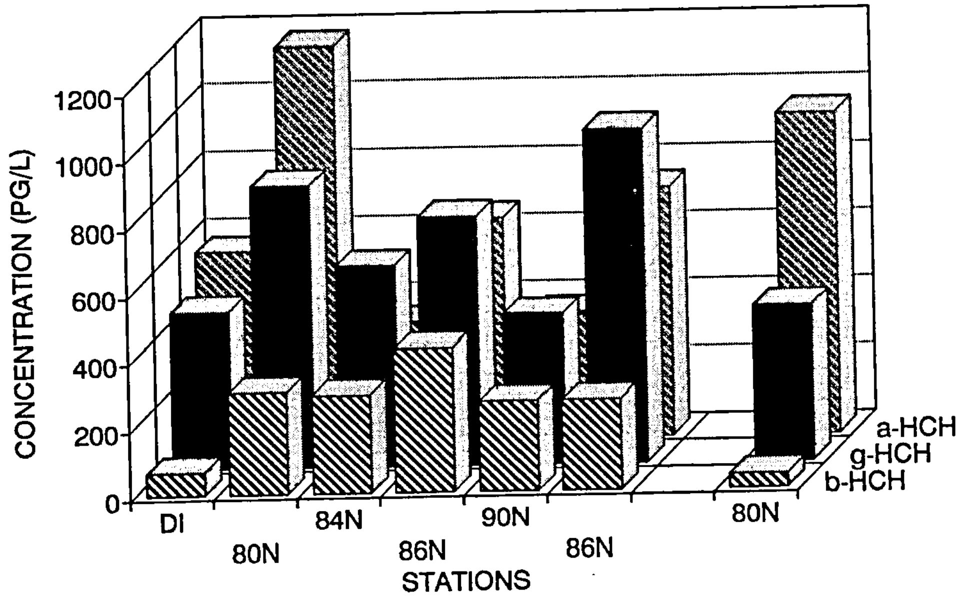


Figure 5b. Comparison of concentrations of heptachlor epoxide (H-epoxide), α-endosulfan (a-endosulf), α-chlordane (a-chlordan) and dieldrin in large volume snow samples collected during the polar transect from Dixon Island, Russia to 86°N plus the Agassiz Ice Cap at 80°N, April/May 1993.

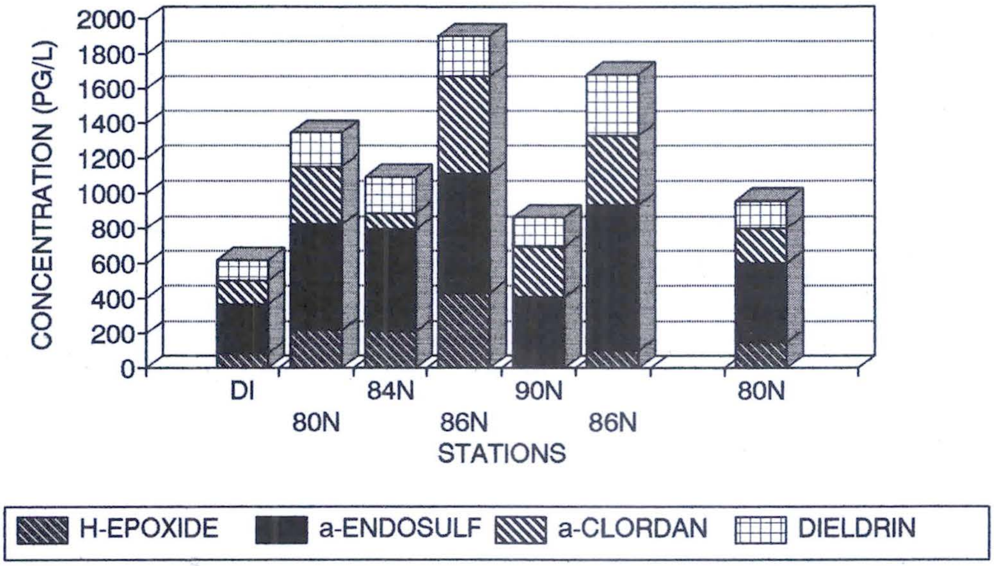
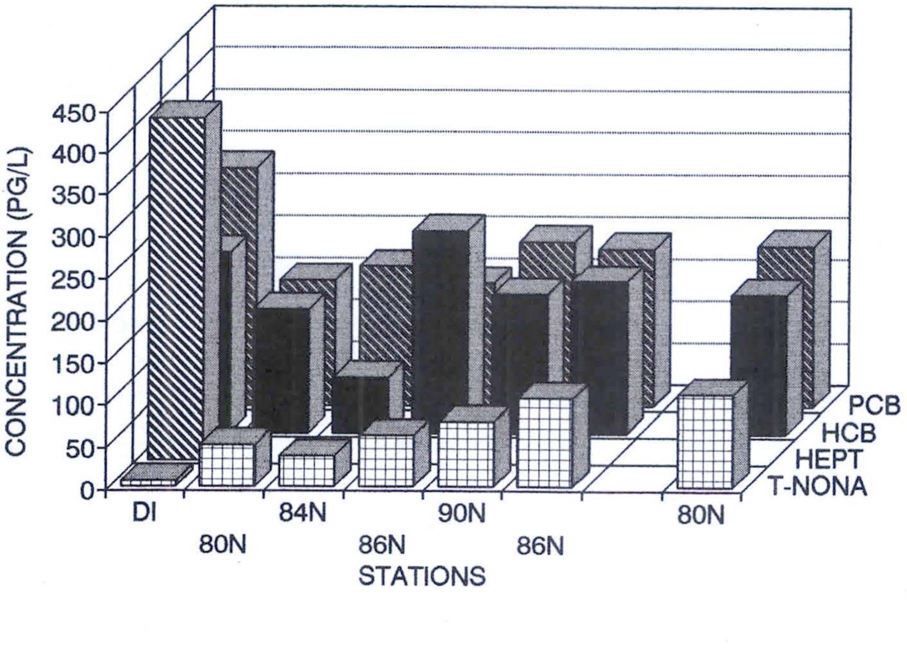


Figure 5c. Comparison of concentrations of trans-nonachlor (t-nona), heptachlor (hept), hexachlorobenzene (HCB) and pentachlorobenzene (PCB) in large volume snow samples collected during the polar transect from Dixon Island, Russia to 86°N plus the Agassiz Ice Cap at 80°N, April/May 1993.



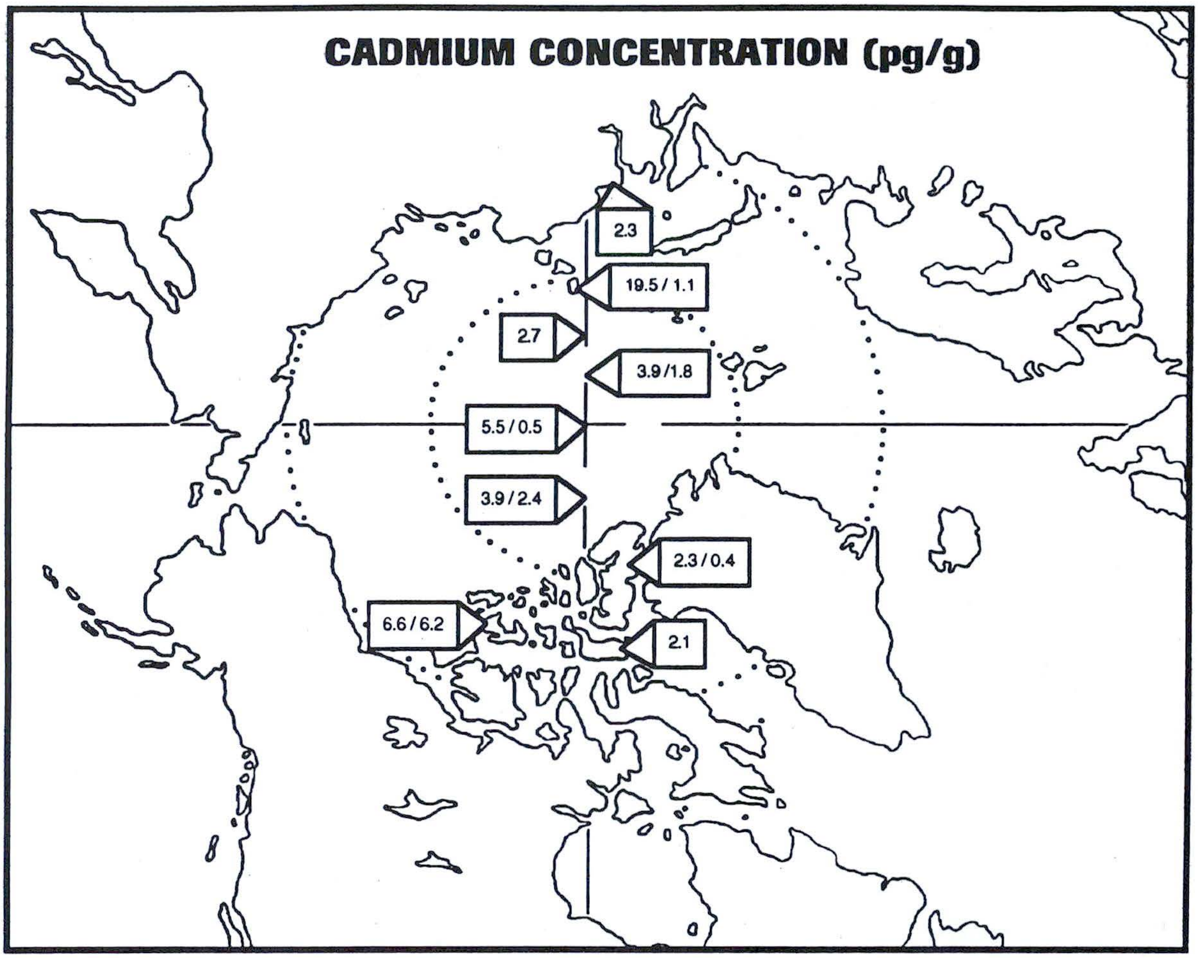


Figure 6. Cadmium concentrations (pg/g). A single value for a site represents the mean value for the August to April/May surface (unmelted) snow layer. Where two values for a site are shown, the first represents a sample collected close to the surface after a cm of snow was scraped from the surface with a PTFE scraper. The second value represents snow collected between the surface layer and the underlying or summer melt sea-ice surface.

THE HISTORICAL RECORD OF PERSISTENT ORGANIC POLLUTANTS AND TRACE METALS IN GLACIAL SNOW/ICE

PROJECT LEADER: D.J. Gregor, University of Waterloo

PROJECT TEAM: R.M. Koerner, D. Fisher, J. Bourgeois, Natural Resources Canada; J. Nriagu, M. Alaee, A. Peters, G. Lawson, N. Jones, National Water Research Institute (NWRI); N. Doubleday, Queen's University

OBJECTIVES

1. To quantify annual residue trends and historical deposition trends of trace organic contaminants and metals in arctic ice caps.

2. To quantify annual variability of deposition of these compounds as a result of variable atmospheric conditions.

3. To determine the major processes controlling the fate of these contaminants in glaciers that could influence the deposition trend including re-volatilization to the atmosphere, transfer between annual layers by gas transfer and melt water and photochemical degradation within the snow layers.

DESCRIPTION

Past work on concentrations of organic contaminants in snow, including the ice caps, has been questioned because this work has previously demonstrated that certain compounds will revolatilize from shallow snow packs. We now know that this is less important for deep snow packs and that the degree of re-volatilization depends on the physicochemical properties of the compound. This information from the Arctic has re-initiated discussion on the cold condensation of low volatile organic compounds in polar regions (Wania and Mackay 1993). Furthermore, recent evidence from studies of agricultural soils in England corroborate indirectly Agassiz Ice Cap findings regarding PCBs. The UK study showed that concentrations in these soils have decreased since a peak in the early 1970s with a move toward greater proportions of the heavier homolog groups (Jones *et al.* 1992, Alcock *et al.* 1993). Where have these PCBs gone? Wania and Mackay suggest that many have probably moved to the Arctic. If the UK situation is typical of Eurasia and North America, an estimated 90 to 95% of PCBs in soils has revolatilized between the 1970s and present day, and it is therefore unreasonable to expect a decline in deposition of PCBs deposited in the Arctic over the past 20 years. Add to this the fact that use in many Eurasian countries has continued past 1970, and the result may be that we may not see a decrease in arctic deposition for some time to come. The ice cap record is the only foreseeable means of effectively monitoring trends of deposition of these contaminants well before they are evidenced in lake sediments and freshwater and marine biota. Additionally, it may be possible to obtain an understanding of the lag time that we can expect in the Canadian Arctic to reduced supply in temperate areas by comparing the initial deposition curve of the ice cap to known information for the supply.

The rationale above applies to PCBs. We also anticipate that temporal trends can be determined for PAHs, toxaphene, the most abundant organochlorine in arctic marine mammals and fish, and selected metals. At the present time we are unable to confidently investigate trends for more volatile OCs such as HCH as we do not understand the factors that control revolatilization sufficiently. For these compounds we will have to be satisfied with residue trends in the ice cap which may eventually be related to deposition.

ACTIVITIES

Methods

In March and May of 1993 an intensive sampling effort was undertaken. Extensive support of the order of $50K was provided by the Polar Continental Shelf Project (PCSP) to cover approximately two thirds of the aircraft charter costs incurred. Through the excavation of an 8.3 m pit into the ice cap, a total of thirty years were sampled in detail for PCBs, PAHs, elemental carbon, toxaphene and other OCs. Selected samples were collected in a special pit for trace metal analyses.

Metal analyses are continuing. To date the Cd data have been published in Nriagu *et al.* (1994). The toxaphene samples remain in storage until extraction procedures have been further refined to improve recoveries. Some of the elemental carbon work has been completed but not all. Two papers, one on PCBs and one on PAHs and elemental carbon, were presented at a Symposium in Iceland in November 1993 and these papers have been accepted for publication in the proceedings (Gregor *et al.* in press, Peters *et al.* in press). Highlights of these two papers are presented here.

The sampling site was located 1.7 km north of the semi-permanent field camp. The snow was excavated manually and lifted to the surface using a battery powered winch. Annual layers were identified on the basis of visual inspection of the firn, the presence of ice layers, plus the conductivity profile in the snow determined from subsamples down the face of the wall at approximately 2 cm intervals and measured at the field camp at 0 °C as outlined in Gregor *et al.* (in press). Samples were collected using a stainless steel shovel that had been rinsed with high purity acetone and hexane. Annually integrated samples were placed into custom made aluminum snow cases that were also rinsed with high purity acetone and hexane at the sampling site. These samples were collected for the analysis of PCBs, organochlorine pesticides and for PAHs.

The snow is melted inside the sealed sampling cases at the field camp in a circulating water bath maintained at 17 °C. The melt water is extracted with a Goulden Large Volume Extractor (GLVE) (Goulden and Anthony 1985, Neilson *et al.* 1988). The flow rate in the GLVE is 250 $ml \cdot min^{-1}$ and the extraction solvent is dichloromethane (DCM). The GLVE is thoroughly cleaned with high purity acetone and hexane between each sample. The initial 150 ml of DCM added to the GLVE is spiked with 60 ng of 2,3,4,5-tetrachlorobiphenyl (PCB #70). Makeup DCM, metered into the GLVE at a nominal rate of 3 $ml \cdot min^{-1}$, is further spiked with 10 ng δ-HCH and 20.32 ng 1,3,5-tribromobenzene in methanol. The DCM is placed in pre-cleaned bottles which are sealed and kept refrigerated during shipment to, and storage at, the analytical laboratory. Finally, the volume of water extracted is measured and recorded. Sample volumes ranged from 14.8 to 20 L of meltwater.

The sample extract is allowed to reach room temperature prior to processing generally following the procedure developed at Environment Canada's National Water Quality Laboratory (Anonymous 1987). Thereafter, excess water is removed by passing the sample through anhydrous Na_2SO_4 in an Alihn filter funnel. A 20 ml volume of DCM is then passed through the Na_2SO_4 with gentle suction. The sample is then spiked with 56.52 ng of 1,3-dibromobenzene and reduced to approximately 5 ml by reduced pressure rotary evaporation at 30 °C. Following solvent exchange with hexane and base wash with 0.1 M K_2CO_3 (aq) the extract is again passed through Na_2SO_4 with three 5 ml hexane rinses. Subsequently the sample is spiked with 40 ng of 2,3,5,6-tetrachlorobiphenyl (PCB #65) and 235 ng of perthane prior to concentration by reduced pressure rotary evaporation to approximately 2 ml. This concentrate is applied to a silica gel column prepared with 10 g of 60-mesh silica gel, fully activated at 500 °C for 12 hours. The sample is eluted to obtain four fractions - F1: 80 ml hexane; F2: 85 ml 35% (v/v) DCM in hexane; F3: 85 ml 60% (v/v) DCM in hexane; and F4: 50 ml DCM followed by 50 ml MeOH. Each fraction is then spiked with 65 ng of octachloronaphthalene (OCN) and concentrated by reduced pressure rotary evaporation to approximately 2 ml, solvent exchanged to iso-octane and finally concentrated to 1.0 ml under a nitrogen stream. The solvent is then transferred to vials and stored at 4 °C until analyses.

Samples are analysed with a HP 5890 Gas Chromatograph equipped with dual ECD detectors. The two 30 m x 0.25 mm fused silica columns are SPB1 (polydimethyl siloxane) and SPB5 (5% phenyl and 95% methyl polysiloxane) (listed as Supelco products) with a phase thickness of 0.25 μm. The sample is injected using an autosampler in splitless mode with a time delay of 0.5 min, after which the injector purged. An initial oven temperature of 80 °C is maintained for 2 min, increasing at 4 $°C \cdot min^{-1}$ to a maximum of 280 °C and holding for 12 min. Injector and detector temperatures are 220 °C and 350 °C, respectively. The carrier gas is helium at 1.0 $ml \cdot min^{-1}$ with nitrogen as the makeup gas at 30 $Ml \cdot min^{-1}$.

Quality Assurance

Mean recovery of the initial DCM spike (2,3,4,5-tetrachlorobiphenyl) is 89%. Mean recoveries for δ-HCH and 1,3,5-tribromobenzene, added during the field extraction are 107% and 46%, respectively. 1,3-dibromobenzene, 2,3,5,6-tetrachlorobiphenyl and perthane, spiked during the cleanup and fractionation procedures, have mean recoveries of 46%, 90% and 125%, respectively. Mean recovery of OCN for the 34 samples analysed is 78%. While recoveries of individual compounds are variable, there is good consistency for each compound and no evidence of major methodological problems. All solvents are pre-checked in the laboratory before accepting them. Standards are carefully prepared and rigorously confirmed through a routine NWRI quality assurance (QA) protocol. The laboratory also participates in the Arctic Environmental Strategy QA program.

A total of 67 PCB congeners were analysed in this study. Of these, only six congeners (5,7,8,16,52,54) were present in the background corrected field blanks at significant concentrations and these have not been included in this analysis. A total of 60 PCB congeners are considered to comprise ΣPCB.

RESULTS

PCB concentrations in the firn can vary for a number of reasons and thus temporal trends of contaminant fluxes may be more informative. The annual flux of PCBs to the ice cap is a function of the concentration, snow thickness and water content of the annual layer. The annual fluxes over the period of record for the PCB homologs are shown in Figure 1. Mean annual ΣPCB deposition to the ice cap over the 30 years is 406 (± 187) $ng \cdot m^{-2} \cdot a^{-1}$. The maximum estimated deposition for the period of record was 930 $ng \cdot m^{-2} \cdot a^{-1}$ in 1967/68. The general temporal pattern of deposition is a period of high deposition prior to 1968/69, in 1968/69 there was a significant decrease in deposition followed by a slow, consistent increase until 1979/80 when a further decrease in deposition occurred with the period of record minimum of 91 $ng \cdot m^{-2} \cdot a^{-1}$ in 1980/81. Subsequently, ΣPCB deposition has again risen with a local maximum of 848 $ng \cdot m^{-2} \cdot a^{-1}$ in 1989/90. The mean annual flux for the last three years of record (1990/91, 1991/92 and 1992/93) is 465 $ng \cdot m^{-2} \cdot a^{-1}$ which is not significantly different but moderately higher than the period of record mean flux (406 $ng \cdot m^{-2} \cdot a^{-1}$), indicating the absence of any overall temporal trend.

In contrast, Peters *et al.* (in press) indicate that ΣPAH deposition at this site has decreased over the period of record (Figure 2). ΣPAH deposition has remained relatively uniform for the past 20 years at approximately 11 (± 6) $\mu g \cdot m^{-2} \cdot a^{-1}$. This is much lower than the mean annual flux of 74 (± 20) $\mu g \cdot m^{-2} \cdot a^{-1}$ measured between 1963/64 and 1970/71. The major temporary decline in ΣPCB flux occurred in 1967/68, three years before the ΣPAH decline, suggesting that these events were real rather than some unique phenomenon of a particular layer of the ice cap.

Deposition of atmospherically transported, semi-volatile organic contaminants to the ice cap can vary annually for a variety of reasons. For example, the southward extent of the polar front over the continental land masses, which, largely defines the potential source area for these pollutants, can vary. As well, emissions to the atmosphere from sources can be highly variable as can the atmospheric transport and deposition processes. On average, the contributing air shed should not change and thus an observable decrease in deposition to the ice cap would have to result from a major change in emissions. Future work will attempt to normalize these ΣPCB fluxes for source, transport and deposition variability.

Peters *et al.* (in press) note that the PAH flux trend may be indicative of changing global fossil fuel use. Analogously, the PCB data may therefore suggest that there has not been a major change to the PCB availability in the northern hemisphere over the past 30 years. This observation is indirectly supported by recent evidence from studies of agricultural soils in England. The UK study estimated that soil residues have decreased by as much as 90 to 95% since a peak in the early 1970s (Jones *et al.* 1992, Alcock *et al.* 1993). Further, volatilization has been determined to be a major cause of this loss resulting in a shift toward greater proportions of the heavier homolog groups comprising the bulk of PCBs remaining in the soils. If northern hemisphere soils are releasing PCBs, a lag can be expected in a corresponding decline in deposition of PCBs deposited in the Arctic. Add to this, the fact that use in many Eurasian countries has continued past 1970 (Barrie *et al.* 1992) and the result may be that a measurable decrease in arctic PCB deposition will not occur for some time.

Gregor *et al.* (in press) published a 17 year trend of ΣPCB (analyses was by packed column gas chromatography using a 1:1:1 mixture of Aroclor 1242, 1254, and 1260 for quantification) in the Agassiz Ice Cap between 1969/70 and 1986/87. This Aroclor mixture consists largely of PCBs with more than three chlorines and thus a direct comparison is not possible with the ΣPCB data reported here. However, by summing only the congeners with more than three chlorine atoms, it is possible to make a crude comparison of the two sets of data (Figure 3). While there are some similarities between the two sets of data, the most notable differences occur in 1983/84 and 1978/79 when the 1993 data show higher fluxes and for the period 1969/70 through 1973/74 when the flux for the 1987 samples was higher. Even with these differences it is possible to see how this earlier work concluded that PCB deposition to the ice cap was decreasing as the low flux rates for the mid-1980s concur in both cases but it could not be foreseen in 1987 that the minimum deposition was reached in the early 1980s and deposition has continued to increase since that time to near the levels of the early 1960s.

CONCLUSIONS AND UTILIZATION OF RESULTS

ΣPCB flux to the Agassiz Ice Cap on north-central Ellesmere Island, Canada for the last three decades shows no clear, continuing temporal trend due in part to the inter-annual variability. Nevertheless, there is some evidence of a pattern to the deposition. Specifically, deposition was generally higher in the early 1960s with a maximum of 930 $ng \cdot m^{-2} \cdot a^{-1}$ in 1967/68, in 1968/69 there was a significant decrease in deposition which increased slowly and consistently until 1979/80 when a further decrease in deposition occurred with the period of record minimum of 91 $ng \cdot m^{-2} \cdot a^{-1}$ in 1980/81. Subsequently, ΣPCB deposition has again risen with a local maximum of 848 $ng \cdot m^{-2} \cdot a^{-1}$ in 1989/90 and a mean flux for the last three years of 465 $ng \cdot m^{-2} \cdot a^{-1}$ which is moderately higher than the period of record mean of 406 $ng \cdot m^{-2} \cdot a^{-1}$. In contrast, PAHs show a distinct decline over the thirty years considered here which more or less corresponds to reductions in fossil fuel combustion.

The PCBs on the ice cap are dominated by the lower chlorinated homologs which also account for a great deal of the inter-annual variability. A normalization procedure that effectively accounts for interannual deposition variability would be very useful in assessing real trends. This topic needs to be investigated further. Recent reports of PCB volatilization from temperate soils indirectly support this observation in that arctic PCB deposition will considerably lag controls in temperate regions due to the presence of the soil reservoir and ongoing use and/or poor disposal practices in other regions. Determination of the PCB trend in arctic ice caps is complicated by variable source and delivery functions, scouring, and revolatilization. Further, longer term investigation of deposition to ice caps in association with process studies will add to the understanding of long term trends of deposition in the Arctic. These ice cap data will provide the first evidence of a clear and sustained decline in the delivery of organic contaminants to the Arctic. This information will also be very useful in calibrating transport and deposition models when they are further developed.

Expected project completion date: March 31, 1996

PARTNERS

Natural Resources Canada, Glaciology; Polar Continental Shelf Project; Modellers (e.g. Wania and Mackay); Transport/Deposition Modellers (e.g. Atmospheric Environment Service); Arctic Monitoring and Assessment Programme

REFERENCES

Alcock, R.E., A.E. Johnston, S.P. McGrath, M.L. Berrow and K.C. Jones. 1993. Long-term changes in the polychlorinated biphenyl content of United Kingdom soils. Environmental Science and Technology 27(9): 1918-1923.

Anonymous. 1987. Analytical protocol for monitoring ambient water quality at the Niagara-on-the-Lake and Fort Erie stations. Unpublished report. National Water Quality Laboratory, Environment Canada, Canada Centre for Inland Waters, 867 Lakeshore Road, Burlington, Ontario.

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. Science of the Total Environment 122: 1-74.

Goulden, P.D. and D.H.J. Anthony. 1985. Design of a large sample extractor for the determination of organics in water. Unpublished report. National Water Research Institute, Environment Canada, Canada Centre for Inland Waters, 867 Lakeshore Road, Burlington, Ontario. Contribution no. 85-121.

Gregor, D.J., J. Dominik and J.-P. Vernet. In press. Recent trends of selected chlorohydrocarbons in the Agassiz Ice Cap, Ellesmere Island, Canada. *In*: Proceedings of the 8th International Conference of the Comité Arctique International on Global Significance of the Transport and Accumulation of Polychlorinated Hydrocarbons in the Arctic, Oslo, Norway, R. Shearer and A. Bartonova (eds.).

Gregor, D.J., A.J. Peters, C. Teixeira and N. Jones. In press. The historical residue trend of PCBs and selected organochlorine pesticides in the Agassiz Ice Cap, Ellesmere I., Canada. Science of the Total Environment.

Jones, K.C., G. Sanders, S.R. Wild, V. Burnett and A.E. Johnston. 1992. Evidence for a decline of PCBs and PAHs in rural vegetation and air in the United Kingdom. Nature 356: 134-137.

Neilson, M.A., R.J.J. Stevens, J. Biberhofer, P.D. Goulden and D.H.J. Anthony. 1988. A large sample extractor for determining organic contaminants in the Great Lakes. Inland Waters Directorate, Ontario Region, Water Quality Branch, Environment Canada, Burlington, Ontario. Technical Bulletin no. 157.

Nriagu, J.O., G.S. Lawson and D.J. Gregor. 1994. Cadmium concentrations in recent snow and firn layers in the Canadian Arctic. Bull. Environ. Contam. Toxicol. 52: 756-759.

Peters, A.J., D.J. Gregor, C.F. Teixeira, N.P. Jones and C. Spencer. In press. The recent historical depositional trend of polycyclic aromatic hydrocarbons and elemental carbon to the Agassiz Ice Cap, Ellesmere Island, Canada. Science of the Total Environment.

Wania, F. and D. Mackay. 1993. Global fractionation and cold condensation of low volatile organic compounds in polar regions. Ambio 22: 10-18.

Figure 1. The annual fluxes over the period of record for the PCB homologs for the Agassiz Ice Cap.

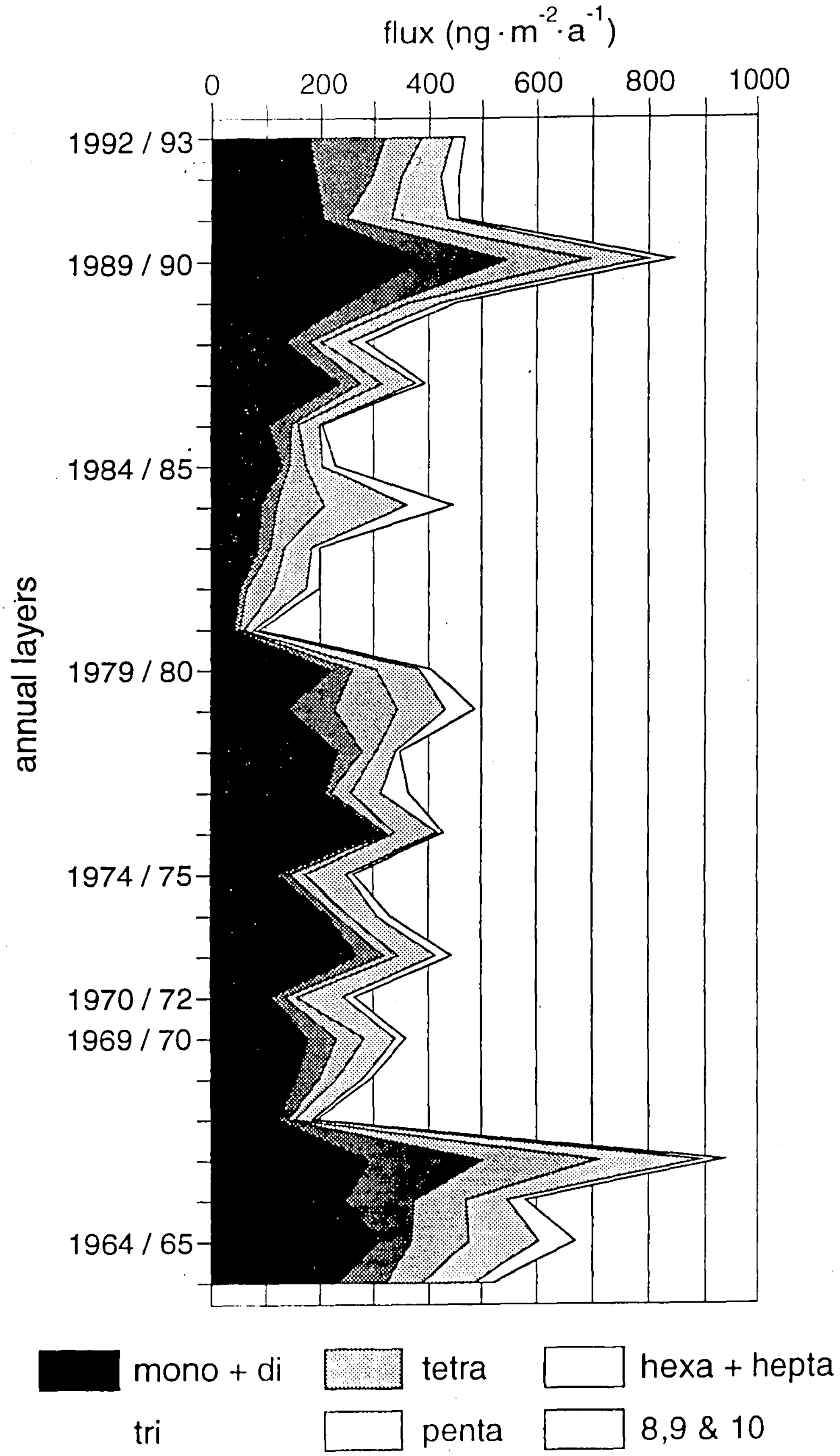


Figure 2. Annual fluxes over the period of record for ΣPAH for the Agassiz Ice Cap.

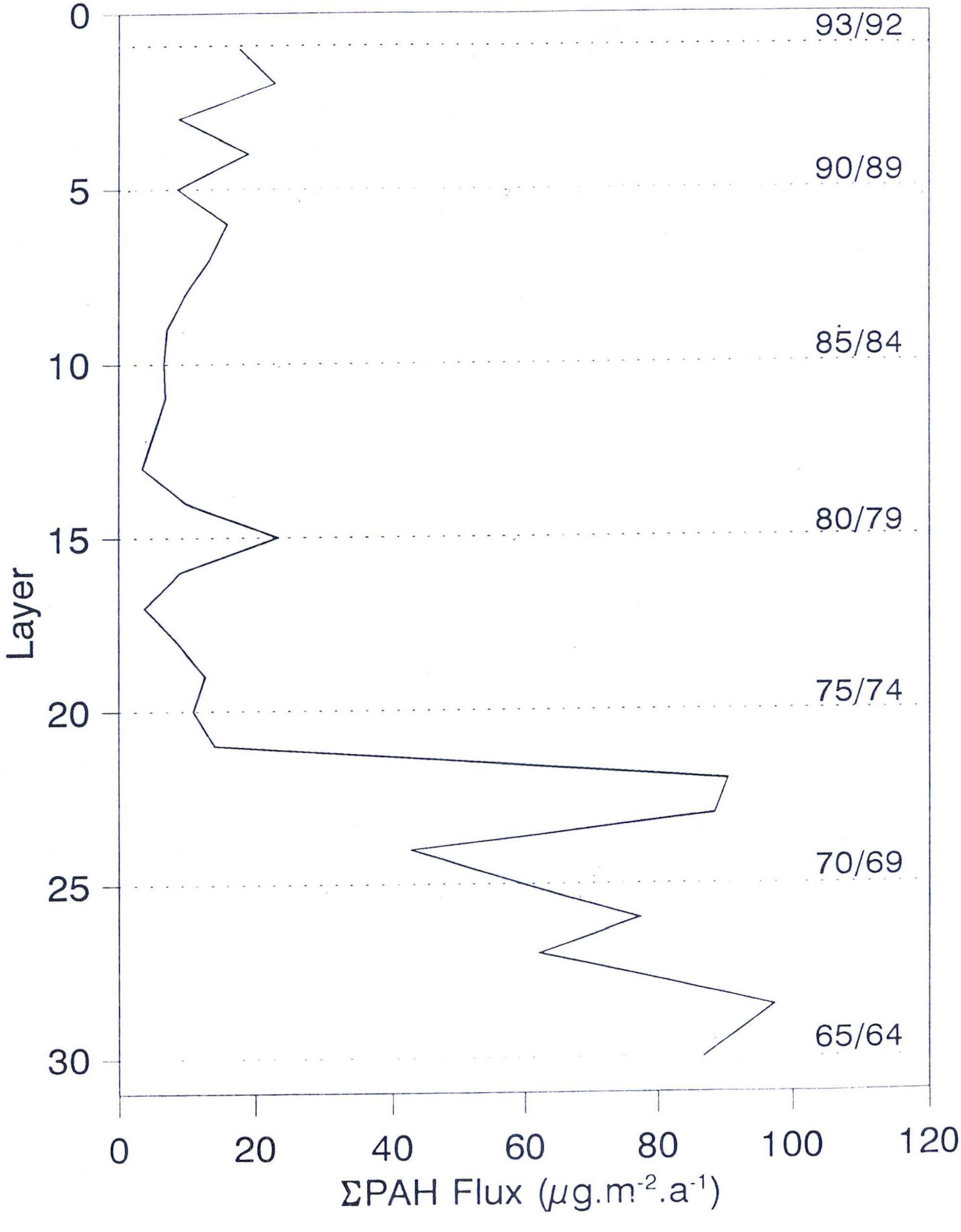
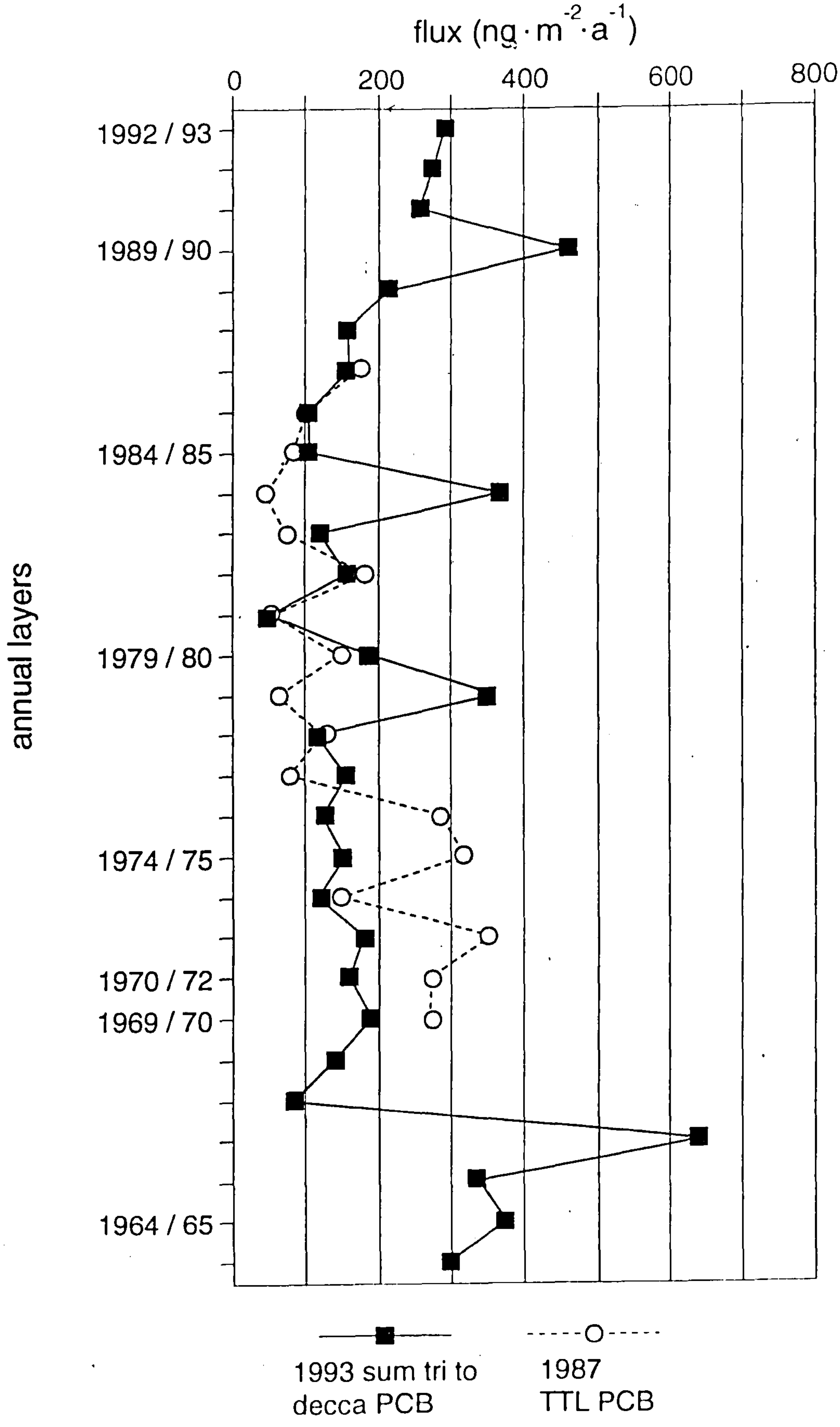


Figure 3. Comparison of ΣPCB profile for homologs with three or more chlorine atoms from the 1993 pit on Agassiz Ice Cap and previous data showing Ttl. PCB deposition from 1969/70 to 1986/87 for a nearby site on Agassiz Ice Cap sampled in 1987.



CURRENT CONTAMINANT DEPOSITION MEASUREMENTS IN ARCTIC PRECIPITATION (SNOW)

PROJECT LEADERS: M. Swyripa, Water Resources Division, Indian and Northern Affairs Canada; and W.M.J. Strachan, National Water Research Institute (NWRI), Environment Canada

PROJECT TEAM: D. Gregor, University of Waterloo; M. Palmer, Indian and Northern Affairs Canada; M. Alaee, D. Burniston, N. Jones, C. Teixeira, NWRI, Environment Canada

OBJECTIVES

To quantify the snowfall deposition of persistent toxic chemicals in the Arctic and to assess the relative importance of this mechanism to the overall input of these chemicals to the region.

PROJECT BACKGROUND AND DESCRIPTION

Atmospheric inputs to aquatic systems elsewhere than the Arctic have been identified as a major means of introducing persistent organochlorine pesticides and industrial compounds to those systems. The chemicals of interest are persistent and semi-volatile and undergo a repeated process of deposition and re-volatilization from water and land surfaces with a slow northerly movement. For such pollutants, the Arctic and Antarctic regions are considered to be the ultimate repositories.

Wet precipitation (rain and snow) is considered a major mechanism whereby the chemicals are transferred from the atmosphere to aquatic or terrestrial surfaces. In southern regions that are largely without anthropogenic influence, wetfall accounts for 90-100% of the chemical input to aquatic systems. In the Arctic, snowfall accounts for the majority of the wetfall (1991, 1992: 38, 59% for Whitehorse, 51, 60% for Baker Lake, 85, 89% for Alert). Earlier work by Gregor *et al.* indicated that accumulated snow contained the target compounds at sub nanogram/litre levels in the snowmelt. These levels, if extended to all snowfall, would indicate annual loadings of 0.02-1 $\mu g/m^2$/year - levels on the average to low level for the Great Lakes. All of this material does not necessarily become incorporated into the aquatic or terrestrial systems into which it is deposited; evidence is available to show that losses from accumulated snow are significant for some toxic chemicals although it is noted that this only makes it available for deposition elsewhere.

The purpose of the overall study is to determine the levels of OC pesticides, PCBs and chlorobenzenes in Arctic snow. Determination of these analytes in accumulated snow was undertaken following the winter of 1991/92; large snow collectors were also employed at Whitehorse and Eureka to determine snow concentrations there on a weekly basis. During winter 1992/93, large snow collectors were established at two additional Yukon sites and at two sites in the Northwest Territories. Bulk samples were also collected at a number of sites during March of 1993 in order to obtain a second synoptic survey of deposition patterns and to compare accumulated results with those which could be calculated using with the weekly levels. In the reporting year, covering the 1993/94 winter, a total of four weekly samplers were operated in the Yukon and five in the NWT. The present report describes some of the results for the sampling period 1991-93 and the collections from 1993/94. The Yukon samples were collected and funded under another project (M. Palmer, this volume) but are presented here for completeness.

ACTIVITIES IN 1993/94

Samples were collected from the sites noted in Table 1. November-March weekly and accumulated snow (to March) samples have been extracted with dichloromethane using Goulden extractors at either Whitehorse or Resolute Bay. Additional weekly samples between March and May from the same locations are in process of extraction. All samples will be further processed and analysed at the NWRI laboratories.

Table 1. Snow Sampling Locations for Winter 1993/94.

Dawson, YKT	Alert, NWT
Tagish, YKT	Baker Lake, NWT
Whitehorse, YKT	Cape Dorset, NWT
	Mould Bay, NWT
White Pass/Fraser, B.C.	Snare Rapids, NWT

Analysis of 1992/93 samples was completed during the reporting year; results for 1991/92 also became available. Most of the analytes occur at trace levels or are non-detectable in most samples. Their numbers, however, require some condensation for reporting purposes. The complete list is provided in Table 2. The atmospheric PCB congeners designated in the table are those which have been found to represent approximately 90% of the total PCB congeners in wetfall samples in the region of the Great Lakes. In the Arctic snow samples, these percentages are much less (60-75%), even in the weekly snow samples. This may reflect degradation on the way north; it may also be the result of losses, even from the weekly samples.

RESULTS

Data for two fluxes (and their corresponding concentrations) are noted in this report. Firstly, deposition at four weekly collection sites (three in the Yukon, one in the NWT), and secondly, accumulated snowfall at 21 NWT locations during winter 1991/92.

The analyte flux via the snow for a given period is:

$$F_{i,j} = C_{i,j} \cdot V_i / A$$

$$= C_{i,j} \cdot P_i$$

where "i" and "j" refer to an individual snowfall event or period, and to the chemical, respectively. $C_{i,j}$ (in ng/L) is concentration of "j" in the snowmelt and P_i (in mm) and V_i (in litres) refer to the amount and volume of precipitation expressed as water equivalent; A (in m^2) is the area of the collector. If the units are as shown, the $F_{i,j}$ will be in ng/m^2.

For a protracted period, e.g. the winter, the flux is the sum of the individual events or collection periods and can also be arrived at by using the volume weighted mean concentration (C_{vwj}):

$$\Sigma Fi,j = \frac{\Sigma\{Ci,j \cdot Vi\}}{\Sigma Vi} \cdot \Sigma Pi$$

$$= C_{vwj} \cdot \Sigma P_i$$

Assuming that a large fraction of the winter snowfall is covered and that the snow is sampled frequently enough that losses are not significant, this derived flux should be a good estimate of the flux via snowfall for the winter. Data on volume weighted concentrations and calculated fluxes based on these are presented in Table 3. For White Pass, the ΣP_i was not available and estimates have been made using the nearest site; it is noted that ΣP_i should be higher than shown for this site and that the flux should also be increased.

Snow accumulating on the ground does not reflect the target analytes in the falling snow due to several potential losses - e.g. with runoff during periods of warming, degradation, volatilization along with subliming snow, and drifting in and out of the collector. Some of these factors will be influenced by temperature and wind conditions. Experience in earlier studies by Gregor has shown that, collectively, these losses may amount to as much as 90% over a few months, depending on the analyte.

Estimation of the flux of the chemicals using the concentration in the accumulated snowfall late in the winter requires the depth of that accumulated snow plus the snow density - or alternatively, the area of the sampled snowpack. For the NWT sampling survey in March-May 1992, data on snow density and depth were collected at the time of sampling. The available fluxes for the winter period can therefore be estimated using the observed concentrations in the snowmelt:

$$F_j = C_j \cdot 10 \cdot \rho_{snow} \cdot d_{snow}$$

where the "ρ" is the snow density measured for the site at the time, and "d" is the depth of the snowpack in cm; the flux will be in ng/m^2 for the specified units. The concentrations and fluxes so estimated are given in Table 4. While these fluxes might be available for release to the underlying ground water, there is no knowledge about what losses may have occurred between collection and final disappearance of the snow. There may also have been additional deposition from snow that fell subsequent to collection.

DISCUSSION

At this stage of the study, the results presented in Tables 3 and 4 must be considered preliminary. There are concerns over whether the ΣP_i terms are representative of the quantity of snow that fell in the respective locations; efforts will be made to determine whether these values are appropriate. It is also the intent of this study to compare the fluxes at the same locations determined from accumulated snowpack and from weekly samples. With these caveats in mind, the following observations are made.

From Table 3 (weekly collections) the most obvious feature is the high concentration (and correspondingly high fluxes) of α-HCH and lindane at Eureka in the High Arctic. Comparison with the Yukon sites is not valid since they are far removed both in time and space. These levels have been checked and do not correspond to high blanks (all results in Tables 3 and 4 are blank corrected).

It is tempting to conclude that the geographic progression in the fluxes and concentrations of the analytes at the Yukon sites during the winter of 1992/93 is real. (A more realistic estimate of the amount of precipitation at White Pass would only accentuate the apparent trend). It is even more interesting to add Eureka to the list (excluding the HCHs) despite the year difference and lack of data at intervening locations. If the trend is real, a conclusion could be that there is a significant input to the area from the Pacific via this route.

In Table 4, data from the Hayes River sample seems anomalously high in fluxes for all analytes reported; mainly this is the consequence of a greater snowcover (i.e. d) at the particular location than was found at other locations. This highlights the difficulty in selecting an appropriate location (and snow depth) at each site. In order to arrive at a representative flux, it might be preferable to have fewer sites and more replications per site. Fluxes of ΣPCBs in samples from the Penny Ice Cap and Lady Melville Lake are also high with only modestly higher concentrations to explain the levels.

Even discounting the anomalies mentioned, the snow survey indicated a pattern of slightly higher fluxes in the eastern part of the study area. This is apparently the case for all of the reported compounds or classes except for the ΣPCBs. It is pointed out that this does not include data for the Yukon region (except for the Peel River site) and an extension westward might change the apparent pattern if the input via the White Pass is real since it would differ from that of the 1991/92 survey.

DATA TREATMENT

All data presented have been corrected for blanks determined using Milli-Q water extracted in the same manner as the samples and shown to be clean in the laboratory. Data also exists for each sample to correct the determined concentrations for recoveries of internal standards. The present report does not include such adjustments since there is no agreement on whether this should be done or what limits should apply. For similar reasons, means and statistical comparisons have not been estimated because there is no agreement among the Northern Contaminants Program participants on how to deal with the question of non-detectables.

PROJECT COMPLETION

At the 1994 meeting of the Northern Contaminants Program Technical Committee, it was decided that the weekly collectors at sites other than those co-located with air samplers of the Atmospheric Environment Service would be dismantled. Following the analyses of the samples collected in 1993/94 (Table 1), sampling in 1994/95 will be continued only at the Alert, Cape Dorset and Tagish sites. It is expected that 1995/96 activities will be limited to analysis of these samples plus preparing reports on the data developed.

ACKNOWLEDGEMENT

In addition to the regional persons who form part of the study team, this study is indebted to the several operators of the weekly snow samplers. Gratitude is also expressed to the Polar Continental Shelf Project at Resolute for provision of accommodation, facilities and transport without which the High Arctic part of the study could not be undertaken.

Table 2. Analytes in the Snow Sampling Programme.

OC Pesticide	Chlorobenzenes	PCB Congeners		
α - HCH	1,3-DCB	1	86	173
γ - HCH (lindane)	1,4-DCB	5*	87*	180
Dieldrin	1,2-DCB	6*	101*	182
Heptachlor epoxide	1,3,5-TCB	7	103	183
α - Chlordane	1,2,4-TCB	8	105*	185
γ - Chlordane	1,2,3-TCB	15	114	187
α - Endosulfan	1,2,3,4-TeCB	16*	118*	189
β - Endosulfan	Penta-CB	17*	121	191
p,p'-DDT	HCB	18*	128	193
p,p'-DDD	1,2,3,5-TeCB	19	129	194
p,p'-DDE	1,2,4,5-TeCB	28*	137	195
o,p'-DDT		31*	138*	196
Heptachlor		32*	141	199
Methoxychlor		33*	143	200
Mirex		40	151	201
trans-Nonachlor		44*	153*	202
Heptachlor		45	154	203
Aldrin		49*	156	205
β-HCH		52*	157	206
o,p'-DDD		54	159	207
		60*	170	208
		77*	171	209

* - atmospheric congeners in the Great Lakes programme

Table 3. Concentrations and Fluxes at Weekly Snow Collection Sites.

	α-HCH		Lindane		Σ-Chlordanes		DDT+DDE+DDD		HCB		ΣPCBs	
	C_{vwj}	ΣF_j	C_{vwj}	ΣF_j	C_{vwj}	ΣF_j	C_{vwj}	ΣF_j	C_{vwj}	ΣF_j	C_{vwj}	ΣF_j
	ng/L	$\mu g/m^2$	ng/L	$\mu g/m^2$	ng/L	$\mu g/m^2$	ng/L	$\mu g/m^2$	ng/L	$\mu g/m^2$	ng/L	$\mu g/m^2$
Fraser/White Pass, B.C. Winter 1992/93 P=186.6 mm*	0.84	0.16	0.30	0.06	1.0	0.19	0.75	0.14	0.25	0.05	22.	4.0
Tagish, YKT Winter 1992/93 P=186.6 mm	0.54	0.10	0.19	0.04	0.72	0.13	0.13	0.02	0.18	0.03	17.	3.2
Whitehorse, YKT Winter 1992/93 P=143.9 mm	0.31	0.05	0.08	0.01	0.38	0.05	0.03	<0.01	0.13	0.02	9.8	1.4
Eureka, NWT Winter 1992/93 P=39.0 mm	13.	0.52	6.8	0.26	0.12	<0.01	0.34	0.01	0.14	0.01	6.8	0.26

Precipitation (P) amounts are data from the Atmospheric Environment Service. They represent the difference between total and rain precipitation for the entire winter period.

Table 4. Concentrations and Fluxes from the NWT Snow Survey in 1991/92.

# snow density & depth unavailable * mean of three	α-HCH		Lindane		Σ-Chlordanes		DDT+DDE+DDD		HCB		ΣPCBs	
	C_j	F_j	C_j	F_j	C_j	F_j	C_j	F_j	C_j	F_j	C_j	F_j
	ng/L	$\mu g/m^2$	ng/L	$\mu g/m^2$	ng/L	$\mu g/m^2$	ng/L	$\mu g/m^2$	ng/L	$\mu g/m^2$	ng/L	$\mu g/m^2$
Peel R. (YKT)#	0.15		0.24		nd		nd		0.07		3.6	
Nahanni Butte	0.23	1.2	0.18	0.93	nd		0.03	0.18	0.24	1.3	2.1	11.
Great Bear L.	0.04	0.15	0.09	0.30	0.11	0.35	0.03	0.11	0.23	0.77	3.6	12.
Slave R.	0.04	0.10	0.05	0.11	nd		0.03	0.06	0.06	0.13	1.9	4.3
Ellice R.	0.21	0.69	0.22	0.74	nd		0.06	0.21	0.31	1.0	4.8	16.
Akasta R.	0.12	0.65	0.09	0.48	nd		0.03	0.15	0.16	0.87	1.9	11.
Reid L.*	0.08	0.38	0.11	0.48	0.02	0.11	0.02	0.08	0.13	0.60	3.4	15.
Kakisa R.	0.06	0.14	0.05	0.10	nd		0.02	0.05	0.26	0.57	4.2	9.2
Ft. Good Hope#	0.03		nd		0.05		0.07		0.06		1.9	
Baker/VOR L.	0.43	2.3	0.47	2.5	0.01	0.05	0.10	0.55	0.11	0.59	3.3	17.
Yathkyed L.	0.13	0.67	0.10	0.54	0.02	0.12	0.02	0.10	0.38	2.0	1.6	8.5
Hayes R.	2.4	33.	1.3	18.	0.09	1.2	0.14	2.0	0.18	2.5	3.6	50.
Back R.	0.02	0.11	nd		0.03	0.15	nd		0.20	1.2	0.9	5.3
Brown R.	0.34	1.4	0.46	2.0	0.03	0.13	0.10	0.43	0.25	1.1	3.1	13.
Thelon R.	0.26	1.3	0.24	1.2	nd		0.05	0.26	0.22	1.1	3.3	16.
Lorrilard R.	0.09	0.22	0.12	0.29	nd		0.02	0.06	0.20	0.47	3.3	8.1
Seal Hole L.	0.44	2.8	0.26	1.6	0.11	0.67	0.04	0.23	0.13	0.81	2.2	14.
Stan.Fletch.L.*	0.92	3.4	0.95	3.4	0.14	0.50	0.39	1.4	0.04	0.15	6.7	24.
Chartrand L.*	1.3	2.7	0.76	1.6	0.17	0.36	0.42	0.86	nd		9.0	19.
Ly Melville L.*	0.31	0.76	0.46	1.1	0.01	0.02	0.20	0.49	0.04	0.10	13.	31.
Penny Ice Cap	0.86	7.7	1.4	12.	nd		0.12	1.1	0.04	0.34	9.0	81.

CURRENT CONTAMINANT DEPOSITION IN SNOW IN THE YUKON TERRITORY

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OBJECTIVES

1. To quantify annual deposition of trace organic contaminants to the Yukon Territory during the winter season through the establishment of a multi-station annual snowpack sampling network.

2. To quantify weekly deposition of contaminants during the winter season by operating three snow collectors at selected intensive sampling locations strategically located within the Territory.

3. To determine spatial variability in contaminant deposition during the winter season within the Territory.

4. To assess source areas and transport vectors for winter-time contaminant deposition in the Yukon through the use of back trajectory calculations.

DESCRIPTION

In the Yukon, and indeed in much of Canada, snowfall is an important component of the total annual precipitation. Consequently, snowmelt during the spring is the single most important hydrological event throughout most of Canada, including the Yukon Territory. Although the Yukon actually receives more than half of its annual precipitation during the May to October period, winter snowfall is significant in the hydrologic cycle, as evidenced by the flow of the Yukon River in the spring and summer seasons. This is due to the large quantity of snow fall in areas of orographic precipitation (precipitation due to the effect of increasing elevation) such as within the mountain ranges of the Yukon. Total annual precipitation in the St. Elias Mountain range can exceed 200 cm per year, more than 4 times more than that in the central part of the Yukon. At least one half of this annual amount can be expected to arrive as snow.

Precipitation is an effective means of removing trace organic contaminants from the atmosphere. These contaminants may be transported long distances in the atmosphere either adsorbed onto or within fine particles or in the gaseous state. Snow crystals in the atmosphere have a much larger surface area than raindrops and thus it follows that snow is an effective scavenger of semi-volatile organic contaminants from the atmosphere. For example, PCBs have been shown to be between 80 and 100% in the vapour phase in urban atmospheres and in the area of the Laurentian Great Lakes (Murphy and Rzeszutko 1977, Doskey and Andren 1981, Eisenreich *et al.* 1981). Duinker and Bouchertall (1989) investigated the partitioning of several PCB congeners and concluded that while only a very small fraction of total PCB was found in aerosols, this compartment accounted for more than 99% of the PCBs in rain. More highly chlorinated congeners were particle-associated while the lower chlorinated congeners remained essentially in the vapour phase. The partitioning of PCBs between vapour and particles in the atmosphere is inversely related to temperature (Bidleman 1988). Consequently, at ambient arctic temperatures, a greater proportion of lower chlorinated PCBs will likely be particle associated than in the temperate source regions. Thus it can be speculated that for the Arctic winter, ice crystals, fresh snowfall and some unknown component of dry deposition scavenge rather effectively the full range of PCB congeners. Nevertheless, the atmospheric concentrations of higher chlorinated PCBs in the Arctic will be less than the lower chlorinated PCBs as they will have been preferentially precipitated during transport (Lunde *et al.* 1977)

It is in this context that measurement of contaminant deposition in snow has been undertaken in the belief that the atmosphere is an important source vector for contaminants to the Yukon. Only through a comprehensive measurement program of atmospheric deposition, will the relative importance of other sources, including local landfills, be able to be assessed relative to the total contaminant burden of the Yukon River system.

ACTIVITIES

Samples

In 1991/92, a single large area snow collector was operated in the vicinity of Whitehorse. Plans to collect large volume snowpack samples from a number of sites in March of 1992 were unfulfilled as a result of early snow melt except for the White Pass site at Frazer, B.C.

In 1992/93, a total of three snow collectors were operated. In addition to the original one at Whitehorse, a second large area collector was installed at Tagish, adjacent to the high volume air sampler operated by Environment Canada. A remote weather station was also installed at this site. The third sampler, with a surface area of 0.25 m^2 and standing approximately 3 m above the ground surface was designed specifically for the high snowfall area of White Pass. During early to mid-March, large volume bulk snowpack samples were collected at five sites in the Yukon. These sites were located at Tagish, White Pass, Beaver Creek, Burwash Creek and Dawson City. All samples are carefully collected into specially constructed aluminum containers and sealed until melted and extracted under contract at Yukon College, Whitehorse. Extracts are forwarded for analyses by NWRI, Environment Canada staff. Thus results are comparable to similar work undertaken in the NWT. All of the samples collected during the 1992/93 winter season have been analysed.

During the winter of 1993/94, a fourth large area snow collector was added at the Midnight Dome site in the area of Dawson City. This location was chosen in part in response to the high bulk deposition of PCBs observed at this location in 1992/93 and in part to provide additional information from the northern part of the Territory. Bulk snow samples were collected at the same sites sampled in 1992/93 plus four additional sites. These sites are Watson Lake (60°4'N 128°46'W), Teslin (60°9'N 132°40'W), Faro (62°12'N 133°32'W) and Ross River (61°57'N 132°29'W) . All samples were handled in an identical manner as in previous years. Again the samples were stored frozen in the Yukon until melting and extraction at the Yukon College with analysis to be undertaken at NWRI. Extraction of the 1993/94 samples has been completed and samples have been delivered to NWRI for analyses.

Methods

The snow is melted inside the sealed sampling cases at the laboratory at Yukon College, Whitehorse. The melt water is extracted with a Goulden Large Volume Extractor (GLVE) using a centrifugal pump to mix and emulsify the sample with the extraction solvent (Goulden and Anthony 1985, Neilson *et al.* 1988). The flow rate in the GLVE is 250 $ml \cdot min^{-1}$ and the extraction solvent is dichloromethane (DCM). The GLVE is thoroughly cleaned with high purity acetone and hexane between each sample. The initial 150 ml of DCM added to the GLVE is spiked with 60 ng of 2,3,4,5-tetrachlorobiphenyl (PCB #70). Makeup DCM, metered into the GLVE at a nominal rate of 1.5 $ml \cdot min^{-1}$, is further spiked with 10 ng δ-HCH, 20 ng of 1,2,4,5-tetrabromobenzene and 20.32 ng 1,3,5-tribromobenzene in methanol. The graduated cylinder containing this spike was always thoroughly rinsed with DCM which was subsequently metered to the GLVE to ensure a quantitative transfer of the spike during the course of the extraction. At the end of the extraction, the DCM is drained from the GLVE into a pre-cleaned 500 ml amber glass bottle. The water remaining in the GLVE is further separated from the DCM using a separatory funnel. The DCM and a small quantity of the water, to minimize volatilization of the DCM, are added to the bottle. The bottles are sealed and kept refrigerated during shipment to, and storage at, the analytical laboratory. Finally, the volume of water extracted is measured and recorded.

The sample extract is allowed to reach room temperature prior to processing generally following the procedure developed at Environment Canada's National Water Quality Laboratory (Anonymous 1987). Thereafter, excess water is removed by passing the sample through anhydrous Na_2SO_4 in an Alihn filter funnel. A 20 ml volume of DCM is then passed through the Na_2SO_4 with gentle suction. The sample is then spiked with 56.52 ng of 1,3-dibromobenzene and reduced to approximately 5 ml by reduced pressure rotary evaporation at 30 °C. Following solvent exchange with hexane and base wash with 0.1 M K_2CO_3 (aq) the extract is again passed through Na_2SO_4 with three 5 ml hexane rinses. Subsequently the sample is spiked with 40 ng of 2,3,5,6-tetrachlorobiphenyl (PCB #65) and 235 ng of perthane prior to concentration by reduced pressure rotary evaporation to approximately 2 ml. This concentrate is applied to a silica gel column prepared with 10 g of 60-mesh silica gel, fully activated at 500 °C for 12 hours. The sample is eluted to obtain four fractions - F1: 80 ml hexane; F2: 85 ml 35% (v/v) DCM in hexane; F3: 85 ml 60% (v/v) DCM in hexane; and F4: 50 ml DCM followed by 50 ml MeOH. Each fraction is then spiked with 65 ng of octachloronaphthalene (OCN) and concentrated by reduced pressure rotary evaporation to approximately 2 ml, solvent exchanged

to iso-octane and finally concentrated to 1.0 ml under a nitrogen stream. The solvent is then transferred to vials and stored at
4 °C until analyses.

Samples are analysed with a HP 5890 Gas Chromatograph equipped with dual ECD detectors. The two 30 m x 0.25 mm fused silica columns are SPB1 (polydimethyl siloxane) and SPB5 (5% phenyl and 95% methyl polysiloxane) (listed as Supelco products) with a phase thickness of 0.25 μm. The sample is injected using an autosampler in splitless mode with a time delay of 0.5 min, after which the injector purged. An initial oven temperature of 80 °C is maintained for 2 min, increasing at 4 °C•min^{-1} to a maximum of 280 °C and holding for 12 min. Injector and detector temperatures are 220 °C and 350 °C, respectively. The carrier gas is helium at 1.0 ml•min^{-1} with nitrogen as the makeup gas at 30 Ml•min^{-1}.

Quality Assurance

Samples are spiked upon collection with 1,2-dibromobenzene and PCB #167 to assess the recovery of these compounds throughout the storage, extraction, fractionation and cleanup procedures. In addition, a total of eight other spikes are added as described in the methods section above. In general, recoveries of these spikes increase the later they are added in the procedure. Thus recovery of the field spikes represents a worst case and these appear acceptable but are still under review by NWRI. The mean recovery and one standard deviation for field spikes added to the initial DCM and the makeup DCM during the extraction process and analytical laboratory spikes are (based on 47 samples):

- Field spikes	- PCB #70	88% ± 35
	- 1,3,5-tribromobenzene	42% ± 19
	- 1,2,4,5-tetrabromobenzene	52% ± 22
	- δ-HCH	71% ± 48
- Laboratory spikes		
	- 1,3-dibromobenzene	45% ± 16
	- PCB #65	90% ± 16
	- perthane	135% ± 34
	- octachloronapthalene	111% ± 18

These data indicate very good and consistent recoveries for these spiked compounds suggesting highly acceptable data.

Routinely, field blanks are prepared consisting of ultra-pure water taken to the field and handled as samples, including the placement of the water in the aluminum snow cases following the standard cleaning processes. For 1992/93 these field blanks were contaminated with PCBs and this is being investigated further. The cause is thought to be shipping or storage of the water as the water was pre-checked in Burlington and the concentrations in the blanks greatly exceeded the actual snow samples suggesting that only the blanks were contaminated. Comparable samples from the NWT have not shown any signs of major PCB contamination thus the procedure is not suspect. Blanks for organochlorine pesticides are routinely non-detectable except for α-chlordane and dieldrin which indicate minor contamination.

In the laboratory, all standards are rigorously pre-tested and compared to other laboratories in an ongoing Environment Canada inter-laboratory comparison study. The NWRI laboratory also participates in the inter-laboratory comparison study of the Arctic Environmental Strategy.

RESULTS

This discussion will be limited to the data derived from the 1992/93 sampling period. In total, 43 samples were collected from the three snow collectors. Due to the relatively low snow fall at the Whitehorse site, only 7 samples were collected here in the period between November 1, 1992 and the end of March 1993. Nevertheless, the PCB congener pattern for all three collectors over the winter season are highly comparable as illustrated in Figure 1. Specific congeners are not labelled in this figure; however a total of 67 congeners are determined in this analysis with a broad representation from the possible 209 congeners that comprise PCB. A comparison of the individual sample PCB homolog composition for the Tagish and White Pass sites is made in Figure 2. Homolog concentrations are generally lower at Tagish but demonstrate a general increase in concentration for the homologs with up to four chlorine atoms (i.e. mono through tetra). Whether such a pattern is significant is unknown at this time.

The five bulk snow samples collected in March are compared in Figure 3. It is quite clear that there is similarity with respect to the homolog concentrations among these samples; but there are also differences. Differences are especially noticeable for the White Pass and Dawson City sites. White Pass has much higher concentrations of 1 and 2 chlorinated congeners. This is possibly a result of the higher elevation of this site, its proximity to the Pacific Ocean resulting in greater scavenging of lower chlorinated PCBs by snow, and/or decreased re-volatilization of these light PCBs from the much deeper snowpack at this site. Also noticeable are the higher concentrations of the higher chlorinated PCBs (greater than four chlorines) present in the sample at Dawson City. This could suggest a different source but any conclusion should be reserved until the 1993/94 snow collector data from the Dawson City site are analysed.

The most obvious difference between the bulk samples and the fresh snow samples from the collectors is the order of magnitude lower concentrations of PCBs in the bulk samples. This again could demonstrate the impact of revolatilization on the concentrations of PCBs in snowpack samples or some combination of other processes.

Due to the highly variable amounts of snow received at each of the three sites, it is more appropriate to compare deposition of PCBs at each site which factors in the amount of snow collected in the snow collector. The computed deposition for each sample in ng/m^2/day is compared among the three collectors in Figure 4. It is very evident here that while concentrations are not greatly different among the sites the amount of snowfall determines the deposition. Mean deposition of ΣPCB at Tagish and Whitehorse, respectively, is 4.9 and 3.6 ng/m^2/day. These values are quite comparable with High Arctic sites from the NWT. In contrast, the mean deposition at Whitepass for the winter of 1992/93 was estimated at 100 ng/m^2/day.

The mean ΣPCB deposition at Tagish and Whitehorse appear to agree well with the calculated deposition in the snowpack samples for Tagish as well as for Beaver Creek and Burwash Creek which range from 2.3 to 5.4 ng/m^2/day (Figure 4). Snow/water equivalent measurements used in determining deposition at these sites are based on snow pillow measurements or snow survey data from early March at Tagish (168 mm), Beaver Creek (120 mm) and the average of the Burwash Airstrip and Burwash Uplands station (71.5 mm). Similarly, the Dawson City site is calculated using snow survey data from Midnight Dome (198 mm) (Indian and Northern Affairs Canada 1993) the site of the bulk snow sample from Dawson City. Unfortunately, we lack snow course data for the White Pass site for the winter of 1992/93 so deposition in the bulk snowpack sample has been calculated using the total amount of water collected in the snow collector, specifically 385 mm. This produces a ΣPCB deposition rate nearly five times that of Tagish but much less than the estimated rate based on the snow collector data. Based on snow survey data from the White Pass site in the spring of 1994, it would appear that the actual bulk snow/water equivalent accumulation at this site between November and March is of the order of 650 mm or nearly twice that collected in the collector in 1992/93. Thus, the bulk snowpack deposition rate may be underestimated by a factor of two. However, this does not explain why there is such a discrepancy between deposition rates determined from bulk snowpack samples and those determined from fresh snow fall samples except for possible losses or relocation external to the snowpack.

Relatively few organochlorine pesticides and related compounds are detected in the snow samples from the Yukon. Those with consistent hits include pentachlorobenzene, hexachlorobenzene, *p,p*-DDE, α-hexachlorocyclohexane, lindane, γ-chlordane, α-endosulfan, α-chlordane and dieldrin. Of these, hexachlorobenzene, α-chlordane and dieldrin have relatively high blanks suggesting that the presence of these compounds may be due to contamination. Lindane and α-hexachlorocyclohexane are commonly detected in the Arctic and in the snow samples from Tagish and White Pass. Once again there is a major difference between the deposition rates calculated for the two sites with daily deposition throughout the winter at White Pass an order of magnitude greater than at Tagish (Figure 5). This is further evidenced by the fact that the bulk snow sample at White Pass had significant concentrations of both α-HCH and lindane while neither were present in the bulk sample from Tagish. This is likely due to differential volatilization from the two snowpacks with the deeper snowpack at White Pass retaining a larger amount of these volatile compounds.

CONCLUSIONS AND UTILIZATION OF RESULTS

In summary, atmospheric deposition rates of organic contaminants to the Yukon are quite variable and apparently depend on the amount of precipitation which in turn determines the degree of scavenging that occurs. Further confirmation of the spatial and seasonal trends observed during 1992/93 will need to be confirmed based on results from subsequent years. Actual delivery of these contaminants to the surface waters and their significance to the mass balance of contaminants in the aquatic systems will require further assessment including modelling and a small watershed mass balance study for rudimentary calibration purposes. This work will be undertaken in future years. Nevertheless, these deposition rates indicate that the atmosphere is a potential source of at least PCBs to the surface waters of the Yukon.

Collaboration with other studies, including air sampling and mass balance work in the upper Yukon River system will be necessary to fully utilize the results from this project.

Expected project completion date: March 31, 1997

PARTNERS

Environment Canada, Inland Waters Directorate, Yukon and NWRI; Yukon Territorial Government; Yukon College; University of Waterloo; Yukon Contaminants Committee

REFERENCES

Anonymous. 1987. Analytical protocol for monitoring ambient water quality at the Niagara-on-the-Lake and Fort Erie stations. Unpublished report. National Water Quality Laboratory, Environment Canada, Canada Centre for Inland Waters, 867 Lakeshore Road, Burlington, Ontario.

Bidleman, T.F. 1988. Atmospheric processes, wet and dry deposition of organic compounds are controlled by their vapor-particle partitioning. Environ. Sci. Tech. 22: 361-367.

Doskey P. and A. Andren. 1981. Modelling the flux of atmospheric polychlorinated biphenyls across the air/water interface. Environ. Sci. Tech. 15: 705-711.

Duinker, J.C. and F. Bouchertall. 1989. On the distribution of atmospheric polychlorinated biphenyl congeners between vapor phase, aerosols, and rain. Environ. Sci. Technol. 23: 57-62.

Eisenreich, S.J., B.B. Looney and J.D. Thornton. 1981. Airborne organic contaminants in the Great Lakes ecosystem. Environ. Sci. Tech. 15: 30-58.

Goulden, P.D. and D.H.J. Anthony. 1985. Design of a large sample extractor for the determination of organics in water. Unpublished report. National Water Research Institute, Environment Canada, Canada Centre for Inland Waters, 867 Lakeshore Road, Burlington, Ontario. Contribution no. 85-121.

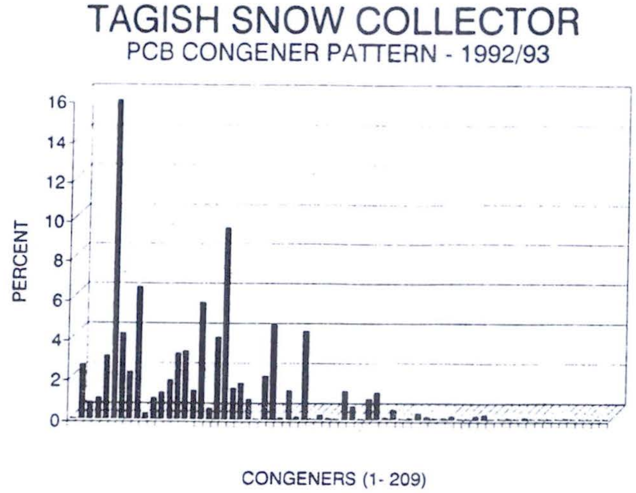
Indian and Northern Affairs Canada. 1993. Yukon Territorial snow survey bulletin and water supply forecast. Water Resources Division, Yukon, Indian and Northern Affairs Canada, Northern Affairs Program, 200 Range Road, Whitehorse, Yukon, Y1A 3V1.

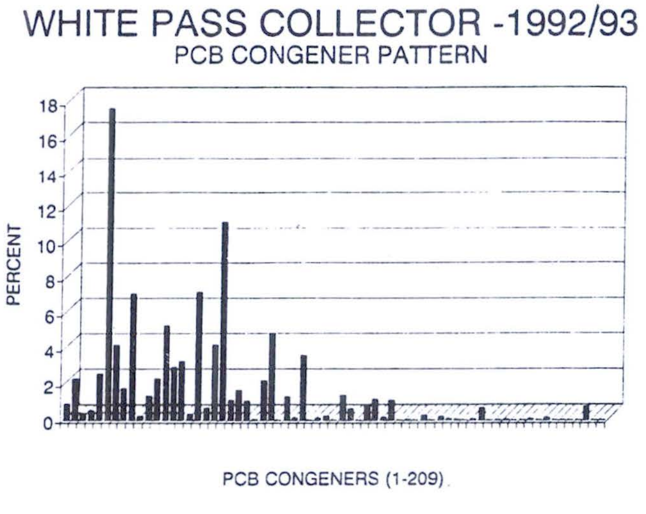
Lunde, G., J. Gether, N. Gjos and S.L. May-Berit. 1977. Organic micropollutants in precipitation in Norway. Atmos. Environ. 11: 1007-1014.

Murphy, T.J. and C.P. Rzeszutko. 1977. Precipitation inputs of PCBs to Lake Michigan. J. Great Lakes Res. 3: 305-312.

Neilson, M.A., R.J.J. Stevens, J. Biberhofer, P.D. Goulden and D.H.J. Anthony. 1988. A large sample extractor for determining organic contaminants in the Great Lakes. Inland Waters Directorate, Ontario Region, Water Quality Branch, Environment Canada, Burlington, Ontario. Technical Bulletin no. 157.

Figure 1: Comparison of the relative contribution of individual PCB congeners averaged for all samples from snow collectors for the winter of 1992/93 for Tagish, White Pass and Whitehorse.





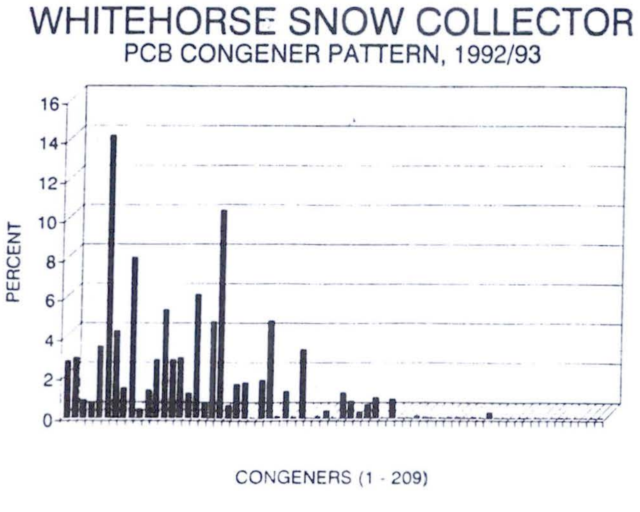
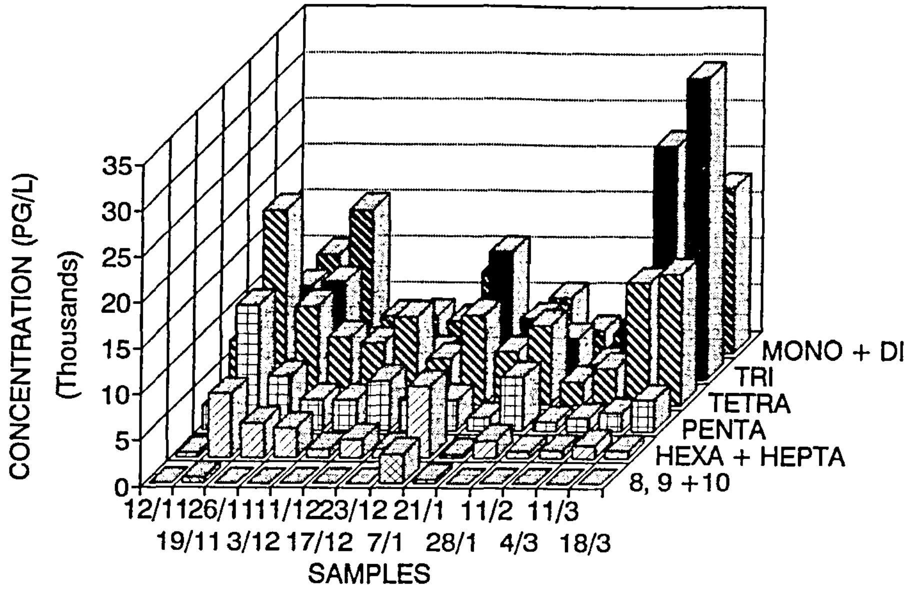


Figure 2: PCB homolog composition of individual samples collected using the large area snow collectors at the White Pass and Tagish sites during the winter of 1992/93. The sample dates shown on the Y-axis are the end dates of the snow sampling period.

WHITE PASS COLLECTOR -1992/93

PCB HOMOLOG DISTRIBUTION



TAGISH SNOW COLLECTOR

PCB HOMOLOG PATTERN - 1992/93

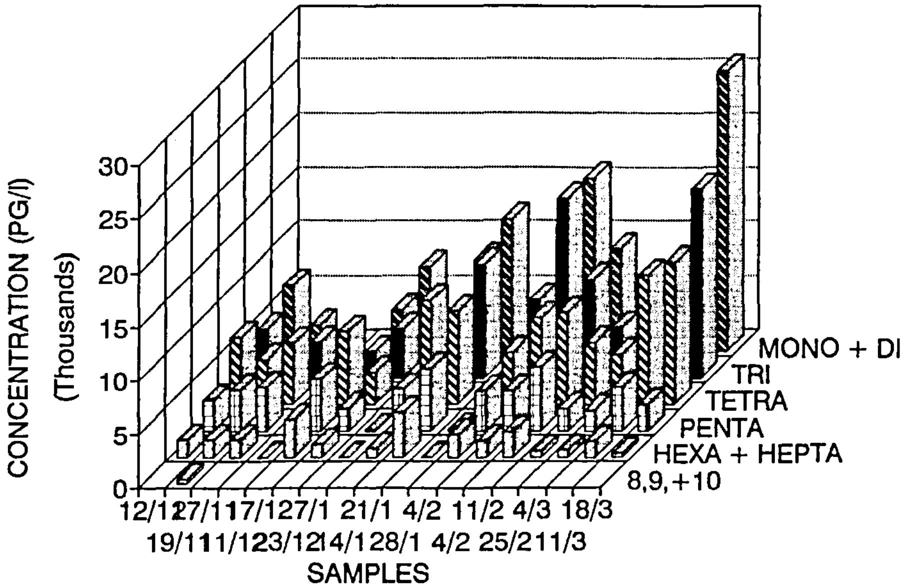


Figure 3: Concentrations of PCB homologs in bulk snow samples collected in early March, 1993 from White Pass (WP), Tagish (TG), Beaver Creek (BeC), Burwash Creek (BuC) and at Dawson City (DC).

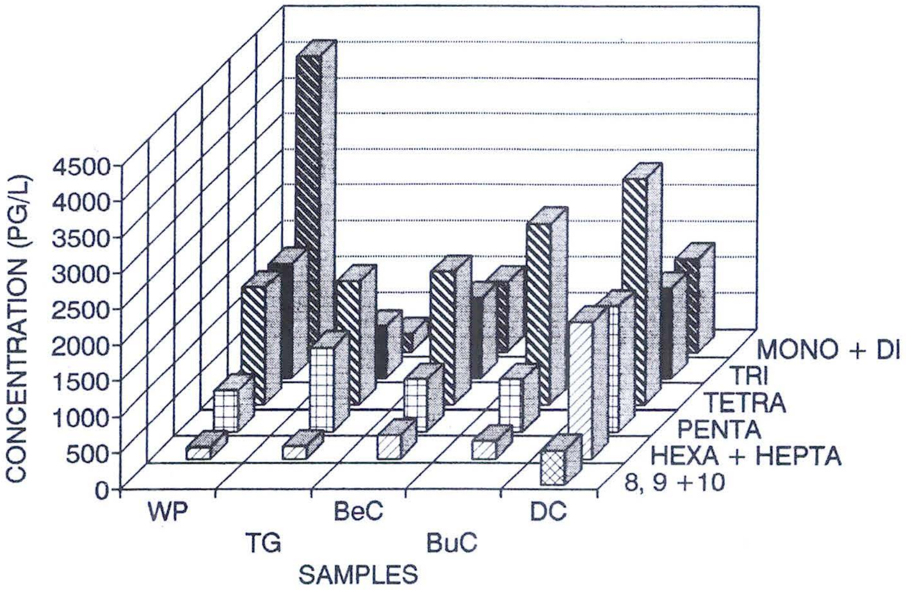
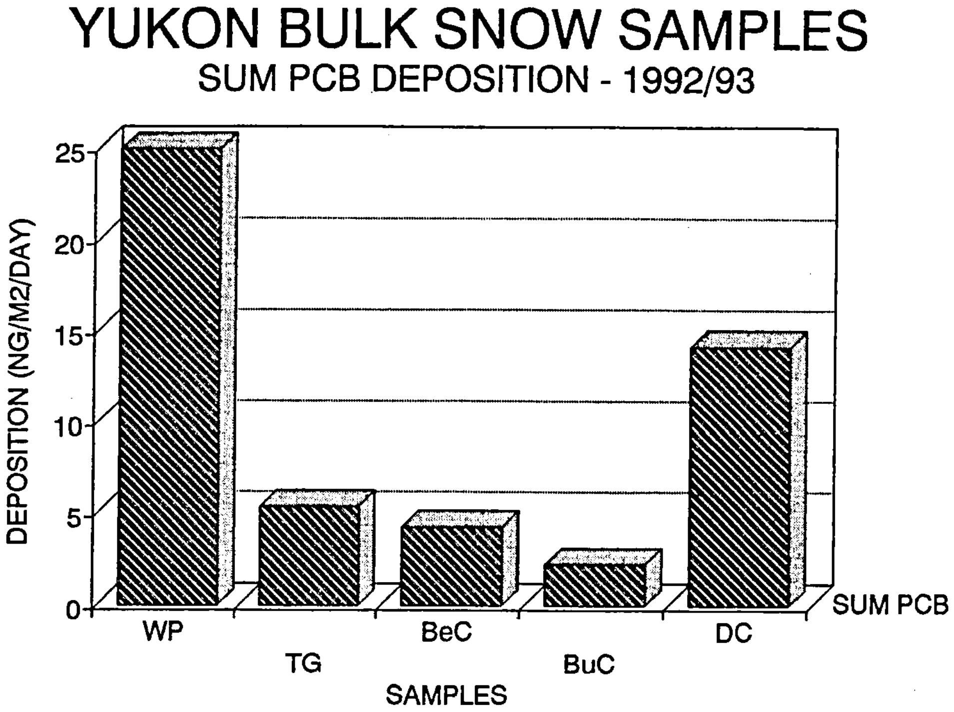


Figure 4: Comparison of ΣPCB deposition as determined for the bulk snowpack samples and for the samples collected from each of the snow collectors.



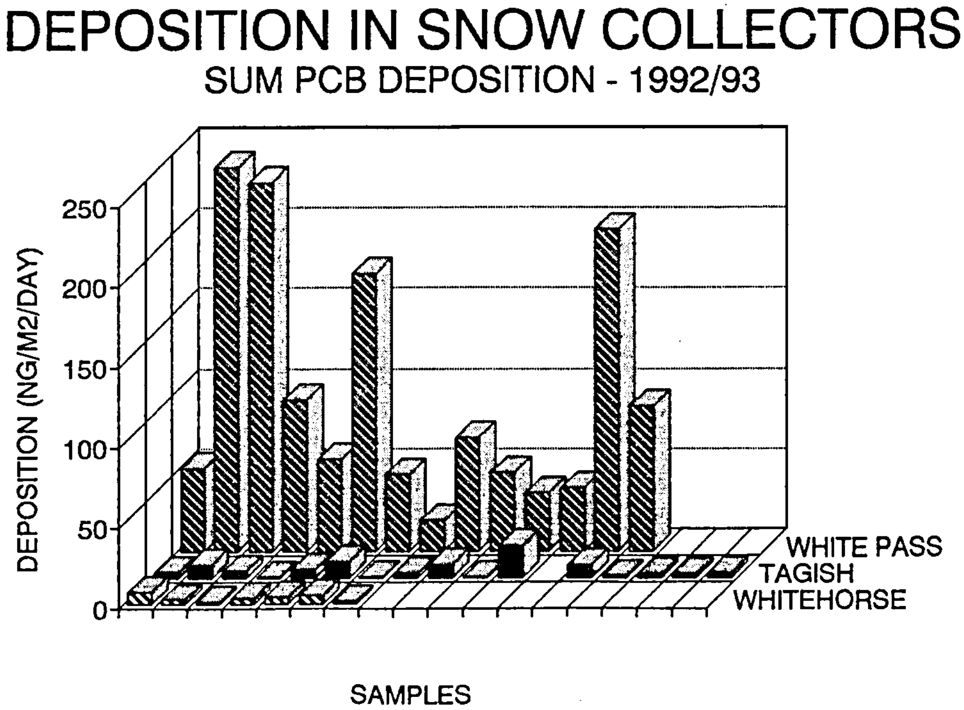
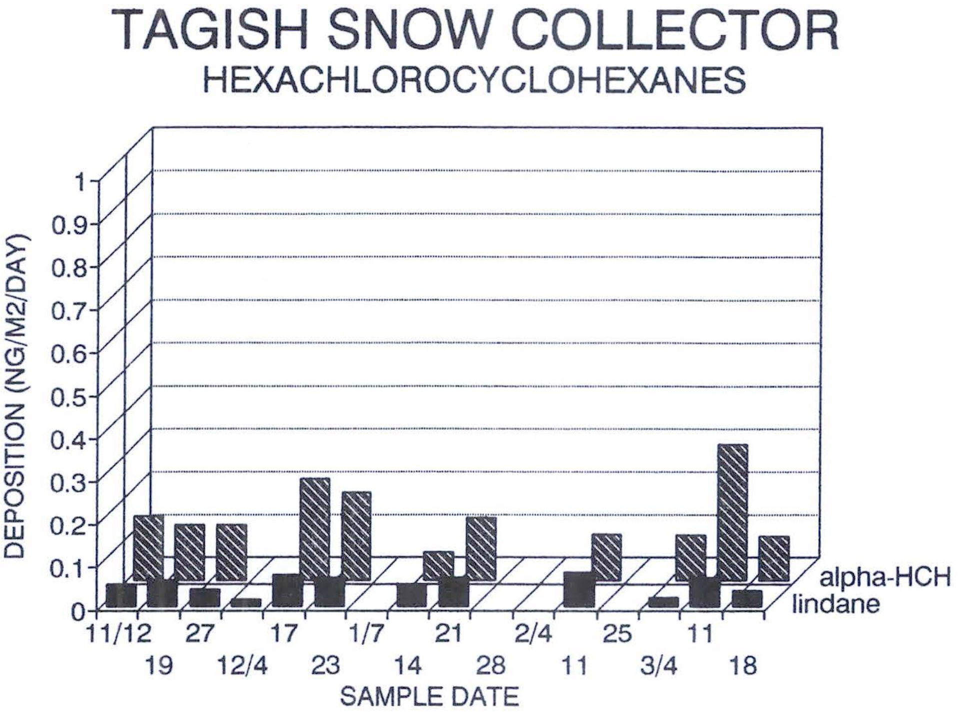
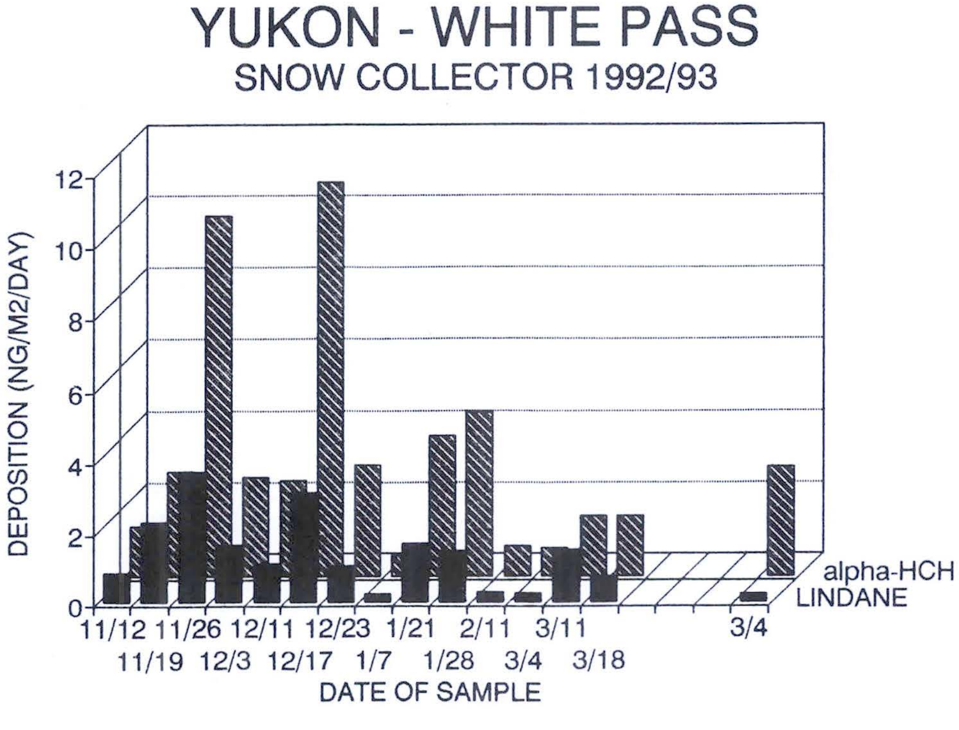


Figure 5. Comparison of calculated daily deposition of α-HCH and lindane for the Tagish and White Pass snow collectors for the winter of 1992/93. Note that the bulk snow sample collected on March 4, 1993 at the Tagish site had no detectable quantities of these compounds present and thus this sample is not included.





LONG-RANGE TRANSPORT OF CONTAMINANTS
TO THE CANADIAN BASIN

PROJECT LEADERS: R.W. Macdonald and E.C. Carmack, Institute of Ocean Sciences, Fisheries and Oceans Canada

PROJECT TEAM: F. McLaughlin, D.W. Paton, M.C. O'Brien, R. Pearson, D. Sieberg

OBJECTIVES

To determine the composition, quantity and distribution of organochlorine contaminants within the Western Arctic and Arctic Ocean Interior (Canada Basin). To measure the relative amounts of these compounds contained within biogeochemical compartments (e.g. particulate, dissolved, biological). To model the rate of transfer of these compounds within the Arctic Ocean.

DESCRIPTION

The various sources and sinks of organochlorine contaminants (OCs) in the Arctic Ocean are listed below.

1. River-borne contaminants enter the Arctic Ocean via the shelves. The quantity and composition of OCs from this source is optimally determined by measurements within the rivers themselves accompanied by river flow estimates. Such measurements on the Canadian River source (essentially the Mackenzie) are planned by others (Gregor). We are also strongly encouraging bilateral work which will lead to similar measurements for Russian rivers.

2. Pacific (Bering Strait) and Atlantic (Fram Strait) waters transport OCs into the Arctic Ocean. These sources are best measured at their points of entry; we propose to accomplish these measurements for the Pacific input through trilateral agreements with Russia and the United States.

3. The atmosphere is thought to be the predominant source for many OCs to the Arctic. Due to the wide distribution of this source and its variability in space and time, it is much more difficult to measure without bias. The Atmospheric Environment Service (Environment Canada) proposes to establish both North American and Eurasian land-based stations to determine this source function/pattern.

4. OCs are lost via outflow through Fram Strait and the Canadian Archipelago (measurements being made by Hargrave), and within the Arctic, OCs are scavenged by shelf sediments and into basin sediments as a component of the particle flux.

Accurate determination of the above sources and how they transport within the Arctic Ocean is necessary to develop models of OC distribution and movement. Models are necessary to predict the consequences of our actions (business as usual, limited use, banning of these chemicals, etc.).

Our work in the western Arctic focuses on the oceanographic processes that control distribution of OCs, and in particular HCH. We are presently making measurements that allow us to determine the source of water masses and their age since ventilation. We are also measuring particle flux at several locations to determine the rate of removal of contaminants from the upper ocean by this mechanism. Lastly, we are maintaining a time series at a deep station to observe variability and trends.

ACTIVITIES AND RESULTS IN 1993/94

This year's work involved a trilateral cruise (Canada, Russia, United States) with several objectives:

1. Service the moorings and collect another profile at our time-series station (A1; see Figure 1). We successfully recovered and redeployed the A1 mooring and several other moorings at the Beaufort Shelf Edge. Continuing the time-series at this station, we were able to collect data on water properties including tritium and CFCs which are used to determine the age of the water and HCHs. Our HCH determinations are now approaching "tracer" quality (Fig. 2) wherein the HCH concentrations reflect the water masses. This strongly suggests that the oceanography must be understood in a broad context before we can make sense of OC water column concentrations.

2. Carry out a long oceanographic section that extends from the Beaufort Sea to the Chukchi Sea to the East Siberian Sea (Fig. 1). Initially, we had hoped to work on the East Siberian Sea shelf. We had two Russian scientists on board and had the necessary permissions from the Russians. However, a last minute requirement to undergo inspection by the Northern Sea Routes Department with uncertain costs and unacceptable loss in time required us to reorganize our cruise. It is indeed fortunate that ice conditions allowed us to make a remarkably deep penetration into the ice along the East Siberian Shelf. Preliminary results are exciting. 1993 was clearly an exceptional year during which an "event" was taking place wherein water was entering the Canadian Basin from both the Eurasian Basin and from the Pacific Ocean at enhanced rates. Both of these phenomena clearly have the potential to "short circuit" contaminant transport. We collected water samples for HCH and for a series of radionuclides (Smith, Bedford Institute of Oceanography (BIO)) and these data promise to shed light on the interbasin connections and the movement of contaminants along the Russian Shelves. Several papers are in progress and more planned as the data become completed. Further, we collected 6 large box cores, which are presently being analyzed for AMAP priority contaminants in collaboration with John Smith (BIO) and Charles Gobeil (Institut Maurice Lamontagne), and biological samples (zooplankton).

3. Carry out specific measurements on the rate of inflow of water into the Arctic through the Barrow Canyon using towed Acoustic profilers. The data collected here confirm the water column measurements from within the Basin itself; the Pacific inflow was particularly strong in 1993. A paper describing the event and estimating flow is in preparation.

DISCUSSION/CONCLUSIONS

We believe these collections to be important due to their location (they fill in a rather large area of unknown territory along the Russian shelves and will help us to evaluate the contaminant issue there) and as a planning background for the Arctic-94 mission which hopefully will extend this study. We are presently working on papers dealing with the anomalies we found in the water, the rates of inflow from the Pacific Ocean and the distribution and sources of HCH to the Canadian Basin. The sediments collected this year will be augmented by approximately 10 more box cores in 1994. This will give us a wide coverage of carefully collected material from which to evaluate several topics such as the loss of radionuclides from the Russian Shelves, the importance of basin and slope sediments as organochlorine sinks, and the distribution and source of PAH and heavy metals in the Arctic Ocean.

Expected project completion date: 1997

Figure 1: 1993 Sampling Sites

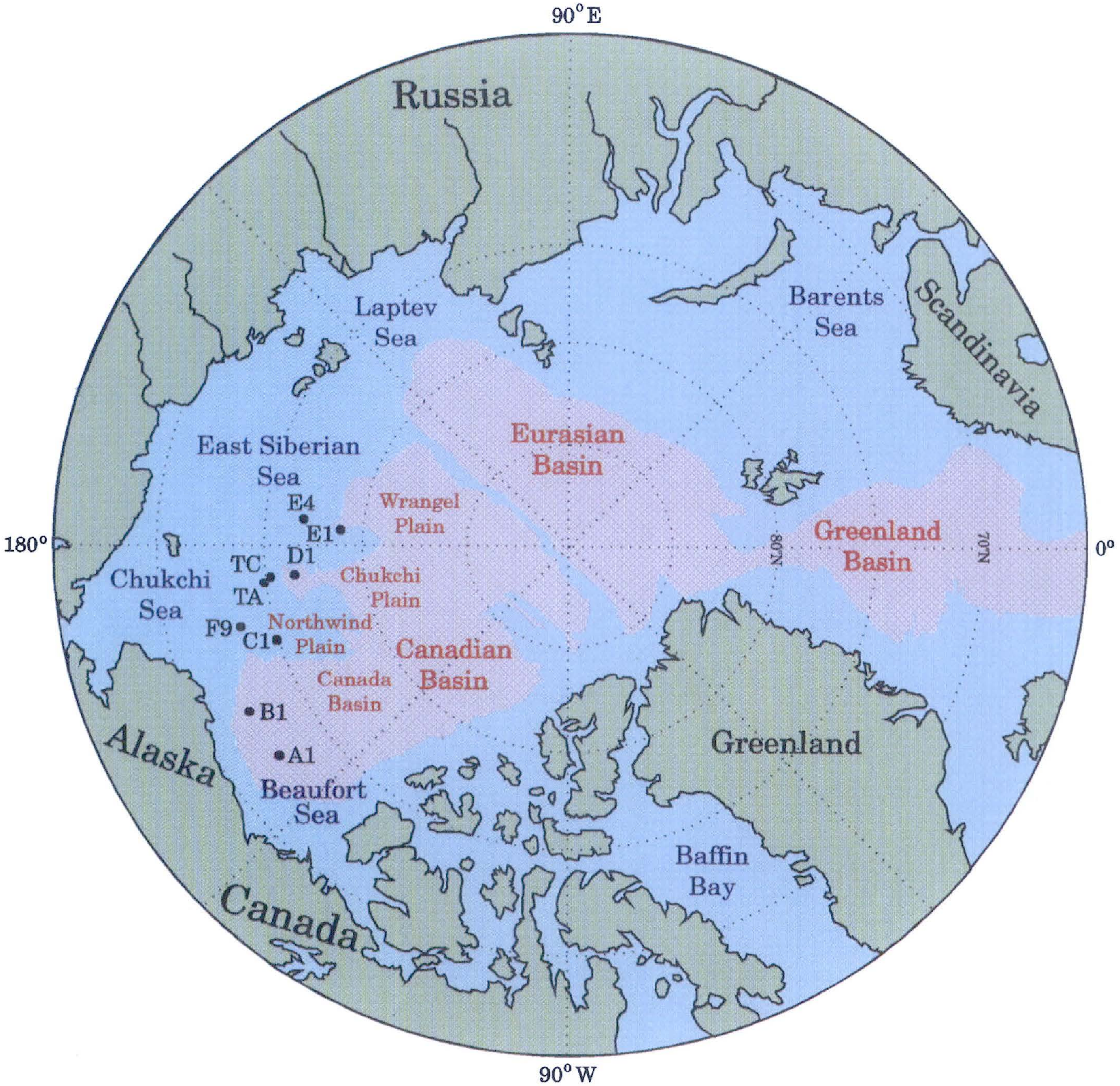
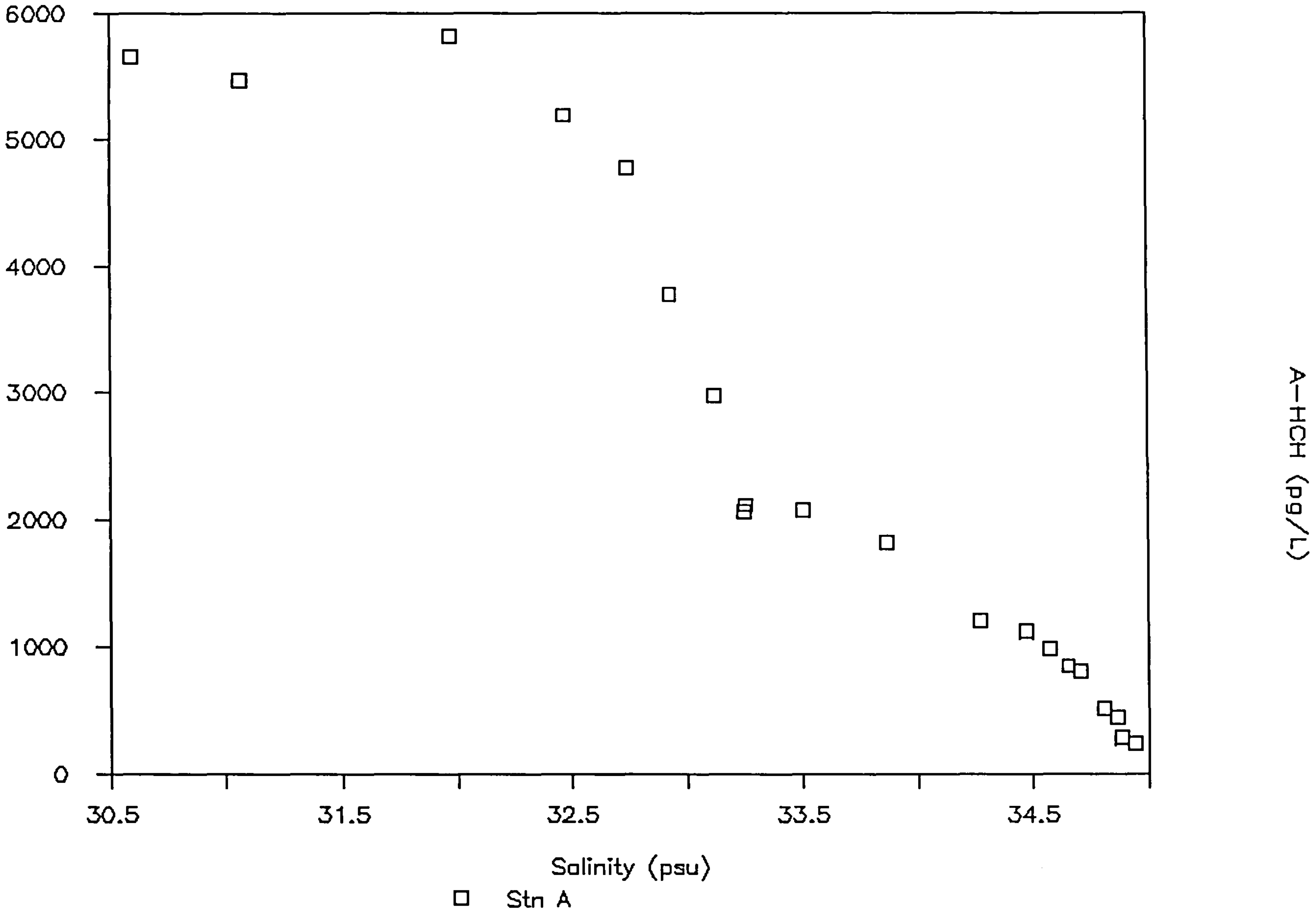


Figure 2: Concentration of αHCH vs. Salinity taken at Station A, 1994.



MEASUREMENTS OF RADIOACTIVE CONTAMINANTS IN THE ARCTIC OCEAN

PROJECT LEADER: J.N. Smith, Bedford Institute of Oceanography (BIO), Fisheries and Oceans Canada

PROJECT TEAM: K. Ellis, R. Macdonald, Institute of Ocean Sciences, Fisheries and Oceans Canada; A. Aarkrog, Riso National Laboratory, Roskilde, Denmark; L. Polyak, Byrd Polar Research Centre, Columbus, Ohio; G. Ivanov, Okeanogeologia, St. Petersburg, Russia; D. Matishov, Murmansk Marine Biological Institute, Murmansk, Russia; S. Dahle, Akvaplan Niva, Tromso, Norway; L. Kilius, University of Toronto

OBJECTIVES

1. To determine source functions for radioactive contaminants in the Arctic Ocean associated with nuclear accidents, nuclear weapons tests and ocean dumping of radioactive wastes.
2. To identify the mechanisms governing radionuclide transport from anthropogenic sources through different environmental phases (sediments, seawater, biota) with special reference to the Russian marginal seas.

DESCRIPTION

Recent reports of the dumping of radioactive wastes on the Russian Continental Shelf have raised concerns regarding the transport of radioactive contaminants through the Arctic Ocean, their uptake in the food chain and the consequent radiological exposures of northern population groups. This project will provide information on: (1) the magnitude of radioactive source terms in the Arctic through site-specific measurements of radioactive contaminants on environmental samples collected within the vicinity of radioactivity sources (i.e. radioactive waste dumpsites, sunken submarines, nuclear weapons accident sites) in the Arctic Ocean, and (2) fluxes of radioactivity and other contaminants (organics, metals) in the arctic marine environment through measurements of natural and artificial radionuclides in sediments, seawater and biota and the application of various models (ventilation, sediment biodiffusion, etc.) to estimate radionuclide transport fluxes. Radionuclides will be used as tracers to estimate inorganic and organic contaminant fluxes in collaborations with other investigators.

ACTIVITIES IN 1993/94

The field and analytical activities in 1993/94 included: (a) the collection of sediment, seawater and biota samples in the Barents and Kara Seas and the Ob and Yenisey River estuaries; (b) the collection of sediment/seawater samples in the East Siberian and Chukchi Seas; (c) analyses of sediment samples collected in 1992 in the Barents Sea for radionuclides; and (d) the analysis of sediment samples collected at Thule, Greenland in 1991. The results of these studies were reported at two international conferences held respectively in June 1993 in Woods Hole, Massachusetts, USA and in August 1993 in Kirkenes, Norway.

RESULTS

Cruise Work

Two cruise operations were conducted in the Arctic Ocean in 1993. A Bedford Institute of Oceanography (BIO) scientist accompanied the Russian Vessel, *Geolog Fersman,* to the Barents and Kara Sea and effectively managed their sediment coring and seawater collection operations. A series of seawater samples and sediment cores were collected from the fjord of Chernaya Bay, a region in which underwater nuclear weapons tests had been conducted and in which sediment plutonium concentrations were known to be extremely high. The *Geolog Fersman* then proceeded to the Kara Sea where a submerged vessel reported to contain 200 curies of radioactive wastes was identified at a water depth of 300 m in the Novaya Zemlya Trough using side-scan sonar. Sediment and seawater samples were collected within the vicinity of the submerged vessel in order to determine the extent to which it represented a radioactive source for long-term releases into the Kara Sea.

A second BIO scientist accompanied the CSS Henry Larsen to the Chukchi and East Siberian Seas where environmental samples were collected in order to determine radionuclide (^{137}Cs, ^{90}Sr, ^{129}I, ^{239,240}Pu) fluxes across the Canada Basin. Sediment samples were collected in shelf and slope sediments of the western Canada Basin while seawater samples from a range of water depths were passed through filters and resins to extract particulate and dissolved radionuclides. The primary focus of this work is to determine the extent to which radioactive contaminants from the Russian marginal seas have been transported through the Canada Basin and onto the North American continental shelf.

Analytical Work

Barents Sea Study

Analyses of ^{137}Cs and ^{239,240}Pu in a suite of surface sediments collected in 1992 from a broad region of the Barents Sea, from the Kola Peninsula to Franz Joseph Land, have revealed little evidence for major sources of radioactive contamination, other than those associated with fallout and inputs from European Reprocessing Plants. In most cases, the magnitude of the radionuclide signal in surface sediments is governed by particle size, with the highest signals being associated with the finer-grained clays and organic matter. The exception to this is in the fjord of Chernaya Bay on the southwestern coast of the island of Novaya Zemlya, the site of three underwater nuclear weapons tests between 1955 and 1961. Plutonium concentrations in surface sediments from this fjord are among the highest recorded anywhere in the marine environment and are equivalent to those measured at the US nuclear test site in the Marshall Islands in the Pacific Ocean. Analyses of plutonium isotopic concentrations has confirmed that the origin of this plutonium is from nuclear weapons tests similar to those carried out between 1951 and 1955 at the Nevada Test Site in the US.

Thule Study

Plutonium inventories measured at the site of a nuclear weapons accident in 1968 in Thule, Greenland, are of the same order of magnitude as those measured in Chernaya Bay, providing an important comparison between the two sites of contamination which are at similar latitudes and have similar water depths. ^{210}Pb sediment-depth profiles indicate that burial of the ^{239,240}Pu has occurred by a combination of sediment accumulation and bioturbation. Applications of a two layer, biodiffusion model to the ^{210}Pb and ^{239,240}Pu profiles at Thule indicate that sedimentation rates range from 0.1-0.5 cm/y throughout the region and that the approximately 1 TBq of ^{239,240}Pu had been buried to mean sediment depths of 3-6 cm by 1984. However, sediment organisms have buried plutonium contamination to depths in excess of 15 cm in the vicinity of the crash site.

1993 Samples

Analyses of samples collected during the 1993 field season are presently underway. Preliminary results indicate that the submerged ship containing radioactive wastes in the Novaya Zemlya Trough is not leaking significant quantities of radioactivity. Levels of radioactivity in sediments of Chernaya Bay are extremely high, as might be expected. Levels of ^{137}Cs in the water column of the Canada Basin are comparatively high, far in excess of any previous values reported for this region, and are apparently due to inputs of radioactivity from European reprocessing plants.

DISCUSSION/CONCLUSIONS

Barents Sea

Applications of a sediment mixing model to radionuclide profiles measured in sediment cores from the Barents Sea indicate that the burial of contaminants occurs mainly as the result of sediment mixing, with sediment accumulation playing a minor role in the removal of contaminants from the sediment-water interface. The plutonium in the sediments of Chernaya Bay is probably in a refractory form that is not readily released into seawater and, despite the high concentrations, probably represents only a minor threat to the Arctic Ocean. This preliminary conclusion will be assessed through measurements on a series of cores collected in 1993 in Chernaya Bay aboard the Geolog Fersman. The plutonium inventory in Chernaya Bay does, however, represent a significant, and previously undocumented inventory of radioactivity in the Arctic Ocean and an important opportunity to evaluate the assimilation of plutonium into arctic food chains.

Thule, Greenland

Analyses of sediment cores collected at a nuclear weapons accident site in Thule, Greenland have indicated that plutonium has undergone only minimal radial dispersion from the crash site, based on successive sediment inventory surveys conducted in 1974, 1979 and 1984. The site does not represent a significant, current source of contamination to proximal environments. The implication is that plutonium contained in nuclear weapons which have been deposited (by accident or design) on the seabed will probably remain relatively immobile and be retained by, and incorporated into sediment matrices. Although ^{239,240}Pu concentrations remain relatively high at the sediment-water interfaces of most cores at Thule, their sediment-depth distributions are simulated by the biodiffusion model using a pulsed input of ^{239,240}Pu to the sediments injected solely at the time of the accident. Relatively high levels of ^{239,240}Pu are maintained in surface sediments by bioturbation processes that act to retain contaminants in the upper surface mixed layer.

Expected project completion date: March 31, 1997

PUBLICATIONS

Smith, J.N. and K.M. Ellis. Radionuclide tracer profiles at the CESAR Ice Station and Canadian Ice Island in the western Arctic Ocean. Deep-Sea Research, submitted.

Smith, J.N., K.M. Ellis, A. Aarkrog, H. Dahlgaard and E. Holm. Sediment mixing and burial of the ^{239,240}Pu Pulse from the 1968 Thule, Greenland nuclear weapons accident. Journal of Environmental Radioactivity, submitted.

Smith, J.N., K.M. Ellis, K. Naes, S. Dahle and D. Matishov. Sedimentation and mixing rates of fallout radionuclides in Barents Sea sediments off Novaya Zemlya. Deep-Sea Research, submitted.

POLYCHLORINATED DIBENZO DIOXINS AND FURANS IN THE ARCTIC ENVIRONMENT

PROJECT LEADER: M. Alaee, National Water Research Institute, Environment Canada

PROJECT TEAM: L. Barrie, Atmospheric Environment Service, Environment Canada; D. Gregor, University of Waterloo; B.K. Afghan, R. Wilkinson, and A. Peters, National Water Research Institute (NWRI)

OBJECTIVES

To survey the presence of polychlorinated dibenzo dioxins (PCDD) and polychlorinated dibenzo furans (PCDF) in air, water, sediment and suspended sediment at Alert (air), Yukon/Laberge system, Mackenzie River, and Amituk Lake, and to provide relevant baseline information.

DESCRIPTION

Atmospheric transport of organochlorine contaminants to the Arctic Ocean has been reported by Hargrave *et al.* (1988), and observed in snow from various locations in the Canadian Arctic by Gregor and Gummer (1989). Polychlorinated dibenzo dioxins and furans, in particular 2,3,7,8 TCDD and 2,3,7,8 TCDF, are among the most toxic anthropogenic compounds. These compounds are produced as a byproduct during the manufacturing of PCB and other organochlorine compounds; and during low temperature incineration of halogenated compounds such as PVC. Currently there are various low temperature incinerators in operation in Canada, US, Japan and many European countries. For example, in Russia about 30 million tons of halogenated sludge is produced annually, some of which is incinerated. Federov (1993) reported concentrations up to 151 ppb of 2,3,7,8 TCDD in soil in Chapevsk, Russia. Lexen *et al.* (1993) reported significantly lower emissions from Swedish industries. Similar to other organochlorine contaminants, emissions of PCDD and PCDF from these operations can be carried atmospherically and deposited in the Arctic.

Co-planar PCBs are a subset of PCB congeners; due to the particular position of the chlorine substituent (3,4,3',4'), co-planar PCBs exhibit biological activities similar to dioxins (Ahlborg *et al.* 1994). The similarities in chemical structure result in a similar analytical procedure. With slight modification in the analytical procedure for dioxin analysis, co-planar PCBs can also be collected and analyzed.

Currently there is a limited amount of information on PCDDs and PCDFs in marine mammals and polar bear available (Norstrom *et al.* 1990). Co-planar PCBs in marine mammals and biota are under study at the Freshwater Institute (Muir 1993). The purpose of the present study is to investigate the presence of these contaminants in physical compartments of the Canadian Arctic.

ACTIVITIES IN 1993/94

This program is an add-on to other programs run by NWRI and the Atmospheric Environment Service. Air samples were collected by L. Barrie from Alert, NWT and Tagish, Yukon. These samples were extracted with hexane and dichloromethane and analyzed for OCs, PCBs and PAHs (Barrie 1993). A portion of these samples are archived for future use. Blank samples (no air though the collector) were obtained and analyzed for dioxins and co-planar PCBs; they did not contain significant amounts of contamination. However, after consulting with M. Oehme, it was decided that the PUF and filters should be extracted with toluene. Additional air samples for dioxin analysis will be collected by L. Barrie from Alert.

A total of nine water samples (ea. >100 L) along with six samples for suspended solids were collected from the Yukon river, Arctic Red on the Mackenzie River and Amituk Lake (water only). Due to sampling difficulties, suspended solids and sediments from Amituk Lake were not collected in 1993/94 but will be collected in 1994/95. To ensure compatibility at the low trace level expected, these samples will be processed together. Method development and checking for blanks is already completed.

Quality Assurance/Quality Control (QA/QC)

All samples were collected by NWRI staff with the exception of air samples which were provided by L. Barrie. Water samples were spiked in the field with ^{37}Cl enriched 2,3,7,8 TCDD, and extracted with LVGE. Additional ^{13}C PCDDs and co-planar PCBs were added to the extracts and processed in the laboratory. Preliminary scans were done on a VG Tribrid MS at 1000 resolution. Preliminary results from a sample from Arctic Red are presented in Figure 1. Using a 3:1 signal to noise criteria results in a detection limit of 30 fg/L (.03 ppq). Better detection limits will be accomplished using HRMS at 10,000 resolution for the final report.

A similar procedure was applied to suspended solids; ^{13}C PCDDs and co-planar PCBs were added to the samples prior to extraction. Since only PUF and filter extracts were available for air samples, the extracts were spiked with ^{13}C PCDDs and co-planar PCBs.

Expected project completion date: March 1995

REFERENCES

Ahlborg, U.H, G.C. Becking, L.S. Birnbaum, A. Brouwer, H.J.G.M. Derks, M. Feeley, G. Golor, A. Hamberg, J.C. Larsen, A.K.D. Liem, S.H. Safe, C. Schatter, F. Wærn, M. Younes and E. Yrjänheikki. 1994. Toxic equivalency factors for dioxin-like PCBs. Report on a WHO-ECEH and IPCS Consultation, December 1993. Chemosphere 28: 1049-1067.

Barrie, L. 1993. Personal communication.

Federov, L.V. 1993. Ecological problems in Russia caused by dioxin emissions from chemical industry. Chemosphere 27: 91:96.

Gregor, D.J. and W. Gummer. 1989. Evidence of atmospheric transport and deposition of organochlorine pesticides and PCB in Canadian Arctic snow. Environ. Sci. Technol. 23: 561-565.

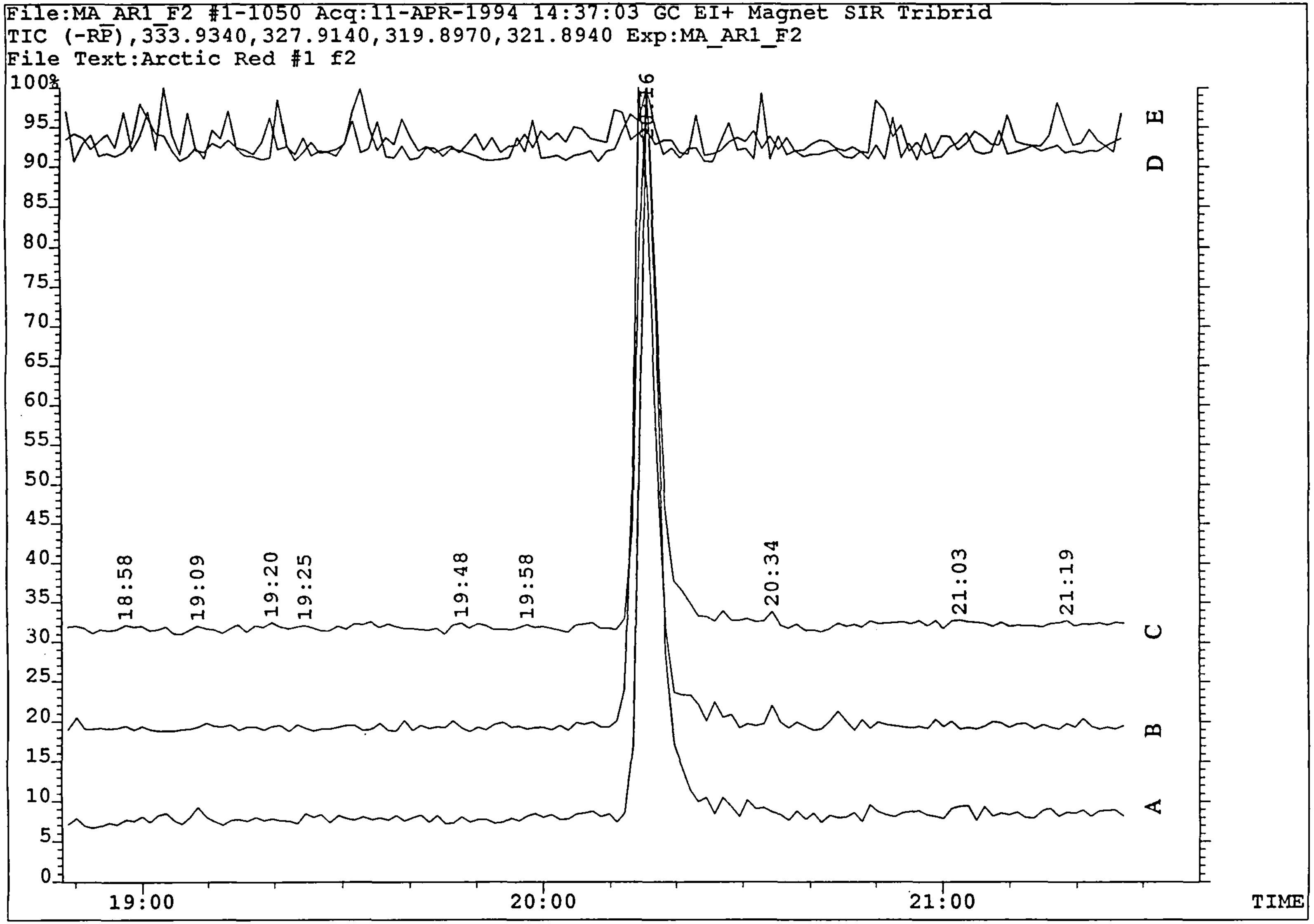
Hargrave, B.T., W.P. Vass, P.E. Erickson and B.R. Fowler. 1988. Atmospheric transport of organochlorines to the Arctic Ocean. Tellus 40B: 480-493.

Lexen, K., C. de Wit, B. Jansson, L.O. Kjeller, S.E. Kulp, K. Ljung, G. Söderström and C. Rappe. 1993. Polychlorinated dibenzo-*p*-dioxin and dibenzofuran levels and patterns in samples from different Swedish industries analyzed within the Swedish Dioxin Survey. Chemosphere 27: 163-170.

Muir, D.C.G. 1993. Co-planar PCBs in arctic marine mammals and fish. Pp. 99-104 *in*: Synopsis of Research Conducted Under the 1991/92 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 70. Indian and Northern Affairs Canada, Ottawa. 285 pp.

Norstrom, R.J., M. Simon and D.C.G. Muir. 1990. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in marine mammals in the Canadian north. Environ. Pollut. 66: 1-19.

Figure 1. Water sample from Arctic Red on the Mackenzie River, Yukon.



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File:MA_AR1_F2 #1-1050 Acq:11-APR-1994 14:37:03 GC EI+ Magnet SIR Tribrid
TIC (-RP),333.9340,327.9140,319.8970,321.8940 Exp:MA_AR1_F2
File Text:Arctic Red #1 f2
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A. TIC (total ion chromatogram); B. Ion chromatogram for mass 334, corresponding to 20 pg ^{13}C, 2,3,7,8 TCDD, laboratory internal standard; C. Ion chromatogram for mass 328 field internal standard corresponding to 20 pg of ^{37}Cl enriched 2,3,7,8 TCDD; D. and E. Ion chromatograms for masses 320 and 322, both corresponding to 2,3,7,8 TCDD. 2,3,7,8 TCDD in this sample is <30 fg/L (.03 parts per quadrillion).

RIVERINE INPUTS OF CONTAMINANTS

PROJECT LEADERS: D. Jeffries, J. Carey, National Water Research Institute, Environment Canada; and M. Swyripa, Water Resources Division, Indian and Northern Affairs Canada, Northwest Territories (NWT) Region

PROJECT TEAM: D. Gregor, University of Waterloo; S. MacDonald, Inland Waters Directorate-Northwest Territories

OBJECTIVES

Short-term:

To estimate and characterize the total contaminant load delivered by major river systems to the arctic marine environment, characterize its source and seasonal variability, and assess the controlling biogeochemical processes.

Long-term:

To investigate and quantify the processes and rates of contaminant transport and transformation in northern riverine systems, assess applicability of existing predictive models and refine as necessary, and develop an understanding of the biogeochemical dynamics of contaminants at the freshwater/marine interface in northern systems.

DESCRIPTION

Northward flowing rivers that drain 10^7 km^2 of northern Asia, northern Europe and North America may be major conduits to the Arctic Ocean of contaminants originating from point sources and/or atmospheric deposition to the terrestrial ecosystem. While the amount of freshwater flowing into the Arctic Ocean is only ~1% of the inflow of water entering through Fram Strait, rivers have an important effect on the oceanography of the region. Freshwater inflows contribute to the stable, less dense, more productive surface layer, and adjacent to river mouths, introduce turbid water and establish horizontal density gradients that drive ocean currents. The processes in river systems that control contaminant mobility, timing and rate of provenance to the arctic marine environment are likely different from those in temperate climates.

Information on contaminant loadings to the Arctic Ocean from any northward flowing river is limited. Prior to the commencement of this study, what did exist for North America focused on the Mackenzie River since it is the only major river system. Beyond simple loading data, however, there is also a need to obtain more extensive information on contaminant fate and effects, both within the river system itself and at the freshwater-seawater interface. Moreover, in order to ensure that no major contaminant pathway has been missed, river systems that drain other ecozones (e.g. tundra) and flow into other marine environments (e.g. estuarine versus deltaic) must be considered. Such information can only be obtained in the short-term through an intensive research survey that effectively extends existing data and anticipates long-term monitoring data.

Once completed, this study will provide: 1) good baseline information on the magnitude, source, and spatial and temporal variability of contaminant delivery by river systems to the Arctic Ocean for use in Canada's Northern Contaminants Program and the Arctic Monitoring and Assessment Programme (AMAP); 2) a basis for assessing and/or refining preliminary transport and fate models; and 3) a basis for identifying remaining information gaps to assist planning of further field work.

Progress Prior to Fiscal 1993/94

In 1991/92, a review of existing trace organic contaminant data was undertaken that included a classification of NWT river systems based on hydrology, suspended sediment loads, geology, geomorphology, vegetation and climate. This information was used to design subsequent field sampling programs. In 1992/93, the Mackenzie River was sampled in June, July and August near Inuvik (East Channel), Aklavik (West Channel) and Arctic Red River (Main Channel) for suspended sediment and filterable solids, temperature, conductivity, pH, major ions, and a suite of organic contaminants (see below). A survey of 11 rivers (the Anderson and 10 rivers in the District of Keewatin) was conducted in August using the Mackenzie sampling protocol except that only water and suspended solid samples were collected due to the low filterable sediment load in these rivers. Sample processing and laboratory analyses commenced in the fall and winter of 1992/93.

ACTIVITIES IN 1993/94

Sample Collection

After consideration of preliminary 1992/93 data, follow-up sampling was conducted at all sites in 1993/94 by Sean Backus (contract), Murray Swyripa, Juanetta Peddle (Indian and Northern Affairs Canada) and assisted by Brian Ferguson (Fisheries and Oceans Canada). See Figures 1 and 2 for sample locations. A greater number of field blanks were collected to improve quality control. The 3 Mackenzie River sites were sampled on 3 occasions as before to permit evaluation of between-year variability. In addition, to enhance evaluation of seasonal variability, sub-ice sampling in the winter was conducted for the first time. Replicate samples were collected at the Arctic Red River site to assess between-sample variability. The Keewatin sites and the Andrews River (substituted in 1993/94 for the Anderson River) were sampled once during peak spring flow in July to repeat the 1992 work. A large volume water sample (108 L at the Keewatin sites, the Andrews, and at Arctic Red and 40 L at Inuvik and Aklavik) and a suspended sediment or filterable solid sample were collected at each site.

RESULTS

Sample Analysis

OCs in water: Procedures for the extraction of large volume water samples using the Goulden extractor are given by Neilson *et al.* (1988) and further details on the extraction and cleanup steps are given by Comba *et al.* (1993).

Sediments: Sub-sets of suspended sediments collected from the Mackenzie River were freeze-dried and analyzed for trace metals and particle size analysis. Wet sediments were extracted with hexane:acetone (41:59) in a Soxhlet apparatus using glass thimbles with sintered glass frits. Internal standards of deuterated PAHs and 1,3,5-tribromobenzene and 1,2,4,5-tetrabromobenzene were added after the extraction step. The extract was chromatographed on a silica column (topped with 1 cm sodium sulphate) and eluted with hexane (to recover alkanes) followed by hexane:dichloromethane (1:1) for 2 to 6 ring PAHs. Organochlorines (OCs) were isolated in the same step.

Capillary gas chromatographic analysis of PCBs, toxaphene, DDT and other organochlorines was carried out on a HP-5890 GC equipped with a 30 m x 0.25 mm x 0.25 μm DB-5 column and a 30 m x 0.25 mm x 0.25 μm OV-1 column. Quantitation of organochlorines was based on dual column confirmation using an external standard. PCBs were measured as individual congeners based on the dual capillary column procedure established at the 1985 PCB workshop in Grosse Ile, Michigan (Mullin *et al.* 1985). Initial quantitation of PCB congeners was carried out using the primary Green Bay (GB) Mass Balance PCB standard (Swackhamer *et al.* 1988) obtained through the University of Minnesota. The GB PCB standard is a mixture of Aroclors 1232, 1248, and 1262 from the Quality Assurance Branch, U.S. EPA, Cincinnati, Ohio, in the ratio of 25:18:18. Individual congener concentrations were calibrated by Mullin (Mullin *et al.* 1985) for this specific PCB standard. A second primary PCB standard was prepared using purchased Aroclor solutions of 200 $\mu g.ml^{-1}$ 1016, 1221, 1242, 1254 and 1262 at ratios of 1:1:1:1:1 and reconstituted in hexane to a concentration of 1 $\mu g.ml^{-1}$. This secondary PCB standard was calibrated with the primary GB standard and verified using all 209 individual PCB congeners. PAHs were quantified by capillary GC-mass spectrometry (HP 5890-5971 MSD) using an external standard technique.

Beyond the physical and inorganic variables, both the dissolved and particulate phase samples have been analyzed for 8 chlorobenzenes, 20 organochlorine pesticides, 120 PCB congeners, 17 PAHs, several alkylated PAHs and acyclic hydrocarbons and are currently being analyzed for toxaphene by GC-NIMS. The currently available raw data show that most samples have total PCBs and other OC values below detection limits after blank correction. A small number of OC variables (e.g. HCH) are occasionally detectable. The PAH concentrations in the particulate phase are shown graphically in Figures 3, 4 and 5. Obviously there are substantial spatial and temporal differences in particulate phase PAH levels found at the 3 Mackenzie sites (Figure 3). Similarly, large differences exist among the 10 Keewatin rivers (Figures 4 and 5).

QA/QC

The laboratories participating in this project include several at Environment Canada's National Water Research Institute (NWRI) and the Indian and Northern Affairs-Water Resources, Water Laboratory in Yellowknife. The NWRI laboratories participate in the Northern Contaminants QA/QC Program. Within study QA/QC is extensive and is designed first, to identify when the entire procedure does not function according to specifications, and second, to determine which sub-procedure has failed (e.g. contaminant isolation, pre-analysis concentration, fractionation, etc.).

General Water Quality and Metals

Results of the analyses for trace metals, nutrients, and physical variables are summarized in Tables 1 and 2. In general, the rivers have low levels of filterable and non-filterable residues, low hardness and alkalinity, and low nutrient levels. Metal levels were also generally very low. The Andrews River water quality differs significantly from the other sites.

DISCUSSION

The analyses of these samples were completed in 1993/94, and the data are still under review and evaluation. In this regard, the data presented in the tables and figures should be considered preliminary at this time. Upon receipt of flow data in early July 1994, river loadings will be calculated.

Expected completion date: March 31, 1997

REFERENCES

Comba, M.E., V.S. Palabrica, S.M. Backus, and K.L.E. Kaiser. 1993. St. Lawrence River Trace Organic Study Part IV, 1989-90 and Summary. National Water Research Institute, Report 93-19, 46 pp.

Mullin, M.D. 1985. PCB Workshop. U.S. EPA Large Lakes Research Station, Grosse Ile, M.I. June.

Neilson, M. and R. Stevens. 1988. Evaluation of a large-volume extractor for determining trace organic contaminant levels in the Great Lakes. Water Poll. Res. J. Canada. 23: 578-588.

Swackhamer, D.L. 1988. Quality Assurance Plan, Green Bay Mass Balance Study. I. PCBs and Dieldrin, University of Minnesota, March 11.

Table 1. Keewatin Rivers Field Data.

	Coppermine	Burnside	Ellice	Dubawnt	Thelon	Back	Kazan	Hayes	Quoich	Lorillard
Latitude (N)	67° 13' 45"	66° 43' 26"	67° 42' 29"	64° 13' 52"	64° 46' 23"	66° 05' 10"	63° 39' 10"	67° 31' 30"	64° 18' 22"	64° 17' 36"
Longitude (W)	115° 53' 11"	108° 48' 40"	104° 08' 19"	99° 28' 37"	97° 04' 04"	96° 30' 15"	95° 51' 19"	94° 05' 19"	93° 55' 02"	90° 26' 49"
Sampling Date	20/7/93	20/7/93	20/7/93	22/7/93	22/7/93	21/7/93	22/7/93	21/7/93	21/7/93	21/7/93

	Coppermine	Burnside	Ellice	Dubawnt	Thelon	Back	Kazan	Hayes	Quoich	Lorillard
pH	8.19	7.94	7.87	7.86	7.74	6.72	7.04	6.23	7.62	7.84
Turbidity	112	0	11	8.0	313	122	0	31	0	2
Salinity	0	0	0	0	0	0	0	0	0	0
D.O. (mg/L)	10.67	11.10	10.53	10.78	14.42	11.16	11.40	9.42	10.07	10.15
Conductivity (ms/cm)	0.056	0.013	0.015	0.013	0.017	0.012	0.018	0.005	0.006	0.006
Temperature (°C)	10.8	11.4	16.4	10.1	6.1	11.5	14.0	17.8	18.7	15.6
SPM (mg/L)	26.4	0.93	8.4	1.2	1.3	1.1	0.3	9.2	0.3	1.1
DIC (mg/L)	7.1	1.6	0.8	1.3	2.1	1.1	1.8	0.6	0.4	0.3
DOC (mg/L)	7.5	4.2	7.6	8.5	21.5	4.2	8.2	8.4	27.3	13.2
POC (mg/L)	0.388	0.121	0.328	0.401	0.262	0.268	0.193	0.414	0.221	0.114
PON (mg/L)	0.041	0.012	0.028	0.040	0.03	0.024	0.017	0.039	0.028	0.013
DOC/POC	19	35	23	20	82	16	42	20	124	94

D.O. = Dissolved Oxygen
SPM = Suspended Particulate Matter
DIC = Dissolved Inorganic Carbon
DOC = Dissolved Organic Carbon
POC = Particulate Organic Carbon
PON = Particulate Organic Nitrogen

Table 2. Major ions, nutrients, metals and physical variables for the Arctic Rivers. Triplicate samples were collected at the Andrews and Hayes Rivers; mean and standard deviation are shown.

	Andrews (n=3)	Coppermine	Burnside	Ellice	Dubawnt	Thelon	Back	Kazan	Hayes (n=3)	Quoich	Lorillard
Sampling Date		20/7/93	20/7/93	20/7/93	22/7/93	22/7/93	21/7/93	22/7/93	21/7/93	21/7/93	21/7/93
Alkalinity (mg/L)	88.7 ± 0.08	27.2	4.2	1.6	3.8	4.7	2.7	6.2	<0.3	<0.3	<0.3
Calcium (mg/L)	26.87 ± 0.09	6.40	1.40	1.00	1.50	1.70	1.00	2.00	0.4 ± 0	0.50	0.40
Chloride (mg/L)	2.02 ± 0.02	0.43	0.37	1.84	0.44	0.90	0.66	0.40	0.67 ± 0.004	0.53	0.63
Colour	18 ± 5	12	<5	12	<5	<5	<5	<5	11 ± 2	<5	<5
Tot. Hardness (mg/L)	95.7 ± 0.5	29.0	6.0	5.0	5.8	7.1	5.0	7.9	<3	<3	<3
Potassium (mg/L)	1.20 ± 0	0.40	0.30	0.30	0.30	0.40	0.30	0.20	0.27 ± 0.05	0.20	0.30
Magnesium (mg/L)	7.00 ± 0.05	3.10	0.60	0.60	0.50	0.70	0.60	0.70	0.20 ± 0	0.20	0.20
Sodium (mg/L)	4.80 ± 0	0.50	0.40	1.20	0.40	0.50	0.40	0.40	0.53 ± 0.05	0.50	0.50
T-Phosphorous (mg/L)	0.006 ± 0	0.007	0.002	0.009	<0.002	<0.002	0.003	<0.002	0.008 ±	0.002	0.014
Non-Filt Res (mg/L)	<3	4	<3	<3	<3	<3	<3	<3	5 ± 2	<3	<3
Ammonia-N (mg/L)	0.014 ± 0.003	0.004	0.005	0.009	0.016	0.011	0.158	0.027	0.017 ±	0.019	0.007
NO_3+NO_2-N (mg/L)	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008
Ortho-Phos (mg/L)	<0.002	<0.002	0.003	0.005	<0.002	<0.002	0.002	0.018	0.006 ± 0	<0.002	<0.002
pH	8.18 ± 0.01	7.40	6.71	6.51	6.63	6.63	6.53	6.89	6.17 ± 0.02	6.14	6.15
Sulphate (mg/L)	14.4 ± 0.6	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3
T. Arsenic-Hyd (μg/L)	0.3 ± 0	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
T. Cadmium-S/E (μg/L)	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
T. Cobalt-S/E (μg/L)	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
T. Chromium- S/E (μg/L)	<1	<1	<1	<1	<1	<1	<1	<1	1 ± 0	<1	<1
T. Copper-S/E (μg/L)	1 ± 0	2	1	1	<1	<1	<1	<1	1 ± 0	<1	<1
T. Iron-S/E (μg/L)	327 ± 40	374	170	397	105	82	152	56	626 ± 30	128	75
T. Mercury-C/V (μg/L)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
T. Nickel-S/E (μg/L)	2 ± 0.5	1	1	<1	<1	<1	<1	<1	1 ± 0	<1	<1
T. Lead-S/E (μg/L)	1 ± 0	<0.7	<0.7	1	<0.7	<0.7	1	<0.7	1.3 ± .5	<0.7	<0.7
T. Zinc-S/E (μg/L)	2.0 ± .8	1.0	3.0	1.0	1.0	<1	1.0	<1	1.3 ± .5	1.0	<1
Turbidity (NTU)	3.0 ± 0.3	4.8	0.8	8.5	0.6	0.7	1.1	0.6	9.0 ± .7	1.1	0.6

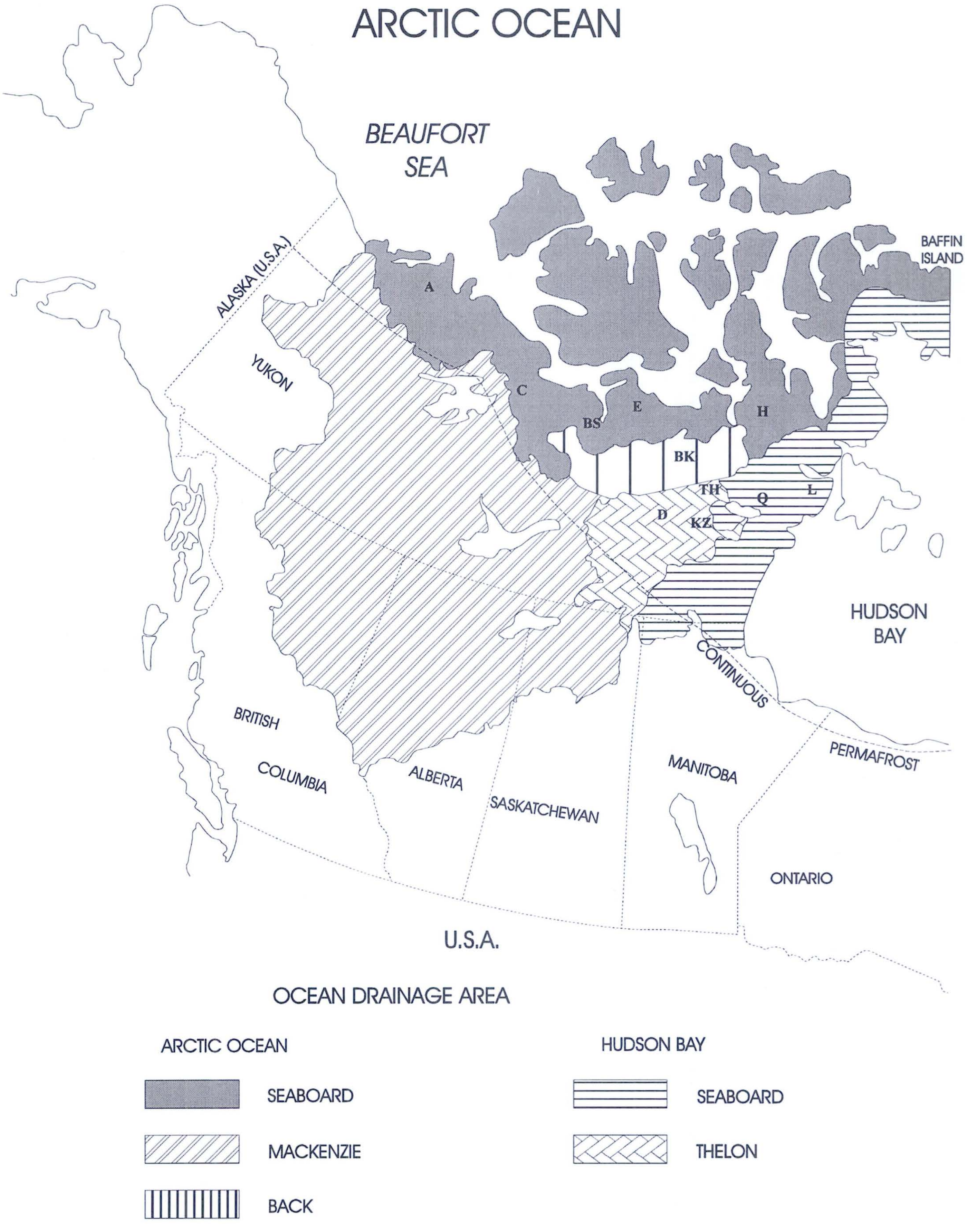


Figure 1. Sampling locations showing drainage basins, 1993/94.

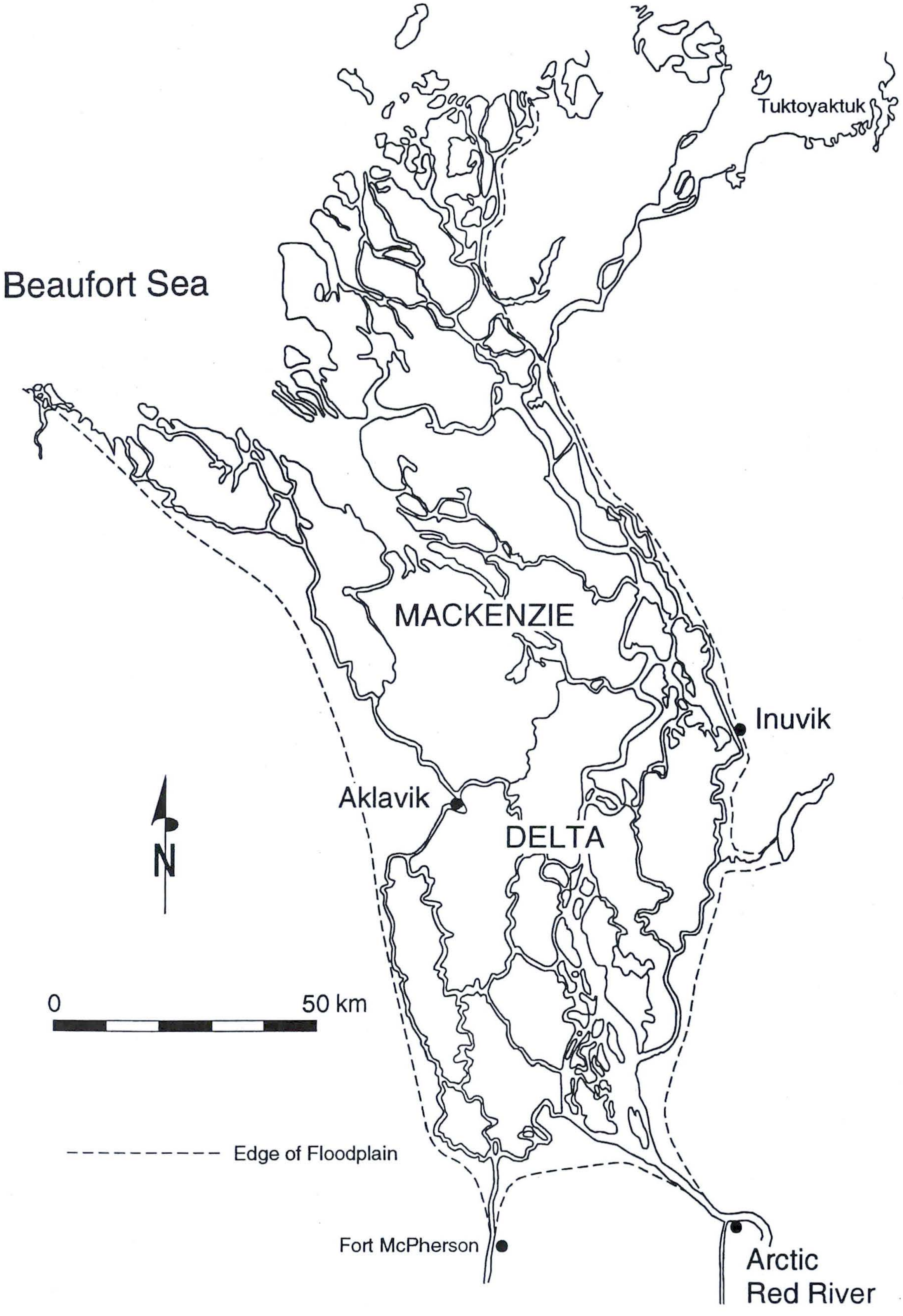
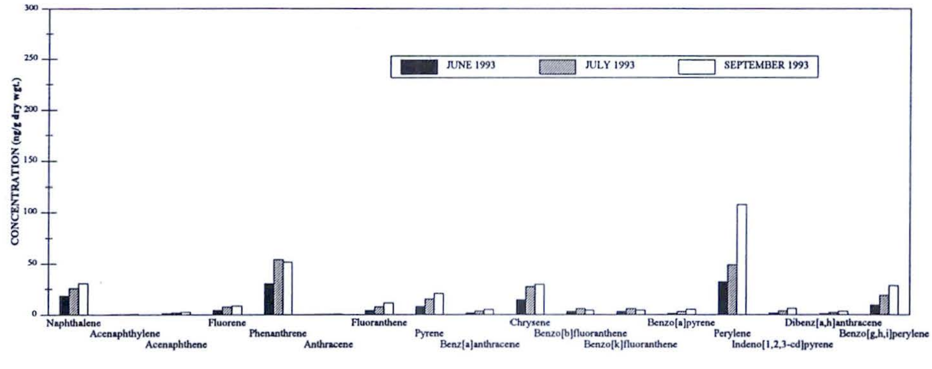
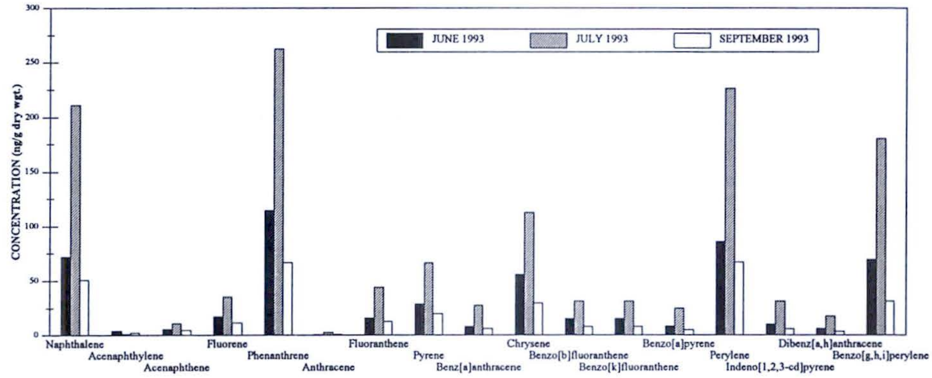


Figure 2. Sampling locations on the Mackenzie River 1993/94.

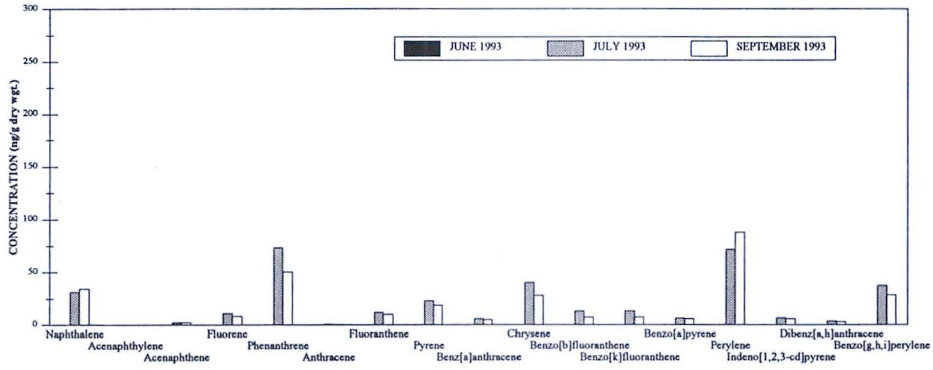
PAH CONCENTRATIONS IN SPM AT INUVIK



PAH CONCENTRATIONS IN SPM AT AKLAVIK



PAH CONCENTRATIONS IN SPM AT
ARCTIC RED RIVER



Note: Sampling at Arctic Red River was not completed in June because of mechanical problems with the centrifuge.

Figure 3. PAH Distributions in Suspended Particulate Matter in the Mackenzie Delta.

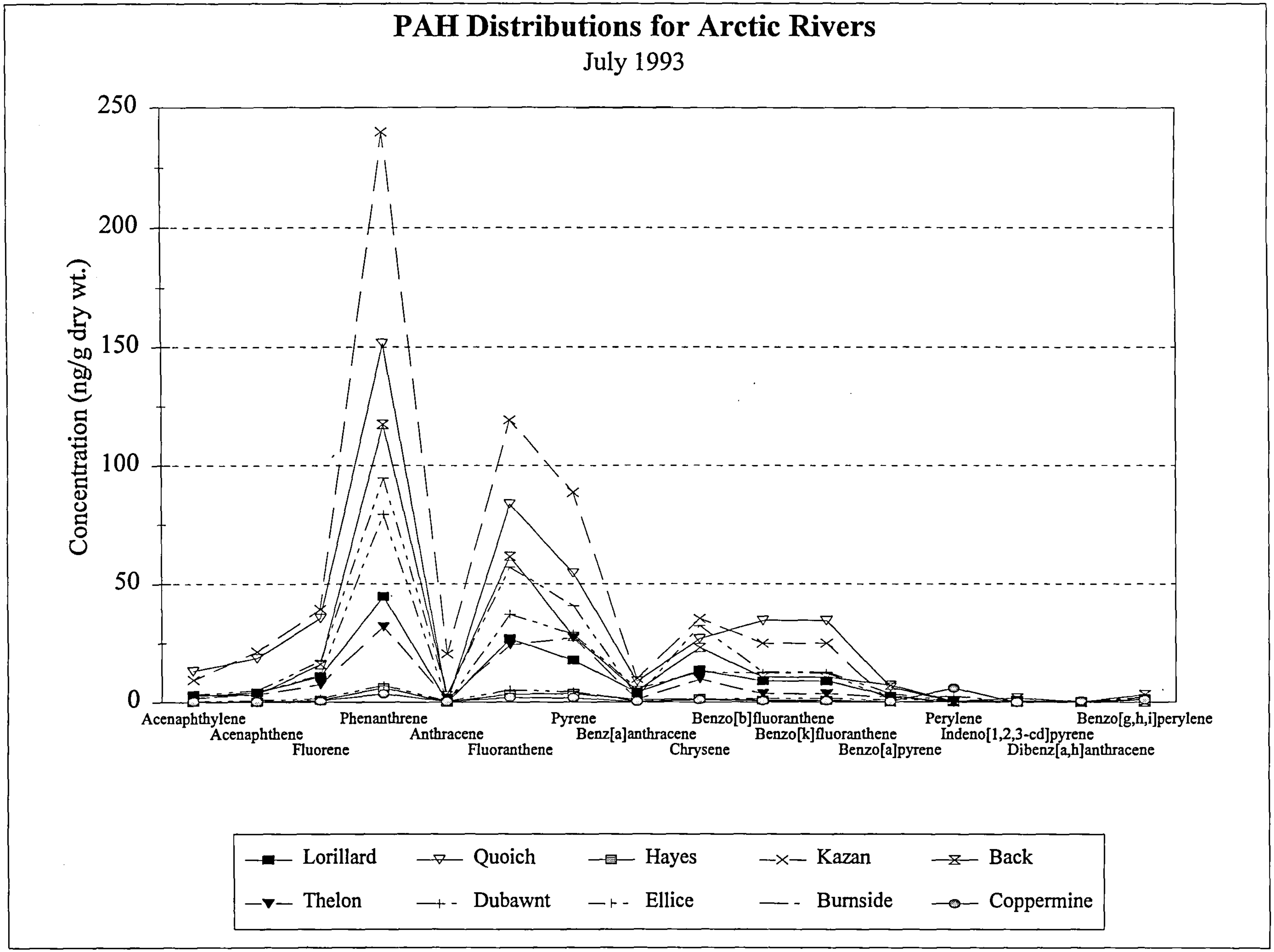


Figure 4. PAH Distributions in Suspended Particulate Matter of Arctic Rivers.

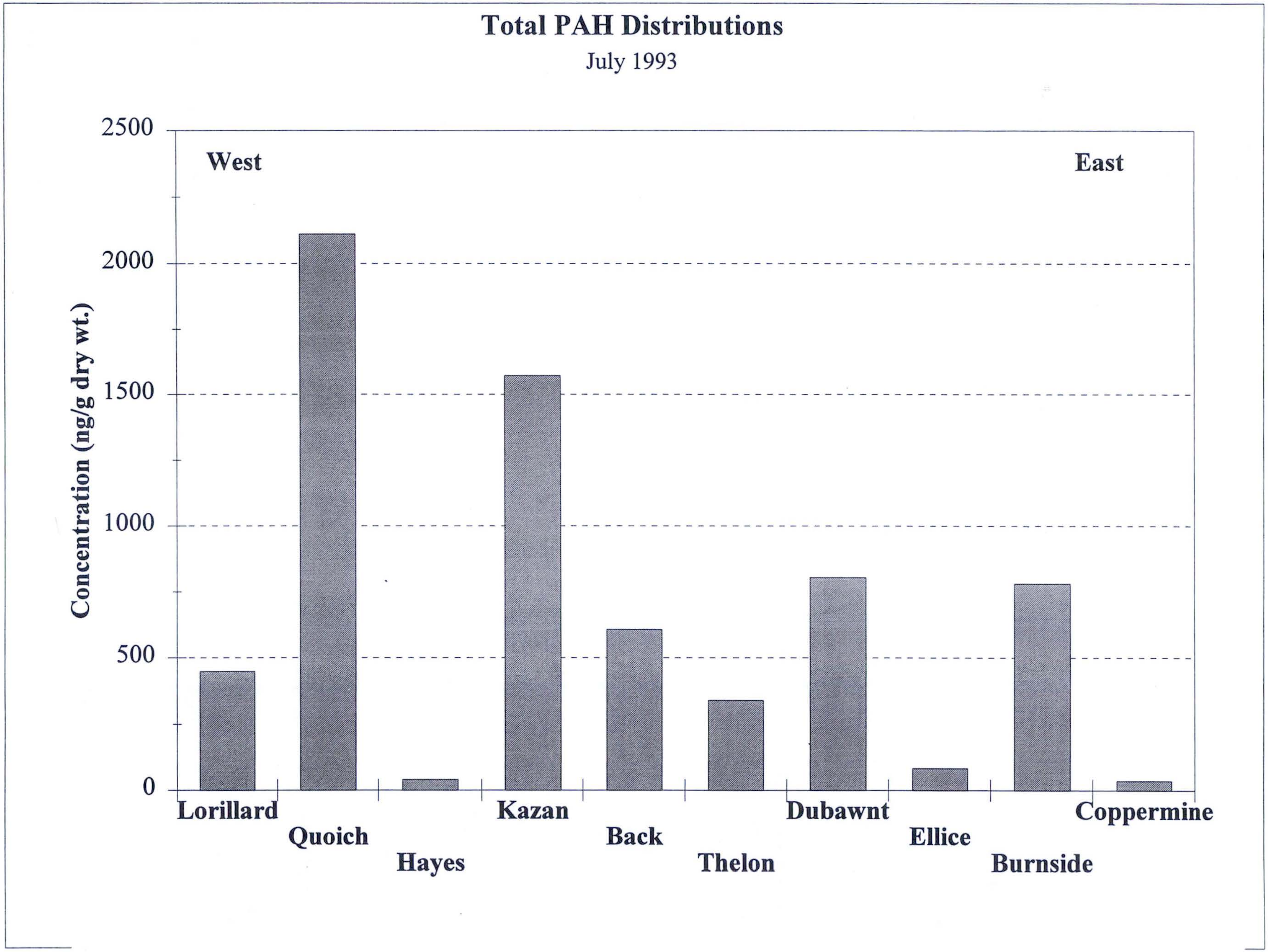


Figure 5. Total (16 Priority) PAH Distributions in Suspended Particulate Matter of Arctic Rivers.

MODELLING INORGANIC AND ORGANIC CONTAMINANTS IN ARCTIC FRESHWATER LAKES

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PROJECT TEAM: D.J. Gregor, R. Semkin, M. Alaee, D.C.G. Muir, T. Bidleman

OBJECTIVES

Short-term:

1. To compile mass balance models to estimate the fate and transport of inorganic and organic contaminants in arctic freshwater lakes, including Char and Amituk Lakes on Cornwallis Island.
2. To investigate key factors controlling contaminant movement and exposure to aquatic organisms.
3. To identify long-term and transient sinks of inorganic and organic contaminants.
4. To estimate the response time of arctic lakes to changes in contaminant loadings.

Long-term:

1. To quantify the fate and transport of various inorganic and organic contaminants in arctic freshwater systems.
2. To evaluate the sensitivity and response of arctic lakes to contaminant loadings.
3. To extend our understanding of contaminant dynamics in arctic lakes to the larger arctic ecosystem.

DESCRIPTION

There are several compelling reasons to examine chemical dynamics in lakes. Firstly, lakes are generally regarded as sinks for chemicals, thereby reducing the movement of chemicals to the surrounding ecosystem. The assumption of lakes acting as chemical sinks, requires examination in Arctic systems. Secondly, chemical concentrations in lake sediments and fish have been used as indicators of chemical loadings, allowing spatial and temporal comparisons to be made. For this comparison to be a valid, we must establish a quantitative link between sediment and fish concentrations, and loadings, and understand factors that may confound or complicate the comparison. Finally, since lakes are contained systems in which inputs, outputs and processes can be relatively easily quantified, and their food chains are simple, they can be viewed as archetypical systems, allowing us to improve our understanding of chemical transport mechanisms within a system, and movement of chemicals from the environment into the food chain. Thus, results obtained from lakes can be used to improve our understanding of the larger Arctic ecosystem.

ACTIVITIES IN 1993/94

1. An unsteady-state version of the lake model was developed which includes the build-up and degeneration of ice cover with the concomitant cryoconcentration of solutes in the unfrozen water.

2. The steady- and unsteady-state models were extended to treat chemicals that exist as multiple, interconverting species such as mercury.

3. The model of species interconversion was applied to groups of related organic chemicals, e.g. DDT, DDD and DDE; α-, β-, and γ-HCH. Application to PCB homologues awaits receiving the data.

4. The food chain model was modified to account for physiological adaptations in Arctic fish (specifically Arctic char), e.g. low growth rate, and low feeding rate but high digestive efficiency.

5. The lake model was used to examine the dynamics of α- and γ-HCH, chlordane, HCB, PCC, DDT and mercury in Amituk Lake. These simulations used 1992 chemical concentration data from Gregor and Semkin for Amituk snow and water, Muir and Lockhart for fish and sediments, and Bidleman for air.

6. H. Freitas, a graduate student funded by this project, participated in field studies at Amituk Lake during summer 1993.

RESULTS

Modelling efforts concentrated on Char and Amituk Lakes. The Char Lake model was recalibrated, again using the phosphorus data set compiled by Rigler, Schindler and co-workers in the early 1970's (e.g. Schindler *et al.* 1974, Rigler 1975). Figure 1 illustrates that correspondence between measured and observed phosphorus concentrations within Char Lake was achieved to within a factor of two by manipulating the fraction of inflow, and hence chemical, that mixes with the water column rather than flowing through the lake during ice melt. The model was then used to estimate contaminant concentrations in Char Lake, comparing the results with measured fish concentrations. A more rigorous test of the model will, hopefully, come with analysis of organochlorines in Char Lake sediments (during summer 1994 efforts will again be made to obtain sediment samples for chemical analysis).

The model of Amituk Lake was updated to include hydrologic and particle dynamics data obtained during the summer of 1993 (organochlorine and mercury data were from the 1992 field season). Results from the steady-state version generally over-predicted water and under-predicted sediment concentrations, the extent of which was chemical-specific (Figure 2). To improve the agreement between measured and estimated water and sediment concentrations, a K_P value (quantifying chemical partitioning between particle and dissolved phases) was used rather than a K_{OC}-based estimate of partitioning based on the organic carbon content of particles and sediment (Karickhoff 1974). Model results suggested that the discrepancy between results obtained using K_P and K_{OC} was greater for less hydrophobic chemicals. This deduction was supported by evidence suggesting that mineral matter sorbs significantly more organic chemicals (particularly the less hydrophobic chemicals) in systems in which the organic carbon content is extremely low, e.g. groundwater aquifers (Curtis *et al.* 1986, Calvert 1989). By using K_P values, agreement between measured and estimated concentrations was achieved to within a factor of two for most organochlorines (Figure 3).

Model results for mercury are purely illustrative at this point since we have limited data with which to parameterize and test the lake model. However, using predicted water and sediment mercury concentrations, good agreement was obtained between measured and estimated fish concentrations using two methods, a simple bioconcentration factor and the mechanistic food chain model (Figure 4). The results indicate the movement of three forms of mercury through the system with, again, minimal total mercury being retained in the lake and some elemental mercury volatilizing during the ice-free season.

Our first attempt to estimate organochlorine concentrations in Arctic char in Char and Amituk Lakes resulted in underestimates of measured values. After a thorough review of the literature on the physiology of Arctic char and related species, the rate constants developed by Gobas (1992) for his model of chemical uptake by fish, were altered to better reflect Arctic conditions. Major changes came in rates of chemical uptake across the gills (due to decreased metabolic rate), egestion (due to increased metabolic efficiency) and growth (Table 1). With these modifications, agreement was improved to within a factor of 2.5 for HCH and DDT (Figure 5).

Table 1. Comparison of rate constants for Arctic char and a related temperate salmonoid of similar size (30 g). Rate constants for the Arctic char are expressed as percentages of that for the temperate counterpart.

Process	Arctic rate constant as % of temperate
Chemical Uptake	
Gill uptake	15%
Food uptake	20%
Chemical "Loss"	
Gill elimination	50%
Fecal elimination	12%
Chemical metabolism	50%
Growth dilution	33%

DISCUSSION/CONCLUSIONS

1. Minimal levels of chemicals are retained in lake sediments, e.g. about 3% and <1% of DDT and ΣHCH, respectively, were estimated to be retained in Amituk Lake. This is due to two factors:

   i) a limited fraction of the inflow actually mixes with the water column of the lake. This fraction is lake-specific and thus determines lake loading,

   ii) low suspended particle concentrations and deposition rates limit the amount of chemical conveyed to and subsequently buried in the sediment.

Thus, unlike temperate lakes, arctic lakes are not significant sinks for chemicals. This implies that contaminant concentrations, at least in the water column, should respond rapidly to changes in loadings. This response will be largely controlled by water residence time. Conversely, chemicals that do enter the sediments are much more persistent because of limited sediment/water exchange, burial and chemical degradation rates. A second implication is that whereas sediment profiles chronicle relative changes in chemical loadings to a lake, the profiles alone cannot be used to deduce total or absolute loadings.

2. Our results suggest that a significant fraction of organochlorines partition into mineral, as well as organic phases, due to the extremely low organic carbon content of suspended particles and sediment (e.g. 3 and 1.2%, respectively). This effect, as seen in groundwater aquifers that typically have minimal organic carbon, is most pronounced for chemicals with low K_{OW}, such as HCH and PCC. Thus, for arctic systems, Karickhoff's (1974) relationship that predicts chemical sorption based on K_{OW} or K_{OC} underpredicts sorption and hence sediment retention.

3. In arctic lakes more chemical is bioavailable (dissolved) in the water column than in temperate lakes for several reasons. Firstly, as noted above, a higher proportion of chemical remains in the water column rather than the sediments of arctic lakes. In the water column most chemical is dissolved because chemical sorption is limited by extremely low suspended particle and dissolved organic carbon concentrations. Secondly, ice cover over 45 weeks of the year impedes the loss of dissolved chemical by volatilization. Thirdly, cryoconcentration (the freeze-out of chemicals from ice and consequent concentration in water) can increase the concentration of chemicals in the water by more than 15% during the long period of ice cover. For fish, an elevated dissolved concentration may result in relatively more of the moderately hydrophobic or hydrophillic chemicals such as HCH, entering via the gills versus the food chain (in comparison to a temperate lake).

4. In high arctic lakes the food chain consists of benthos (mostly chironomids) and Arctic char. The adult char may consume their young thereby adding another link in the food chain. The relatively high fish contaminant concentrations in these lakes is due principally to the longevity and slow growth and, secondarily, the high digestive efficiency of the char. For hydrophobic chemicals such as DDT, fish concentrations will respond very slowly to changes in loading because of the slow growth rate of the fish and because most chemical enters via the benthic-driven food chain. As noted above, chemicals are estimated to be very persistent in sediment due to restricted sediment/water exchange.

5. Chemicals appear to be relatively more mobile in Arctic lakes, than their temperate counterparts. Lakes do not act as efficient sinks, and Arctic fish appear to be less able to bioconcentrate and biomagnify organic chemicals than similar temperate species. Nonetheless, Arctic fish do achieve high concentrations, largely attributable to their age. In this respect, it is suggested that these simple ecosystems are illustrative of other, more complex ecosystems in the Arctic.

Expected project completion date: We expect to complete the project in 1996 or 1997, depending on availability of chemical concentration data from Amituk Lake.

REFERENCES

Calvert, R. 1989. Adsorption of organic chemicals in soils. Environ. Health Perspectives 83: 145-177.

Curtis, G.P., P.V. Roberts and M. Reinhard. 1986. A natural gradient experiment on solute transport in a sand aquifer. 4. Sorption of organic solutes and its influence on mobility. Water Res. Res. 22: 2059-2067.

Gobas, F.A.P.C. 1992. Modelling the accumulation and toxicity of organic chemicals in aquatic food chains. Pp. 129-151 *in*: Chemical Dynamics in Fresh Water Ecosystems, F.A.P.C. Gobas and J.A. McCorquodale (eds.). Lewis Publ., Chelsea, MI.

Karickhoff, S.W. 1984. Organic pollutant sorption in aquatic systems. J. Hydraulic Eng. 110: 707-735.

Rigler, F. 1975. The Char Lake Project: an introduction to limnology in the Canadian Arctic. Pp. 171-198 *in*: Energy Flow - Its Biological Dimensions. A Summary of the IBP in Canada, T.W. Cameron and L.W. Billingsley (eds.). Royal Society of Canada, Ottawa.

Schindler, D.W., H.E. Welch, J. Kalff, G.J. Brunskill and N. Kritsch. 1974. Physical and chemical limnology of Char Lake, Cornwallis Island (75° N). J. Fish. Res. Board Can. 31: 585-607.

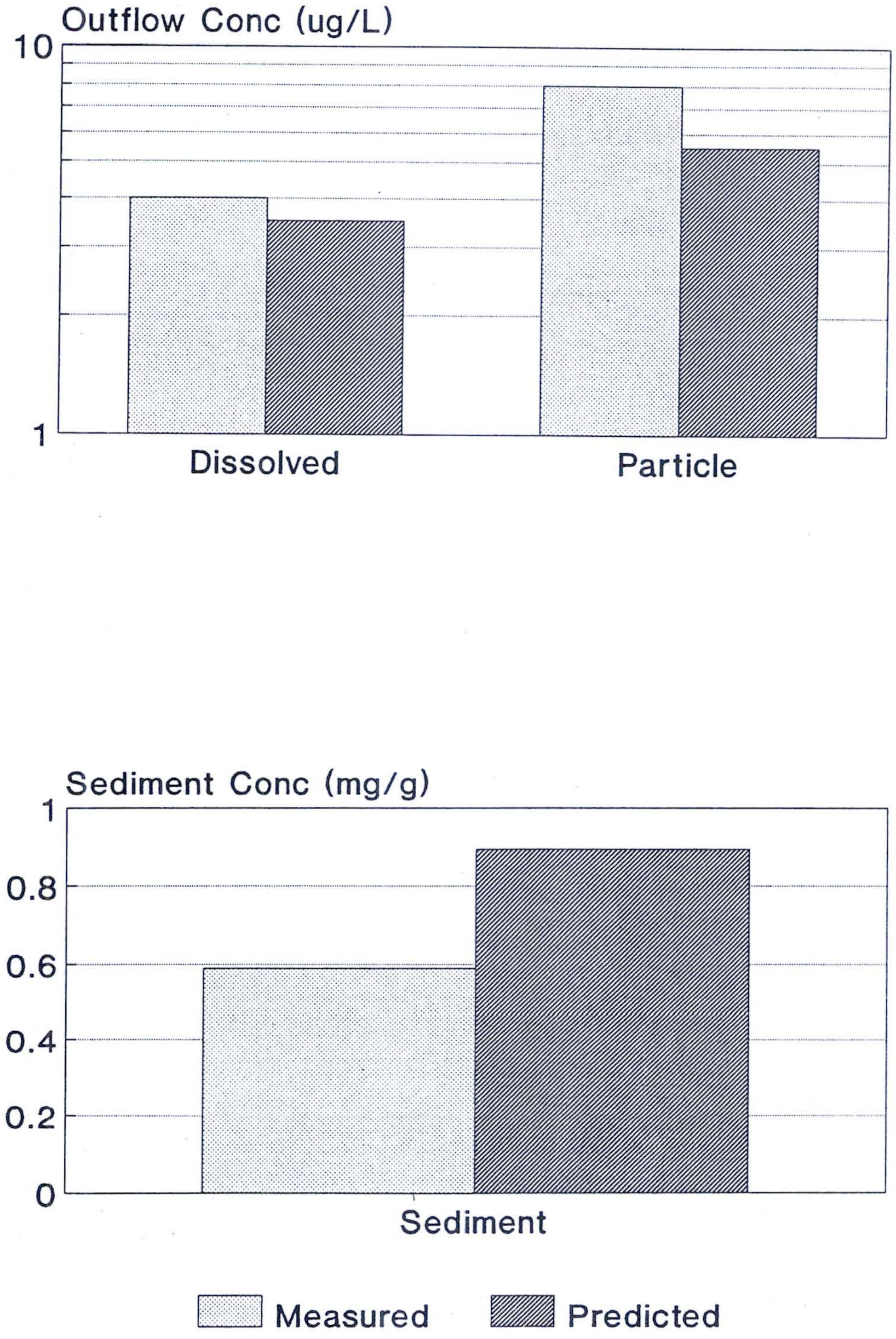
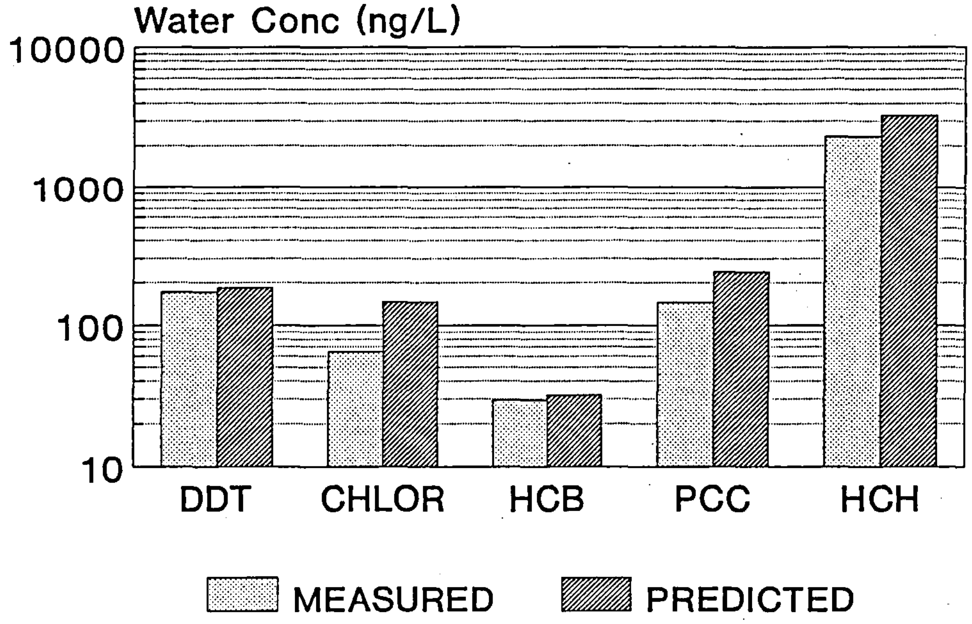


Figure 1. Phosphorus concentrations in Char Lake.



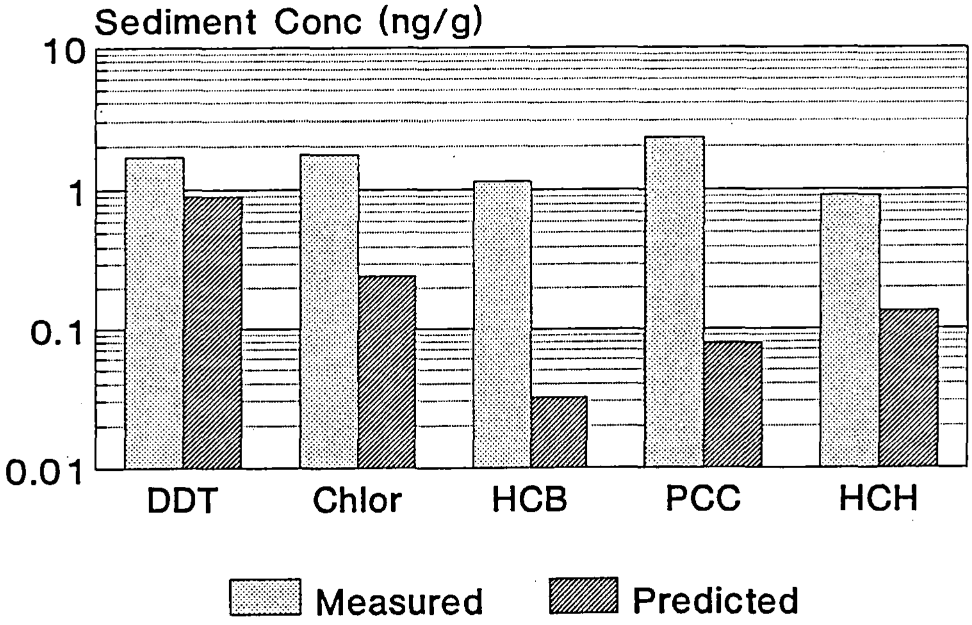


Figure 2. Measured versus predicted organochlorine concentrations in Amituk Lake water and sediment. Predicted values were obtained with K_{oc}-based partition coefficients.

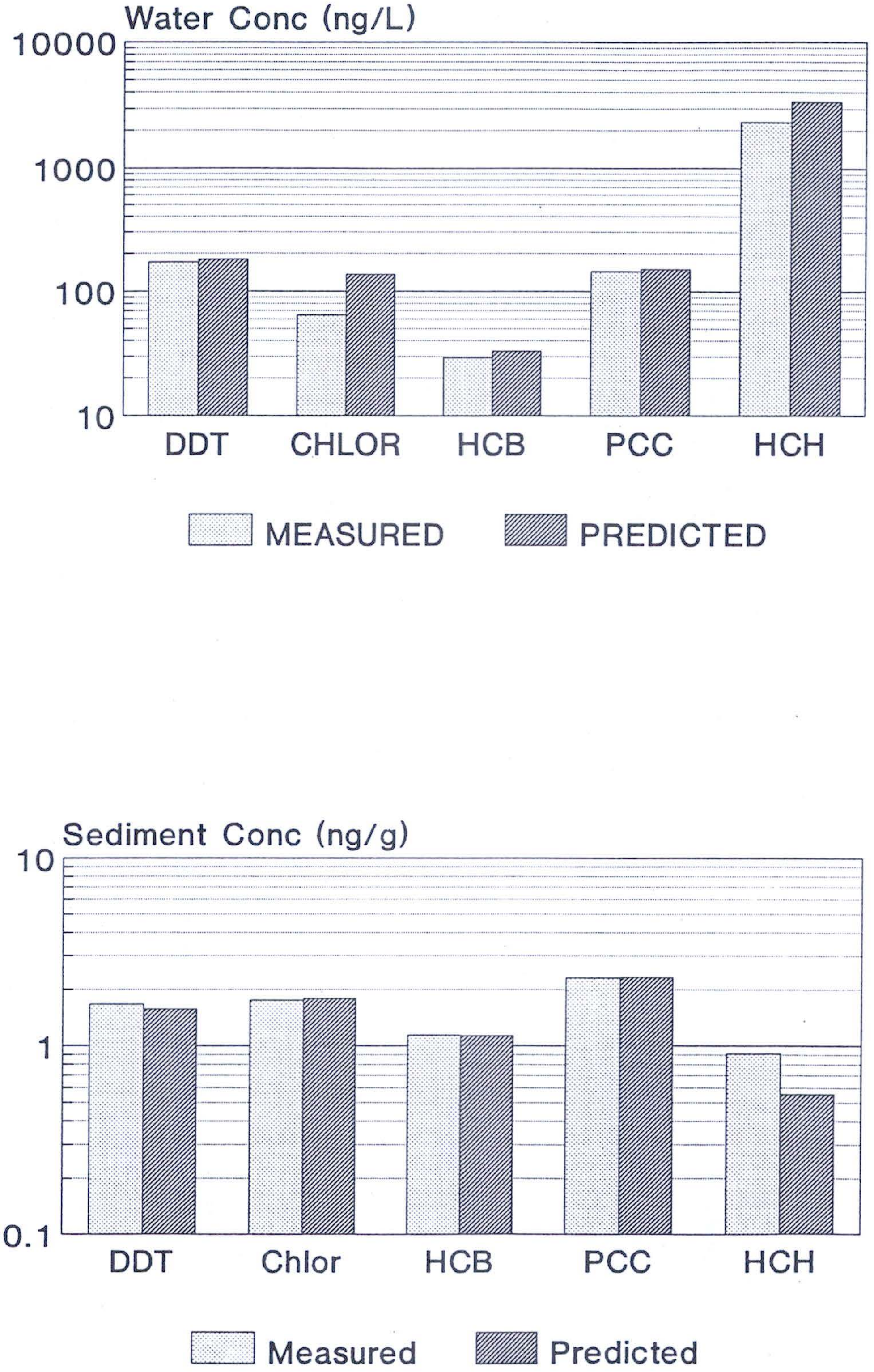


Figure 3. Measured versus predicted organochlorine concentrations in Amituk Lake water and sediment. Predicted values were obtained with empirical partition coefficients.

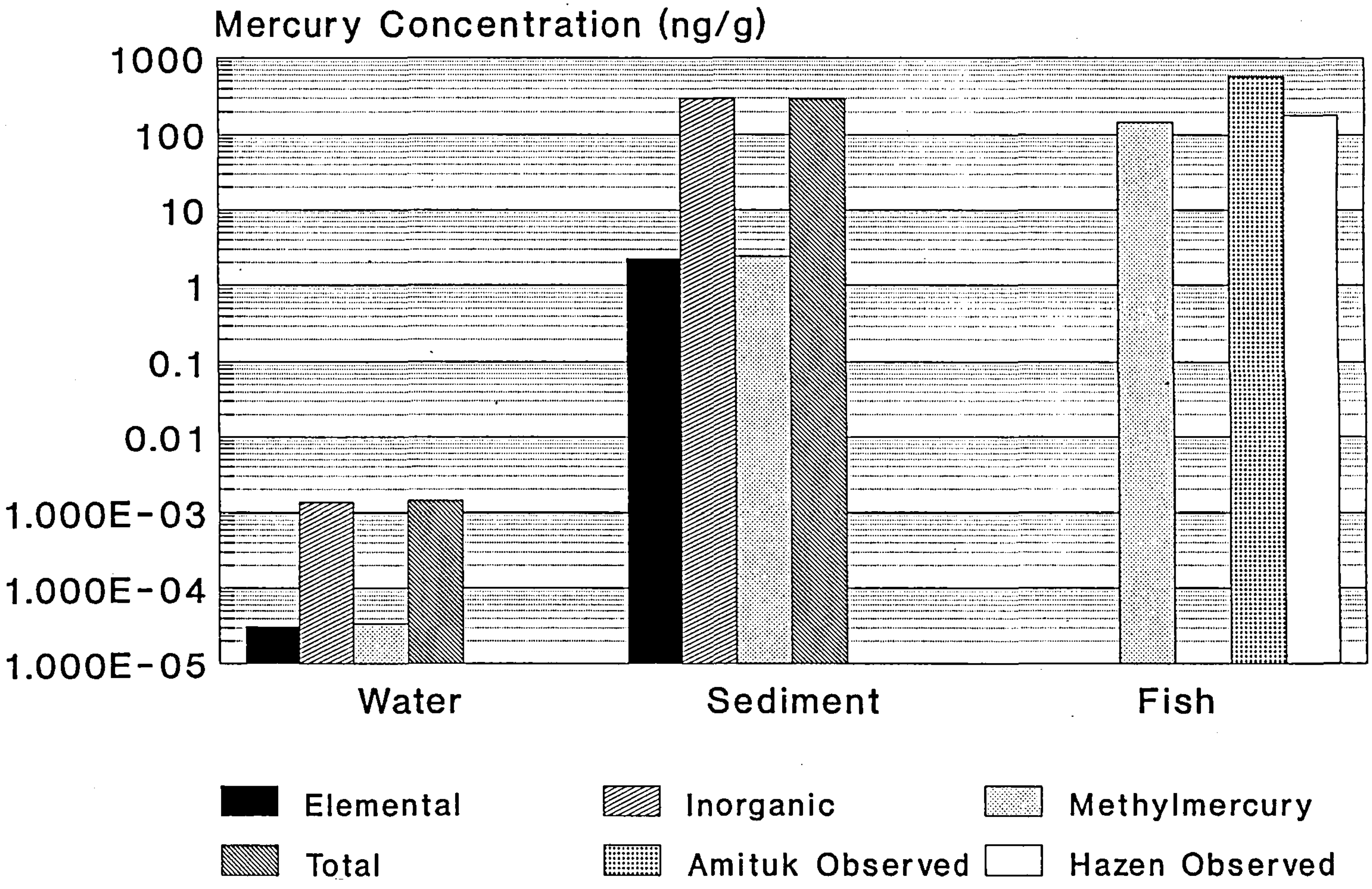


Figure 4. Mercury concentrations.

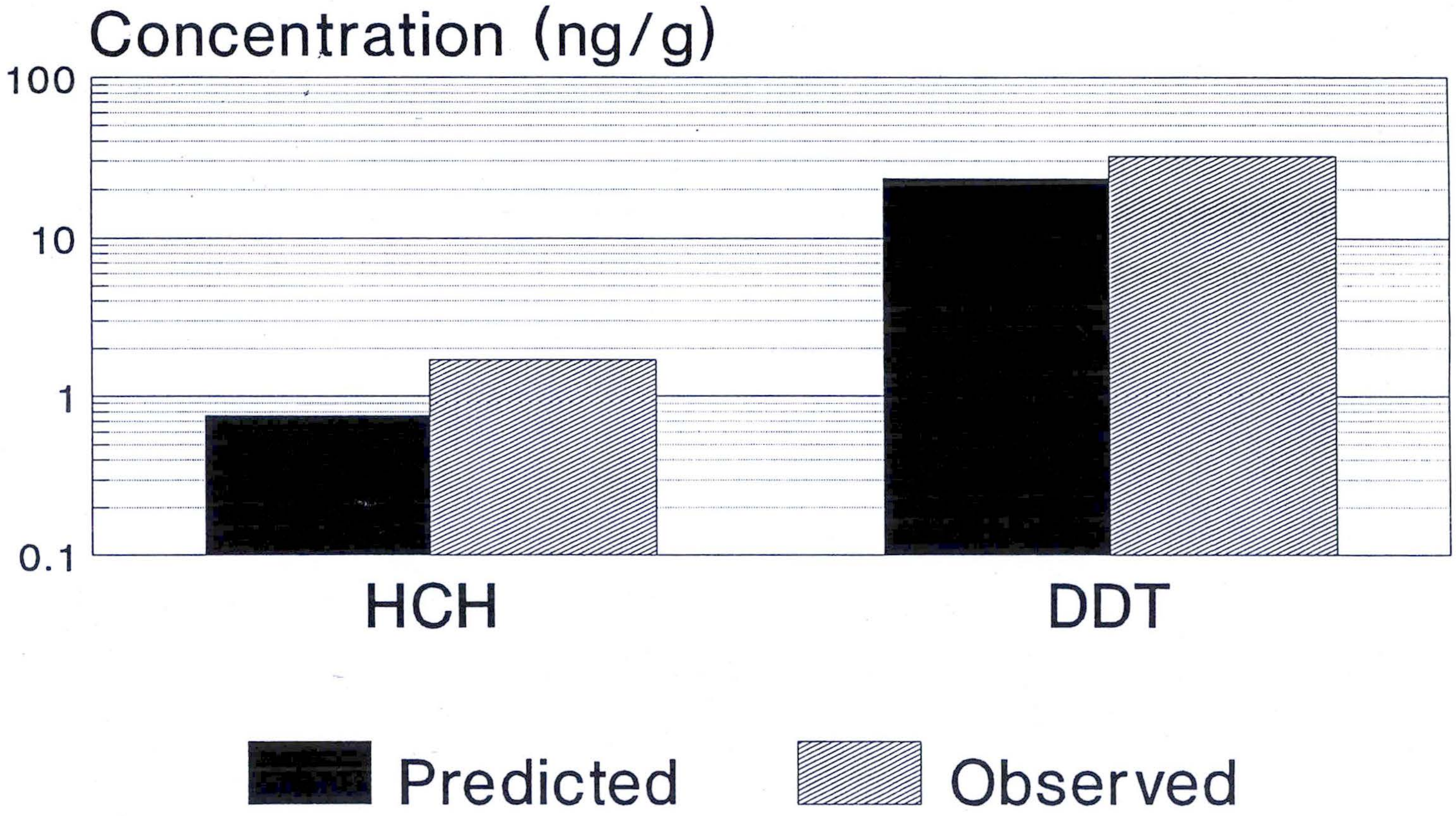


Figure 5. Contaminant concentrations in Arctic Char at Amituk Lake.

DEPOSITIONAL TRENDS - LAKE AND MARINE SEDIMENTS

PROJECT LEADER: W.L. Lockhart, Freshwater Institute, Fisheries and Oceans Canada

PROJECT TEAM: P. Wilkinson (radiochemical dating); E. Slavacek (contractor, radionuclides); B.N. Billeck (PAHs and hydrocarbons); D. Muir, N. Grift, A. Yarechewski, C. Ford (organochlorines); R. Hunt (metals); H. Kling (biogenic remains); J. Smol and N. Doubleday (Queen's University, carbon particles).

OBJECTIVES

1. To obtain sediment core samples from a grid of arctic headwater lakes in sufficient quantities to permit determinations of layer ages using radionuclide concentrations and down-core profiles of polycyclic aromatic hydrocarbons, organochlorines, and metals. In addition, sediments from marine locations will also be taken in instances where the availability of ships and equipment permit. The target collecting program is two or more sites per year, with the aim of generating a grid of locations throughout the Canadian Arctic. Initial work was on a north/south transect, from the U.S. border to Northern Ellesmere, and work is now underway in the western Arctic to initiate an interlocking east/west transect.

2. To derive the LRTAP input rates of each contaminant at each site, set current rates of supply in the context of those which have been taking place over the last century and longer, and compare accumulations with information on sources and transport processes. The history of contaminant supplies determined from the sediment records will be tested to see whether it predicts contaminant levels (subproject on contaminants in fish). Where possible, contributions of contaminants from within the drainage basin will be determined.

DESCRIPTION

Lake sediment cores have been collected from several grid locations in the Northwest Territories and the Yukon Territory over the period from 1987 to the present. The basic methodology of coring in arctic lakes (through the ice in waters up to 300 m deep) uses a newly designed box corer and large-diameter KB-corers; these obtain large enough quantities of sediment per slice to permit extensive chemical analyses. Cores are sliced at the time of collection and slices are dated using radiochemical analyses before being analyzed for a series of contaminants (metals, hydrocarbons, organochlorines). Dating allows the calculation of the rate of input of each contaminant to a given slice and the down-core profiles of contaminants give changes in the rate of supply over time, and allow extrapolation into the future.

Lack of reliable bathymetric maps of many northern lakes has required that we develop technology to make them. The first of these was made on a summer expedition to Lac Belot, NWT using equipment and personnel from U.S. EPA. We have obtained the appropriate Global

Positioning System (GPS)/SONAR equipment and software to produce these ourselves, and it is now being 'ground-truthed' during 1994.

In 1992 and 1993 marine cores were obtained by participating with Fisheries and Oceans Canada ship cruises to Hudson Bay. These have been taken using conventional box corers, with 10-cm diameter push cores being taken from the box cores. Cores are sliced at sea.

It is intended to extend the geographic coverage throughout the Canadian Arctic along the lines of Norwegian work (i.e. along grid points covering the major regions), as required by the Arctic Monitoring and Assessment Programme (AMAP). External cooperation is encouraged, and a number of Russian marine sediment samples were obtained from the Murmansk Marine Biological Institute late in 1993.

ACTIVITIES IN 1993/94

During 1993/94, efforts were given to several activities: collection of additional cores, resolution of difficulties with the GPS/SONAR technology, chemical analysis of samples, preliminary modelling of core sedimentation parameters, and communication of results.

We were able to place two members of the team on board the *M.V. Fogo Isle* (on charter to Institut Maurice Lamontagne) for further coring in Hudson Bay during September 1993. Several cores were collected at points from near the entrance to James Bay to near the entrance to Hudson Strait. Limited samples of marine invertebrate organisms were also obtained. Late in the fiscal year, additional cores were obtained from three lakes in the southern Yukon/British Columbia area (Lindeman, Bennett and Marsh). Several grab samples of marine sediment from the Russian Arctic were obtained from T. Savinova, Murmansk Marine Biological Institute.

Initial difficulties with custom electronics and software with the GPS/SONAR system were finally solved in the fall of 1993, and the system was successfully deployed in a test on the lower part of the Winnipeg River and southern Traverse Bay. Further 'ground truthing' of this system is slated for the open water season of 1994.

A number of cores on hand have been analyzed for unsupported ^{210}Pb and ^{137}Cs. Where the radionuclide profiles indicate datable sequences, core slices are partitioned to several laboratories for bulk sediment chemistry, organochlorines, polycyclic aromatic hydrocarbons, and several metals. A contract taxonomist (P.L. Wong) was retained to classify biological material from the Hudson Bay samples. All completed core sequences have also been subjected to mathematical mixing models by A. Omelchenko, using models provided by J. Robbins (NOAA, Ann Arbor).

Results were communicated through several scientific and public channels.

RESULTS

With the number of data being produced, only a few selected examples can be presented here. Below are sample results with mercury, PAHs and biogenic remains.

New cores

The Canadian sites for which cores have now been collected until the end of 1993/94 are shown in Figure 1. Not shown on the map are the Russian marine dredge samples, and a small sample from the former Canadian ice island off Axel Heiberg. The map includes cores taken at Lac Ste. Therese south of Great Bear Lake and at Alexie Lake near Yellowknife, both sampled early in 1994/95. In related work, we anticipate obtaining some cores from Lake Winnipeg. This still leaves several large gaps in our coverage, notably northern Quebec, the eastern, central, and western archipelago, the southern Keewatin, and central and northern Yukon. Plans are underway (with Makivik Corp.) to try coring some sites in northern Quebec in 1995/96. The list of cores collected since the last report (Lockhart 1993) is shown in Table 1. Cores from Buchanan Lake (Axel Heiberg Island) and Hazen Lake (northern Ellesmere Island) did not have satisfactory ^{210}Pb profiles; neither of these lakes had a good bathymetric map at the time of the expedition, and so it may be necessary to visit these sites again with state-of-the-art differential GPS/sonar technology to produce these maps. New core sites may have to be selected in light of known bathymetry.

Table 1. Cores collected since the last report (Lockhart 1993).

Core Number	Core Type	Location	Date	Latitude and Longitude
LIN1	KB-10	Lindeman Lake	10 Mar 94	59 47 47N/135 03 46W
LIN2	KB-10	Lindeman Lake	10 Mar 94	59 48 36N/135 02 01W
BEN1	KB-10	Bennett Lake	11 Mar 94	59 56 16N/135 55 29W
MAR1	KB-10	Marsh Lake	14 Mar 94	60 29 08N/134 19 02W
MAR2	KB-10	Marsh Lake	15 Mar 94	60 30 21N/134 20 49W
LST1	KB-10	Lac Ste. Therese	13 Apr 94	64 37 32N/121 39 10W
LST2	KB-10	Lac Ste. Therese	13 Apr 94	64 37 32N/121 39 10W
LST3	KB-10	Lac Ste. Therese	14 Apr 94	64 37 33N/121 31 06W
LST4	KB-10	Lac Ste. Therese	14 Apr 94	64 38 01N/121 35 24 W
ALX1	KB-10	Alexie Lake	16 Apr 94	62 40 37N/114 06 15W

Sedimentation Rates

The key measurement allowing the dating of cores, and hence the calculation of sedimentation rates, are the radionuclides ^{210}Pb and ^{137}Cs. The ^{210}Pb (half-life 22 y) should show an exponential decline with depth in the core for several half-lives. Cesium should show a peak in the early 1960s from atmospheric testing of nuclear bombs, and a subsequent decline. Figure 2 shows some typical profiles of these radionuclides from sediments taken by this project. The sedimentation rates for sites can be calculated in a number of ways, using a simple regression equation or using different models to accommodate physical mixing. The sedimentation rates calculated for a number of our cores are listed in Table 2 using three different methods of calculation.

Table 2. Calculated sedimentation rates in several lake and marine sites using different methods of calculation

	Sedimentation rate (g/sq.m/yr)		
Lake & core	Linear fit(1)	RSSM(2)	CFM(3)
Lac Belot			
BEL-1	70	104	102
BEL-2	57	97	144
Fox Lake			
CORE 1	120	126	114
CORE 2	80	81	73
Little Atlin Lake			
CORE 1	840	703	695
CORE 2	390	421	405
Hudson Bay			
HUD4	1180	1101	1059
Lake 382:			
BOX CORE	104	111	136
Far Lake:			
BOX CORE A	77	101	
BOX CORE B	74	84	100
Hawk Lake			
BOX CORE A	51	47	31
BOX CORE B	65	80	57
Hawk Inlet			
BOX CORE A	320	483	535
BOX CORE B	947	551	574

Table 2 (continued). Calculated sedimentation rates in several lake and marine sites using different methods of calculation

	Sedimentation rate (g/sq.m/yr)		
Lake & core	Linear fit(1)	RSSM(2)	CFM(3)
Lake 375			
BOX CORE			
Sophia Lake			
BOX CORE A			
BOX CORE B			
KB CORE A			
KB CORE B			
Amituk lake			
KB CORE A			
KB CORE B			
Hazen Lake			
BOX CORE A	92	278	380
Sydney Lake	269	268	300
Green Lake			
KB CORE GL-10	129	121	134
Lake Laberge			
KB CORE LAB1	591	732	814
KB CORE LAB2	656	669	583
KB CORE LAB3	650	611	480
KB CORE LAB4	561	595	414
Kusawa Lake:			
KB CORE KUS1	227	218	190
Lake Nipigon:			
KB CORE NIP1	560	411	477
KB CORE NIP3	921	835	756
KB CORE NIP4	649	599	574

(1) Based on regression analysis of the exponential part of "excess ^{210}Pb vs. depth" curves.

(2) RSSM-calculated with the rapid steady-state mixing model.

(3) Mean value for sedimentation rates estimated for each slice with the constant flux - alternative sedimentation rate model.

Profiles of chemical contaminants

Metals

The down-core profiles of metals that give the greatest cause for concern are those for mercury; several of these are shown in Figure 3. With the exception of Lac Belot, all the lakes with interpretable ^{210}Pb profiles showed striking increases in mercury in recent slices. (Lakes Hazen and Buchanan had no gradients in mercury, but the ^{210}Pb profile suggested that the chronologies there could not be interpreted confidently). These profiles suggest that many arctic locations are receiving loadings of mercury that are considerably higher than those in the past. Similar increased loadings have been reported for lakes on the Belcher Islands (Hermanson 1993). The biological consequences of these increased loadings are not known, but it is difficult to imagine how these systems could sustain ongoing high loadings without some of the mercury finding its way into aquatic food chains and ultimately into people. Failure to find increasing mercury inputs to Lac Belot was unexpected in view of clear indications of these increases in other northern locations (Figure 3). Mercury levels in the fish there are also quite low (see Contaminants in Freshwater and Marine Fish, this volume).

Polycyclic aromatic hydrocarbons

As analytical methods have been refined over several years, the list of PAHs identified in sediments has grown. Initial analyses were restricted essentially to the EPA priority list (naphthalene, acenaphthylene, acenaphthene, fluroene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(a)pyrene, indeno(1,2,3-*cd*)pyrene, dibenzo(*ah*)anthracene, benzo(*ghi*)perylene). The sums of these compounds in core slices from several locations are shown in Figure 4. Retene and perylene are not included in the sums plotted because perylene often increases with depth in a core, probably because of *in situ* formation in the sediments. Retene has been used as a tracer for smoke from burning wood from deciduous trees.

PAH data from Lake Hazen on Ellesmere Island and Buchanan Lake on Axel Heiberg Island were complicated by the presence of large amounts of coal in the sediments. A sample of coal recovered from the Gillman River Valley at Lake Hazen contained deposits of amber, and these were particularly rich in retene.

The pattern of PAH accumulation in Lakes 375 (Experimental Lakes Area, Northwestern Ontario) and Hawk Lake (near Chesterfield Inlet, NWT) have been described (Lockhart *et al.* 1993); Hawk Lake data are included in Figure 4. These two lakes both showed a pattern with sub-surface maxima similar to others from eastern North America (Gschwend and Hites 1981), indicating that recent inputs are lower than inputs earlier this century. The other lakes in Figure 4, however, did not show this pattern; there was no consistent pattern throughout the histories represented by cores from Lakes Amituk, Belot and Kusawa. On this basis, the pattern of deposition of PAHs appears to differ regionally, with sites in eastern North America differing from more northern and northwestern North America. In some instances, there were consistent patterns in individual PAHs; for example, retene, sometimes used as a trace for wood smoke, showed consistent increases in some of the Yukon cores (see "Food Chain Accumulation and Biological Effects of Organochlorines in Fish from Lake Laberge and Other Yukon Lakes", this volume).

PAH levels in Lake Belot were relatively high in comparison with other northern lakes sampled to date. Phenanthrene, naphthalene, fluoranthene and pyrene were the most important contributors to the total shown in Figure 4. The reasons for the high levels of these compounds in Lac Belot are unknown but the lack of a down-core gradient suggests that it is not a recent pollution event.

The PAHs in the two marine samples taken from the Canadian ice island (supplied by the Geological Survey of Canada, Institute of Sedimentary and Petroleum Geology, Calgary) had total PAH (excluding perylene and retene) contents of 147 and 175 ng g^{-1}, in relatively good agreement with most of the northern lake sediments (Figure 4).

Biogenic remains

In addition to records of contamination, lake sediments also contain a wide variety of biogenic remains. The most common of these are pollen grains and siliceous microfossils (diatoms and chrysophyte cysts). The surface sediment from three arctic lakes, Belot, Colville and Fox, have been analysed for siliceous and non-siliceous microfossils using light (LM) and scanning electron microscopy (SEM). The quantity and quality of microfossils in the three lakes indicate that these lakes are very different from one another. Total numbers of microfossils per gram of sediment (dry wt) in Belot was 20-30x lower than in Fox and Colville. This indicates a very nutrient poor, deep shield lake with very little littoral zone. The dominance of planktonic chrysophytes and low abundance of diatoms also supports this.

Colville Lake had the highest number of microfossils per gram of sediment. It also had a large number of non-siliceous microfossils, i.e. Dinoflagellate cysts, bluegreen akinetes and desmids. The presence of the dinoflagellate cysts indicates that this lake receives a higher nutrient load than Belot. Dinoflagellates are know to bloom when arctic lakes receive nutrient additions (Schindler *et al.* 1974, O'Brien *et al.* in press). Fox Lake, southern Yukon, had the greatest diversity of planktonic diatoms; several centric diatom species occur with a very limited geographic distribution were found. Several unique taxa were also found. A good population of a new taxon (Fig. 5), possibly a new genus in the family Thalassiosiraceae was discovered. It is closely related to the genus *Stephanodiscus* and in external view to the species *S. subtransylvanicus* and *S. oregonica*. However, the presence of a central labiate process is not known from the genus *Stephanodiscus*. This taxon will be dealt with in a future publication. Other taxa unique to Fox Lake were: a population of *Cyclotella bodanica* with initial valves 1/3x larger than in lakes in neighbouring areas (Alaska, Shield areas of NWT, Manitoba and Ontario). The size of these initial valves is reminiscent of ancient populations and of the initial valve of the populations of lakes in the Swiss alps. *Cyclotella ocellata* pant. often confused with *C.tripartita* was abundant in Fox Lake. In Fox lake the overall density of planktonic diatoms and small number of benthic taxa would indicate a deep lake.

DISCUSSION/CONCLUSIONS

The coverage of northern lakes is improving as we attempt to expand the original north/south transect to a grid covering the Canadian North, but several very large areas are still not represented. In future, we hope to add several more sites, notably northern Quebec, large parts of the eastern, central, and western archipelago, the southern Keewatin, and central and northern Yukon.

Regional differences appear to be emerging for mercury and PAH deposition, both considered to be largely byproducts of combustion processes at lower latitudes. Regional differences have also been reported in Scandinavia (e.g. Johansson 1985). Determining the sizes and patterns of these differences will require an increased number of grid locations. The observation of increasing mercury in sediments of Hudson Bay off the Grande Baleine Delta was something of a surprise, since it was anticipated that these sediments would be too badly mixed to produce a good ^{210}Pb profile. However, this was not the case. A second core taken from the North Belcher Islands from M.V. Fogo Isle during the summer of 1993 showed a similar profile for mercury. Given the potential for hydroelectric development in the Grande Baleine basin, it seems very important to document changes such as that shown in Figure 3 (lower left) before development occurs.

An unexpected finding was the discovery of an apparently unnamed genus of diatoms abundant in Fox lake. Processes which might offer an explanation for the geographic distribution of these organisms are not clear.

Expected project completion date:

Scientifically the project will not be complete until a more detailed grid has been completed. Practically, about seven more core locations are required, and the two most northerly locations will have to be re-visited some time during the open-water season to try to obtain good bathymetry. The core profiles are being used to try to determine whether sites with unusually high levels of contaminants in the fish are the result of basin geology or pollution, especially pollution by aerial fallout. Given this application, it is likely that the projected seven sites will change depending on the needs for answers to particular site problems. For example, Peter Lake near Rankin Inlet has high levels of toxaphene, PCBs and mercury, and it may be necessary to take cores from that lake earlier than some of the proposed sites.

REFERENCES

Gschwend, P.M. and R.A Hites. 1981. Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the northeastern United States. Geochim. Cosmochim. Acta. 45: 2359-2367.

Hermanson, M.H. 1993. Historical accumulation of atmospherically derived pollutant trace metals in the Arctic as measured in dated sediment cores. Wat. Sci. Technol. 28: 33-41.

Johansson, K. 1985. Mercury in sediment from Swedish forest lakes. Verh. Internat. Verein. Limnol. 22: 2359-2363.

Lockhart, W.L. 1993. Depositional trends - lake and marine sediments. Pp. 46-56 *in*: Synopsis of Research Conducted under the 1992/93 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 70. Indian and Northern Affairs Canada, Ottawa. 285 pp.

Lockhart, W.L., P. Wilkinson, B.N. Billeck, G.J. Brunskill, R.V. Hunt and R. Wagemann. 1993. Polycyclic aromatic hydrocarbons and mercury in sediments from two isolated lakes in central and northern Canada. Wat. Sci. Technol. 28: 43-52.

Schindler D.W., J. Kalff, H.E. Welch, G.J. Brunskill, H.J. Kling and N. Kritsch. 1974. Eutrophication in the high arctic - Meretta Lake, Cornwallis Island (75 N Lat) J. Fish. Res. Board Can. 301: 647-662.

O'Brien J.W., M. Bahr, A. Hershey, J.Hobbie, G. Kipphut, G. Kling, H. Kling, M. McDonald, M. Miller and P. Rublee. In Press. The Limnology of Toolik Lake.

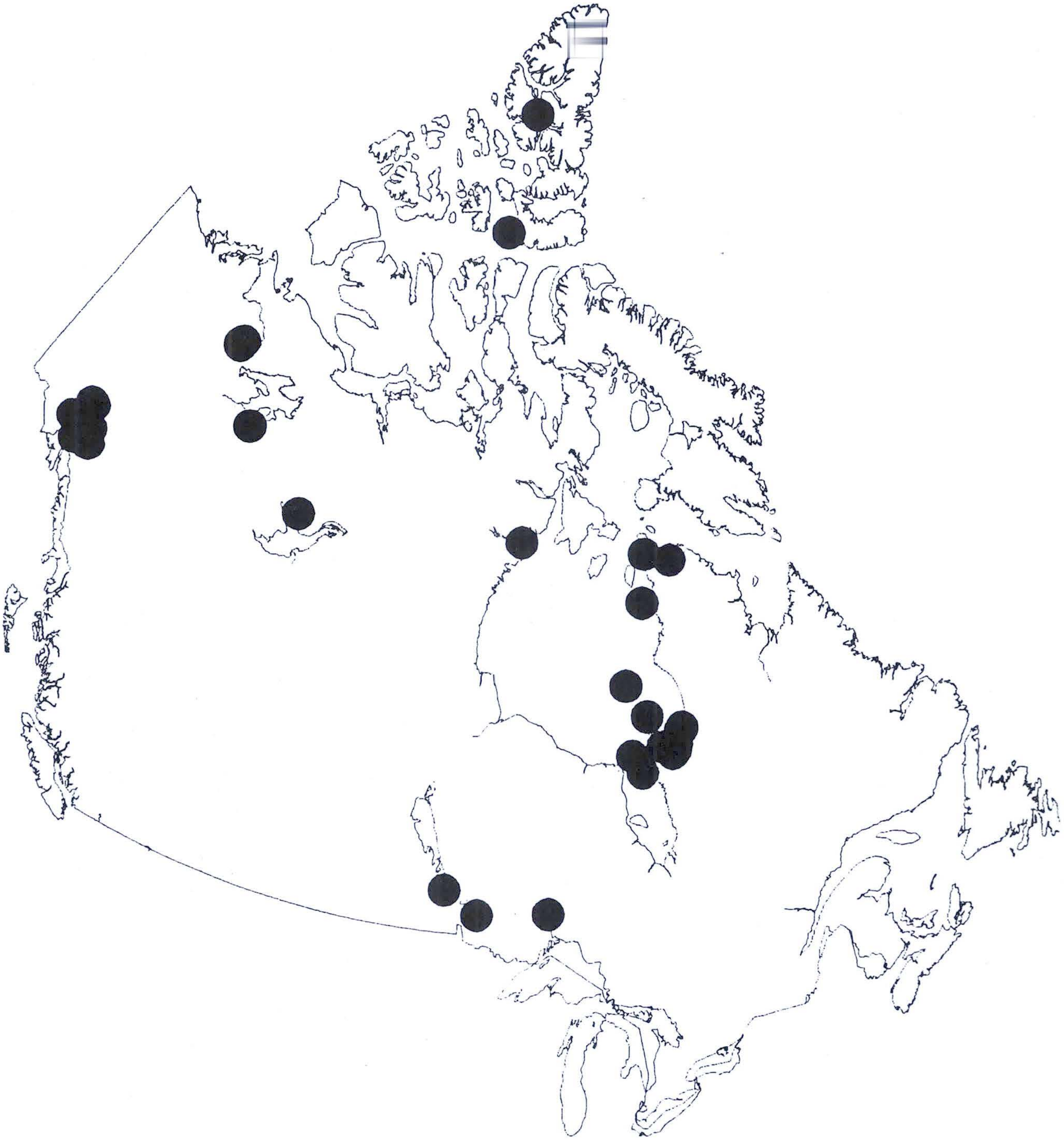


Figure 1.
Locations of cores taken from 1987 until May, 1994.

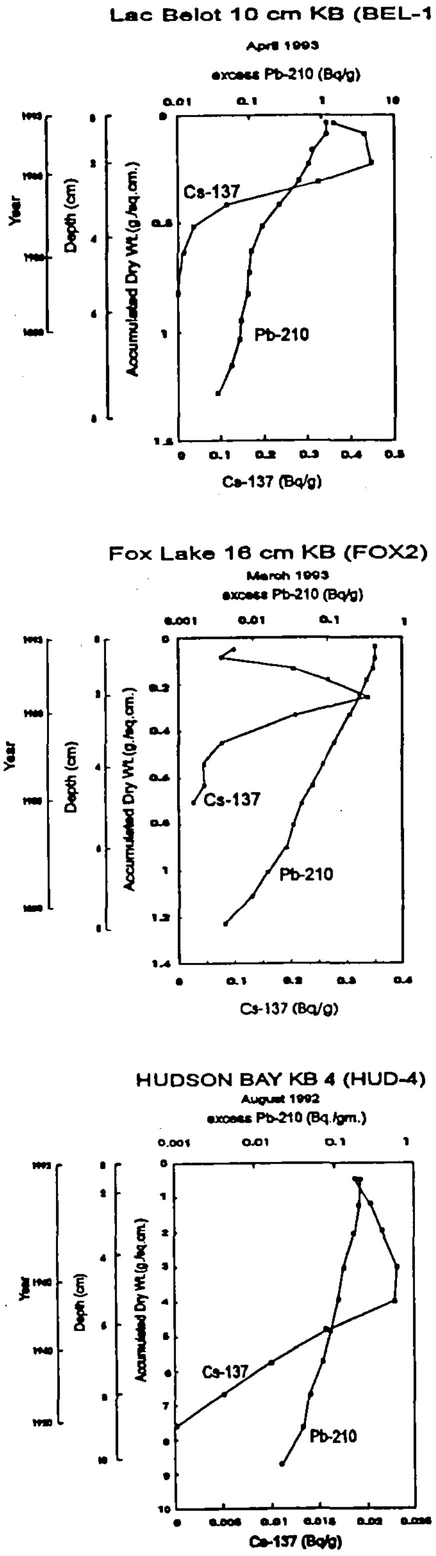


Figure 2. Sample ^{210}Pb and ^{137}Cs profiles from two lakes (Belot near Great Bear and Fox in the southern Yukon) and one marine site in Hudson Bay near the Grande Baleine Delta.

Figure 3. Mercury levels in core slices from several sites. Dates in italics are extrapolations.

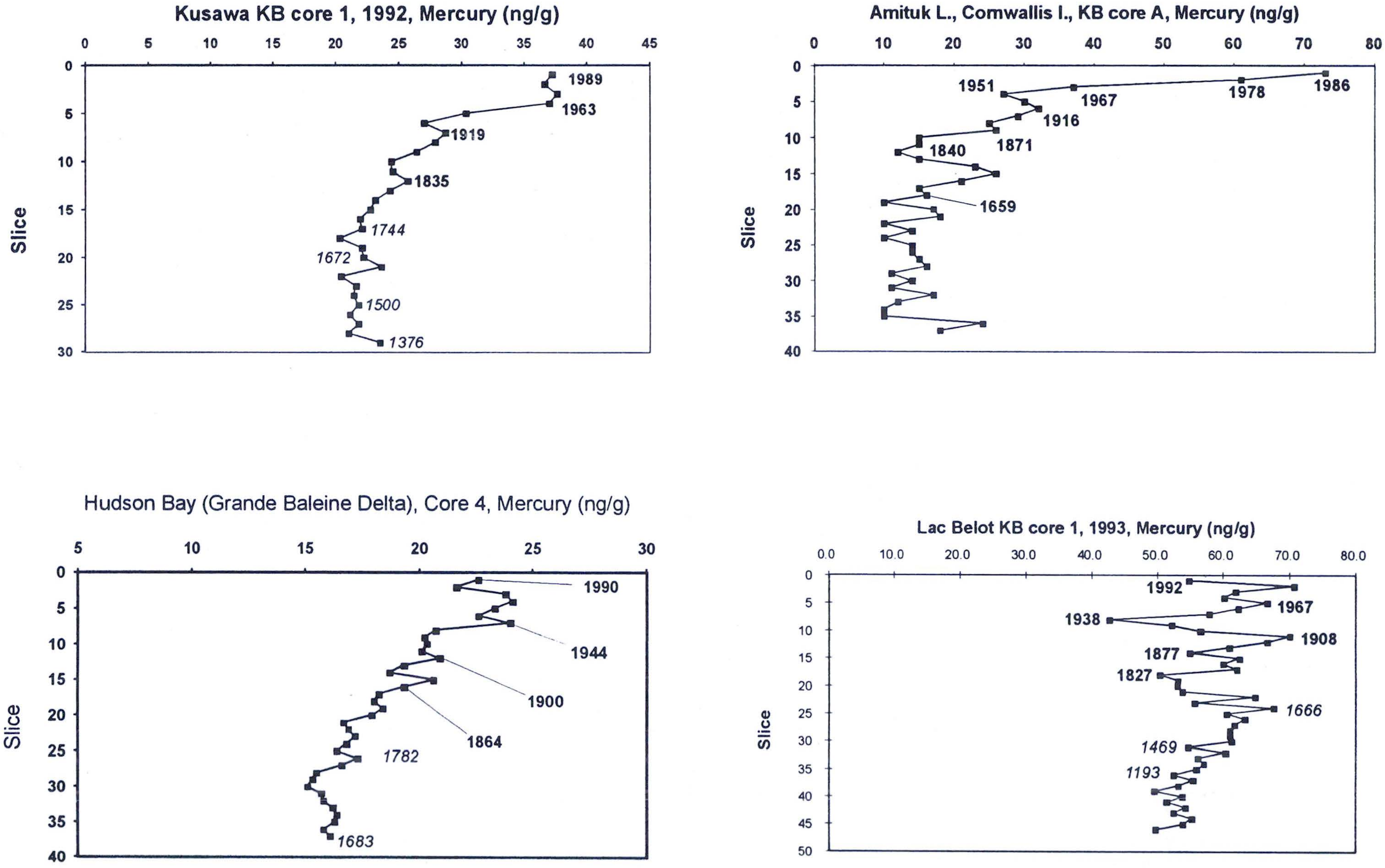
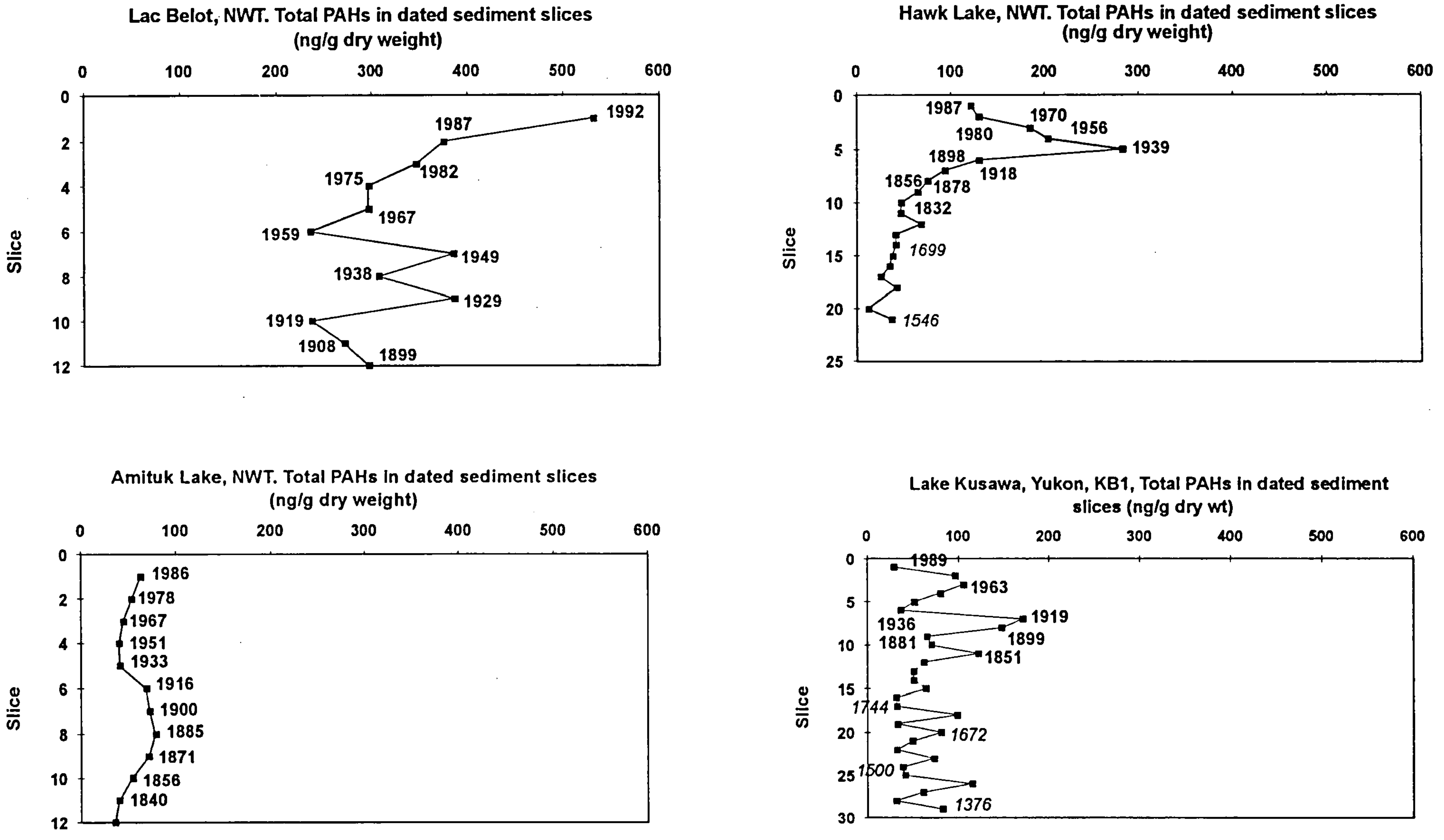


Figure 4. Sum of PAHs (excluding perylene and retene) in sediment slices from several northern lakes. Dates in italics are extrapolations.


Lac Belot, NWT. Total PAHs in dated sediment slices (ng/g dry weight)

Hawk Lake, NWT. Total PAHs in dated sediment slices (ng/g dry weight)

Amituk Lake, NWT. Total PAHs in dated sediment slices (ng/g dry weight)

Lake Kusawa, Yukon, KB1, Total PAHs in dated sediment slices (ng/g dry wt)

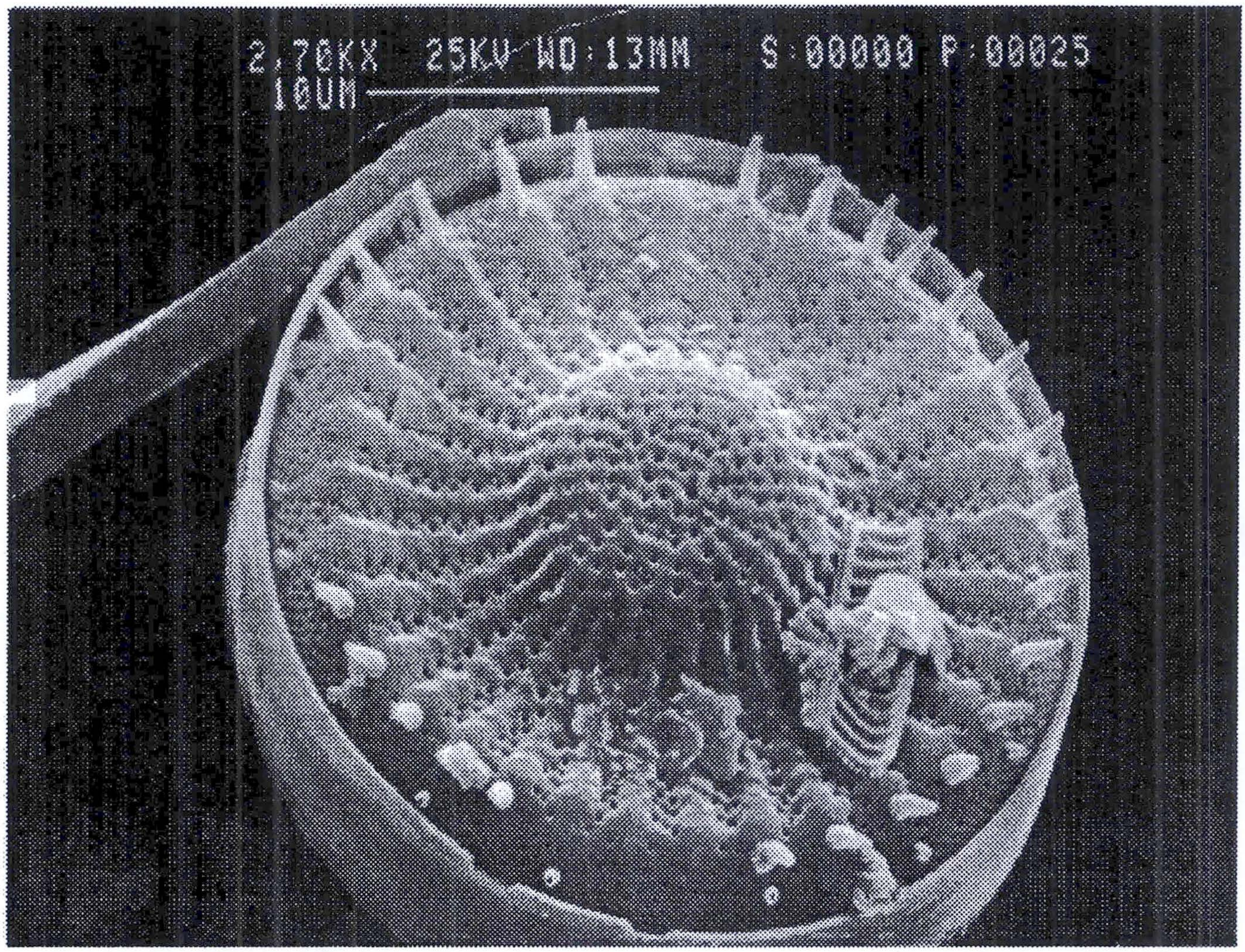


Figure 5. Scanning electron micrograph of previously undescribed genus of diatom found by Ms. H. Kling in Fox Lake, 1993.

A STUDY OF THE SOURCES AND FATE OF ORGANOCHLORINE CONTAMINANTS IN THE YUKON RIVER BASIN

PROJECT LEADER: M. Alaee, National Water Research Institute, Environment Canada and D. Gregor, University of Waterloo

PROJECT TEAM: M. Palmer, Indian and Northern Affairs Canada; J. Eamer, Environmental Protection, Environment Canada; C. Spencer, C. Hauta, G. Lawson and J. Azcua, National Water Research Institute (NWRI), Environment Canada

OBJECTIVES

1. To determine the source(s) of high levels of organochlorine (OC) contamination in Laberge, Atlin, Bennet, Fox, Kusawa, and Marsh Lakes along with the Yukon and Takhini Rivers.

2. To determine the fate of the contaminants in the Yukon River Basin.

3. To quantify the historical trend of organochlorine deposition within the basin.

DESCRIPTION

Relatively high concentrations of toxaphene and other organochlorines have been detected in fish from Lake Laberge and other lakes in the Yukon River basin (Kidd *et al.* 1993). This has led to the closure of local fisheries. Further studies from other lakes in southern Yukon, including Lake Hansen (where toxaphene was applied) indicate lower concentrations of toxaphene (Eamer 1994). This anomaly can be explained by two different hypotheses. The first hypothesis, currently under study by the Freshwater Institute (FWI) and University of Alberta, is based on changes in the food web caused by extensive fishing. The second hypothesis is based on possible use and disposal of organochlorine contaminants in certain areas. Historical uses of organochlorine compounds have been documented by the Yukon Contaminants Committee (Nordin *et al.* 1994). This document indicates that compounds such as DDT were used in aerial sprays between 1949-1969. Unknown quantities of household organochlorine pesticides and PCB-containing electrical components were abandoned at various sites along the Yukon River basin (Davidge 1994, pers. comm.).

Long-range atmospheric transport has been identified as a major source of contaminants to the Arctic (Bidleman *et al.* 1989). Atmospheric contaminants are delivered by dry and wet (rain and snow) deposition or by gas exchange. Snow deposition is currently measured under other Northern Contaminants Program projects, however, rain deposition is measured in this project. Gas exchange can be estimated using the fugacity model developed by D. Mackay at the University of Toronto (Mackay and Shiu 1981). Using water concentrations and air concentrations, along with Henry's Law Constant and mass transfer coefficients, the flux of gaseous contaminants into the water is estimated.

In order to access a historical record of OCs and heavy metals a peat sample was collected from ombrotrophic bogs. Bogs are precipitation fed, therefore the record of contaminants found within the peat should represent a historical account of atmospheric deposition.

Through a mass balance study of significant compartments in the ecosystem, we will be able to identify inputs and the fate of contaminants. In turn, we believe that this will allow inferences about sources and the model of transport into this ecosystem.

In this study, contamination levels in air, water, suspended solids, and precipitation at Lake Laberge, Atlin, Bennet and Fox Lakes were compared to the less contaminated Kusawa Lake. This project complements studies such as that on the Lake Laberge food web (this volume), and provides a complete data set from which to examine the contaminant mass balance of the ecosystem.

ACTIVITIES IN 1993/94

Spring/Summer 1993

Water sampling started in the last week of May. During the 1993/94 sampling season (mid May-mid August), a total of 8 water samples (≈ 100 L) along with suspended sediments (5-20 g) were collected from the Takhini River using a continuous flow centrifuge. Large volume water samples from the Takhini and Yukon Rivers were extracted with dichloromethane using the Goulden Large Volume Extractor (GLVE). Thirty-six lake water samples were collected from the six lakes using the Infiltrex II solid phase extractor. All suspended solid and river samples are processed and analyzed for PAHs. OC analysis on these samples are in progress. Fifty percent of the lake samples are currently processed and being analyzed for PAHs.

Peat

To access the historical trends of atmospheric deposition, a peat sample was collected from the area (64°3' N and 139°4'30" W). The peat sample collected was approximately 35 cm long. The peat sample was divided into 17 segments (2 cm/segment except 4 cm for top layer). 0.25 g of each sample was dissolved in Aqua Regia using the microwave digestion technique and analyzed using ICP-AED, GF-AA for Cd, and Cr, and CV-AA for Hg. Concentrations of 15 metals as a function of depth are presented in Table 2 and Figure 3. ^{210}Pb dating on the same core is in progress at NWRI. The remainder of the peat sample will be analyzed for trace organic contaminants in 1994/95.

Winter 1994

Due to the relatively warm fall and winter season (unsafe ice conditions), only one set of water samples was collected during the winter season (February 1994). This sample set was collected during the period in which lake and river surfaces were covered with ice, and the inputs from runoff and rivers to the lakes were minimal. A total of 28 samples, along with 6 field and laboratory blanks were collected from the same sampling locations in summer 1993. Due to cold weather conditions all samples were processed using the LVE technique. Analysis of this data set is completed for PAHs and OCs. A subset of these samples was analyzed for toxaphene by G. Stern at FWI. Preliminary results were presented at the 24th International Symposium on Analytical Environmental Chemistry in Ottawa (Alaee *et al.* 1994).

Quality Assurance/Quality Control (QA/QC)

All samples were processed and analyzed for OCs using dual column GC/ECD, and for PAHs using GC/MS at NWRI. Toxaphene analysis, using HRGC/ECNI/HRMS, was done by G. Stern at FWI. To ensure the data quality and consistency with other participants in the Northern Contaminants Program (NCP) the following measures have been taken:
a) participated in various QA/QC programs offered by the QA/QC coordinator of NCP;
b) water samples collected were spiked with internal standard prior to extraction with a Goulden extractor in the field. XAD columns were spiked with internal standards in the laboratory and shipped to the field. Other sets of internal spikes were added during the extraction procedure; and c) at least three field blanks during each sampling period, and one in every six samples processed in our laboratory is a procedure blank. Each new set of standards used during this study was checked against previous and commercial standards. Standard reference materials were used for metals analysis.

RESULTS AND DISCUSSION

Concentrations of Organochlorine in Water

Results from OC and PAH measurements are presented in Table 1. HCHs, in particular α (0.9-1.8 ng/L) and γ (0.2-0.4 ng/L) isomers, are the most predominant OC in the Yukon River system. These values are comparable to those reported in Amituk Lake by Falconer *et al.* (1.3 ng/L for α-HCH and .280 ng/l for γ-HCH) and in Lake Ontario (1-2 ng/L for α-HCH and 0.5-0.75 ng/l for γ-HCH) reported by Strachan (1994). Using an average air concentration of 114 pg/m^3 α-HCH and 9.8 pg/m^3 γ-HCH reported by Falconer *et al.* (1994) and an average water temperature of 6-8 °C, fugacity gradients of 0.9 and 1.5 are obtained for α- and γ-HCH, respectively, which indicate near equilibrium for α-HCH and outgassing for γ-HCH.

Enantiomeric ratios of α-HCH determined on two different chiral columns (β- and γ-cyclodextrin) are presented in Figure 4. The enantiomeric excess is due to selective enzymatic decomposition, resulting from biological activity. The Yukon River system shows high biological activity from Atlin Lake towards Lake Laberge, and no significant biological activity in Kusawa Lake and Takhini River.

High levels of toxaphene in fish from Lake Laberge and Atlin Lake raised the question of whether there were local sources for direct input to these lakes. However, as shown in Table 1, toxaphene concentrations range from 12 to 27 pg/L, less than values observed by Bidleman

(1994) at Resolute Bay (48 pg/L) and Amituk Lake (145 pg/L). Muir *et al.* (1994) reported 70-200 pg/L in northern Ontario lakes. The similarity among these concentrations and the similarities in the toxaphene pattern shown in Figure 1, suggest that the source is atmospheric. Atmospheric fluxes of toxaphene can be estimated using Henrys' Law Constant and Mass Transfer Coefficients provided by Hoff *et al.* (1993). Air concentrations of toxaphene at Alert of 2-25 pg/m^3 (annual average) were reported by Barrie *et al.* (1993), and at Resolute of 6.9 pg/m^3 (August 1992) reported by Bidleman (1994). Using these values the water/air fugacity ratio is 0.15. This indicates that the water is undersaturated with respect to air and the flux direction of toxaphene from air to water has an annual vapour flux of 2.8 μg/m^2. As more data becomes available a more detailed model will be constructed to provide a better representation of the current situation.

Peat Analysis

Ombrotrophic peat has been used as an atmospheric indicator for heavy metals (Glooschenko 1989) and organic contaminants by Rapaport and Eisenreich (1986). Peat samples were originally collected for OC analysis. However, concern due to high levels of Cd in caribou promoted us to do a metal survey as well. An ICP-AES scan provided reasonable results for a few metals such as iron, manganese, barium, molybdenum and zinc. In order to measure Cd levels in the peat, the samples were reanalysed using GF-AA. Metal concentrations in peat are presented in Table 2. As shown in Figure 3, Cd increases from 20 ppb to 150 ppb at about 20-25 cm depth; and Cr values peak at 15 cm depth. Interpretation of these results will be possible when the dating is finished. However, a preliminary observation indicates a reduction in the atmospheric input of Cd in recent years, which can be caused by reduction in coal burning. Analysis for other heavy metals such as lead and mercury along with dating is in progress.

CONCLUSION

All of the results so far indicate that atmospheric deposition is the major source of contaminants into the Yukon River basin. Similar concentrations of toxaphene in various lakes indicates that there is no point source in this system. Peat samples indicate a reduction of atmospheric deposition of cadmium in recent years.

REFERENCES

Alaee, M., C. Spencer, C. Hauta and M. Palmer. 1994. Contaminants in Yukon River Basin, 24th International Symposium on Environmental Analytical Chemistry, Ottawa, Ontario, May 16-19, 1994.

Bidleman, T.F., G.W. Patton, M.D. Walla, B.T. Hargrave, W.P. Vass, P. Erickson, B. Fowler, V. Scott and D.J. Gregor. 1989. Toxaphene and other organochlorines in arctic ocean fauna: Evidence for atmospheric delivery. Arctic 42: 307-313.

Davidge, D. 1994. Personal communication.

Falconer, R.L., T.F. Bidleman and D.J. Gregor. 1994. Air-water gas exchange and evidence for metabolism of hexachlorocyclohexanes in Resolute Bay, N.W.T., Canada. Sci. Tot. Environ. in press.

Eamer, J.E. 1994. Organochlorine in Yukon fish. The Yukon contaminants workshop. Whitehorse, Yukon, January 29-31.

Hoff, R.M., T.F. Bidleman and S.J. Eisenreich. 1993. Estimates of PCC loadings from the atmosphere to the great lakes. Chemosphere 27: 2047-2055.

Glooschenko, W.A. 1989. Sphagnum fuscum moss as an indicator of atmospheric cadmium deposition across Canada. Environ. Pollut. 57: 27-33.

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: 1975-1986.

Kucklick, J.R., D.A. Hinckley and T.F. Bidleman. 1991. Determination of Henry's law constants for hexachlorocyclohexanes in distilled water and artificial seawater as a function of temperature. Marine Chem. 34: 197-209.

Mckay, D. and W.Y. Shiu. 1981. A critical review of Henry's law constant for chemicals of environmental interest. J. Phys. Chem. Ref. Data 10: 1175-1199.

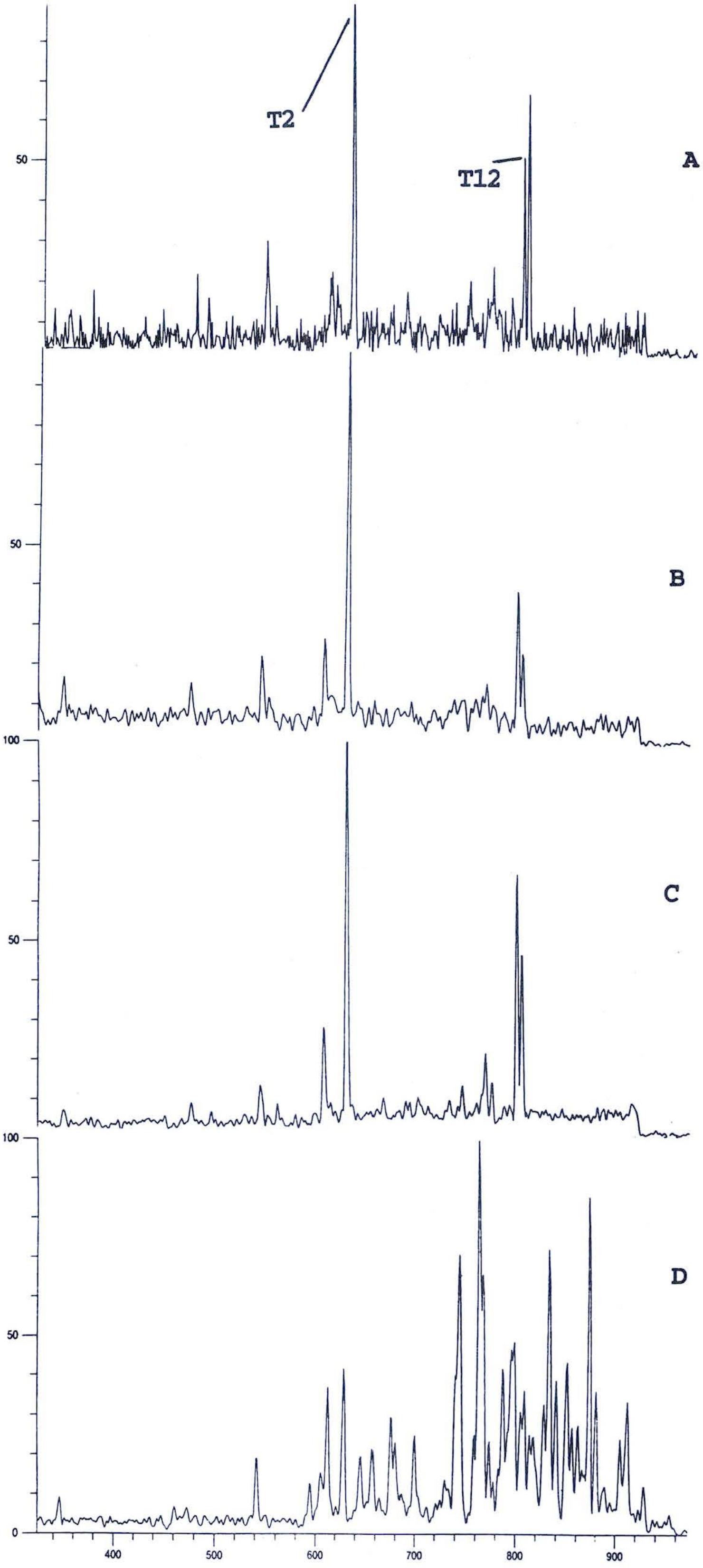
Muir, D.C.G., B. Roseberg, N.P. Grift and G.A. Stern. 1994. Biomagnification of specific octa- and nonachlorobornanes (toxaphene) in aquatic food webs. 24th International Symposium on Environmental Analytical Chemistry, Ottawa, Ontario, May 16-19, 1994.

Nordin, K., B. Burns and B. Lendrum. 1993. Use, disposal, and Transportation of selected contaminants in Yukon. Department of Indian Affairs and Northern Development, Ottawa.

Rapaport, R.A. and S.J. Eisenreich. 1986. Atmospheric deposition of toxaphene to eastern North America derived from peat accumulation. Atmos. Environ. 22: 2367-2379.

Strachan, W.M.J. 1994. Personal communication.

Figure 1. Total ion chromatogram ECNCI/MS of Toxaphene in the Yukon River Basin.



A. Lake Laberge, B. Atlin Lake, C. Kusawa Lake, D. Toxaphene Std. ECNI/MS analysis was done by G. Stern at FWI using HRGC/HRMS at 15000 resolution.

Figure 2. Toxaphene in the major lakes of the Yukon River Basin.

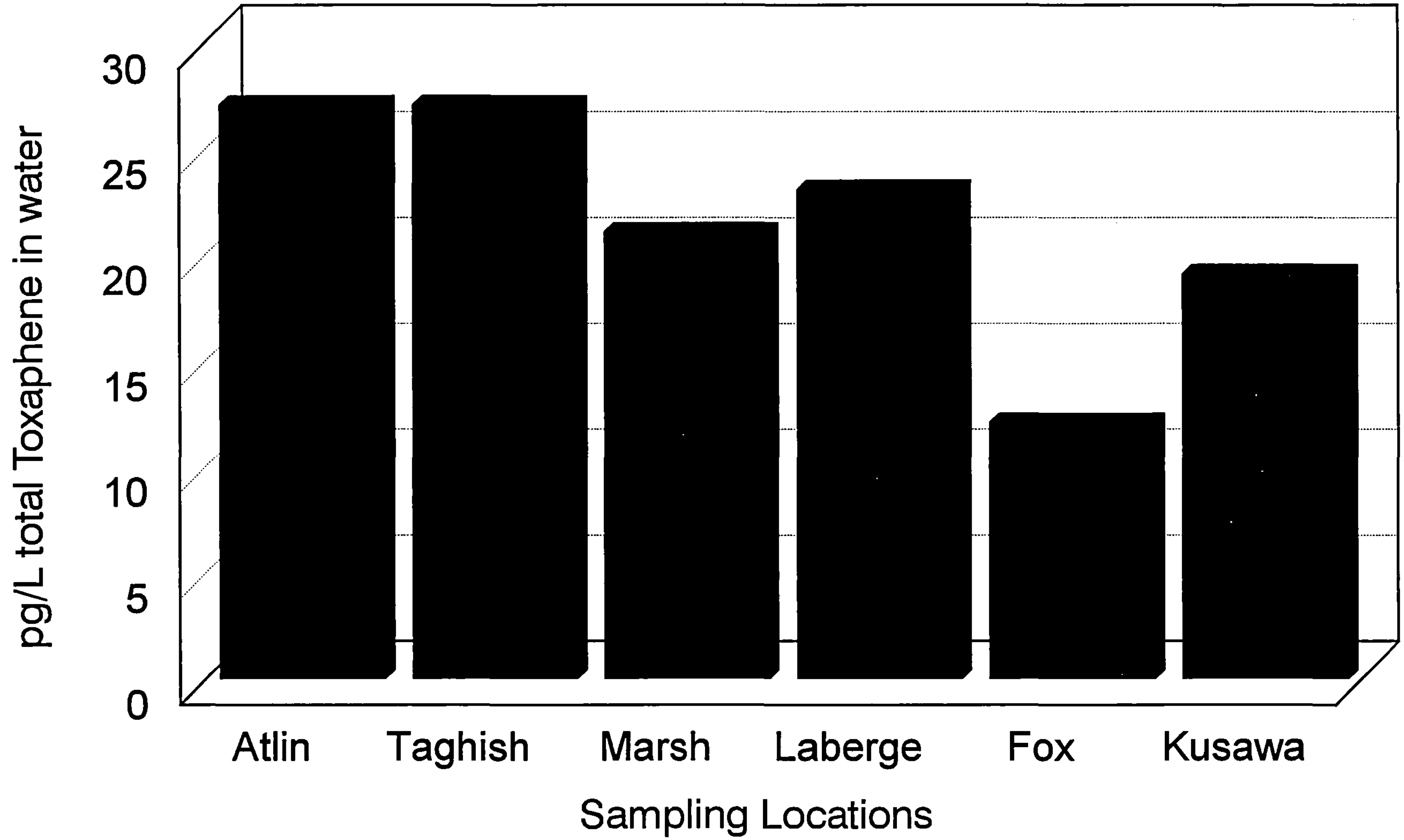


Figure 3. Concentrations of Cadmium and Chromium in the peat sample.

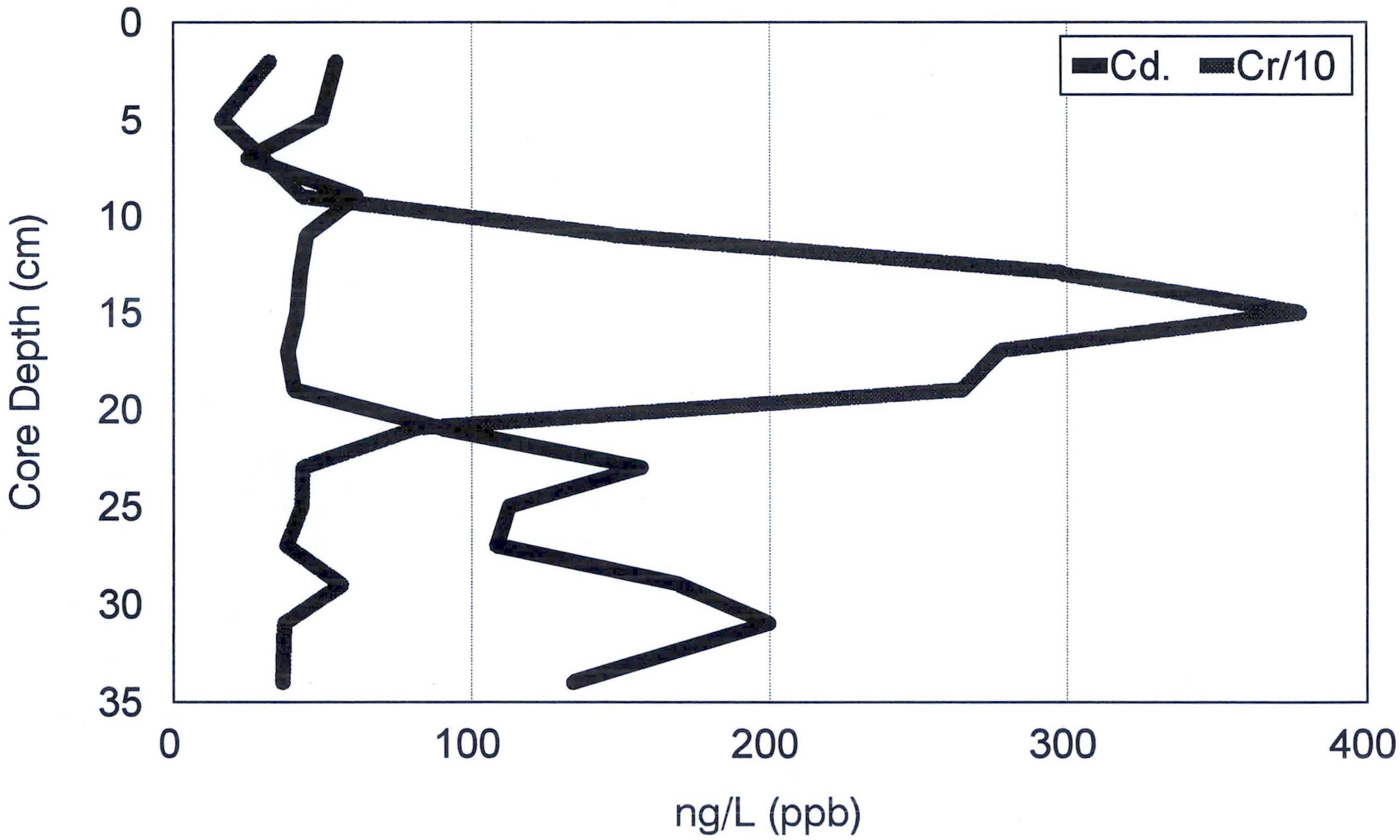


Figure 4. Enantiomeric ratios of *α*-HCH in Yukon river basin.

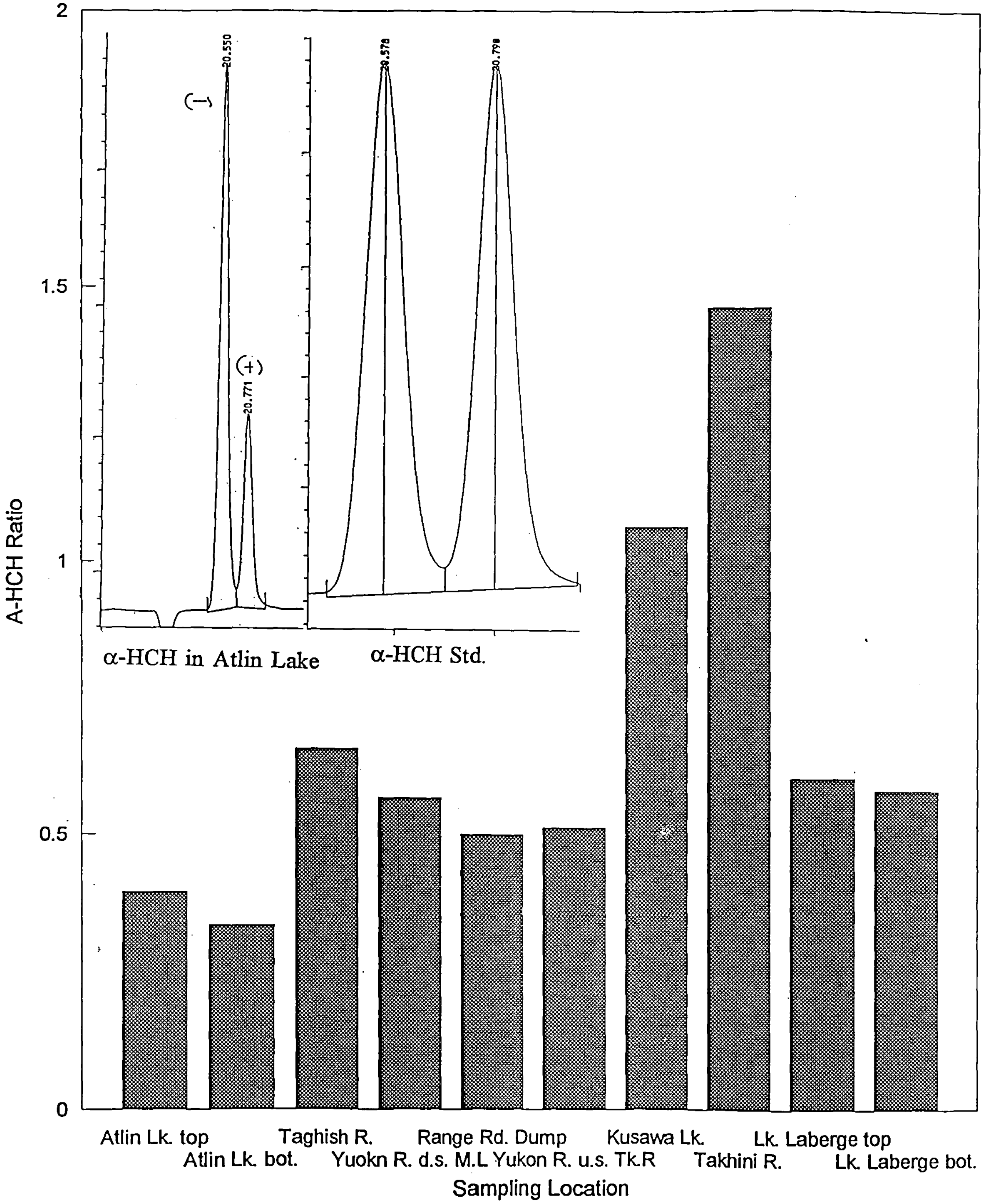


Table 1. Organochlorines and polycyclic aromatic hydrocarbon concentrations in the Yukon River basin.

Compounds Location	Atlin	Tagish	Bennett	Marsh	YK abv Whs	U Dump	L Dump	YK @ Tk	Takhini R	Kusawa	Fox	Laberge
PAHs Concentration in ng/L (ppb)												
Naphthalene	2.24	2.03	3.63	1.89	3.96	2.67	2.35	4.62	1.64	2.14	1.76	1.65
Acenaphthylene	0.07	0.06	0.01	0.11	0.13	0.12	0.17	0.22	0.03	0.07	0.07	0.00
Acenaphthene	0.03	0.01	0.00	0.07	0.08	0.45	0.46	0.17	0.04	0.06	0.04	0.02
Fluorene	0.10	0.09	0.12	0.20	0.22	0.64	0.57	0.34	0.13	0.28	0.06	0.03
Phenanthrene	0.41	0.93	0.94	0.72	1.33	1.48	1.95	1.49	0.40	1.23	0.66	0.39
Anthracene	0.47	1.06	1.13	0.89	1.60	1.66	2.18	1.72	0.48	1.42	0.76	0.46
Fluoranthene	0.31	0.57	0.69	0.36	1.10	0.56	0.67	0.35	0.15	0.52	0.34	0.30
Pyrene	3.78	3.11	3.59	1.37	7.71	1.81	3.06	2.47	0.46	2.88	1.74	1.33
Benz[a]anthracene	0.00	0.00	0.00	0.00	0.00	0.12	0.25	0.00	0.00	0.00	0.00	0.00
Chrysene	0.00	0.00	0.00	0.00	0.00	0.10	0.20	0.00	0.05	0.00	0.00	0.00
Benzo[b+k]fluoranthene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Benzo[a]pyrene	0.00	0.00	0.00	0.00	0.00	0.15	0.00	0.00	0.00	0.00	0.00	0.00
Perylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Indeno[123-cd]pyrene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dibenz[ah]anthracene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzo[ghi]perylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OCs												
PENTA-CB	0.52	0.52	0.65	0.39	0.67	0.59	0.35	0.70	0.20	0.61	0.41	0.42
HCB	1.21	1.45	2.22	1.86	1.57	1.00	1.09	1.94	1.31	2.70	1.09	1.36
ALDRIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
DIELDRIN	0.49	0.58	0.37	0.41	0.47	0.81	0.00	0.98	0.61	0.00	0.49	1.17
MIREX	0.00	0.12	0.11	0.00	0.00	0.00	0.00	1.55	0.00	0.00	0.07	0.40
t-nanochlor	0.00	0.00	0.00	0.00	0.06	0.22	0.20	0.00	0.09	0.32	0.20	0.14
A-BHC	154.88	110.46	71.83	107.07	113.47	24.75	28.47	124.60	39.31	109.48	101.74	82.18
B-BHC	1.08	0.91	0.49	0.78	0.78	0.00	0.24	1.63	0.40	0.34	0.70	0.76
G-BHC	31.74	22.38	9.92	21.67	22.50	3.46	5.00	27.31	5.12	9.75	12.85	9.21
HEPTACHLOR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HEPT. EPOX	0.00	0.17	0.00	0.00	0.08	0.00	0.00	0.19	0.06	0.00	0.25	0.39
G. CHLOR	0.00	0.10	0.00	0.00	0.06	0.00	0.18	0.00	0.05	0.49	0.20	7.34
A. CHLOR	0.00	0.35	0.34	0.12	0.24	0.23	0.32	0.43	0.16	0.75	0.30	0.17
OP-DDE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.80	0.51	0.00
PP-DDE	1.17	0.27	1.09	1.12	1.36	8.76	9.33	2.09	1.45	0.00	1.52	2.41
OP-DDD	0.75	0.00	1.82	0.44	0.70	2.10	3.80	0.00	0.97	3.74	0.00	0.33
PP-DDD	0.00	0.00	0.00	0.00	0.00	9.46	10.45	1.26	0.00	0.00	0.00	2.62
PP-DDT	0.00	0.00	0.40	0.00	0.00	0.00	0.49	0.00	0.00	0.00	0.00	1.29
CHBs (Toxaphene)	0.03	0.03		0.02						0.02	0.01	0.02
PCBs												
#18	0.35	0.89	2.03	1.48	0.85	1.36	2.33	1.52	1.21	7.15	1.05	1.22
#54	0.00	0.00	0.42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
#31	0.49	1.32	0.56	1.11	1.21	0.67	3.23	1.60	1.48	3.42	1.39	1.35
#49	0.64	1.11	2.30	1.60	0.81	0.78	1.32	1.97	1.74	3.67	1.00	0.42
#44	0.90	1.86	3.06	1.99	1.64	1.35	2.18	3.66	2.25	4.52	1.45	1.40
#40	0.66	0.00	1.48	0.00	0.00	0.00	0.00	0.00	0.89	1.22	0.00	0.00
#87	0.34	0.68	0.92	0.52	0.45	0.29	0.49	0.91	0.38	1.68	0.49	0.46
#77	0.00	0.39	0.38	0.48	0.00	0.00	0.00	0.75	0.22	1.21	0.93	0.00
#153	0.13	0.30	0.30	0.52	0.14	0.13	0.17	0.52	0.19	0.85	0.17	0.23
#159	0.00	0.00	0.02	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
#209	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
#15	0.00	3.97	4.34	4.26	0.00	0.00	5.34	3.52	2.65	18.95	1.77	2.86
#52	2.44	2.75	6.00	3.92	3.64	2.41	1.10	6.43	5.69	11.79	3.93	3.43
#60	0.00	0.15	0.28	0.22	0.10	0.65	0.00	0.36	0.26	0.70	0.00	0.23
#143	0.00	0.00	0.00	0.00	0.00	0.30	0.44	0.73	0.00	0.00	0.00	0.33
#105	0.00	0.17	0.15	0.00	0.00	0.00	0.00	0.41	0.33	0.73	0.00	0.00
#182	0.00	0.09	0.00	0.18	0.00	0.00	0.00	0.00	0.00	0.21	0.00	0.00
#153	0.15	0.34	0.34	0.59	0.16	0.14	0.00	0.58	0.40	0.95	0.30	0.62
#183	0.00	0.00	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
#209	0.00	0.00	0.55	0.00	0.00	0.00	0.00	0.79	0.00	0.00	0.00	0.00
#101	0.00	0.21	0.39	0.30	0.14	1.19	2.06	0.50	0.36	0.97	0.00	0.31
#118	0.00	0.94	0.00	0.00	0.00	0.30	0.00	0.09	0.00	0.00	0.00	0.59

YK abv. Whs.: Yukn River above Whitehorse

U. Dump : Upper Range Road dump

L. Dump : Lower Range Road dump

YK. @ Tk : Yukon River at the junction with Takhini River

PROCESSES AND FLUXES OF CONTAMINANTS IN AQUATIC SYSTEMS

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OBJECTIVES

Short-term:

1. To obtain scientific information from an experimental basin in the High Arctic for the purpose of determining a detailed hydrologic and organic/inorganic contaminant budget.

2. To investigate and quantify the major processes affecting contaminant transformation, transport and fate in the Amituk Lake watershed in order to provide predictive capability for basin mass balances.

3. To develop and calibrate contaminant transport models utilizing the results from this basin study and to compare the results with other basin studies.

Long-term:

1. To quantify mass balances of contaminants and selected inorganic substances for specific Arctic watersheds in the Canadian north.

2. To investigate and quantify the key abiotic processes controlling contaminant fate and dynamics in Arctic freshwater systems.

3. To utilize the study results from all basins studied in the Arctic for model development and calibration in order to estimate contaminant transport and flux in larger northern aquatic systems.

DESCRIPTION

The Amituk Lake study began in 1992 under the auspices of the Arctic Environmental Strategy (AES). The objective of the multidisciplinary research activities was to document the distribution, pathways and sinks of inorganic and organic contaminants in an Arctic snowpack and in the meltwaters as they move through a terrestrial lake basin. By recording the occurrence and movement of these chemicals in a freshwater system, a better understanding of the migration of contaminants to the marine environment can be attained. Furthermore, scientific information from a relatively small basin such as Amituk Lake will be used in model development and calibration for the behaviour of contaminants in larger northern aquatic ecosystems.

Amituk Lake is located on the eastern coast of Cornwallis Island at latitude 75° 02' 57" and longitude 93° 45' 51". The basin is underlain by Ordovician and Silurian carbonate rocks. The overall basin is approximately 26 km^2 and contains 6 small watersheds (Figure 1) of which Gorge, Cave and Mud Creek account for 78% of the drainage area contributing to Amituk Lake. The climate on Cornwallis Island is typical of High Arctic regions with an annual mean temperature of -16.6°C and total annual precipitation of 131.4 mm reported at Resolute Bay (Environment Canada 1990).

ACTIVITIES IN 1993/94

The 1993 field season at Amituk Lake extended from early June to mid-August. Forty-seven snow samples were collected from stream valleys, lake ice and upland areas to record the spatial variability in water content and chemical composition. An additional 15 samples from deep and shallow snow were collected for organochlorine (OC) determinations.

Some 268 water samples were collected from the 6 influent streams and from the lake outlet. Samples for inorganic analyses (major ions, nutrients, suspended solids) were collected at least daily to coincide with the major influx of snowmelt and less frequently during periods of low flow. OC analyses were carried out on another 36 stream samples. Instantaneous flow measurements were combined with stream levels to generate stage-discharge rating curves for the seven gauging sites. Daily stream discharge values were then derived from the continuous level record for mass balance calculations.

Lake sampling was carried out weekly from June 16 to August 11, 1993. Chemical profiling for major ions and nutrients was done at this time. Weekly samples for TP, TKN and suspended solids were also collected at 0.5 m below ice level, 20 m and 41 m. Fourteen OC samples were taken at the same time and from two depths — 3.0 and 21.0 m. Chemical measurements were accompanied by weekly profiles of temperature, specific conductance, dissolved oxygen and light penetration. Sediment traps were installed at four sites in Amituk Lake ranging in depth from 13 to 41 m. Collectors were placed at the surface mid-depth and 1 m off the bottom; samples were tested for total solids and organic carbon content. Sediment cores were also collected at three lake stations for the analysis of organic contaminants and heavy metals.

Biological surveys at Amituk Lake in 1993 investigated the seasonal variation in the phytoplankton community. Measurements included species variability with time and lake depth, chlorophyll and lipid concentrations. Zooplankton samples were also collected by hauling a net (150 μm mesh) through the water column; species enumeration and OC determinations were carried out.

Continuous meteorological measurements were made at the Amituk Lake base camp and at a satellite station to provide data for modelling snowmelt and for the generation of streamflow. In terms of atmospheric chemistry, two large solar panels were deployed at the west end of Amituk Lake to power a high-volume air sampler for contaminant analysis.

RESULTS

Snow surveys at Amituk Lake in 1993 recorded a marked heterogeneity in both physical and chemical attributes. Snowpack depths ranged from 0.10 m in the upland areas to several metres in the stream valleys. The major ion composition of the snow changed greatly in the watershed, primarily as a result of the presence of rock flour which became incorporated into the snowpack by the strong prevailing winds. Calcium and alkalinity, the dominant ions in the pre-melt snow cover and products of erosion, both varied in concentration across the basin by factors of 50 (Table 1).

Streamflow was first detected in Mud Creek and at the lake outlet on June 18, 1993, eight days earlier than in the 1992 season. The high discharge period lasted for approximately 20 days at the Amituk Lake outflow (Figure 2). The temporal variation in stream chemistry was characterized by elevated major ion concentrations at the initiation of snowmelt, possibly reflecting early chemical fractionation of ions in the parent snowpack (Figure 3). Concentrations decreased with increasing streamflow as snowmelt of lower ionic strength entered the stream channels. The major ion levels returned to higher values under the low flow conditions of late summer.

Amituk Lake was sampled weekly from June 16, 1993 when a reverse thermal stratification was evident until early August, 1993 when isothermal conditions were observed (Figure 4). As in 1992, the major ion composition of the water column was dominated by $Ca^{2+}$and HCO_3^- as a result of chemical/mechanical weathering of limestone and dolomite in the watershed (Semkin and Gregor 1992). The depth of mixing of cold meltwaters with the lake water varied over time, reaching depths of 6 to 7 m in mid-July. Complete mixing in the water column occurred with the break-up of the thermocline in early August (Table 2).

Limnological studies in 1993 included an assessment of the phytoplankton and zooplankton populations in Amituk Lake. With respect to the phytoplankton community, summer surveys revealed five main algal groups in the water column — Chrysophyceae, Bacillariophyceae, Dinophyceae, Cryptophyceae and Chlorophyceae (Table 3).

Sixty-five water samples (snow, stream and lake) were collected for organochlorine analyses at Amituk Lake in 1993. Additional samples were collected from the bottom sediments, from suspended sediment matter and from the zooplankton population. As the OC analytical results are preliminary at this time only data for hexachlorocyclohexane (HCH) will be presented in this report. HCH is one of the most ubiquitous and commonly reported OC compounds in the High Arctic. Concentrations of total HCH ranged from about 300 pg/L in shallow snow on lake ice to greater than 4000 pg/L in deep (5 m) valley snow (Table 4). Total HCH levels in a small influent stream averaged 765 pg/L over the study period, although an initial stream concentration of 2008 pg/L was measured at the onset of snowmelt. This high concentration in Rock Creek was comparable to that observed in Mud Creek on June 23, 1993 (2161 pg/L) and may be explained by chemical fractionation of dissolved species in the snowpack at the initiation of melt — a phenomenon also observed for Cl^- in the lake outflow (Figure 3). Lake concentrations of total HCH were similar at depths of 3.0 and 20.0 m — 1422 and 1351 pg/L, respectively, although earlier data from the shallow depth may have increased the 3.0 m average value. The relative proportions of α- and γ-HCH were quite variable in the different sampling media at Amituk Lake. α/γ-HCH ratios ranged from 1.6 - 3.1 in shallow to deep snow to 5 - 6 in Rock Creek and Amituk Lake and to 9 in the lake outflow (Table 4).

CONCLUSION AND UTILIZATION OF RESULTS

The analysis of contaminants in the snowpack has resulted in an effective measure of atmospheric deposition over the winter months at Amituk Lake and in an important estimator of the contaminant loading available to a freshwater ecosystem. Processes that control the timing of contaminant release to melt waters and the efficiency of release relative to the total deposition are being quantified. The mechanisms that regulate the movement and fate of contaminants from snowmelt into stream and lake waters and aquatic biota are being investigated so that contaminant pathways and sinks can be determined. By calculating contaminant mass balances at Amituk Lake, the development and calibration of deposition and fate models at this site and elsewhere in the High Arctic will be greatly facilitated.

Expected project completion date: March 31, 1996.

REFERENCES

Environment Canada. 1990. The Climates of Canada. Ottawa, Canada

Semkin, R. and D. Gregor. 1993. Processes and fluxes of contaminants in aquatic systems. Pp. 57-68 *in*: Synopsis of Research Conducted Under the 1992/93 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 70. Indian and Northern Affairs Canada. 285 pp.

Figure 1. Drainage areas in the Amituk Lake basin

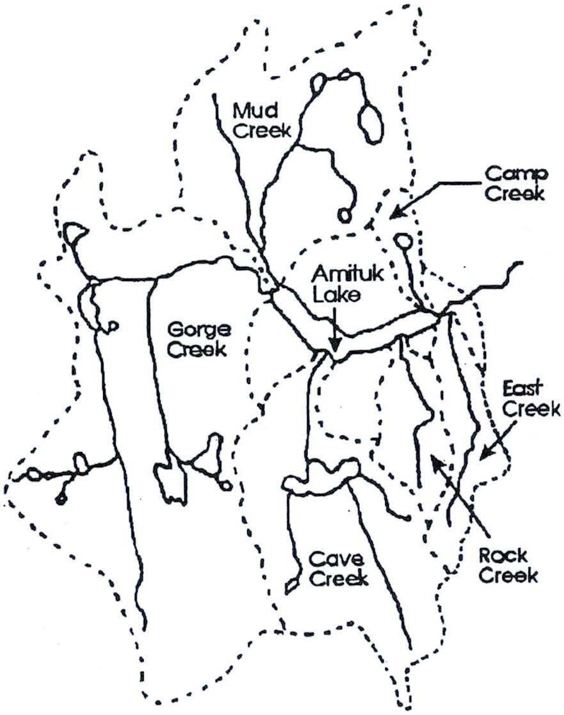


Table 1. Composition[1] of the Pre-Melt Snowpack, Amituk Lake, 1993

	Mean	Min.	Max.	C.V.%
Depth (m)	0.821	0.099	3.3	96
SWE(mm)	363	35	1620	106
pH	6.7	5.84	9.57	131
Ca^{2+}	1.66	0.14	6.36	86
Mg^{2+}	0.53	0.05	1.57	67
Na^+	1.85	0.12	5.29	72
K^+	0.17	0.04	0.76	78
NH_4±N	0.005	N.D.	0.021	101
ALK meq/L	0.0926	0.0082	0.3987	99
SO_4^{2-}	0.46	0.05	1.02	38
Cl^-	3.94	0.3	12.48	76
NO_3^-	0.03	N.D.	0.085	53
SiO_2	0.009	N.D.	0.053	135
DOC	1.54	0.25	23.2	226

[1] All concentrations as mg/L unless otherwise specified.

Fig.2 Amituk Lake Outflow 1993

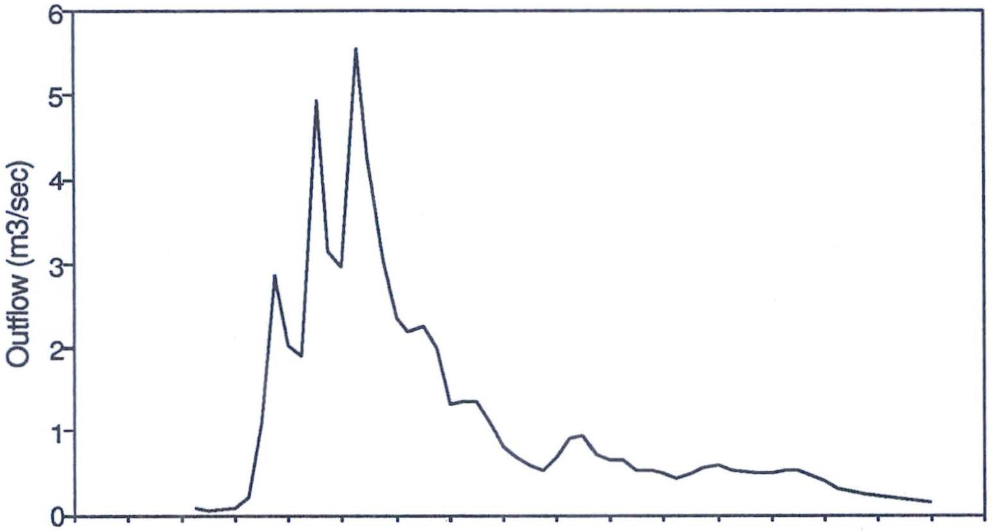


Fig.3a Major Cations in Lake Outflow

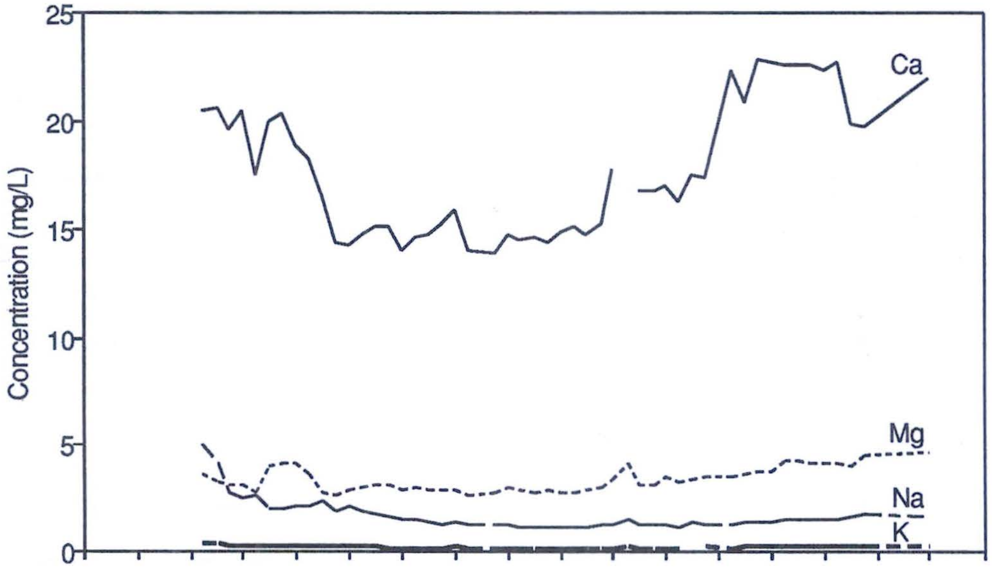


Fig.3b Major Anions in Lake Outflow

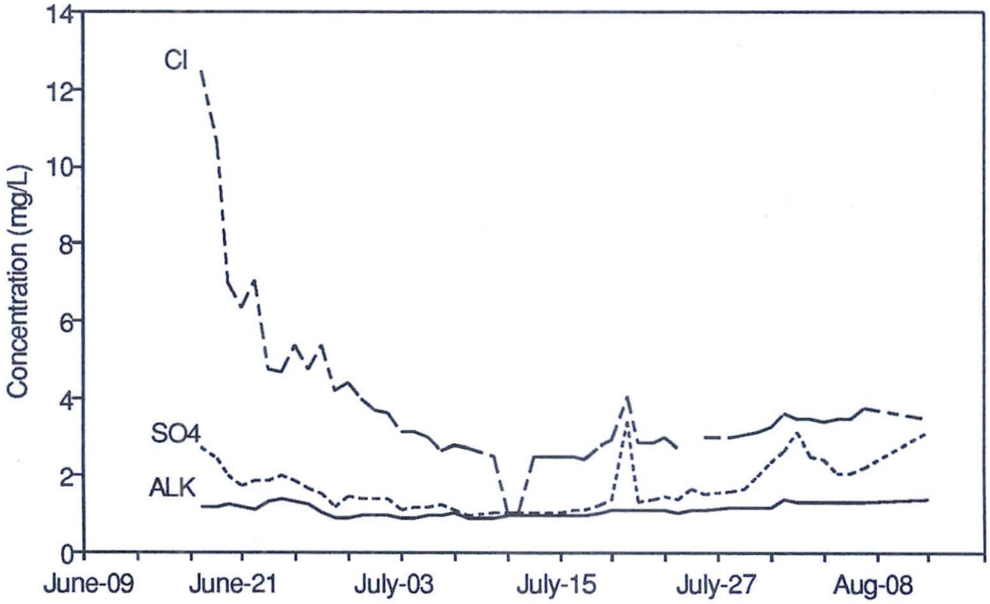


Table 2. Mixing in Amituk Lake 1993				
	July 7/93 Ice Thickness 1.17m		August 4/93 Ice Thickness O m	
Depth (m)	Cond. (μS/cm)	Ca (mg/L	Cond. (μS/cm)	Ca (mg/L)
0	----	----	128	19.4
1	----	----	131	19.8
1.2	15	1.9	----	----
2	87	13.4	132	19.6
3	95	15.1	132	19
4	97	14.8	132	19
5	113	17.1	133	19.6
6	119	18.5	131	19.6
7	146	21.7	132	18.8
8	146	22	131	19.2
9	147	21.7	131	19
10	146	22.1	132	18.6
20	145	21.5	132	19
30	146	22.3	132	19.1
40	170	26.3	133	20.2

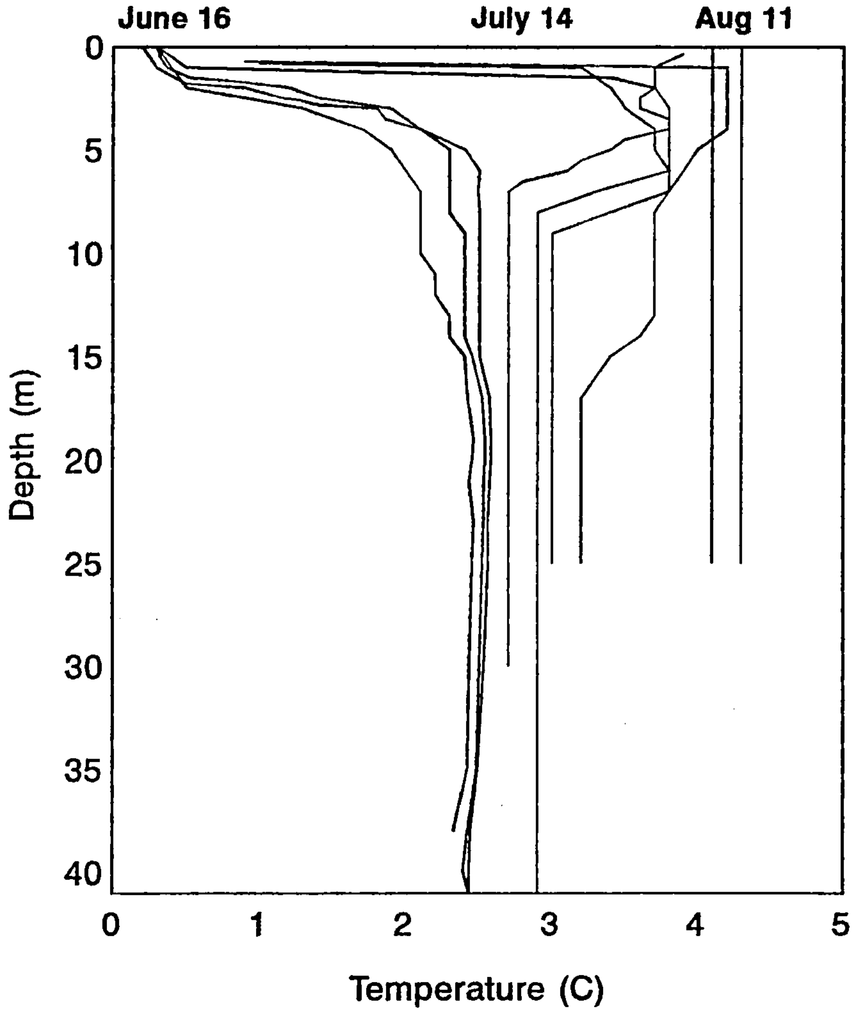
Table 3. Dominant algae found in Amituk Lake (July 11, August 4)

CHRYSOPHYCEAE	Chromulina sp. Chrysococcus rufescens Dinobryon divergens Dinobryon cf. crenulatum Kephyrion sp. Pseudokephyrion cf. entzii Ochromonas sp.
BACILLARIOPHYCEAE	Cyclotella comta Cyclotella cf. meneghiniana Cyclotella sp. Navicula sp. Nitzshia sp. Synedra ulna Stephanodiscus sp. Suriella sp.
DINOPHYCEAE	Gymnodinium cf. bohemicum Gymnodinium sp. Peridinium inconspicuum Peridinium cf. umbonatum Peridinium sp.
CRYPTOPHYCEAE	Cryptomonas cf. marasonii Cryptomonas obovata Cryptomonas sp. Rhodomonas lacustris
CHLOROPHYCEAE	Chlamydomonas sp.

Table 4. HCH Variation at Amituk Lake 1993

Site	No. Samples	Mean sumHCH pg/L	Std Dev sumHCH pg/L	Mean A/G-HCH	Std Dev A/G-HCH
Shallow Snow	7	288.8	71.1	1.62	0.54
Rock Valley Snow	4	4139.1	704	3.05	0.11
Rock Ck	5	764.8	646.5	4.85	1.68
Amituk Lk-3.0m	6	1422.2	341.4	5.9	0.87
Amituk Lk-20.-m	8	1350.5	369.5	6.49	2.22
Outflow Amituk Lk	8	1620.8	486.9	9.03	3.77

Fig.4 Temperature Profile
Amituk Lake 1993



ECOSYSTEM CONTAMINANT UPTAKE AND EFFECTS

ECOSYSTEM CONTAMINANT UPTAKE AND EFFECTS
NEW FINDINGS

1. Marine Environment

Organochlorines

1) Concentrations of PCBs in blubber of female ringed seals, collected in 1992 and 1993, from Arviat and Inukjuaq were similar (1093±472 and 1457±1648 ng/g, respectively) while females from Pangnirtung had much lower levels (467±195 ng/g). Similar trends were observed for other OCs. The observation of higher levels of OCs in Hudson Bay animals is consistent with previous reports.

2) Concentrations of ΣPCBs and ΣDDT increase with age in male ringed seals from Arviat but not in females. This has been observed previously but a large number of samples from Arviat has enabled a thorough test of the age/concentration relationship.

3) Reproduction represents an important pathway of contaminant transfer between generations in marine mammal populations. This assessment is based on the elevated levels observed in young animals, reduced levels observed in mature females, and through modelling exercises using estimated values of contaminant partitioning from maternal tissue to the fetus and milk. This transfer occurs primarily during nursing for beluga and ringed seals.

4) A study on harp seals, sampled at various points down Hudson Strait as they migrated from Ungava Bay to the Gulf of St. Lawrence, indicates that the bulk of OC accumulation by these animals occurs during intensive feeding in the northern Gulf of St. Lawrence. However, concentrations are much lower than a decade ago. In contrast, levels of major OCs in ringed seals from Hudson Bay and Baffin Island do not appear to have declined significantly in females over the last 6 years.

5) In a study of biomarkers in arctic seals, correlation analysis demonstrated several associations between enzymatic activities and blubber residues in the same seals; all four biochemical measurements (ethoxyresorufin-O-deethylase, EROD; aryl hydrocarbon hydroxylase, AHH; cytochrome-P450; and aminopyrene-N-demethylase, APND) were correlated with dieldrin residues, and these associations were not artifacts due to other biological covariates (age, sex, blubber lipid content).

6) The concentration of PCBs and chlordanes in polar bears tends to increase as the fasting period progresses. A recent study showed that levels in pregnant females approximately doubled during the 5 month fasting period. To a lesser extent, chlorobenzene levels also increased, but HCH and dieldrin levels were similar at both time points, indicating a faster equilibration. Cubs had higher levels than their mothers.

7) Levels of total methylsulfone-PCBs and -DDE in polar bear liver were 100 times higher than those in the brain, and 10-20 times higher than in the other tissues. The distribution of PCBs

in the polar bears was similar to that of methylsulfone-PCBs. There was much more selective retention of methylsulfone-DDE in liver, in which average levels were 0.3 ppm (lipid wt. basis), which was nearly half the level of DDE itself.

8) As found in a previous study of the geographical distribution of organochlorines in polar bears undertaken between 1982-84, there is a tendency for HCH to be higher in the western Arctic, reflecting a probable Asian source. It is the only chlorinated compound class to have this type of distribution. All other residues are relatively evenly distributed (e.g. chlorobenzenes), or tend to increase from west to east, with highest levels being found in eastern Greenland and Svalbard. The highest levels of total methylsulfone-PCBs were found in east Greenland bears.

9) Retrospective analysis of adult polar bear fat samples from northern Hudson Bay has shown that levels of all residues tended to be lower in 1969 than in 1982-84. However, this apparent increase over time was only significant for ΣChlordanes. Similarly, levels of all residues appear to have declined between 1982-84 and 1989-91, but only the decrease in ΣDDT was significant. It is probable that the peak in concentration of most organochlorines and PCBs was shifted several years later in the Arctic than at mid-latitudes, where it occurred in the late 1960s or early 1970s, so the peak may have been any time between 1969 and 1982. Every indication suggests that levels of all organochlorines in polar bears are now in decline in this area.

Metals

1) In the muscle of narwhal from Pond Inlet and Iqaluit the mean methylmercury (and total mercury) concentration was significantly higher than the Federal Guideline for fish as set by Health Canada (0.50 μg/g wet wt.) and was somewhat higher also in Repulse Bay narwhal. In all narwhal combined, the mean methylmercury concentration in muscle was 0.82 μg/g wet weight. However, the number of animals from each site was relatively small, and additional samples should be analyzed before the results are utilized for dietary calculations.

2) Methylmercury levels in muscle of ringed seals from Sachs Harbour exceeded the Federal Guideline for fish (0.50 μg/g wet wt.) in approximately one third of the animals sampled. Methylmercury was much higher in liver than in muscle in both ringed seals (e.g. 2.11 μg/g wet wt. at Sachs Harbour) and narwhal (e.g. 3.02 μg/g at Iqaluit) and far exceeded the guideline.

3) In muktuk of narwhal from Iqaluit, the mean total mercury concentration (0.61 μg/g wet wt.) exceeded the Federal Guideline for fish. However, mercury was not distributed homogeneously but was highest in the outermost stratum (degenerative epidermis) and progressively declined in successive strata. The mean concentrations of lead and cadmium were quite low in muktuk of narwhal from Repulse Bay and Iqaluit and appear not to pose a problem for consumers or animals.

4) In a survey of mercury, cadmium and selenium in country foods in the eastern Hudson Bay, it was determined that levels in mussels were low, and concentrations in muscle of freshwater fish were generally below guideline levels for mercury and cadmium. Some marine mammal liver samples presented high levels of all metals (e.g. levels of Cd, Hg and Se in beluga liver

reached levels of 13.24, 98.56 and 24.97 ppm, respectively). Mercury levels in some liver samples exceeded consumption guidelines. A concern had been raised that beluga muktuk might be high in Cd, but this study showed that muktuk contained very low concentrations of this metal.

2. Freshwater Environment

Organochlorines

1) Mean levels of OCs in lake trout muscle, burbot liver and lake whitefish muscle from Lake Laberge, Yukon are up to 150-, 45- and 43-fold higher, respectively, than found in the same species from Fox Lake, situated beside Lake Laberge. OC concentrations in lake trout and whitefish muscle are up to 21- and 13-fold higher, respectively, in fish from Lake Laberge than those from Kusawa Lake. The top predators in Lake Laberge feed at a higher trophic level than those from the other lakes. This trophic difference between lakes provides an explanation for the higher concentrations of DDT, PCBs and toxaphene found in the fish from Lake Laberge.

2) A survey of whitefish, lake trout and burbot in the east and west arms of Great Slave Lake revealed relatively low concentrations of organochlorines (including dioxins and furans) and PAHs. Toxaphene was the predominant organochlorine detected.

3) Lake whitefish collected from Lake Laberge, Yukon in 1974 had 3-fold higher concentrations of ΣDDT (390 ng/g), 4-fold lower toxaphene (22 ng/g) and 2-fold lower PCBs (61 ng/g) than those from 1992. HCH, dieldrin and chlorobenzenes were significantly higher in 1974 samples than in 1992, while chlordane showed the opposite trend. The higher DDT in 1974 is in agreement with results for sediments which show higher DDT concentrations at that time than in present day sediments.

4) It has been suggested that the presence of toxaphene in Laberge fish is almost certainly the result of atmospheric input. In the case of PCBs and DDT, however, the consistently higher levels in Lake Laberge than other locations suggests a local influence as well as atmospheric sources.

5) In a survey of organochlorines in fish from 9 locations in the NWT and from the Ob River in Russia, toxaphene was the major OC contaminant in all fish except whitefish from the Ob River. The other major OCs in the fish were PCBs, DDT and chlordane.

Metals

1) Concentrations of mercury in char muscle in 5 lakes on Cornwallis Island, NWT exceeded the Health Canada guideline of 0.2 μg/g for subsistence fisheries, but were well below the 0.5 μg/g Federal Guideline level.

3. Terrestrial Environment

Organochlorines

1) Glaucous Gull eggs collected from the High Arctic (Prince Leopold and Browne Islands) generally contain the highest concentrations of organochlorine residues (e.g. PCB 3.326 ppm; DDT 2.367 ppm), whereas eggs of eiders and Black-legged Kittiwakes contain the lowest levels. The highest residue concentrations of organochlorines are also found in Glaucous Gull chicks (e.g. PCB 1.635 ppm; DDT 1.139 ppm) and livers of adult Glaucous Gulls (e.g. PCB 2.506 ppm; DDT 1.965 ppm) compared to other species. This is to be expected since this species is highly predatory, often feeding on the eggs and chicks of other birds or scavenging on carcasses.

2) In a study of contaminants in arctic waterfowl, the most commonly detected residues were the chlordanes, DDT and dieldrin, although the chlorobenzenes and PCBs were also prevalent in the diving species. Those species which feed at a lower trophic level, such as grazers (geese), browsers (ptarmigan) and dabbling ducks (Mallard), contain the least amount of contaminants. Diving ducks, such as the eiders and Oldsquaw which feed mainly on invertebrates, reflect a higher exposure to organochlorine contaminants (e.g. levels of ΣDDT and ΣPCB in Oldsquaw from Baker Lake of 0.142 and 0.173, respectively).

3) A preliminary comparison of 1993 egg residue data from Prince Leopold Island with data for the same location from the 1970s and mid-1980s shows a stabilization of PCB and DDT residues for Thick-billed Murres, a continuing decline in levels for Black-legged Kittiwakes, and possibly an increase in DDE levels in Northern Fulmars.

4) Results from data collected from 1991 to 1993 indicate a continued presence of organochlorines in arctic peregrine falcons and their prey near Rankin Inlet. The highest level of DDE found was 4.71 ppm wet wt. in a nestling some 3 weeks old. There is evidence that organochlorine contamination of peregrine eggs has decreased since the early 1980s and that the mean levels are under the levels considered critical. However, peregrine eggshell fragments collected since 1991 are still thinner than those laid in the Nearctic prior to the introduction of pesticides. Contrary to predictions, there has not been an increase in eggshell thickness since the early 1980s.

5) In a study of caribou from Arviat, Cape Dorset, Lake Harbour, Southampton Island and the Bathurst herd, HCB, HCH, chlordane, and DDT were the predominant organochlorine compounds detected. HCB residues ranged from a lipid corrected mean of 32.83 ng/g in fat of Bathurst caribou to 129.41 ng/g in Lake Harbour animals. α-HCH was the predominant hexachlorocyclohexane, with levels ranging from 8.11 ng/g in Bathurst animals to 37.9 ng/g in Cape Dorset caribou. Total chlordane levels ranged from 0.81 ng/g in Bathurst caribou to 5.01 ng/g at Cape Dorset, with oxychlordane the dominant chlordane compound. The levels of total DDT ranged from 0.46 ng/g at Arviat to 2.58 ng/g at Cape Dorset, consisting largely of *p,p*'-DDE. ΣPCB residues ranged from 6.24 ng/g in fat of Arviat caribou to 31.68 ng/g at Cape Dorset, with congeners 153 and 138 most dominant of the 43 congeners tested. The patterns of PCB congener distribution were generally similar at all sites, although the levels of lower

chlorinated PCB congeners were generally higher in the Bathurst and Arviat caribou than in those at the other three sites.

Long-range atmospheric transport appears to be the primary source of the contaminants detected in this caribou study, and the air-plant-animal (e.g. air-lichen-caribou) contaminant pathway is the most likely route of contaminant deposition into the terrestrial food chain. Overall, organochlorine residue levels in NWT caribou were substantially lower than levels found in arctic marine mammals.

6) A survey of caribou (liver, muscle and fat) in the Yukon and Northwest Territories revealed extremely low levels of PCDDs, PCDFs and non-ortho substituted PCBs. Levels of PCDDs and PCDFs were less than 1 ng/kg and were frequently not detected at 0.1 ng/kg or lower. Non-ortho PCBs were detected in most samples, but did not exceed 25 ng/kg. The results reported in this study indicate that PCDDs, PCDFs and non-ortho PCBs do not pose a threat to the caribou herds studied. The levels observed are among the lowest ever reported in wildlife. PCDDs, PCDFs and PCBs are globally distributed and long-range atmospheric transport, with some minor local inputs, can probably account for the PCDD/PCDF and non-ortho PCB levels found in the caribou. The high levels reported in 1993 were probably the result of sample contamination either in the field or the laboratory.

7) Many of the pesticides and PCB congeners recently detected in mink and martens from the Northwest Territories were found at very low levels. ΣPCB residues ranged from a mean of 5.32 ng/g wet wt. in the livers of Inuvik mink (most northerly site) to 27.67 ng/g in mink from Fort Smith (most southerly site), and averaged 32.58 ng/g in the Fort Good Hope marten sample. There was a doubling of mean ΣPCB levels in Inuvik mink from 5.32 ng/g in 1991/92 to 10.69 ng/g in 1992/93. In all but two mink (n=90) and two marten samples (n=20), DDT was below detection limits. Of the more toxic non-ortho substituted PCB congeners, PCB-77 was detected in no mink samples (n=90) and only two marten samples (n=20), PCB-169 was only detected in one Fort Smith mink, and residues of PCB-126 were found in two mink and six marten samples. Dioxins/furans were not detected in any mink liver samples, and were detected in only three cases in Fort Good Hope marten liver samples. Total toxaphene in mink was 1.42 and 7.85 ng/g (wet weight) for mink from Ft. Good Hope and Ft. Rae, respectively.

There was a distinct trend of decreasing organochlorine contaminant burdens in mink with increasing latitude. At present, long-range atmospheric transport appears to be the primary source of the contaminants detected, due to the even distribution across a wide geographic area. Local point sources are not suspected.

While organochlorine residues were present in mink in the NWT, the observed burdens were generally low in comparison with wild mink from other areas of North America. Overall, PCB levels observed in NWT mink were considerably lower than levels shown to cause reproductive impairment. Population indices derived from age and sex ratios of the harvest, coupled with the comparatively low levels of contaminants, suggest little or no effects on mink reproduction or population health as a result of these contaminants.

Metals

1) Lead and cadmium were virtually not detected in eggs of arctic seabirds and lead was only minimally detected in the chicks and livers of adult birds. The highest levels of total mercury were found in eggs of Glaucous Gulls from Prince Leopold Island (4.89 ppm). Burdens of total mercury increase from egg to chick for all species, however, much of the mercury is concentrated in the feathers. Cadmium and, to a lesser extent, lead are taken up by the chick after hatch, indicating that transfer of these elements from parent to egg is minimal.

2) Moderately elevated levels of Cd and Hg were detected in kidney and liver of caribou from Arviat, Cape Dorset, Lake Harbour, Southampton Island and the Bathurst herd. Cd levels in kidney tissue ranged from 9.68 μg/g dry wt. in Bathurst animals to 33.87 μg/g in Arviat caribou. Hg levels in kidney tissue ranged from 0.52 μg/g wet weight in Bathurst caribou to 2.93 μg/g in Arviat animals. Cadmium levels detected in this study were similar to those found in caribou from Norway and northern Quebec. Moderately elevated levels of Cd in caribou from the NWT are comparable with findings in other big game species in Canada, and are most consistent with long-range atmospheric transport. A human health hazard assessment was conducted on the data by Health Canada. The results of this assessment were published by the Government of Northwest Territories Department of Health in an issue of EPINORTH.

Radionuclides

1) Radionuclide levels in Caribou at five sites within the NWT were generally low or non-detectable, with the exception of ^{137}Cs, ^{40}K, and ^{134}Cs. ^{137}Cs was the most predominant nuclide, with activity ranging from 34.86 Bq/kg in the Bathurst herd to 184.10 Bq/kg in Lake Harbour caribou. ^{40}K was also consistently found in all samples. Levels ranged from 115.20 Bq/kg in Bathurst caribou to 123.80 Bq/kg in Lake Harbour animals. Levels of ^{134}Cs ranged from <0.37 Bq/kg in Bathurst caribou to <1.50 Bq/kg in Lake Harbour animals. The levels of ^{137}Cs, the predominant nuclide in this study, supports the conclusion that levels of ^{137}Cs are steadily declining in the Canadian Arctic.

SOURCES AND SINKS OF ORGANOCHLORINES IN THE ARCTIC MARINE FOOD WEB

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OBJECTIVES

1. To quantify the long-range atmospheric and marine transport of organic contaminants and their incorporation into lower trophic level organisms of the marine food web in the Arctic Ocean.

2. To provide baseline measurements of major semi-volatile organics (chlorinated pesticides, PCBs) in the Canadian high Arctic Ocean environment by sampling seawater (dissolved and particulate phases), plankton, benthos and fish.

3. To assess the relative importance of atmospheric versus oceanic input of these contaminants to Arctic Ocean biota by seasonal measurements.

4. To evaluate the seasonal bioconcentration of these compounds for comparison with data from more southern latitude ocean sites in order to assess input of organochlorines to food webs utilized as food by native populations.

DESCRIPTION

Chlorinated hydrocarbon pesticides (OCs) and polychlorinated biphenyls (PCBs) are produced and used primarily in temperate and tropical latitudes, but long-range atmospheric transport, as well as surface ocean currents and river drainage, have introduced these compounds into the Arctic and other ocean basins (Barrie *et al.* 1992). The semi-volatile nature of many of these compounds and their resistance to photolysis or biodegradation has resulted in a global distribution with OC pesticide residues such as DDT and PCBs detectable in marine plankton and higher trophic level organisms from a wide variety of oceanic areas (Woodwell *et al.* 1971; Harding 1986; Muir *et al.* 1992).

Many OCs have a low water and high lipid solubility. Bioaccumulation (the partitioning of compounds between an aqueous phase and tissues of organisms) should be greatest in small-bodied aquatic organisms where equilibrium conditions are established between internal lipid pools and external ambient OC concentrations (Bidleman *et al.* 1989). In most aquatic animals, however, uptake of these organic contaminants occurs through food ingestion. Bioconcentration (calculated as the ratio of concentrations for predators over their prey) occurs in food webs where predators store the ingested compounds in lipids with slow rates of excretion or metabolism (Woodwell *et al.* 1971, Harding 1986). Bioconcentration should be favoured in arctic marine ecosystems where there is a summer maxima of lipid synthesis and storage.

While the present distribution and mechanisms for transfer of OCs between various compartments of the arctic marine environment and food web are poorly understood, it is known that concentrations of organic matter (particulate and dissolved) in the Arctic Ocean are extremely low (Gordon and Cranford 1985). Since there is no photosynthesis during months of darkness, marine organisms must store energy-rich lipids to survive. The high fat content of tissues used for lipid synthesis and storage make these organisms more likely to accumulate OCs that have a high fat solubility. This in turn may result in a greater bioconcentration of these contaminants by higher trophic levels than occurs in more temperate regions. The seasonal dynamics of accumulation and storage of potentially toxic and persistent OCs has human relevance in the Canadian Arctic where native people rely on marine mammals and fish for a large portion of their protein and caloric intake.

Published observations of the distribution of OCs in the Arctic Ocean are restricted primarily to measurements of concentrations in the atmosphere and tissues from large mammals (Muir *et al.* 1992). Measurements from the Canadian Ice Island between 1986 and 1989 (Hargrave *et al.* 1992) were restricted to summer months due to logistics of sampling throughout the year. The main objective for this project in 1993/94 was to provide the first seasonal measurements of OCs in seawater and lower trophic level marine organisms in Barrow Strait near Resolute Bay. The distribution and relative concentrations of OCs and PCBs in air, snow, seawater and various marine food web organisms sampled earlier from the Ice Island (Hargrave *et al.* 1988, 1992) over a restricted range of seasons could be compared with the new data set covering a full annual period.

ACTIVITIES IN 1993/94

Sampling Schedule

A 12-month over-wintering sampling program for organochlorines was initiated using the Department of Fisheries and Ocean's (DFO) facilities at South Camp, Resolute Bay, NWT in January 1993. Monthly sample collection was carried out for seawater (1 and 50 m depth), epontic particulate matter, various size classes and species groups of planktonic and benthic crustaceans and fish (Table 1). The work was coordinated with other DFO studies during the POLARPRO project to measure biomass and productivity of plankton and benthos in Barrow Strait over an annual cycle. Observations of hydrographic variables (temperature, salinity, dissolved nutrients), chlorophyll *a*, zooplankton biomass, lipid content and species composition were made at monthly or more frequent intervals. The data set is unique in providing seasonal observations of marine food web dynamics over an annual cycle.

Table 1. Sampling schedule for OCs during POLARPRO-1993

Date	Sample Collection seawater	epontic particulates	zooplankton	amphipods	fish
Jan 23 - Feb 1	+		+	+	+
Feb 25 - Mar 1	+		+	+	
Mar 30 - Apr 1	+		+	+	
Apr 28 - May 3	+		+	+	
May 19 - 23	+		+	+	
June 1 - 3	+	+	+	+	+
June 26 - 30	+	+	+	+	
July 29 - 30	+	+	+	+	+
Sept 7 - 8	+		+	+	
Oct 15 - 18	+		+	+	
Nov 13 - 15	+		+	+	+
Dec 9 - 13	+		+	+	

Methods

The start-up date for POLARPRO was delayed to January 1993 from the planned date of September 1992 to allow food, laboratory supplies and equipment to be shipped to Resolute Bay by sea-lift. This also ensured that ice was sufficiently thick to allow establishment of a research base-camp on the ice. Monthly sampling of organochlorines in seawater and lower trophic level organisms commenced in January 1993 using a 1 m^2 ice hole covered by a heated sampling hut placed approximately 6 km off Cape Martyr in Barrow Strait. A local Inuit technician (Peter Amarualik) assisted with sampling and sample processing throughout the study.

XAD-2 resin columns attached to Seastar (Infiltrix) *in situ* pumps were used to concentrat dissolved and colloidal OCs from 150 to 250 l of seawater. Seawater was pumped

(150 ml$\cdot$min^{-1}) through a baked GFC filter (1 μm pore dia) to remove particulate matter. Previous analyses of samples from both coastal and offshore Arctic Ocean water have shown that the small amounts of material present on filters does not allow accurate determination of OCs associated with suspended particulate matter accumulated on filters. Columns were capped and held refrigerated until extracted. Biota samples, after removal of excess water, were weighed and frozen (-18 °C) in solvent-clean jars. Subsamples were preserved in 2% buffered formalin for taxonomic identification. Extraction and clean-up procedures for XAD-2 columns and biota are described in Hargrave *et al.* (1989 and 1992).

Analytical procedures for sample extraction and identification and quantification of OCs in the present study performed by Axys Analytical Services (AAS), Ltd. (formerly Seakem Oceanography Ltd.), Sidney, B.C., are the same as were used in previous studies from the Canadian Ice Island (Hargrave *et al.* 1989). This ensures internal consistency in data collected in different years for intercomparison of data sets. In addition, a four-laboratory intercalibration for 18 different OC residues in arctic marine crustaceans collected between 1986 and 1989 was completed in 1992 (Phillips and Hargrave 1992). Data from replicate samples analyzed by AAS and two DFO laboratories (Bedford Institute of Oceanography and Freshwater Institute) were consistent for seven major OC compounds or groups of compounds.

RESULTS

Due to the sampling schedule from January to December 1993 (Table 1), material for OC analyses was not prepared for extraction until January 1994. In addition, expenses associated with the year-long field season restricted funds available for sample work-up during 1993/94. Approximately half of the samples (from alternate months over the annual period) were delivered to AAS in February 1994. Preliminary results are being prepared in spreadsheets for transfer to a database but the data has not been analyzed.

Toxaphene (PCCs) measurements which were carried out as part of the intercalibration study provided data that was included in a primary paper (Hargrave *et al.* 1993) published in Chemosphere in 1994 (Table 2). The distribution of PCCs among organisms in the marine food web shows biomagnification between predators and prey. Biomagnification factors (BMFs) (predator:prey PCC concentrations) were highest (65) for the potential transfer link between ringed seals to the benthic scavenging amphipod *Eurythenes gryllus*, and for zooplankton to arctic cod and char (37).

DISCUSSION/CONCLUSIONS

Five classes of compounds (hexachlorocyclohexanes, cyclodienes, isomers of DDT and its metabolites and congeners of PCBs and toxaphene (PCCs)) have been detected in under-ice epontic particulate matter and tissue samples of marine biota from lower trophic levels of the Arctic Ocean (Hargrave *et al.* 1992). PCCs, PCBs, isomers of DDT and DDE, chlordane, dieldrin, alpha-endosulfan, HCB and α-HCH were present in quantifiable levels. Traces of β- and γ-HCH and the cyclodienes aldrin, endrin, heptachlor, heptachlor epoxide, methoxychlor and mirex were present but small sample sizes for epontic particles and various zooplankton size fractions did not allow concentrations to be determined.

The OCs in samples of epontic particles, and pelagic and benthic crustaceans are also present in the Arctic atmosphere, particulate and dissolved fractions of snow, ice melt water and seawater samples collected from the Ice Island between 1986 and 1988 (Hargrave *et al.* 1988). The data show that small-bodied organisms which are short-lived generally have a lower lipid content for storage of OCs than larger sized animals. The large storage potential for OCs in lipids of fish, seal and mammal tissues, where lipid content may amount to < 50% of tissue fresh weight contrasts average values for lipid expressed as a percentage of wet weight in benthic amphipods (6.4%), zooplankton (3.1%) and epontic particles (< 1%) melted from the undersurface of the ice.

Seasonal differences in bioaccumulation of OCs are expected due to changes in marine food web productivity as the source of primary production shifts from under-ice epontic algae to phytoplankton during the open water period in Barrow Strait between July and September. The sampling program completed in Barrow Strait provides the first opportunity for seasonal measurements of the major OCs in the Canadian arctic marine environment. The study will provide additional information for mass budget calculations to assess the relative importance of atmospheric versus ocean sources.

Expected project completion date: March 31, 1997.

REFERENCES

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. 122: 1-74.

Bidleman, T.F., G.W. Patton, W.D. Walla, B.T. Hargrave, W.P. Vass, P. Erickson, B. Fowler, V. Scott and D.J. Gregor. 1989. Toxaphene and other organochlorines in Arctic Ocean fauna: evidence for atmospheric delivery. Arctic 42: 307-313.

Gordon, D.C. Jr. and P.J. Cranford. 1985. Detailed distribution of dissolved and particulate organic matter in the Arctic Ocean and comparison with other oceanic regions. Deep-Sea Res. 32: 1221-1232.

Harding, G.C.H. 1986. Organochlorine dynamics between zooplankton and their environment, a reassessment. Mar. Ecol. Prog. Ser. 33: 167-191.

Hargrave, B.T, W.P. Vass, P.E. Erickson and B.R. Fowler. 1988. Atmospheric transport of organochlorines to the Arctic Ocean. Tellus 40B: 480-493.

Hargrave, B.T., W.P Vass, P.E. Erickson and B.R. Fowler. 1989. Distribution of chlorinated hydrocarbon pesticides and PCBs in the Arctic Ocean. Can. Tech. Rep. Fish. Aquat. Sci. #1644, 224 pp.

Hargrave, B.T., G.C. Harding, W.P. Vass, P.E. Erickson, B.R. Fowler and V. Scott. 1992. Organochlorine pesticides and polychlorinated biphenyls in the Arctic Ocean food web. Arch. Environ. Contam. Toxicol. 22: 41-54.

Hargrave, B.T., D.C.G. Muir and T.F. Bidleman. 1993. Toxaphene in amphipods and zooplankton from the Arctic Ocean. Chemosphere 27: 1949-1963.

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. Total Environ. 122: 75-134.

Phillips, G.A. and B.T. Hargrave. 1992. Intercalibration of organochlorine residues in biota. Can. Data Rep. Fish. Aquat. Sci. #879, 65 pp.

Woodwell G.M., P.P. Craig and H.A. Johnson. 1971. DDT in the biosphere: where does it go? Science 174: 1101-1107.

Table 2. PCCs in benthic amphipods, zooplankton and a benthic fish (Glacial eelpout, *Lycodes frigidus*) collected in the present study from abyssal and continental shelf regions of the Arctic Ocean between 1986 and 1989. [a] Data reported in Bidleman *et al.* (1989). [b] Lipid content from Muir *et al.* (1988). [c] Data for Arctic cod (*Boreogadus saida*), Arctic char (*Salvelinus alpinus*), ringed seal (*Phoca hispida)*, beluga (*Delphinapterus leucas*), and narwhal (*Monodon monoceros*) from Muir *et al.* (1992). [d] Lipid content from Muir *et al.* (1990). All values represent single analyses except where ranges are presented for multiple (n=number) samples. Data presented in Hargrave *et al.* (1993).

Organism	Body Length (cm)	Percent Water	Percent Lipid	PCCs ($ng \cdot g^{-1}$ wet weight)
Amphipods				
Eurythenes gryllus	4.31	59.1	19.5	1764
	3.37	56.0	14.3	3025
	1.85	65.1	8.4	2923
	2.52	65.4	14.4	3083
	2.41	57.2	21.1	3884
	3.18	68.0	14.7	1725
	3.61	59.5	17.6	2585
	6.18	58.2	16.2	2085
	5.30	68.8	9.3	1233
	5.35	68.8	9.3	741
Tmetonyx cicada	1.1	75.9	5.0	69
	0.9	74.1	6.6	96
	0.7	75.7	5.1	420[a]
Anonyx nugax	1.5	80.0	2.4	93
	1.2	78.9	6.2	77
	1.0	50.9	14.4	216[a]
Onisimus sp.	0.3	70.1	4.7	32
Zooplankton	0.15	74.6	8.2	3.2
	0.15	70.8	14.6	3.5[a]
	0.15	79.2	5.1	8.1[a]
	0.05	87.8	4.1	2.3
	0.025	85.8	4.9	2.0
	0.025	87.1	4.6	3.1
	0.025	90.8	3.9	3.3
Glacial eelpout (liver)	47.7	52.7	26.0	470
Arctic cod (muscle) n=3	10±5	(-)	1.5[b]	14-46[c]
Arctic char (whole body) n=5	50±10	(-)	5[b]	44-157[c]
Ringed seal (blubber) n=15	100±20	(-)	90[b]	130-480[c]
Beluga (blubber) n=10	500±50	(-)	80[d]	1380-5780[c]
Narwhal (blubber) n=2	500±50	(-)	85[c]	2440-9160[c]

IDENTIFICATION OF TOXAPHENE COMPONENTS IN ARCTIC AIR, MARINE MAMMALS, AND HUMAN MILK SAMPLES

PROJECT LEADER: D. Muir, Freshwater Institute, Fisheries and Oceans Canada

PROJECT TEAM: G. Stern and M. Loewen, Fisheries and Oceans Canada

OBJECTIVES

1. To isolate and identify major toxaphene components in arctic air, biota and human milk samples.

2. To contribute to an assessment of the toxicological significance of the major toxaphene components by determining their actual molecular structure.

DESCRIPTION

Toxaphene is the major OC contaminant in Arctic abiotic and biotic samples yet little is known about the identity of the chlorinated bornanes that make up the "toxaphene" that analysts are measuring. The profile of components in the environmental samples consists of 10 to 20 peaks and does not resemble the technical material, which consists of several hundred of difficult to resolve chlorobornanes. Only two peaks, a nonachlorobornane (T12) and an octachlorobornane (T2) have been identified to date using beluga whale blubber (Stern *et al.* 1992). The identification is complicated by the fact that so many possible chlorobornane congeners exist due to the presence of multiple Cl or H substituents on each carbon. As a result, NMR as well as mass spectrometry must be employed and mg quantities must be isolated. Studies by Bidleman *et al.* (1993) have indicated that seal blubber contains a slightly different profile of chlorinated bornanes compared with whale blubber. The profile differs due to the presence of a major octachlorobornane that elutes between T2 and T12 on a capillary GC column. This octachlorobornane and other toxaphene related components in seal blubber are the first priority for isolation and identification.

Participants at the workshop on toxaphene (Burlington, February 1993; see Chemosphere Vol. 27, Issue No. 10), which was sponsored by the Northern Contaminants Program of the Arctic Environmental Strategy, recommended that further work be done to identify toxaphene components as a prerequisite to developing an accurate method of quantifying toxaphene.

This project was approved for funding as a new project by the Science Managers Committee of the NCP in October 1993. Work began on the project in December 1993. The work forms part of an M.Sc. project (M. Loewen, Dept. of Chemistry, Univ. of Manitoba).

ACTIVITIES IN 1993/94

Samples

Ringed seal blubber from samples collected at Arviat (NWT) was selected for isolation of chlorobornanes. Sample extracts (hexane) were subjected to polyethylene tube dialysis and HPLC as described by Stern *et al.* (1992).

Analysis

Isolation of samples is in progress. Purified components will be identified by ^{1}H-NMR and mass spectrometry (MS) using techniques described by Stern *et al.* (1992, 1993). For air and human milk samples where limited sample is available, various MS techniques (including linked scanning of fragment ions) will be used to characterize the toxaphene components (Stern *et al.* 1993). The mass spectrometry will be performed on a Kratos HRGC-high resolution mass spectrometer. Installation of the mass spectrometer was completed in March 1994.

RESULTS

To date 5 kg of blubber has been extracted and the chlorinated components isolated by polyethylene tube dialysis and HPLC as described by Stern *et al.* (1992). The GC-electron capture negative ion mass spectrometry chromatogram (GC-ECNIMS) of the crude ringed seal blubber extract shows the major chlorobornanes (Fig. 1). The large octachlorobornane peak eluting between T2 and T12 is the first compound we are attempting to analyse. Work is underway to separate these chlorobornanes from other chlorinated organics (DDT, chlordane, PCBs) which are present in the same extract.

Work is in progress on the analysis of Arctic lake sediments as well as air and human milk samples. Preliminary HRGC-ECNIMS analysis of human milk samples from Northern Quebec has confirmed the presence of the two major chlorobornanes (T2 and T12) also found in marine mammal samples. Further work will be done using MS/MS (i.e. linked scanning; Stern *et al.* 1993) to characterize components because sufficient quantities are not available for analysis by NMR.

The laboratory also recently analysed toxaphene in lake water from Yukon lakes by GC-ECNIMS in collaboration with M. Alaee (NWRI).

CONCLUSIONS AND UTILIZATION OF RESULTS

Although no results are available for the identification of new toxaphene components from ringed seal blubber it is anticipated that sufficient material will have been isolated by September 1994 for MS and NMR work to begin. The availability of high resolution electron capture negative ion MS has given this laboratory the capability to examine low concentrations of chlorobornanes (and other highly chlorinated organics) with greater accuracy than is possible with low resolution negative ion MS. The presence of chlorobornanes in lake waters from the Yukon and in human milk from Northern Quebec has been confirmed with the instrument. Results of the work will be provided to Health Canada who may be able to followup the identification of major chlorinated bornanes with chemical synthesis and toxicological studies.

Expected project completion date: March 31, 1996

PARTNERS

Partners in the project are L. Barrie (Atmospheric Environment Service) and E. Dewailly (Centre Hospitalier de l'Université Laval) who have provided air sample extracts and human milk, respectively, for toxaphene analysis.

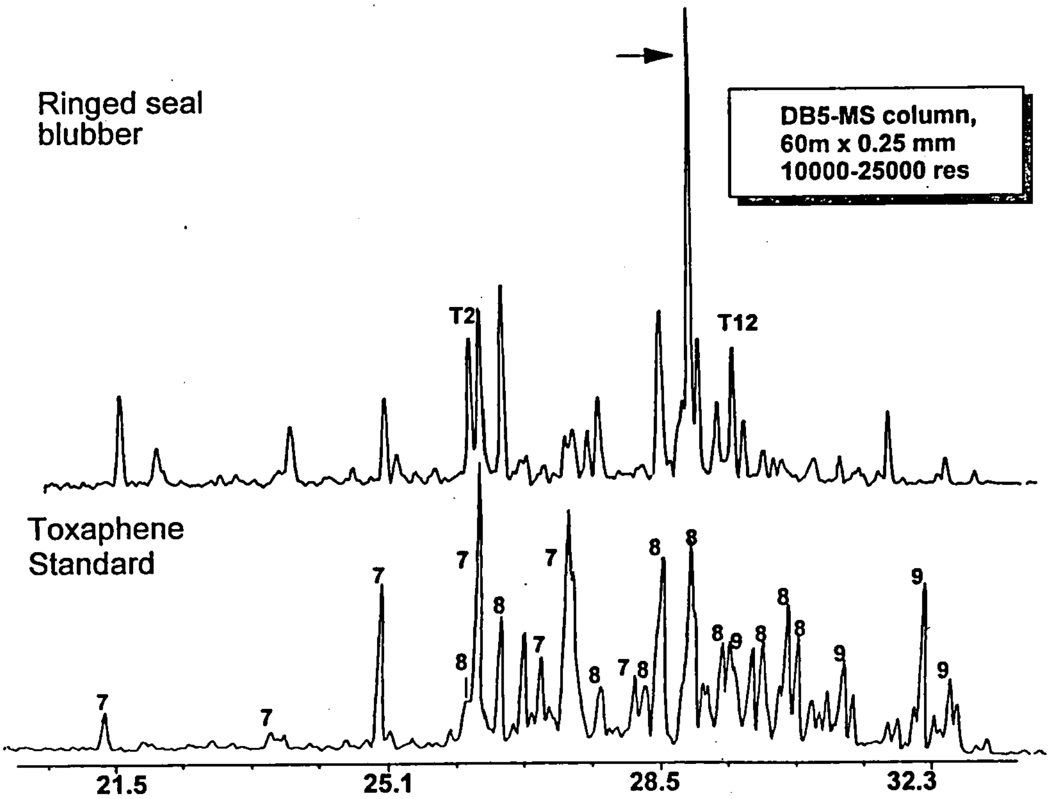
REFERENCES

Bidleman, T.G., M.D. Walla, D.C.G. Muir and G.A. Stern. 1993. Selective accumulation of polychlorocamphenes in aquatic biota from the Canadian Arctic. Environ. Toxicol. Chem. 12: 701-709.

Stern, G.A., D.C.G. Muir, C.A. Ford, N.P. Grift, E. Dewailly, T.F. Bidleman and M.D. Walla. 1992. Isolation and identification of two major recalcitrant toxaphene congeners in aquatic biota. Environ. Sci. Technol. 26: 1838-1840.

Stern, G.A., D.C.G. Muir, J.B. Westmore and W.D. Buchannon. 1993. Mass spectrometric studies of the toxaphene components 2-exo,3-endo,5-exo,6-endo,8,8,10,10-octachlorobornane (T2) and 2-exo,3-endo,5-exo,6-endo,8,8,9,10,10-nonachlorobornane (T12). Biol. Mass Spectr. 22: 19-30.

Figure 1. GC-Electron-capture negative ion mass spectrometry chromatograms of ringed seal blubber and the toxaphene standard showing the octachlorobornane targeted for identification.



SPATIAL AND TEMPORAL TRENDS OF ORGANOCHLORINES IN ARCTIC MARINE MAMMALS

PROGRAM LEADER: D. Muir, Freshwater Institute, Fisheries and Oceans Canada, Winnipeg, Manitoba

PROJECT TEAM: D. Muir, M. Segstro, B. Grift, C. Ford, R. Stewart, S. Innes, G. Stern

OBJECTIVES

1. To determine temporal and spatial trends in PCBs and other organochlorines in arctic marine mammals on a circumpolar basis, with special emphasis on beluga whales, ringed seals and walrus.

2. To provide data for use in surveys of dietary contamination by circumpolar countries and for use by the Arctic Monitoring and Assessment Programme (AMAP).

DESCRIPTION

People in arctic coastal communities consume marine mammals as part of their traditional diets. Information is needed to evaluate current risks of exposure to PCBs via consumption of skin, blubber and other tissues. Surveys have shown the presence of a wide range of organochlorine contaminants in arctic marine mammals throughout the Arctic. There is relatively complete data on organochlorine levels in ringed seals and beluga in the Canadian Arctic (especially for N. Quebec, W. Hudson Bay, Baffin Island, and the southern part of the Arctic archipelago) for samples collected in the mid-1980s. There is little information on geographic trends in other pinnipeds, e.g. Bearded, Harp and Harbour seals and walrus. Information is also limited on variations of contaminants with age and sex because of small sample sizes analysed from most locations, and on temporal trends at all locations except Holman Island where R. Addison has reported results beginning in 1972.

The specific objectives for 1993/94 were: (1) analysis of additional ringed seals from Arviat to thoroughly examine variations with age, blubber thickness and sex in one population, (2) to analyse more walrus and ringed seals from Inukjuak in northern Québec to follow up findings of high PCBs and organochlorine pesticide residues, (3) further temporal and spatial trend studies to include seals from Resolute, Pangnirtung, Grise Fiord and possibly Eureka, (4) further interpretation of results of organochlorines in Greenland beluga tissues and in walrus via preparation of papers on these topics, and (5) isolation of additional toxaphene components from seal blubber.

ACTIVITIES IN 1993/94

Samples

Work continued on Ringed seal samples were collected from Arviat in Spring and Fall 1992 and the winter of 1993 from Resolute (B. Welch, Fisheries and Oceans Canada) and Pangnirtung (R. Stewart). Beluga and narwhal blubber were obtained from the Mackenzie delta and from Iqaluit and Repulse Bay during 1993. Walrus and ringed seals were obtained by hunters at Inukjuak with the help of biologists with Makivik Corp. (Kuujjuak).

Methods

All animals were aged by counting growth layers. Samples of blubber were analysed for 90 PCB congeners and 40 other organochlorine (OC) compounds (see attached list in Table 1).

The extraction and separation of analytes from lipid coextractives were the same as those described in Muir *et al.* (1990). Blubber extracts were chromatographed on a GC-ECD with a 60 m x 0.25 mm DB-5 column using H_2 carrier gas. GC conditions are described in previous studies (Muir *et al.* 1988). Total PCB (ΣPCB) was the sum of all congeners. Total chlordane (ΣCHLOR) was the sum of all chlordane-related compounds including heptachlor epoxide while total DDT (ΣDDT) was the sum of 4,4'- and 2,4'-DDE, -DDD, -DDT isomers. Toxaphene (polychlorobornanes) were quantified using a single response factor based on 19 peaks in the standard (obtained from US EPA repository, Cincinnati, OH).

Quality assurance

Internal standard recoveries (aldrin and octachloro-naphthalene) were uniformly greater than 90%. The Cod liver standard reference material (SRM-1588) from NIST (Gaithersburg, VA) was used as a laboratory control sample for major organochlorine pesticides and PCB congeners. Blank samples were run approximately every 10 samples to check contamination of reagents and glassware. During 1993 the laboratory participated in the intercomparison on PCB congeners for the Northern Contaminants Program, the toxaphene round robin using a certified cod liver oil (P. Andrews, Health Canada), a check sample program for the analysis of OC pesticides and PCBs (Atmospheric Environment Service, Downsview), and an ICES (International Council for Exploration of the Sea) interlab comparison of PCBs in fish and seal oil.

RESULTS

Approximately 130 organochlorine compounds could be detected in walrus and seal blubber. Concentrations of major organochlorine groups are listed in Table 1 for the 111 samples analysed in 1993/94. Total PCBs (ΣPCB) were present in the highest concentrations of all the major OC that were determined. The analysis of Ringed seal blubber samples from Arviat, Pangnirtung and Inukjuak (all collected during spring 1992) enabled comparison of geographic variation in levels of OCs. Concentrations of PCBs in females from Arviat and Inukjuaq were similar (1093±472 and 1457±1648 ng/g, respectively) while females from Pangnirtung had much lower levels (467±195 ng/g). Similar trends were observed for other OCs (Table 1). The observation of higher levels of OCs in Hudson Bay animals is consistent with previous reports (Muir *et al.* 1994 in press).

The variation of ΣPCBs and ΣDDT with age in Arviat ringed seals is illustrated in Fig. 1. Concentrations increase with age in males but not in females. This has been observed previously (Addison and Smith 1974) but the large number of samples from Arviat enabled a thorough test of the age/concentration relationship.

The lack of variation of ΣDDT and ΣPCB with age in females is thought to be due to excretion of the OCs during lactation (Addison and Smith 1974). Geographical comparisons are thus best done with adult female ringed seals.

Eleven harp seal blubber samples from the White sea were provided by V. Savinov (Murmansk Marine Biological Institute). The samples were collected during the annual hunt in the region. The harp seal pups are distinguished from young ringed seals from Arviat by having higher toxaphene and lower ΣHCH levels while levels of other OCs were within the same range (Table 2). Further work is necessary to determine whether the higher toxaphene in the Russian seals is due to metabolic differences between ringed and harp seals or to local sources.

Additional work was also carried out during 1993/94 to confirm the elevated levels of OCs in walrus blubber samples from Inukjuak. K. Hobson (Canadian Wildlife Service, Saskatoon) provided nitrogen and carbon stable isotope ratios (^{15}N and ^{13}C) on most of the seals and walrus that had been analysed for OCs. The graph of $\delta^{13}C$ versus $\delta^{15}N$ (Fig. 2) shows that Inukjuak walrus are distinguished from most Akulivik walrus and from ringed seals (from Inukjuak) by $\delta^{13}C$ values and to a lesser extent by $\delta^{15}N$. The trend towards lighter $\delta^{13}C$ values with higher $\delta^{15}N$ values indicates a shift from a primarily benthic feeder to a primarily pelagic feeder. The lack of major differences in $\delta^{15}N$ (differences of 3-4 ‰ per trophic level are expected) suggests that the walrus from Akulivik and Inukjuak share similar diets, although walrus from Inukjuak may also feed on ringed seals, resulting in slightly higher $\delta^{15}N$ values. The ringed seals (which feed mainly on arctic cod and crustaceans) are clearly feeding at a higher trophic level than the Akulivik walrus. Values for marine clams, the assumed diet of walrus, average 7.9±0.4 ‰ at Lancaster Sound (Hobson and Welch 1992). The $\delta^{15}N$ values of 10-11 ‰ for most walrus at Akulivik are consistent with the expected 3-4 ‰ increase in $\delta^{15}N$ per trophic level if they are eating strictly clams. Based on the relative amounts of ^{15}N, we concluded that the average walrus from Inukjuak (averaging a $\delta^{15}N$ of 11.5 ‰) had ≈26% seal tissues in their diet. The PCB intake from such a diet is much higher than from a clam diet, assuming seal blubber and skin to be the main tissues consumed. ΣPCB concentrations in the seal blubber are about 500 times higher (wet weight basis) than in benthic marine mussels.

In Table 3 results for 1992 animals are compared with those from samples collected in (spring) 1986 at Rankin Inlet (200 km north of Arviat) and at Pangnirtung. Concentrations of the four OC groups have not declined significantly at Pangnirtung over the 6 year period. Levels in animals from Rankin Inlet from 1986 were about 50% lower than observed in the (spring) Arviat samples except for toxaphene. This difference is not consistent with trends elsewhere in ringed seals (for e.g. at Holman Island) or in polar bears and may be due to different feeding habits of the Arviat group. If the seals were feeding more on fish than invertebrates, higher OC levels would be expected. Unfortunately no samples from Arviat are available from 1986. The spring/fall comparison for female ringed seals at Arviat reveals that there may be significant annual variations in concentrations of OCs in blubber. These variations may be due to blubber thickness and to changes in diet.

CONCLUSIONS AND UTILIZATION OF RESULTS

Results of the project during 1993/94 have added to the spatial and temporal information available on ringed seals from Hudson Bay and Baffin Island. Levels of major OCs do not appear to have declined significantly in females over the 6 year period. Future temporal trend work planned for 1994/95 will examine ringed seals from Resolute (previously sampled in 1984) and in narwhal and beluga. Further spatial trend work will include analysis of ringed seal blubber samples from Grise Fiord and Eureka. Sampling of these latter sites was planned for 1993/94 but was postponed until this year following community consultations. Results of the studies were presented at the International Conference on Marine Mammal Biology, Galveston TX, November 1993 and at the Indian and Northern Affairs Canada workshop on Arctic Contaminants in Winnipeg (December 1993). Information on the work has also been given by S. Innes and R. Stewart (Fisheries and Oceans Canada, Winnipeg) during consultations with hunter/trapper associations in the eastern Arctic.

Expected project completion date: March 31, 1997

PARTNERS

Communities of Arviat, Pangnirtung and Grise Fiord; Fisheries Joint Management Committee of Inuvialuit Settlement Region; Murmansk Institute of Marine Biology and other Soviet scientists.

REFERENCES

Addison, R.F. and T.G. Smith. 1974. Organochlorine residue levels in Arctic ringed seals: variation with age and sex. Oikos 25: 335-337.

Hobson, K.A. and H.E. Welch. 1992. Determination of trophic relationships within a high Arctic marine food web using $\delta^{13}C$ and $\delta^{15}N$ analysis. Marine Ecol. Prog. Ser. 84: 9-18.

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.

Muir, D.C.G., C.A. Ford, R.E.A. Stewart, T.G. Smith, R.F. Addison, M.E. Zinck and P. Béland. 1990. Organochlorine contaminants in beluga (*Delphinapterus leucas*) from Canadian waters. Can. Bull. Fish. Aquat. Sci. 224: 165-190.

Muir, D. 1992. Spatial trends in organochlorines in arctic ringed seal and walrus. Pp. 121-125 *in*: Synopsis of Research Conducted Under the 1991/1992 Northern Contaminants Program, J.L. Murray and R.G. Shearer, (eds.). Environmental Studies No. 68. Indian and Northern Affairs Canada, Ottawa. 213 pp.

Muir, D.C.G., C.A. Ford, R.J. Norstrom and M. Simon. In press. Geographical variations of organochlorine contaminants in Canadian arctic marine food chains. In: Proceedings of the 7th International Conference of Comité Arctique Internationale on the Global Significance of the Transport and Accumulation of Polychlorinated Hydrocarbons in the Arctic. Oslo, September 1989. Plenum Press, N.Y.

Table 1. Concentrations (ng/g) (arithmetic means ± SD) of major organochlorine groups in arctic marine mammal blubber analysed during 1993/94.

	Species	sex		N	%Lipid	ΣCBz	ΣHCH	ΣCHLOR	ΣDDT	ΣPCB	Toxaphene	Dieldrin
White Sea	Harp seal	pups	Mean	11	80.4	110.0	69.3	697.9	710.2	1367	2103	82.2
			SD		9.7	64.8	22.0	300.3	437.0	725.5	1131	35.2
Arviat	Ringed	F	Mean	30	92.7	51.9	272.4	676.3	722.2	959.8	248.9	79.5
	Seal		SD		4.9	34.6	196.1	375.4	454.9	526.7	266.8	50.7
		M	Mean	35	93.5	62.8	320.9	1444	1852	1852	601.3	103.3
			SD		4.0	35.2	126.0	1083	1359	1359	1816	67.8
Pangnirtung	Ringed	F	Mean	10	95.4	37.6	178.6	322.0	359.0	466.8	175.0	71.3
	Seal		SD		2.4	9.4	21.8	129.2	166.1	195.0	65.8	33.5
		M	Mean	10	95.3	36.1	209.6	469.5	703.4	675.2	179.5	64.4
			SD		2.7	7.1	36.9	324.3	889.8	596.7	83.9	21.2
Inukjuaq	Ringed	F	Mean	6	94.1	61.8	314.1	1128	1139	1457	294.9	92.3
	Seal		SD		4.6	54.4	227.4	1425	1215	1648	342.5	105.6
		M	Mean	4	94.7	61.6	274.9	708.1	1143	1234	220.5	86.6
			SD		2.0	17.5	123.0	452.5	680.9	636.4	111.6	101.9
Inukjuaq	Walrus	F	Mean	3	87.2	50.8	194.2	3068	2297	5604	1183	306.9
			SD		2.3	24.9	94.3	1204	896.0	1941	785.7	77.8
		M	Mean	2	87.1	43.1	151.4	5657	3640	10403	3922	663.1
			SD		4.0	31.3	113.5	7226	4845	13916	4073	566.3

Table 2. Comparison of OCs in blubber of young-of-the-year seals (ng/g).

	N	%lipid	ΣHCH	ΣCHLOR	ΣDDT	ΣPCB	Toxaphene
White Sea (whitecoats)	11	80.4±9.7	69.3±22.0	698±300	710±437	1370±726	2100±1130
Arviat (0-1 yrs)	8	93.9±5.4	426±224	1020±1320	935±1250	1310±1590	157±112

Table 3. Comparison of temporal trends in major OCs in female ringed seals from West Hudson Bay and Pangnirtung (ng/g).

Location	Year	N	Age	ΣCHLOR	ΣDDT	ΣPCB	Toxaphene
Arviat (spring)	1992	21	9.1±4.3	806±330	840±398	1115±425	297±304
Arviat (fall)	1992	9	6.3±0.7	373±302	448±483	599±587	136±80
Rankin Inlet	1986	10	4.1±4.4	392±198	450±287	570±307	292±139
Pangnirtung	1992	10	5.7±3.9	322±129	359±166	467±195	175±66
	1986	10	2.9±3.6	264±101	243±67	373±97	247±189

Fig. 1. Variation of s-DDT and s-PCB in Ringed Seal blubber (Arviat, NWT) with age.

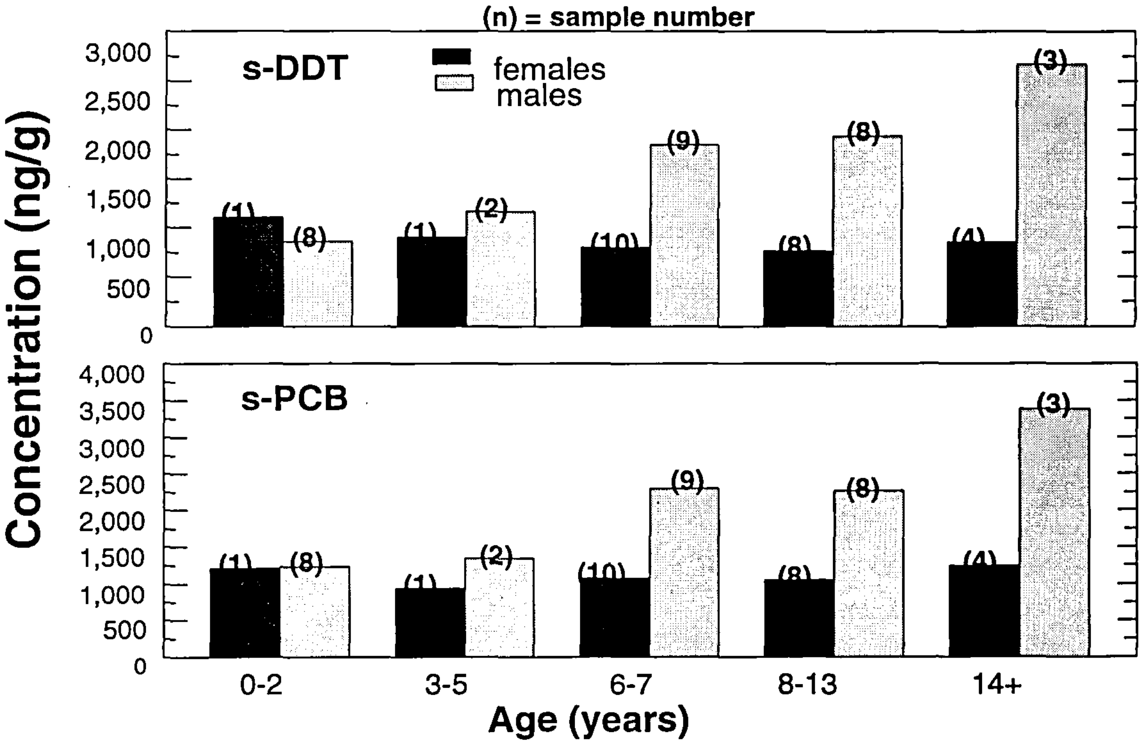
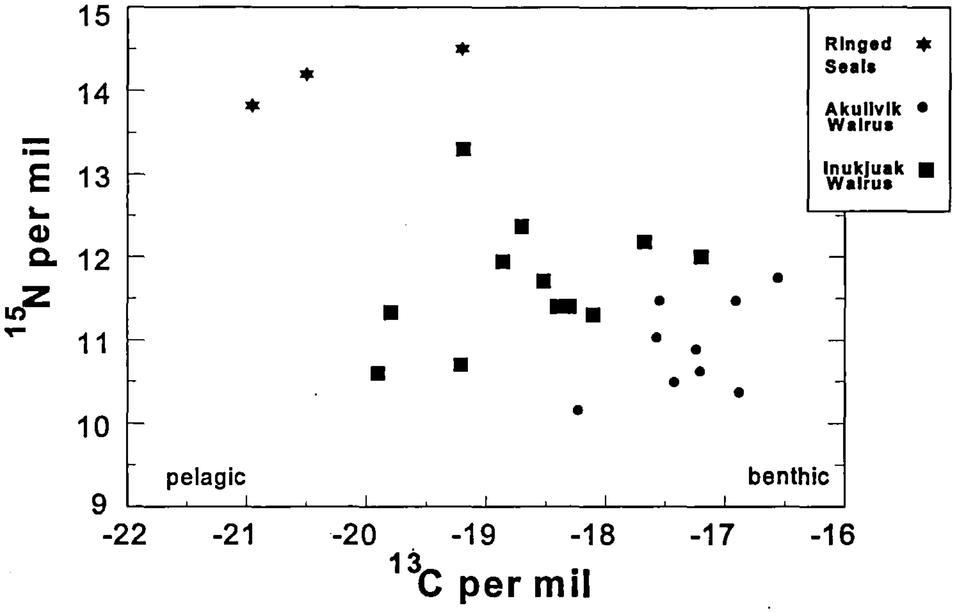


Fig. 2. ^{15}N and ^{13}C ratios in muscle samples of walrus and ringed seal from Northern Quebec



LONG-TERM TRENDS IN ORGANOCHLORINE RESIDUES IN EASTERN AND WESTERN ARCTIC SEAL BLUBBER

PROJECT LEADER: R.F. Addison, Institute of Ocean Sciences (IOS), Fisheries and Oceans Canada

PROJECT TEAM: R.F. Addison, T.G. Smith, Pacific Biological Station, Fisheries and Oceans Canada

OBJECTIVES

To measure temporal trends in levels of PCBs, the DDT-group and other organochlorines from the early 1970s to the present in Arctic seals.

Specifically for 1993/94:

1. To develop methods at IOS to measure DDT-group insecticide residues and major PCBs;
2. To revise a paper summarising PCB, DDT-group, HCB and HCH concentrations in Holman Island ringed seals sampled in 1972, 1981 and 1989; and
3. To publish a paper in which the extent of contamination in harp seals migrating to and from the eastern Arctic is assessed.

DESCRIPTION

Organochlorine (OC) residues are now known to have been introduced to the Arctic by various routes, including local use and long-range atmospheric transport, and these compounds have contaminated Arctic food chains at all trophic levels. Contamination of marine mammals, particularly ringed seals, is of particular interest because of the extent to which these animals are used by native populations as a food resource. Previous analyses by Fisheries and Oceans Canada have suggested that the OC concentrations observed in western Arctic ringed seals may be declining; the main objective of this project is to build on the extensive data set from the Holman Island ringed seal population and to monitor changes in contamination over intervals of several years.

ACTIVITIES IN 1993/94

Three major activities have been undertaken during the past year. Since the Ocean Chemistry Division at IOS had not previously analysed major OC residues, methods for doing so were developed and assessed at IOS (by contract). Secondly, the annual sampling of Holman Island ringed seals during a spring hunt was continued; blubber samples from a range of male and female adults were obtained and sent to IOS, and relevant biological data for the samples was recorded. A manuscript dealing with long-term changes in DDT-group and PCB concentrations in this population was revised extensively. Finally, a paper describing the pattern of OC residue accumulation in harp seals migrating to and from the eastern Arctic was published.

RESULTS

The first two activities of 1993/94 focused on sampling and on method development. The last project examined the distribution of OCs in harp seals sampled at various points down Hudson Strait as they migrated from Ungava Bay to the Gulf of St. Lawrence. The picture which emerged was that the bulk of OC accumulation by these animals occurs during intensive feeding in the northern Gulf of St. Lawrence. However, OC concentrations in harp seals are much lower than those in beluga found stranded in the Gulf of St. Lawrence, probably because of differences in feeding habits, and in the length of time the harp seals feed in the Gulf. Although appreciable accumulation of OCs occurs when the harp seals are in the Gulf, concentrations in these animals are much lower than a decade or so ago.

CONCLUSIONS

1. Continued sampling of the Holman Island ringed seal population for the past several years, now carried out by contract with the Holman Inuit Co-operative, has provided Fisheries and Oceans Canada with a reliable "time series" of samples which are well-defined in terms of age, sex and condition.

2. Analysis of migrating harp seals from the eastern Arctic has shown that most OC residue accumulation in this species occurs during feeding at the relatively contaminated sites of the northern Gulf of St. Lawrence.

REFERENCES

Beck, G.G., T.G. Smith and R.F. Addison. 1994. Organochlorine residues in harp seals *Phoca groenlandica* from the Gulf of St. Lawrence and Hudson Strait: an evaluation of contaminant concentrations and burdens. Can. J. Zool. 72: 174-182.

MODELLING AND EVALUATION OF CONTAMINANT ACCUMULATION AND EFFECTS IN MARINE MAMMALS

PROGRAM LEADER: M. Kingsley, Institut Maurice-Lamontagne, Fisheries and Oceans Canada, Mont-Joli, Quebec

PROJECT TEAM: B. Hickie, Environmental and Resource Studies Program, Trent University, Peterborough, Ontario

OBJECTIVES

1. To develop contaminant accumulation models for Arctic marine mammals.
2. To understand contaminant pathways.
3. To provide a framework for directing contaminant monitoring programs concerned with marine mammals of significance to the diet of native peoples.

DESCRIPTION

Marine mammals are long-lived top-level predators with high maintenance-energy requirements. They therefore have the capability of both concentrating and accumulating persistent contaminants (including fat-soluble organochlorines and some metals) from background and local sources. In many parts of the Canadian Arctic, they form a significant component of human diets. The potential consequences of this situation include unacceptable levels of contaminant intake among people consuming traditional diets in Arctic coastal communities. Monitoring programs are essential for assessing possible direct toxic effects and for assessing the human health implications of contaminants in Arctic marine mammals. It is important that we develop an understanding of the sources, pathways, and factors controlling rates of contaminant accumulation by marine mammals if we wish to relate ecosystem contaminant levels and loadings with those in marine mammal species.

Energetics-based contaminant accumulation models provide the basis for understanding and quantifying the importance of factors such as age, sex, reproductive effort, growth and diet on contaminant concentrations at the level of the individual animal for beluga, narwhal, ringed seal, and walrus. Development and refinement of models of contaminant accumulation will aid in identifying data gaps, directing contaminant sampling programs, interpreting data from monitoring programs in terms of spatial and temporal trends, and in relating contaminant levels in marine mammals to those in other components of their food web.

ACTIVITIES IN 1993/94

Sensitivity Analyses

Sensitivity analyses were conducted on the individual-based models developed for the beluga and ringed seal to evaluate the effects that each variable or variable group has on model predictions. Variables were classified into three groups: biological (life history, growth, energetics, compartment composition, diet); contaminant/pharmacological (rates of absorption and clearance, partitioning, dietary concentration); reproduction (age at maturity, birth rate, growth of progeny, lactation, contaminant partitioning to fetus and milk). Analysis for the beluga whale model included the examination of 23 variables or groups. The variable set examined for the ringed seal model was more extensive owing to the addition of variables used to describe growth and to regulate blubber dynamics during lactation and the summer moult.

Contaminant partitioning to milk

Work to date has demonstrated that reproduction represents an important pathway of contaminant transfer between generations in marine mammal populations. This assessment is based on the elevated levels observed in young animals, reduced levels observed in mature females, and through modelling exercises using estimated values of contaminant partitioning from maternal tissue to the fetus and milk. Matched samples of maternal blubber and milk were obtained from four belugas and were analysed to characterise contaminant partitioning. Attempts to obtain samples to quantify mother:fetus partitioning, and samples for other species were not successful this year. Further analysis will be done when additional samples become available.

Population-based contaminant accumulation model

The models developed previously attempt to define flux rates of contaminant accumulation, distribution among tissues, and losses in relation to all aspects of life-history at the level of the individual animal. These models demonstrate that a number of important factors such as reproductive rates and contaminant transfer to progeny are expressed, and must be understood, at the level of the population. Development of population-based contaminant flow models will also provide a means of relating the knowledge derived from individual-based models with food web contaminant models and marine mammal contaminant monitoring programmes.

The initial population model is being developed for the beluga whale. It incorporates contaminant flux rates and other information derived from the individual-based models into a population life-history matrix model. Work has involved modifying the individual-based model coding, conducting a literature review on the population biology of beluga, and developing coding for the population model. The structure of the model will allow for easy adaptation to other species. the model is being refined presently and, hence, little in the way of tangible results are available.

RESULTS AND DISCUSSION

Sensitivity analyses for the beluga and ringed seal models show that response to changes in many variables are proportional to or less than proportional to the change in the value of the variable itself. Variables which are used as direct factors to calculate food and contaminant intake yield proportional responses in contaminant intake. These include: activity multipliers, food caloric density, digestibility, and contaminant concentration in food. The energy cost of growth is a notable exception, where a two-fold change in the variable has virtually no effect on predicted contaminant levels. The use of growth curve parameters in the beluga model suggests that differences in sizes and rates of growth can contribute to the variability in contaminant concentration within a population, and can affect comparisons of contaminant levels made between populations. The model predicts that larger whales will have higher contaminant burdens, but their concentrations should be lowest owing to greater growth dilution.

Since there are no published reports of contaminant clearance rates by any marine mammal, these models provide a useful tool to examine the importance of clearance rates and to estimate values for various contaminants. Sensitivity analysis suggests that the contaminant clearance rate (or biological half-life) is one of the most important variables in determining the net accumulation of organic contaminants such as PCBs. For example, the beluga model suggests that for the concentration of an organic contaminant to increase with age in mature males, the half-life must be greater than 12 years.

The sensitivity analysis for reproductive variables show that contaminant transfer to the fetus is low relative to the mass transfer during nursing for both beluga and ringed seals. For the beluga model, predictions of contaminant transfer to progeny through milk (about 40 to 60% of maternal burden) are surprisingly resilient to changes in the values of most of the variables considered. For the ringed seal model, contaminant mass transfer over a 40-day lactation period is similar to that for beluga whales over a 12- to 18-month lactation. The high efficiency of contaminant transfer from mother to pup in the ringed seal can be attributed to the mobilization of maternal blubber during nursing. Thus, predicted values are dependent of the interaction of variables regulating blubber depletion, contaminant partitioning, and milk demand.

CONCLUSIONS

Overall, the range of predicted values that emerge from these analyses is similar in magnitude to the levels and variability observed in contaminant data sets and reproduce the patterns of contamination associated with age and sex of beluga whales and ringed seals from the Canadian Arctic. Future work with the individual-based models will involve modelling of an array of PCB congeners and other dominant contaminants and will include analysis to estimate their clearance rates. Development and application of the population-based model will match those for the individual-based models. Application of these models to address questions of spatial and temporal trends of contaminants are limited by the scarcity of data on contaminant levels in the prey of Arctic marine mammals. Key prey species for which there are few or no data include: Arctic cod (*Boreogadus saida*), Greenland halibut (*Reinhardtius hippoglossoides*), *Parathemisto* spp., and bivalves (*Mya truncata*, *Serripes groenlandicus*). Development of sampling and analysis programmes directed to lower levels in Arctic marine food webs would also yield benefits in terms of greater spatial and temporal resolution of contaminant trends.

Expected project completion date: March 31, 1997

PARTNERS

Arctic marine mammal scientists have made available information on food habits and life history variables; contaminant chemists have provided access to contaminant data.

PLANAR PCBS, CHLORINATED DIOXINS/FURANS AND RELATED COMPOUNDS IN ARCTIC MARINE MAMMALS AND FISH

PROGRAM LEADERS: D. Muir and C. Ford, Freshwater Institute, Fisheries and Oceans Canada, Winnipeg, Manitoba

PROJECT TEAM: D. Muir, C. Ford, B. Rosenberg, and B. Grift

OBJECTIVES

1. To provide geographic and temporal information on toxic PCB congeners and chlorinated dioxins/furans.

2. To compare arctic results with mid-latitude levels of co-planar PCBs

3. To provide a linkage to biomarker studies in the same fish and marine mammals and to assessments of dietary contamination.

DESCRIPTION

Previous studies (Muir and Ford 1990, Norstrom *et al.* 1990, Muir 1993) have shown that co-planar PCBs and mono-ortho PCBs, are present in fatty tissues of ringed seal, walrus, narwhal and polar bear as well as arctic char. Chlorinated dioxins and furans are also present. However, coplanar PCBs account for most of the "TCDD equivalents" in arctic diet samples using the Toxic Equivalent Factors (TEFs) of Safe (1990). The objectives of this work for 1993/94 were to broaden the limited database by determining non-ortho PCBs, as well as chlorinated dioxins and furans, in additional fish and in whale and seal tissues to develop a larger data base than is available at present, and to provide support for biomarker studies in fish and marine mammals. PCB congeners with 3,4,3',4'-chlorine substitution are the most biologically active and are referred to as co-planar or "non-ortho" PCBs (Ahlborg *et al.* 1994). They lack chlorine substituents in the 2 and 6 (or ortho) positions and can therefore assume a planar configuration. These congeners are isostereomers of 2,3,7,8-TCDD and have similar mode of action; induction of hepatic mixed function oxidase (MFO) enzymes, immunotoxicity, teratogenicity and embryotoxicity (Safe 1990). The toxicity of Aroclor mixtures (commercial PCB formulations) is thought to be due almost entirely to these co-planar PCBs (Kannan *et al.* 1988).

Mono-ortho PCBs, which have a single chlorine in the 2- position also have MFO enzyme induction potencies which are similar to those of the co-planar molecules. Toxic equivalent factors (TEFs) of mono-ortho and non-ortho congeners, which are a measure of the biological potency relative to 2,3,7,8-TCDD, range from 0.1 for PCB-126 (3,3',4,4',5-pentachlorobiphenyl) to 0.0005 for PCB-77 (3,3',4,4'-tetrachloro-biphenyl) (Ahlborg *et al.*

1994). These TEFs were used to calculate the contribution of co-planar PCBs to total toxic equivalents in arctic tissue samples.

ACTIVITIES IN 1993/94

Samples

Samples of walrus blubber along with ringed seal blubber were obtained from Inukjuak, Québec. Arctic char, that had previously been analysed for ortho-substitituted PCBs, were obtained from Charr Lake near Resolute. Burbot liver were obtained from the Fisheries and Oceans Canada Lake Laberge collection in Winnipeg.

Analytical methods

The analytical procedure for non-ortho PCBs is described by Ford *et al.* (1993). Briefly: fish tissues were extracted with hexane:dichloromethane (1:1), lipid removed with automated gel permeation chromatography. Fish extracts were split into two portions, one for determination of non-ortho PCBs and the other for determination of all other organochlorines. Extracts were then chromatographed on a silica-gel column to remove additional lipid coextractives then subjected to carbon-column chromatography to isolate the planar PCBs. Marine mammal blubber extracts were chromatographed on a silica gel column to separate PCBs (hexane elution) from most organochlorine pesticides. The hexane eluate was then subjected to chromatography on carbon to isolate non-ortho PCBs and were analysed for all other PCBs. The carbon column eluates were then analysed by GC-MS analysis and non-ortho PCBs quantified with the aid of ^{13}C-internal standards for PCB-77, 126 and 169 (3,3',4,4',5,5'-hexachlorobiphenyl). Mono-ortho PCBs (congeners 105, 118, 114, 156) in discarded fractions from the carbon column were determined by GC-ECD. Samples of ringed seal blubber from Arviat were also prepared for analysis of chlorinated dioxins/furans (PCDD/PCDFs) but results are not yet completed.

Quality Assurance

The NIST cod liver oil SRM 1588 was used as an internal control sample. An interlab comparison of coplanars in cod liver oil SRM 1588 was made with AXYS Analytical Labs (Sidney, BC) and with T. Metcalfe (Trent University). Results obtained by low resolution GC-MS were compared with those obtained by high resolution GC-MS in collaboration with S. Huestis (Fisheries and Oceans, Burlington).

RESULTS

An interlaboratory study with C. Metcalfe (Trent University) showed relatively good agreement between the two labs on the analysis of the non-ortho PCBs in cod liver oil. Good agreement was also obtained for the analysis of non-ortho PCBs ringed seal and arctic char samples between the low resolution (our procedure) and high resolution GC-MS techniques.

In our 1992/93 report (Muir 1993), 8 walrus blubber samples from Inukjuak in northern Quebec were analysed for non-ortho PCBs because of their very high levels of total PCBs. During 1993/94, 13 additional samples of walrus blubber were analysed from two communities, Inukjuak and Akulivik (Table 1). Levels in female walrus from Akulivik were 20-fold lower than in females from the Inukjuak collection consistent with their much lower ΣPCB values. The proportion of non-ortho PCBs differed among the two groups with the Inukjuak group having relatively high CB126 and low CB77 and CB169 (Table 1) while the Akulivik animals had similar proportions of CB 126 and CB77. These results are consistent with our hypothesis that these walrus are consuming ringed seals for a portion of their diet (See Muir 1994, this volume). Ringed seals from Inukjuak had much lower non-ortho PCB levels than the walrus from the same location (Table 1). Levels in ringed seal blubber were similar to those in walrus from Akulivik and also to other results from Broughton Island (Muir and Ford 1990, Ford *et al.* 1993). The proportion of ΣPCB for each coplanar congener in Inukjuak ringed seals was lower than found for ringed seals Broughton Island (Muir 1992) while total PCB levels were higher. This may be a reflection of different dietary exposure of the seals at the two locations.

Coplanar PCBs were determined in landlocked char from Char lake near Resolute and in Amituk Lake (Cornwallis Island). Mean concentrations of PCB 126 in fish from Charr Lake (73 pg/g wet wt) were 4 times higher than in Amituk Lake char muscle. The pattern of non-ortho congeners differed from that in Amituk Lake fish with PCB 126 and differed from that found previously in sea run char where CB77 to be the major coplanar congener (Ford *et al.* 1993). CB 77 was the major non-ortho PCB congener in Arctic cod from Resolute. These samples had very low (<1 pg/g) concentrations of CB126 and CB169.

Levels of coplanar PCBs in burbot liver from Great Slave lake were much lower than we found in Lake Laberge burbot where concentrations of CB 126 and 169 exceeded 1000 pg/g (Muir 1993). The proportions of non-ortho PCBs (of ΣPCB) in burbot liver differed from char or whitefish with much higher CB169. Whitefish from Great Slave Lake had similar levels of CB77 as burbot but 5-fold lower levels of CB169 (Table 1).

CONCLUSIONS AND UTILIZATION OF RESULTS

As more non-ortho PCB data are obtained in this study a consistent pattern is emerging in which fish-eating fish (burbot, some char and lake trout) have relatively high proportions of CB126 and CB169 (of ΣPCB). Lowest proportions of these two toxic PCB congeners are found in fish feeding at lower trophic levels such as Arctic cod, whitefish and sea-run char. But given the huge variation in levels of PCBs, toxaphene and other organochlorines observed in char and other fishes in NWT and the Yukon it seems prudent to examine additional samples. In the coming year we intend to analyse coplanar PCBs in additional samples from the Yukon and from Great Slave Lake. A major study of non-ortho-PCBs in ringed seal blubber is planned using samples from Arviat which have been analysed for total PCBs (and for hepatic mixed function enzyme induction). Further work will also be carried out on PCDD/Fs in the Arviat samples and in other selected samples. Results for PCDD/Fs, which have been reported in past years by this project were not available in time for this report as we attempt to set up our own dioxin/furan analytical capability in-house now that a high resolution GC-MS is available to do the work. The results of the work are used in the "Biomarkers and Stress Effects in Arctic Marine Mammals" project (this volume) to examine relationships between planar PCBs and cytochrome P450 hepatic mixed function enzyme induction activity in marine mammal livers as well as in the assessment of human dietary contamination.

Expected project completion date: March 1997

REFERENCES

Ahlborg, U.G., G.C. Becking, L.S. Birnbaum, A. Brouwer, H.J.G.M. Derks, M. Feeley, G. Golor, A. Hanberg, J.C. Larsen, A.K.D. Liem, S.H. Safe, C. Schlatter, F. Wærn, M. Younes and E. Yrjänheikki. 1994. Toxic equivalency factors for dioxin-like PCBs. Chemosphere 28: 1049-1067.

Ford, C.A., D.C.G. Muir, R.J. Norstrom, M. Simon and M.J. Mulvihill. 1993. Development of a semi-automated method for non-ortho PCBs: Application to Canadian Arctic marine mammal tissues. Chemosphere 26: 1981-1991.

Kannan, N., S. Tanabe and R. Tatsukawa. 1988. Toxic potential of non-ortho and mono-ortho coplanar PCBs in commercial PCB preparations: 2,3,7,8-T_4CDD toxicity equivalence factors approach. Bull. Environ. Contam. Toxicol. 41: 267-276.

Muir, D.C.G. and C.A. Ford. 1990. Analysis of "co-planar" PCBs in arctic dietary samples. Report to Government of the Northwest Territories, Health Canada and Indian and Northern Affairs Canada.

Muir, D.C.G. 1992. Co-planar PCBs in arctic marine mammals and fish. Pp. 110-115 *in*: Synopsis of Research Conducted Under the 1991/92 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 68. Indian and Northern Affairs Canada, Ottawa. 213 pp.

Muir, D.C.G. 1993. Co-planar PCBs in arctic marine mammals and fish. Pp. 99-104 *in*: Synopsis of Research Conducted Under the 1992/93 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 70. Indian and Northern Affairs Canada, Ottawa. 285 pp.

Norstrom, R.J., M. Simon and D.C.G. Muir. 1990. Chlorinated dioxins and furans in marine mammals from the Canadian arctic. Environ. Pollut. 66: 1-20.

Safe, S. 1990. Polychlorinated biphenyls (PCBs), dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and related compounds: Environmental and mechanistic considerations which support the development of toxic equivalency factors (TEFs). Crit. Rev. Toxicol. 21: 51-88.

Table 1. Mean concentrations (±SD) of non-ortho PCBs (pg/g wet weight) and percent of ΣPCB in samples of arctic biota.

							Concentration (pg/g wet weight)				Percent of ΣPCB		
Location	Species	Tissue	Sex	N		% lipid	CB81	CB77	CB126	CB169	CB77	CB126	CB169
Charr Lake	Arctic char	muscle	M&F	5	Mean	4.3	2.31	22.0	73.4	3.38	0.011	0.032	0.002
					SD	1.9	0.87	8.66	31.1	1.23			
Amituk Lake	Arctic char	muscle	M	6	Mean	3.9	0.69	7.20	10.4	1.59	0.013	0.015	0.002
					Sd	1.8	0.42	3.00	7.14	1.60			
Amituk Lake	Arctic char	muscle	F	6	Mean	4.9	0.53	6.95	8.25	0.68	0.011	0.011	0.001
					SD	2.5	0.60	4.32	3.93	0.47			
Resolute Bay	Arctic cod	whole fish	M&F	3	Mean	7.3	0.31	5.52	0.55	0.46	0.107	0.010	0.007
					SD	0.5	0.20	1.44	0.77	0.53			
Great Slave L	burbot	liver	M&F	7	Mean	35.5	0.66	4.97	6.74	10.1	0.003	0.004	0.006
					SD	7.5	1.39	2.60	2.09	5.13			
Great Slave L	whitefish	muscle	M&F	4	Mean	18.8	0.09	3.02	2.57	1.94	0.014	0.011	0.009
					SD	3.4	0.01	0.57	1.28	1.63			
Akluvik	walrus	blubber	M	6	Mean	83.7	4.30	34.4	160	6.18	0.015	0.019	0.006
					SD	6.4	2.72	22.4	206	8.90			
Akluvik	walrus	blubber	F	2	Mean	87.4	4.46	37.7	33.9	2.76	0.021	0.021	0.001
Inukjuak	walrus	blubber	F	3	Mean	87.2	15.1	105	789	9.86	0.002	0.016	0.001
					SD	2.3	4.54	13.7	216	11.8			
Inukjuak	walrus	blubber	M	2	Mean	87.1	3.74	207	1190	13.2	0.004	0.011	0.003
Inukjuak	Ringed seal	blubber	F	7	Mean	92.8	24.2	51.0	183	20.4	0.007	0.015	0.003
					SD	5.3	22.7	29.3	199	9.90			
Inukjuak	Ringed seal	blubber	M	4	Mean	94.7	17.7	53.7	258	34.3	0.005	0.020	0.004
					SD	2.0	13.0	29.5	267	21.9			

MERCURY AND OTHER INORGANIC CONTAMINANTS IN COUNTRY FOODS IN EASTERN HUDSON BAY

PROGRAM LEADER: M. Kingsley, Institut Maurice-Lamontagne, Fisheries and Oceans Canada, Mont-Joli, Quebec

PROJECT TEAM: L. Lockhart, Freshwater Institute, Fisheries and Oceans Canada; Resource Development Division, Makivik Corporation, Kuujjuak, Quebec; C. Metcalfe, Trent University, Peterborough, Ontario

OBJECTIVES

To evaluate baseline levels of mercury and other heavy metals in country foods available to native people in communities on the southeast coast of Hudson Bay, and to evaluate health risks associated with heavy or exclusive dependence on such foods.

DESCRIPTION

Rivers flowing into eastern Hudson Bay do so over material containing mercury and other heavy metals, in some cases recently flooded by hydroelectric dams. Marine mammals in other northern areas have been found to contain levels of mercury, cadmium and other heavy metals that exceed recommended limits. Potential human health risks justify verification of levels in species commonly used as country foods. Such data would also provide baseline data of value to an eventual evaluation of the environmental impact of further hydroelectric development in the hinterland of eastern Hudson Bay.

This project includes a sampling programme on the major marine and freshwater country food species, including marine shellfish, marine and freshwater finfish, and marine mammals. For sampled specimens, age and size determinations will be carried out, and standardized tissue samples will be taken. These samples will be taken at the two communities considered most at risk of increased mercury levels from hydro development, namely Umiujaq and Kuujjuaraapik. Sampling strategies will consider the following desiderata: species and tissues should be those used as country food in the largest quantities; the same tissues should be sampled in common across a range of species and trophic levels; sample sizes should allow estimation of present health risks and assurance that significant changes would be detected if they were to occur after development. Samples will be analysed for mercury (total and methyl-, if levels are high), selenium and cadmium.

ACTIVITIES IN 1993/94

A sampling programme was arranged with the cooperation of Makivik Corporation to collect samples of beluga whale, ringed seal, Greenland cod, whitefish, brook trout and blue mussels from the communities of Kuujjuaraapik and Umiujaq; walrus samples were obtained from Inukjuak, further north, where that species is more readily available. The following samples were obtained and analysed for metals: walrus (1♂, 3♀), beluga whales (5, 1), ringed seals (3 total), mussels (39 total), brook trout (45), and lake whitefish (33). For mussels, whole body soft tissue was analysed, for all other species muscle, for all marine mammals liver, and for belugas muktuk as well. In addition, 27 liver and 26 muscle samples for ringed seals from the Belcher Islands were obtained from archival material by courtesy of Dr Metcalfe at Trent University.

All tissue samples were analysed for the target metals--mercury, selenium and cadmium--except for the Belcher Island ringed seals, which were small and were only analysed for mercury. In addition, results were obtained for copper, zinc and lead. We obtained results only for total mercury, not for methylmercury.

RESULTS AND DISCUSSION

The results obtained from the 1993 sampling programme are summarized in Table 1. Levels of metals determined for mussels were low and uniform, and levels of metals in the fish muscle samples were generally below guideline levels for mercury and cadmium. Some marine mammal liver samples presented high levels of all metals; this is not unexpected, but clearly indicates a need for more extensive sampling. Mercury levels in some marine mammal liver samples and muscle and muktuk samples from beluga exceeded consumption guidelines. High mercury was often associated with high levels of selenium. One of the concerns that motivated this project was the fear that beluga muktuk, like marine mammal liver, might tend to be high in cadmium, but this was not the case; muktuk was in fact very low in cadmium.

Kidney was not sampled in this programme, which was directed specifically toward species and organs used as food. Kidney, from any species, is not much consumed. However, the tendency of metals to be concentrated in kidney tissue may make it a sufficiently useful indicator to be worth including in the sampling programme.

CONCLUSIONS

Levels of mercury and cadmium in liver of marine mammals are high enough to warrant a more thorough examination. The sampling programme should be continued, particularly for marine mammals, to better evaluate the relation of metal levels to age and sex, to describe the correlation between levels in different organs, and between different metals, and to identify regional or local variation. This is especially true for beluga and walrus. Although kidney is not commonly eaten, it would be useful to extend the ambit of the sampling to include it so as to more fully describe the distribution in the organism. There were no marine fish in the samples collected this year, and this gap will be filled in 1994 sampling.

Expected project completion date: March 31, 1997

Table 1. Concentrations of Mercury, Cadmium, and Selenium in Country Foods from Eastern Hudson Bay, 1993.

Species	Tissue	#	Metals (ppm)		
			Cadmium	Mercury	Selenium
Mussels	Soft Tissue	39	0.076-0.224	0.020-0.048	0.45-1.07
Lake Whitefish	Muscle	33	<0.005	0.053-0.176	0.29-0.56
Brook Trout	Muscle	29	<0.005	0.041-0.253	0.036-0.061
Walrus	Muscle	4	0.006-0.058	0.053-0.092	0.65-1.26
	Liver	4	1.086-5.489	0.351-3.718	1.23-2.24
Ringed Seal (Gt Whale)	Muscle	3	0.009-0.201	0.058-0.093	0.54-0.69
	Liver	3	0.871-5.839	0.441-2.68	2.04-2.9
Ringed Seal (Belcher Is)	Muscle	26		0.054-0.349	
	Liver	27		0.131-25.67	
Beluga	Muscle	5	0.015-0.191	1.08-2.551	0.38-0.72
	Liver	4	1.829-19.24	14.63-98.56	4.34-24.97
	Muktuk	5	<0.001-0.047	0.16-1.458	5.22-10.02

Note: range is sensitive to sample size. Where ranges are small, in spite of large samples, as for mussels, or Se in fish, it is a good indication that variability is low. Large ranges indicate high variability, for small or large samples. Small range, for small samples, does not necessarily indicate low variation.

METHYLMERCURY AND HEAVY METALS IN TISSUES OF NARWHAL, BELUGA AND RINGED SEALS

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OBJECTIVES

1. To determine spatial and temporal trends of toxic metals (lead, cadmium, mercury) in tissues of ringed seals and Arctic whales.
2. To provide a data base for estimating dietary contamination with toxic metals in ringed seals and other Arctic marine mammals.
3. To provide a data base of methylmercury in Arctic marine mammals exhibiting high total mercury concentrations.

DESCRIPTION

This project is aimed at providing information on metals in marine mammals across the Arctic as a basis for determining spatial variability, deducing temporal trends by comparison with past and future data, and providing a basis for dietary calculations. Past information on methylmercury is very spotty for Arctic marine mammals, and nonexistent for contaminants in muktuk of Canadian Arctic whales. This report addresses these information gaps. High mercury levels have been reported in ringed seals, bearded seals, and belugas from the western Arctic (Smith and Armstrong 1975, Wagemann *et al.* 1990), significantly exceeding the Health Canada Guideline of 0.5 ppm (μg/g wet weight). The marine mammals in the western Arctic appear to have much higher concentrations of mercury in some tissues than those in the eastern Arctic. On the other hand, cadmium appears to be higher in the eastern (and central) Arctic than the western Arctic. Lead was reported higher in belugas from Hudson Bay than from the Mackenzie Delta, and was very high in dolphins off the coast of Newfoundland (Muir *et al.* 1988) and in some ringed seals from the Strathcona Sound area, Northwest Territories (NWT) (Wagemann 1989), although the latter may have been affected by mining activities in that area. Cadmium in the kidneys of belugas from the eastern Arctic was higher than in belugas from the Mackenzie Delta, and cadmium in narwhal from the vicinity of Pond Inlet, NWT was higher than in any other group of marine mammals (Wagemann *et al.* 1983).

In the previous two years we reported on data for total metals in ringed seals from the eastern Arctic, Hudson Bay (Wagemann 1991) and the western Arctic (Wagemann 1993). This report deals primarily with metals in ringed seals from the central Arctic (Resolute Bay), metals in muktuk of Arctic whales, and methylmercury in ringed seals and whales. Metal data for muktuk from arctic marine mammals has not been collected to date, notwithstanding the importance of this tissue as a country food. The data reported here are from small sample sizes of animals and therefore represent only a start in obtaining a larger data set of metal contaminants and some metal compounds in muktuk and other tissues needed for dietary intake calculations, as bench marks for comparison with past and future studies, and for determining temporal trends and ecosystem health.

ACTIVITIES IN 1992/93

Samples

Liver, kidney and muscle tissues of narwhal from Iqaluit (14 animals) and Repulse Bay (7 animals) were obtained in 1993 by B. Dunn (Fish and Marine Management, Freshwater Institute, Winnipeg) through contracts with Hunters and Trappers Associations. Additionally, tissue samples of narwhal from Pond Inlet (9 animals) obtained in 1992 were available. Muktuk of narwhal was taken during the 1993 hunt at Repulse Bay and Iqaluit but not in 1992 at Pond Inlet. The 1993 hunt at Pond Inlet was to provide the bulk of narwhal tissue samples for this investigation but all samples were lost in transit and were never received at the Freshwater Institute. Tissues from 35 ringed seals from Resolute Bay were received in 1993 through H. Welch. Well over 100 ringed seals from Sachs Harbour were available from previous collections for further analyses.

Methods

Narwhal tissues from Pond Inlet, Repulse Bay and Iqaluit, and ringed seal tissues from Resolute Bay and Sachs Harbour (liver, muscle) were analyzed for methylmercury, and liver, kidney and muscle for total metals (lead, cadmium, mercury, selenium, zinc and copper). Muktuk samples of narwhal from Repulse Bay and Iqaluit were analyzed for total metals. Total mercury was determined by cold-vapour flameless AA, and other metals by direct-current plasma emission spectrometry or Zeeman graphite furnace AA, depending on tissue concentration. Lead and cadmium in muscle required pre-concentration by complexing (diethyldithiocarbamate) and extraction (butyl acetate). Methylmercury was determined by extracting the homogenized tissue with an organic solvent, digesting the extract and analyzing it for mercury by cold vapour AA as for total mercury. These determinations were verified by capillary GC with ECD using a modified method (capillary GC rather than packed-column GC) of Uthe *et al.* (1972). A certified reference material was analyzed with good results along with samples.

Quality assurance

Certified reference materials (Bovine Liver, NBS; DOLT, NRC; DORM, NRC) were used with every set of digests (~40) as a check on accuracy of total metals. High-purity reagents were used. Water for working standards and reagents was triply distilled in a quartz still, and reagent-grade acids were re-distilled in a Teflon still. Results were inspected, and seeming outliers were reanalysed using a fresh sample. This laboratory has participated in an international inter-laboratory trace metal analysis comparative study (Wagemann and Armstrong 1988) with a good outcome. Methylmercury determination by AA was verified by capillary gas chromatography with an ECD. The certified reference material DORM-1 was used as a methylmercury standard. Analysis of the reference material for methylmercury by this method was within the specified error limits of the certified value.

RESULTS

The primary focus in this study was on marine mammals from the eastern and central Arctic. For comparison, metals and methylmercury data for ringed seals from the western Arctic (Sachs Harbour) are included. Ringed seal data for Resolute Bay, collected in 1993 (35 animals) and Sachs Harbour, collected in 1987 (57 animals) and 1988 (60 animals) are compared for methylmercury and total metals in Table 1. Mean concentrations of some metals were significantly different between these areas, i.e. the western and central Arctic (Table 1), although the mean ages of the Resolute Bay ringed seals (5.9±5.0 years) and Sachs Harbour ringed seals (6.5±3.6 years, 1987 and 1988 combined) (Wagemann 1993) were similar.

The data are presented for narwhal collected in 1992 at Pond Inlet (9), and 1993 at Repulse Bay (7) and Iqaluit (14); none were received from the 1993 narwhal hunt at Pond Inlet. Mean total metal concentrations are expressed on a dry weight basis and can be converted to a wet weight basis by multiplying with the following factors: 0.310 for liver; 0.238 for kidney; 0.307 for muscle, for ringed seals; 0.265 for liver, 0.217 for kidney, 0.289 for muscle, for narwhal.

Methylmercury in Ringed Seals and Narwhal (Table 2)

In muscle, methylmercury concentrations did not differ significantly between ringed seals from Resolute Bay and Sachs Harbour (0.45 and 0.43 μg/g wet wt, respectively). Some individual animals did exceed the Health Canada Guideline for fish consumption, 0.50 μg/g (wet wt), however, the means did not. The methylmercury concentration in the liver of ringed seals was significantly higher than in the muscle, at both sites (1.80 and 2.11 μg/g wet weight for Resolute Bay and Sachs Harbour, respectively), but as for muscle, the means for liver did not differ significantly between the two sites. This was in sharp contrast to total mercury, which was significantly higher in the liver of Sachs Harbour than Resolute Bay ringed seals. In ringed seals methylmercury represented 87-93% in muscle, and 12-18% in liver, of the total mercury concentration in these tissues.

The mean methylmercury concentration in muscle of narwhal (0.85, 0.56 and 0.94 μg/g wet wt) from Pond Inlet, Repulse Bay and Iqaluit, respectively, was significantly higher than in ringed seals, and represented 90-100% of the total mercury concentration in this tissue. In all narwhal from all three sites (18 animals), the methylmercury concentration (expressed in terms of μg Hg/g wet weight) exceeded the 0.50 μg/g (wet weight) guideline, and the mean for all the animals (three sites combined) was 0.81 μg/g wet weight (Figure 1). Methylmercury was measured in liver of narwhal from two sites, Repulse Bay and Iqaluit. As for muscle, the mean concentration of methylmercury in liver was highest in Iqaluit animals (3.02 μg/g wet wt) and represented 37-51% of the total mercury in this tissue, somewhat higher than in ringed seals.

The sample sizes were, unfortunately, not sufficiently large to confidently reflect levels in the larger population. The significant difference of methylmercury in the liver and muscle of narwhal between Repulse Bay and Iqaluit may simply reflect a different age bias in the hunted animals at the two sites. However, from a consumer's point of view, it simply reflects the reality of the hunt at each site. Larger sample sizes are required to determine if any such differences between sites are intrinsic or are indeed a consequence of a bias resulting from too small sample sizes being compared.

Metals in Muktuk of Narwhal (Table 3)

No contaminants data were available in the literature on muktuk of narwhal or beluga from the Canadian Arctic, a serious knowledge gap, considering that this is a favoured country food. This report constitutes a beginning in filling this knowledge gap. Metals were measured in muktuk of narwhal from two sites, Repulse Bay and Iqaluit. Muktuk was not available from Pond Inlet animals. The mean concentration of Pb and Cd was quite low in muktuk of narwhal from both sites and appears not to pose a problem for consumers or animals. Of the tissues analyzed, muktuk had the highest concentration of zinc, and is obviously a good source of this essential element for consumers.

The mean total mercury concentration was significantly higher in muktuk of the Iqaluit group (0.61 μg/g wet weight) than the Repulse Bay group (0.34 μg/g wet weight), the mean of the former group exceeding somewhat the guideline for fish. The results were derived from a limited number of tissue samples, as a consequence of an unforeseen loss of samples from the 1993 hunt. More samples of muktuk need to be analyzed to obtain a better data base of metals for this tissue. Beluga muktuk from the western Arctic had relatively high concentrations of mercury (Wagemann 1994). Beluga muktuk from the eastern Arctic should therefore also be analyzed to see if these relatively high levels are peculiar to the species, or are a site-dependent phenomenon. Muktuk was not analyzed for methylmercury in this preliminary survey.

In both narwhal and beluga it was found that mercury was not homogeneously distributed throughout the approximately 3 cm-thick skin (Figure 2). The skin consists essentially of four different strata of tissue (St. Aubin *et al.* 1990): the outermost, degenerative epidermis, underlain by the stratum externum, which in turn is underlain by the stratum intermedium and finally the dermis, which is underlain by blubber. The highest concentration of mercury was found in the outermost membrane (degenerative epidermis), in both, narwhal and beluga, and the lowest in the dermis and blubber. Muktuk from all the available animals examined showed such a mercury gradient, a fact apparently not known before. This gradient may be part of a mechanism by which the animals rid themselves of some mercury. Cellular material from the degenerative epidermal layer, containing the highest concentration of mercury, is naturally sloughed off periodically during the lifetime of the animal.

Total Mercury (Table 4)

The mean total mercury concentration in muscle of narwhal from Pond Inlet, 4.47 μg/g dry weight (1.27 μg/g wet weight), considerably exceeded the guideline for fish (0.50 μg/g wet weight), and was significantly higher than in muscle of ringed seals from Resolute Bay, 1.79 μg/g dry weight (0.55 μg/g wet weight) or Sachs Harbour, 1.43 μg/g dry weight (0.44 μg/g wet weight). In liver, the mean concentration of total mercury in narwhal from Pond Inlet was 36.2 μg/g dry weight (10.0 μg/g wet weight), similar to that in the liver of Resolute Bay ringed seals, 39.5 μg/g dry weight (12 μg/g wet weight). However, the ratio of total mercury in the muscle to that in the liver was more than twice as high in narwhal as in ringed seals.

The results presented for narwhal are based on the few available samples from the 1992 hunt. A larger data base is obviously needed for a more valid assessment, and larger sample sizes are expected from the 1994 hunt. There is also a need to determine the ages of narwhal in conjunction with contaminant surveys. The most useful hard tissue for ageing is the tusk, but its high monetary value precludes its use for this purpose.

Sachs Harbour ringed seals, notwithstanding their relatively young age (6-7 years, average), had the highest concentration of total mercury in the liver, 107 μg/g dry weight (33.9 μg/g wet weight), more than twice that in ringed seals from Resolute Bay (12.0 μg/g wet weight) or narwhal (10 μg/g wet weight), but the mean methylmercury concentration was not any different than in ringed seals from Resolute Bay (Table 4). Most of the "excess" mercury in the liver of Sachs Harbour ringed seals was therefore inorganic mercury. The selenium concentration in the liver of Sachs Harbour ringed seals was also relatively high, and positively correlated with mercury (Figure 3). This lends support to the idea that much of the mercury in the liver of Sachs Harbour ringed seals may have been associated with selenium in the form of mercuric selenide (HgSe), presumed to be a biologically inert form of mercury. It appears that the Sachs Harbour ringed seals while possibly exposed to higher concentrations of mercury in their environment than ringed seals at other sites, may have been able to detoxify most of the mercury in this way. Martoja and Berry (1980) had shown that mercuric selenide (HgSe) occurs as such in the liver, in the form of microscopic black, inert particles, visible under the microscope (see also Pelletier 1985). Although mercury when present in the liver in this form is probably relatively non-toxic to the animals themselves, it does not follow that consumers would be similarly protected from mercury when consuming this tissue.

Cadmium in Narwhal and Ringed Seals (Table 4)

Tissues from nine narwhal from the Pond Inlet area from the 1992 hunt (none from the 1993 hunt) were available for analysis and comparison. Earlier work (Wagemann *et al.* 1983) had indicated that narwhal from the eastern Arctic (Pond Inlet) had high cadmium concentrations in liver, 133 ug/g dry weight (34.1 ug/g wet weight) and especially so in the kidney, 298 ug/g dry weight (63.5 ug/g wet weight). The cadmium concentration in the 1992 animals was somewhat higher, 170 g/g dry weight (47.1 ug/g wet weight) in liver, and 346 ug/g dry weight (75.8 ug/g wet weight) in kidney, than in the 1979 animals reported previously (Wagemann *et al.* 1983). However, the small number of animals in this survey (9) compared to the earlier one (63 animals), does not allow making a definitive statement about any temporal change. A larger sample from the 1994 Native hunt is expected and will be used for analysis and comparison.

Cadmium concentrations in liver and kidney were lower in ringed seals from the western Arctic than in seals from the central (and eastern) Arctic (Table 1), 19.5 ug/g dry weight (6.18 ug/g, wet weight) in Sachs Harbour ringed seals and more than twice that in Resolute Bay ringed seals, 50.3 ug/g, dry weight (15.3 ug/g, wet weight); similarly in kidney, 90.9 ug/g, dry weight (21.9 ug/g, wet weight) in Sachs Harbour ringed seals, 203 μg/g dry weight (47.7 ug/g, wet weight) in Resolute Bay ringed seals and even higher in narwhal. Cadmium concentrations in tissues of marine mammals therefore do seem to be related to the geographic area and site where the animals are hunted in the summer. This implies that these sites do reflect to some degree the predominant environment and habitat of these animals notwithstanding the fact that marine mammals are not sedentary, although ringed seals are more so than narwhal. A similar spatial trend was also observed for other marine mammals (Wagemann *et al.* 1990).

Lead in Narwhal and ringed seals (Table 4)

Judging by the low concentration of lead in liver and muscle of the 1992 animals, and similarly low values reported for the 1979 animals (Wagemann *et al.* 1983), high lead concentrations in soft tissues of narwhal are not a problem now and were not in the past. The lead concentration was in fact very low in soft tissues of the presently surveyed animals. However, hard tissues where lead accumulates preferentially have not been analyzed. Significantly higher mean lead concentrations were found in the soft tissues of ringed seals from Sachs Harbour 0.064 μg/g dry weight (0.02 μg/g wet weight), than in ringed seals from Resolute Bay 0.028 μg/g dry weight (0.009 μg/g wet weight) or narwhal 0.013 μg/g dry weight (0.004 μg/g wet weight), but even in Sachs Harbour ringed seals the concentrations are still relatively low. In the liver lead was correlated with Cd. Unlike mercury and cadmium, lead in muscle did not differ greatly from that in liver. It is generally the case that lead concentrations are comparable in different soft tissues. Kidney was not analyzed for lead.

Selenium

Selenium in ringed seals from Sachs Harbour was on average, 48.0 ug/g dry wt. (15.5 ug/g wet wt) in liver and 1.68 ug/g dry wt. (0.52 wet wt) in muscle, and much less in Resolute Bay ringed seal liver, 15.1 μg/g dry weight (4.59 μg/g wet weight), which undoubtedly reflects the higher concentration of mercury in Sachs Harbour seals than Resolute Bay seals. In general, the outstanding feature of selenium is that it is significantly, positively correlated with mercury in liver (Figure 3) in marine mammals. Although selenium is an essential element, it is clear that the tissue concentration of total selenium can vary considerably depending on the exposure of the animal to mercury.

CONCLUSIONS AND UTILIZATION OF RESULTS

In the muscle of narwhal from Pond Inlet and Iqaluit the mean methylmercury (and total mercury) concentration was significantly higher than the Health Canada Guideline for fish (0.5 ppm) and was somewhat higher also in Repulse Bay narwhal. In all narwhal combined, the mean methylmercury concentration in muscle was 0.82 μg/g wet weight. However, the number of animals from each site was relatively small, and additional samples should be analyzed before the results are utilized for dietary calculations. In ringed seals the mean methylmercury concentration was approximately at the level of the guideline and was essentially the same in animals from the western and central Arctic. Mercury in muscle was nearly all methylmercury and was essentially the same in western and eastern Arctic ringed seals. In individual ringed seals from Sachs Harbour, the Health Canada Guideline was exceeded in approximately one third of the animals. Methylmercury was much higher in liver than in muscle in both ringed seals and narwhal and far exceeded the guideline, however, the means for ringed seals from the western and central Arctic were not significantly different, in contrast to the total mercury means. The mean total mercury concentration was significantly higher in Sachs Harbour ringed seals than Resolute Bay (central Arctic) ringed seals. The "excess" mercury in Sachs harbour ringed seals was likely in the form of a relatively non-toxic (to animals) compound (HgSe), but not necessarily to the consumers.

In muktuk of narwhal from Iqaluit, the mean total mercury concentration exceeded the Health Canada Guideline for fish. Further examination of this tissue revealed that mercury was not distributed homogeneously but was highest in the outermost stratum (degenerative epidermis) and progressively declined in successive strata. These results have implications for the assessment of dietary exposure via consumption of marine mammal tissues, particularly muktuk and flesh of Arctic whales and ringed seal liver. The data for narwhal are derived from relatively small sample sizes and as such are tentative. Additional work, based on larger sample sizes of Arctic whale tissues (beluga, narwhal), is required to confirm the data on methylmercury in muscle and liver, and total metals in muktuk, and to ascertain if cadmium concentration is indeed increasing in narwhal kidney as indicated by the relatively small sample used in this study.

In conjunction with contaminant studies in tissues of narwhal, there is a need for determining the ages of these animals. Research should be undertaken to find a suitable hard tissue for this purpose other than the tusk.

Expected project completion date: March 31, 1997

PARTNERS

Makivik Research Corp., Kuujjuak, Quebec; Inuit of NWT; Indian and Northern Affairs Canada; Fisheries and Oceans Canada; Health Canada; Native Hunters and Trappers Associations.

REFERENCES

Martoja, R. and J.P. Berry. 1980. Identification of tiemannite as a probable product of demethylation of mercury by selenium in cetaceans. Vie Milieu 30: 7-10.

Muir, D.C.G., R. Wagemann, N.P. Grifth, R.J. Norstrom, M. Simon, and J. Lien. 1988. Organochlorine chemical and heavy metal contaminants in white-beaked dolphins (*Lagenorhynchus albirostris*) and pilot whales (*Globicephala malaena*) from the coast of Newfoundland, Canada. Arch. Environ. Contam. Toxicol. 17: 613-629.

Pelletier, E. 1985. Mercury-selenium interactions in aquatic organisms: a review. Mar. Environ. Res. 18: 111-132.

Smith, T.G., and F.A.J. Armstrong. 1975. Mercury in seals, terrestrial and principal food items of the Inuit, from Holman, NWT. J. Fish. Res. Board Can. 32: 795-801.

St. Aubin, D.J., T.G. Smith, and J.R. Geraci. 1990. Seasonal epidermal molt in beluga whales, *Delphinapterus leucas*. Can. J. Zoo. 68: 359-367.

Uthe, J.F., J. Solomon and B. Grifth. 1972. Rapid semi-micro method for the determination of methylmercury in fish. JOAC 55: 583-589.

Wagemann, R. 1989. Comparison of heavy metals in two groups of ringed seals (*Phoca hispida*) from the Canadian Arctic. Can. J. Fish. Aquat. Sci. 46(9): 1558-1563.

Wagemann, R. 1991. Contaminants in northern Quebec marine mammals and fish: lead and other heavy metals. Pp. 30-40 *in*: Synopsis of Research Conducted Under the 1990/91 Northern Contaminants Program, R.G. Shearer (ed.). Indian and Northern Affairs Canada, Ottawa. 84 pp.

Wagemann, R. 1993. Lead and other heavy metals in tissues of walrus and ringed seals. Pp. 105-116 *in*: Synopsis of Research Conducted Under the 1992/93 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 70. Indian and Northern Affairs Canada, Ottawa. 285 pp.

Wagemann, R. 1994. Metal contaminants in muktuk of belugas and methylmercury in liver and muscle of belugas and ringed seals from the western Arctic. Progress report to the FJMC of the Inuvialuit Settlement Region, March 28, 1994.

Wagemann, R., N.B. Snow, A. Lutz, and D.P. Scott. 1983. Heavy metals in tissues and organs of the narwhal (*Monodon monoceros*). Can. J. Fish. Aquat. Sci. 40: 206-214.

Wagemann, R. and F.A.J. Armstrong. 1988. Trace metal determination in animal tissues: an inter-laboratory comparison. Talanta 35: 545-551.

Wagemann, R., R.E.A. Stewart, P. Béland, and C. Desjardins. 1990. Heavy metals and selenium in tissues of beluga whales, *Delphinapterus leucas*, from the Canadian Arctic and the St. Lawrence estuary. Can. Bull. Fish. Aquat. Sci. 224: 191-206 *in*: Advances in Research on the Beluga Whale, *Delphinapterus leucas*, D.J. Smith, St. Aubin, and J.R. Geraci (eds.).

Table 1. Outcome of test[†], $\alpha = 0.05$, comparing mean metal and methylmercury (MeHg) concentrations in Resolute Bay and Sachs Harbour ringed seals.

LIVER

	Pb	Cd	MeHg	Hg	Se	Cu	Zn
Resolute Bay		Higher	Same			Same	Higher
Sachs Harbour	Higher			Higher	Higher		

KIDNEY

	Pb	Cd	MeHg	Hg	Se	Cu	Zn
Resolute Bay	---[1]	Higher	----[1]		---[1]	Same	Higher
Sachs Harbour	---[1]		---[1]	Higher	---[1]		

MUSCLE

	Pb	Cd	MeHg	Hg	Se	Cu	Zn
Resolute Bay		Same	Same	Same		Same	
Sachs Harbour	Higher				Higher		Higher

[†] Scheffe, 1959

[1] kidney was not analysed for Pb, Se and MeHg.

Table 2. Mean±SD, number of animals (n) and range of methylmercury concentration (wet wt) in muscle and liver of ringed seals and narwhal from different sites.

	Muscle		Liver		
	MeHg, μg Hg/g	MeHg %	MeHg μg Hg/g	MeHg %	Site
Ringed Seals	0.45±0.15 31 0.17-0.85	87.0±7.3 31 72-100	1.80±1.10 23 0.38-4.04	17.6±9.0 23 5.5-43.9	Resolute Bay
Ringed Seals	0.43±0.40 12 0.11-1.49	92.5±5.5 12 81.8-99.6	2.11±1.79 41 0.33-6.20	11.8±11.2 41 2.1-63.3	Sachs Harbour
Narwhal	0.85±0.25 9 0.52-1.43	99.9±9.0 9 87-116	---[1]	---	Pond Inlet
Narwhal	0.56±0.06 6 0.51-0.68	92.6±15.7 6 66.6-107	1.58±1.14 5 0.33-2.82	51.3±37.0 4 25.4-104	Repulse Bay
Narwhal	0.94±0.16 9 0.66-1.17	104.8±9.2 9 90.3-117	3.02±0.65 10 2.13-3.92	36.7±17.3 10 12.6-77.2	Iqaluit

[1] --- not determined

Table 3. Mean±SD and range of metal concentrations (μg/g, wet weight) in muktuk of narwhal from Repulse Bay and Iqaluit in the Canadian Arctic.

Location	Pb	Cd	Hg	Cu	Zn
Repulse Bay	$(1.0\pm1.5)\times10^{-3}$ 7 $(0.2\text{-}4.3)\times10^{-3}$	$(2.6\pm2.5)\times10^{-2}$ 7 $(0.3\text{-}6.1)\times10^{-2}$	0.34±0.05 7 0.27-0.42	0.42±0.07 7 0.33-0.52	61.5±14.0 7 43.2-79.7
Iqaluit	$(1.1\pm1.8)\times10^{-3}$ 14 $(0.2\text{-}6.1)\times10^{-3}$	$(1.1\pm0.4)\times10^{-2}$ 14 $(0.4\text{-}2.0)\times10^{-2}$	0.61±0.08 14 0.48-0.77	0.35±0.08 14 0.26-0.54	61.5±8.2 14 48.1-80.6

Table 4. Comparison of mean metal concentrations (μg/g, dry wt) in liver, kidney and muscle of ringed seals between Resolute Bay and Sachs Harbour in the Canadian Arctic.

Muscle

Pb	Cd	Hg	Se	Cu	Zn	Species/ Site
0.028±0.018 35 0.008-0.086	0.32±0.28 35 0.08-1.36	1.79±0.66 35 0.73-3.37	1.08±0.13 35 0.88-1.39	3.92±0.64 35 2.78-5.51	75.8±19.9 35 45.8-130	Ringed Seals/ Resolute Bay
0.064±0.049 86 0.007-0.20	0.14±0.15 99 0.0-0.89	1.43±0.99 106 0.16-6.59	1.68±0.47 97 0.81-2.96	3.75±0.55 100 2.4-5.2	94.2±18.3 100 57.5-141	Ringed Seals/ Sachs Harbour
$(13\pm6)\times10^{-2}$ 9 $(3\text{-}21)\times10^{-3}$	0.82±0.86 9 0.15-2.77	4.47±1.67 9 3.18-8.58	1.28±0.13 9 1.10-1.46	3.14±1.14 9 1.95-5.36	85±43 9 49-192	Narwhal/ Pond Inlet

Table 4. Continued

Liver

Age (Years)	Pb	Cd	Hg	Se	Cu	Zn	Species/ Site
5.9±5.0 33 0.1-22	0.044±0.030 35 0.008-0.19	50.3±27.4 35 6.0-120	39.5±32.0 35 5.48-127.2	15.1±10.7 35 3.2-40.1	32.1±23.5 35 7.6-95.4	165±25 35 109-221	Ringed Seals/ Resolute Bay
6.5±3.6 122 0.1-19	0.098±0.125 115 0.007-0.79	19.5±9.9 86 0.3-49.5	107±115 117 0.72-636	48.0±41.4 117 4.04-204	32.8±21.5 117 9.8-129	129±19.0 117 85.1-223	Ringed Seals/ Sachs Harbour
—	(13±6)*10^{-2} 9 (5-25)*10^{-2}	170±145 9 20.4-525	36.2±21.0 9 7.53-64.5	19.5±9.5 9 6.5-37.3	28.1±16.5 9 17.7-70.5	150±37 9 89-217	Narwhal/ Pond Inlet

Kidney

Pb	Cd	Hg	Se	Cu	Zn	Species/ Site
—[1]	203±99 35 38.2-474	6.2±2.4 35 2.65-12.0	—[1]	25.1±7.0 35 14.3-38.7	210±46 35 123-295	Ringed Seals/ Resolute Bay
—	90.9±62.5 117 0.74-363	8.7±5.4 118 1.1-29.8	—	26.0±8.50 115 13.5-54.8	157.6±40.2 115 92-321	Ringed Seals/ Sachs Harbour
—	346±145 9 98-494	8.72±3.21 9 3.09-13.2	—	13.6±2.01 9 1.95-5.36	85±43 9 49-192	Narwhal/ Pond Inlet

[1] — kidney was not analysed for Pb, Se.

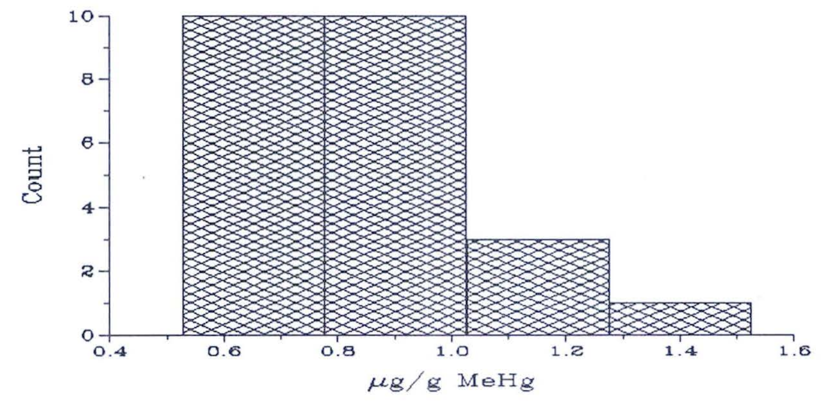


Figure 1. Frequency distribution of methylmercury concentrations in muscle of narwhal from Pond Inlet, Repulse Bay and Iqaluit in the eastern Canadian Arctic.

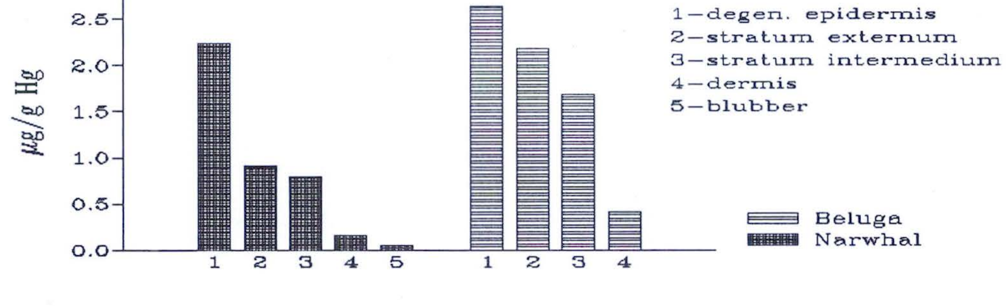


Figure 2. Total mercury concentration in the four tissue strata of the skin (muktuk) of a narwhal and beluga.

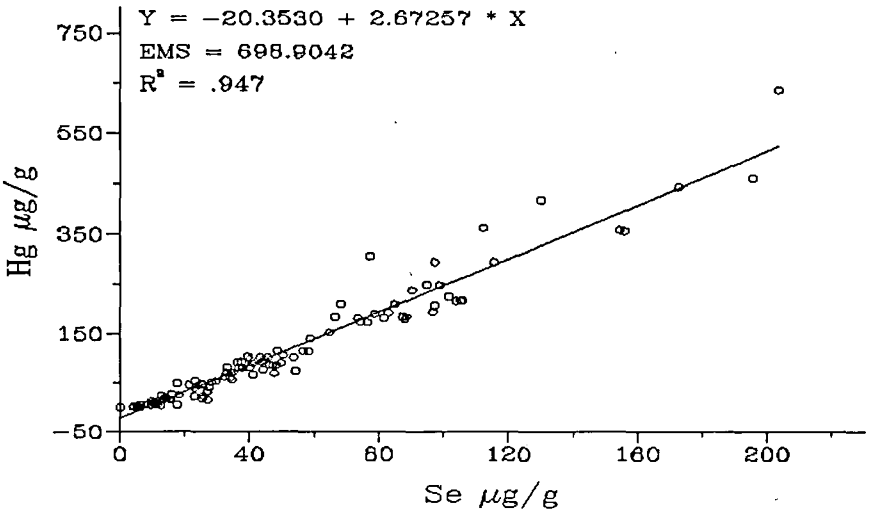


Figure 3. Relationship between selenium and mercury in liver of ringed seals from Sachs Harbour in the western Canadian Arctic.

CONTAMINANT TRENDS IN POLAR BEARS

PROJECT LEADER: R.J. Norstrom, Canadian Wildlife Service (CWS), Environment Canada

PROJECT TEAM: M. Simon, M. Mulvihill, A. Iddrissi, Environment Canada; R. Letcher, J. Zhu, Carleton University; I. Stirling, Canadian Wildlife Service and University of Alberta; S. Polischuk, M. Ramsay, University of Saskatchewan; M. Taylor, Government of Northwest Territories

OBJECTIVES

Short-term:

1. To analyze data on circumpolar geographic distribution of persistent organochlorine contaminants in the polar bear.

2. To examine geographic differences in polar bear bioaccumulation patterns using multivariate statistical analyses.

3. To quantify temporal trends in contaminant levels through a retrospective analysis of contaminant levels in archived polar bear samples.

4. To determine structures of unidentified contaminants and quantify levels of previously ignored chemicals such as dioxins, furans and non-ortho PCBs.

Long-term:

To determine spatial and temporal trends of persistent and toxic organochlorine chemicals in a species at the top of the arctic marine ecosystem food web as an indication of the time constants and effectiveness of global controls of these chemicals.

DESCRIPTION

Polar bears have proven their value as geographic indicators of organochlorine (OC) contamination of the arctic marine ecosystem. Relatively high levels of PCBs and the pesticide metabolite, oxychlordane, are present in polar bears, along with lesser amounts of DDE, dieldrin, HCB and α-HCH. A number of chlordane-related compounds remain unidentified. Levels of most OCs in a sample of Hudson Bay and Baffin Bay bears were higher in 1984 than 1969, therefore it is important to establish long term trends. Knowledge of the circumpolar distribution of contaminants is also important in determining the sources, trends and potential significance of these contaminants to Arctic marine and maritime wildlife. The polar bear could also be a surrogate for human exposure to contaminants because both ingest seal meat.

A proposal for a circumpolar survey of contamination in polar bear fat was presented and approved at a meeting of the International Union on Conservation of Nature, Polar Bear Specialists Group in Sochi, USSR in October 1988. The samples were collected between the autumn of 1989 and the winter of 1990/91. In addition to samples obtained from hunted bears, a number of adipose tissue samples were obtained by biopsy from tranquillized bears as part of other research projects in Viscount Melville Sound, Hudson Bay and Svalbard. Approximately 700 samples were received from a variety of sources from Alaska in the West to Svalbard in the East. Most of the Samples have come from the Northwest Territories. Chemical analysis of these samples was completed in 1992/93. The data were verified and entered into QuattroPro and descriptive statistics completed in 1992/93. More detailed analysis is required. In 1993/94, it was planned to extend the survey to other geographical areas, especially Russia, as part of ongoing research activities of polar bear biologists. It was also planned to extend knowledge of temporal trends through analysis of archived samples and by following levels in individual bears from year to year by biopsy techniques. An older mass spectrometer was upgraded in 1992/93 for full-time operation in the negative-ion chemical ionization mode with the assistance of M. Oehme from Norway. This instrument was applied to the identification and determination of unknown chlorinated contaminants in the arctic marine food chain.

ACTIVITIES IN 1993/94

There were three main blocks of activities in 1993/94: 1) determination of the geographical distribution of HCH and chlorobenzenes, analysis and reporting of the existing data set and collecting additional samples to expand the geographical extent of the survey; 2) continuing to identify and quantify unknown organochlorine compounds by GC/MS techniques and studying their geographical distribution and bioaccumulation in the food chain; and 3) determination of long term temporal trends of organochlorine residues in northern Hudson Bay by analysis of archived samples. Besides these activities, CWS provided the infrastructure support for the Northern Contaminants Program QA/QC program.

Methods

1) Archived fat extracts from adult polar bears left over from analysis of PCBs and chlordanes were pooled from 12 areas from Alaska to east Greenland and analyzed for HCHs, chlorobenzenes, methylsulfone PCB metabolites, PCB-163/138 ratios, PCDDs, PCDFs and non-ortho PCBs. The single-fraction analytical method for determination of OCs and PCBs by GC/MSD was modified to include fully ^{13}C-labelled internal standards of pentachlorobenzene, hexachlorobenzene, PCB-28, PCB-52, PCB-118, PCB-153, PCB-180 and PCB-194. This group of compounds encompasses the whole range of volatility of analytes, allowing determination of recoveries for the whole set of analytes by interpolation of GC retention times. An analytical method for determination of methylsulfone PCBs was completed and validated, as described in the project, "Assessment of Arctic Ecosystem Stress: Effects on Polar Bears". The method was applied to determine the geographical distribution of methylsulfone PCBs in the pooled samples. Relatively high levels of OCDD were found in the pooled samples, in complete disagreement with previous analyses; non-ortho PCB levels seemed erratic and too high. Analysis of freshly-made pools from three of the areas showed that the archived fat extracts had become

contaminated with PCDDs, PCDFs and possibly non-ortho PCBs during sample handling or storage. It is therefore necessary to start with freshly made pools from all areas in order to determine these analytes. The data for HCHs, chlorobenzenes, methylsulfone PCBs and PCB-163/138 were not affected.

The geographical extent of the survey was expanded westward by collection of 23 biopsies from Wrangel Island in Russia by Ted Garner, U.S. Fish and Wildlife Service, Alaska, and northward to the Arctic Ocean near Prince Patrick Island by collection of 25 biopsies by Ian Stirling, CWS, as part of their ongoing studies on polar bear population ecology. Analysis of these samples is proceeding, and will be reported next year.

2) The Hewlett-Packard NICI-GC/MS instrument was applied to the identification and estimation of levels of polychlorinated camphenes (PCCs) in polar bear fat and ringed seal blubber. The PCC levels were compared to those of other major residue classes. A commercial toxaphene mixture was separated into 5 fractions by semi-preparative HPLC on silica gel. Each fraction was analyzed by NICI-GC/MS and electron capture detector (ECD) to determine the overall composition and feasibility of creating a toxaphene standard. Nearly complete identification of the methylsulfone PCB metabolites in polar bears was accomplished by comparison to authentic standards obtained from Å. Bergman, U. of Stockholm. A weighable quantity of photoheptachlor was synthesized by irradiation of heptachlor at 350 nm. The identity of the compound was confirmed by GC/MS and NMR, and a standard was prepared. Results of quantitative analysis of Arctic biological samples for photoheptachlor will be reported next year.

3) Archived adult male and some female polar bear fat samples collected from northern Hudson Bay in 1969 and 1982-84 were retrieved from the CWS Specimen Bank and analyzed individually for chlordanes, PCBs, DDTs, HCHs and chlorobenzenes in order to determine the long term temporal trends in this area, and their statistical significance.

Quality Assurance

The CWS laboratory participated in the Northern Contaminants Program check sample round-robin. CWS also participated in the Swedish intercalibration program on non-ortho PCBs in ringed seal blubber. The quality of the results from both studies showed very good accuracy. Analysis of recoveries of ^{13}C internal standards in the organochlorine/PCB methodology showed that non-volatile compounds (RT longer than PCB-52) were normally recovered >85%. Because of the extremely small sample size of biopsies, and the necessity for evaporating the final extract under a nitrogen stream, recoveries of chlorobenzenes and lower chlorinated PCBs were frequently lower, but were corrected by the internal standards or could be calculated by interpolation of recoveries by retention time.

RESULTS

1) The geographical distribution of HCH and chlorobenzenes in pooled polar bear fat from 12 areas is shown in Fig. 1. As found in the previous study conducted between 1982-84, there is a tendency for HCH to be higher in the west, reflecting a probable Asian source. It is the only

chlorinated compound class to have this type of distribution. All other residues are relatively evenly distributed, as shown in Fig. 1 for chlorobenzenes, or tend to increase from west to east, with highest levels being found in eastern Greenland and Svalbard. The distribution of methylsulfone-PCBs and ratio to total PCBs in the same pooled samples is given in Table 1. Total methylsulfone PCBs are 0.14 to 0.63 ppm in lipid, with the highest levels being in east Greenland bears. Methylsulfone PCBs were present at 5% to 8% of total PCBs. Low levels (1-10 ppb) of 3-methylsulfone-DDE were found in adipose tissue for the first time (Table 1).

2) A total of 15 PCC congeners were found in polar bear fat and ringed seal blubber (Fig. 2). Several of these coeluted with PCB or chlordane components, but could be identified by ECNI mass spectrometry (Zhu and Norstrom 1994). The pattern was more complicated than that previously described for cetaceans and fish in the Arctic and elsewhere. Levels of total PCCs, PCBs, DDT and HCHs were similar in ringed seal, ca. 250-300 ppb. Although PCBs were an order of magnitude higher relative to PCCs in polar bear, total PCC concentration was still approximately 1 ppm. Analysis of the five toxaphene fractions from semi-preparative HPLC using silica gel revealed that approximately 290 compounds could be baseline-separated, distributed throughout the fractions (Zhu *et al.* 1994). The majority of the compounds found in biological samples occurred in Fraction 1. This leads to the possibility that a standard of known concentration of individual peaks, but unknown structures, could be prepared from this fraction using universal detector techniques, such as the flame ionization detector (FID).

Four new methylsulfone PCBs were positively identified: 4M-CB64, 3M-CB70, 4M-CB70 and 3M-CB149, where CBXX identifies the precursor PCB structure (Letcher *et al.* 1994). A total of 18 congeners have now been identified. Only one pentachloro, one tetrachloro and two trichloromethylsulfones remain to be identified.

Using the authentic photoheptachlor standard, it was confirmed that the compound found in ringed seal and polar bear, labelled as U-1 in Norstrom *et al.* (1988), was photoheptachlor.

3) The results of the retrospective analysis of adult polar bear fat samples from northern Hudson Bay are shown in Fig. 3. As previously found for pooled samples of unknown age composition, levels of all residues tended to be lower in 1969 than in 1982-84, although the differences were not as great as found in the pooled samples. However, this apparent increase over time was only significant for s-Chlordanes. Similarly, levels of all residues appear to have declined between 1982-84 and 1989-91, but only the decrease in s-DDT was significant. It is probable that the peak in concentration of most organochlorines and PCBs was shifted several years later in the Arctic than at mid-latitudes, where it occurred in the late 1960s or early 1970s, so the peak may have been any time between 1969 and 1982. Every indication suggests that levels of all organochlorines in polar bears are now in decline in this area.

DISCUSSION AND CONCLUSIONS

In accordance with the Guidelines for Responsible Research of this program, a summary report on the geographical distribution of PCBs, DDTs and chlordanes was submitted to the NWT Contaminants Committee, and a narrative of the findings in English and Inuktitut was sent to participating Inuit communities by NWT Renewable Resources in April 1994. A review of the distribution of organochlorines and PCBs in Arctic marine mammals, which was presented at the International Symposium on the Effects of Marine Pollutants in Kamogawa, Japan in February 1993, is in press (Norstrom and Muir 1994). An invited paper on Bioaccumulation of organochlorines and PCBs in the Arctic marine ecosystem was presented at the International Symposium on Ecological Effects of Arctic Airborne Contaminants in Reykjavik, Iceland October 4-8, 1993. A summary of the geographical distribution findings to date was presented at the SETAC'93 Conference in Houston, November 14-18, 1993.

The polar bear continues to be one of the most effective spatial and temporal monitors of organochlorine contamination in the Arctic marine ecosystem. We have now shown that chlorobenzenes are very evenly distributed throughout the western hemisphere Arctic, and that HCHs tend to be higher in the west, presumably because of continued use of benzene hexachloride (BHC) and/or lindane in Asia. New samples from Russia (Wrangel Island) and the Arctic Ocean (Prince Patrick Island) will be analyzed in 1994/95.

A paper on the initial identification of methylsulfone PCBs was published (Bergman *et al.* 1994). It was shown that there are 22 methylsulfone PCB congeners in polar bears, of which 18 have been positively identified. Levels of these compounds are 5-10% of total PCBs. The geographical distribution of levels was similar to that of the PCBs, i.e., the highest levels were found in bears from Viscount Melville Sound and Scoresby Sound in East Greenland (Letcher *et al.* 1994). DDE levels were notably higher in Davis Strait, Hudson Bay and East Greenland than in the western and high Arctic, indicating the influence of long-range transport of DDT and DDE from North America. However, methylsulfone DDE levels in adipose tissue did not appear to correlate well to DDE levels probably because of varying preferential storage in liver. These results were presented at the International Symposium on Ecological Effects of Arctic Airborne Contaminants in Reykjavik, October 4-8, 1993.

Using NICI-MS techniques, 15 toxaphene-related compounds were identified in ringed seal and polar bear (Zhu and Norstrom 1994). Toxaphene was separated into 5 fractions by HPLC, and it was found that most of the biologically important compounds are in fraction 1 (Zhu *et al.* 1994). In 1994/95, an attempt will be made to prepare a quantitative standard from Fraction 1 using preparative HPLC and FID. An unknown compound in ringed seal and polar bear, U-1, was positively identified as photoheptachlor by synthesis of the authentic compound. Analysis of this compound in ringed seal, polar bear and human plasma has been completed, and a publication will be submitted in 1994/95.

Temporal trends of chlordanes, PCBs, DDTs, HCHs, dieldrin, and chlorobenzenes were established for northern Hudson Bay with three time points: 1969, 1982-84 and 1989-92. Levels of all chemicals except DDT were highest in 1982-84, but there were few statistically significant trends with the small sample sizes used, except for an increase in chlordane, 1969 to 1982-84, and a decrease in DDT, 1969 to 1989-92. In 1994/95, recent temporal trends (1982-84 to 1989-92) will be established for other areas of the Arctic using Specimen Bank samples.

Expected project completion date: End of the Arctic Environment Strategy in 1997. Hopefully another broad-scale survey can be conducted around the year 2000 to establish long-term trends.

REFERENCES

Bergman A., R.J. Norstrom, K. Haraguchi, H. Kuroki and P. Beland. 1994. PCB and DDE methyl sulphones in mammals from Canada and Sweden. Environ. Toxicol. Chem. 13: 121-128.

Letcher, R.J., R.J. Norstrom and Å. Bergman. 1994. Geographical distribution of $MeSO_2$-PCB and -DDE metabolites in pooled polar bear (*Ursus maritimus*) adipose tissue from western hemisphere arctic and subarctic regions. Sci. Total Environ. (in press).

Norstrom, R.J., M. Simon, D.C.G. Muir and R. Schweinsburg. 1988. Organochlorine contaminants in Arctic marine food chains: identification, geographical distribution and temporal trends in polar bears. 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. (in press).

Zhu, J.P and R.J. Norstrom. 1994. Identification of polychlorocamphenes (PCCs) in the polar bear (*Ursus maritimus*) food chain. Chemosphere 27: 1923-1935.

Zhu, J.P., M.J. Mulvihill and R.J. Norstrom. 1994. Characterization of technical toxaphene using combined HPLC-GC.ECNIMS techniques. J. Chromatog. (in press).

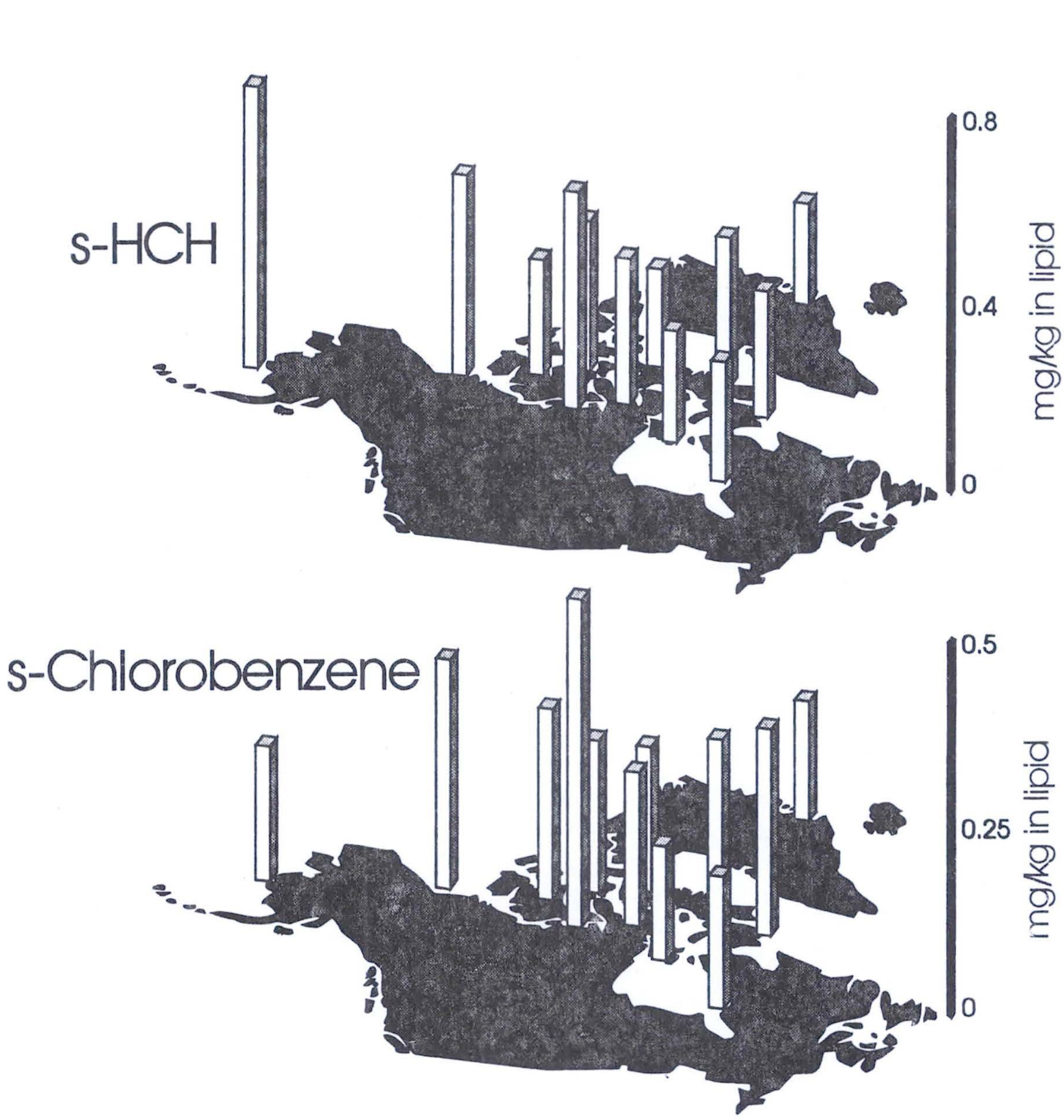


Fig. 1. Geographical distribution of sum of hexachlorocyclohexanes (s-HCH) and sum of chlorobenzenes in pooled adult male polar bear adipose tissue from the western hemisphere Arctic and Subarctic.

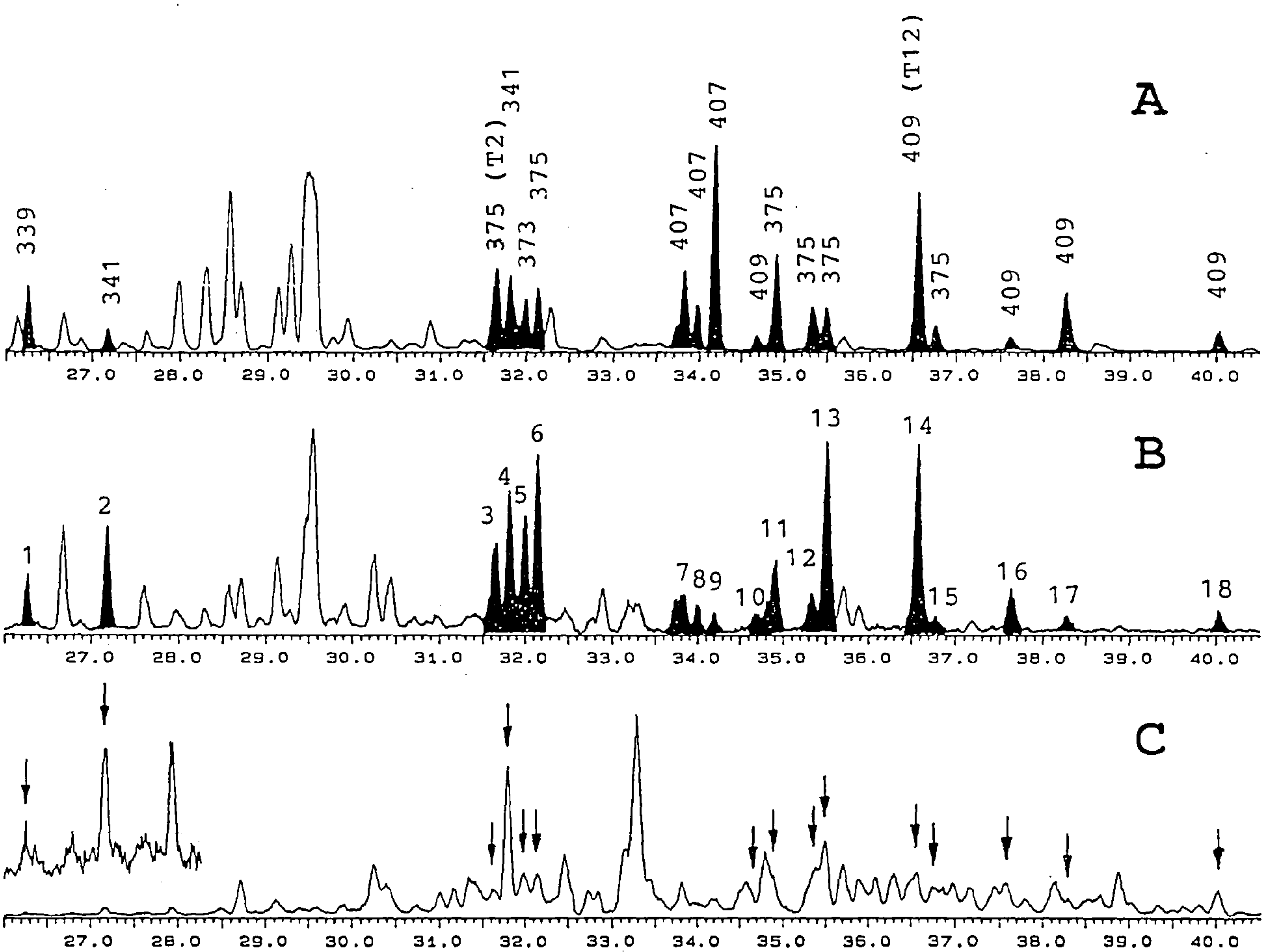


Figure 2: Reconstructed ion chromatograms (m/z 343+377+413) of polar bear adipose tissue (A), ringed seal blubber (B) and technical toxaphene standard (C). Peaks identified as PCCs in (A) and (B) were filled. Numbers above each peak in (A) show the mass of the [M-Cl] ion and in (B) are the peak numbers used in table 2 and figure 3.

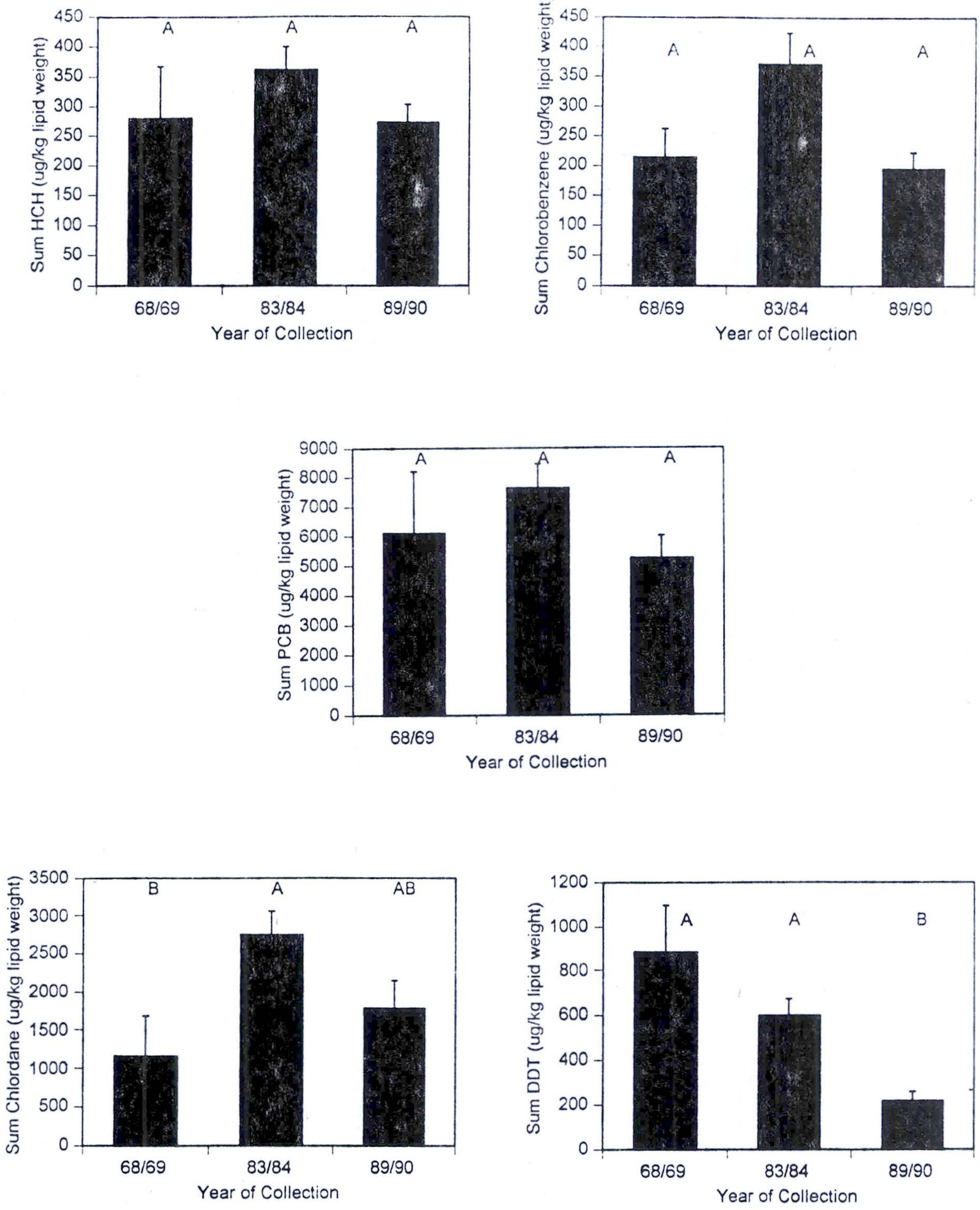


Fig. 3. Mean contaminant levels (+1 std. error) in adult male polar bears collected near Coral Harbour, northern Hudson Bay. Significant differences among time periods are indicated by the letters above the histograms. Time periods with the same letter are not significantly different ($\alpha=0.05$, Tukey's Studentized Range Test).

Table 1. Sum (s-) MeSO$_2$-PCB and 3-MeSO$_2$-DDE levels (ng/g lipid) and ratios to sum of PCBs and DDE in adult male polar bear adipose tissue pools from arctic and subarctic regions.

Geographical Area	Bering Sea	Beaufort Sea	V. Melville Sound	Queen Maud Gulf	Barrow Strait	Boothia Gulf	North Baffin Bay	South Baffin Bay	Davis Strait	North Hudson Bay	South East Hudson Bay	Scoresby Sound
Location in figures	1	2	3	4	5	6	7	8	9	10	11	12
S-MeSO$_2$-PCBs	138.2	246.8	444.8	283.7	215.1	144.7	287.1	470.2	286.3	218.3	326.0	632.7
S-PCBs	1737	5396	6181	4595	3361	2529	4720	8863	7637	4280	6690	13730
Ratio	0.080	0.046	0.072	0.062	0.064	0.057	0.061	0.053	0.038	0.051	0.049	0.046
3-MeSO$_2$-DDE (ng/g)	0.8	1.8	2.7	1.1	1.9	0.6	3.6	4.4	3.2	2.1	2.8	11.0
p,p'-DDE	24.3	50.5	55.1	20.1	74.6	32.6	88.3	82.5	170.1	185.2	314.3	209.0
Ratio	0.031	0.035	0.049	0.056	0.025	0.017	0.041	0.053	0.019	0.011	0.009	0.052

ASSESSMENT OF ARCTIC ECOSYSTEM STRESS: EFFECTS ON POLAR BEARS

PROJECT LEADER: R.J. Norstrom, Canadian Wildlife Service, Environment Canada

PROJECT TEAM: R. Letcher, J. Zhu, Carleton University; M. Ramsay, S. Polischuk, University of Saskatchewan; S. Bandiera, University of British Columbia; D. Muir, Fisheries and Oceans Canada; A. Bergman, University of Stockholm; M. Taylor, Government of Northwest Territories; Inuit hunters; I. Stirling, M. Simon, M. Mulvihill, S. Kennedy, Environment Canada

OBJECTIVES

Short-term:

1. To determine the presence, identity, concentrations and tissue distribution of potentially toxic sulfur-containing metabolites of halogenated aromatic compounds and their precursors in the polar bear and other arctic marine mammals.

2. To determine cytochrome P450 monooxygenase enzyme activity levels in polar bear tissues and compare to Western Blot analysis of P450 proteins.

3. To determine EROD- and porphyrin-inducing capability of fractionated tissue extracts in chick hepatocyte bioassay.

4. To determine the effect of season and adipose tissue size on contaminant levels in adipose tissue, milk and blood and correlate levels of contaminants in females and cubs.

Long-term:

1. To determine the effects, at the individual and population level, of persistent toxic organochlorine chemicals and their metabolites in the polar bear.

2. To collaborate with the Department of Fisheries and Oceans (DFO) in assessing effects on other marine mammals at the top of the arctic marine ecosystem food web.

3. To determine the potential for exposure of the human population to persistent PCB and DDT metabolites through ingestion of wild foods.

DESCRIPTION

There are several possible ecologically-based factors which may reduce fertility in polar bears, such as poor nutritional status as result of poor hunting due to unsuitable ice conditions much of the year. Persistent organochlorines (OCs) may also be a contributing factor. Utilization of fat reserves causes relocation of these compounds from adipose tissue, therefore during times of nutritional stress, organochlorine toxicity might be much more expressed than under more favourable conditions. It is probable that pregnant females, fetuses and cubs are most at risk for toxic effects of organochlorines because of mobilization from fat to target organs in the female and fetus during gestation, and to the cubs via milk for the first year or two after birth. Denning female polar bears fast for up to seven months of the year.

Levels of PCBs, DDT and chlordanes are highest in Hudson Bay bears, reaching several ppm levels in adipose tissue and liver (Norstrom *et al.* 1988). PCBs and DDT, or their metabolites, are the suspect compounds in the reproductive failure of grey and ringed seals in the Baltic Sea. The significance of these results to polar bear ecotoxicology is difficult to determine. Mean PCB levels in fat are generally four to ten times below those which are associated with reproductive effects in most wild mammals such as mink and grey seal. However, some individual bears have PCB levels (20-30 mg/kg in lipid) which are approaching the level of concern.

There is some evidence that the pathologies in Baltic seals associated with PCB and DDT compounds are due to methylsulfone (MSF) metabolites. The 3-MSF-DDE metabolite has been shown to have an extremely high binding affinity for adrenal cortex of mice. Furthermore, it is the suspect cause of hyperadrenocorticism in Baltic seals. We have identified 22 methylsulfone PCB congeners and 2 methylsulfone DDE congeners in polar bear tissues (Bergman *et al.* 1993; Letcher *et al.* 1994). Concentration of total MSFs was nearly 1 ppm in fat in some areas. Concentrations were even higher in liver, suggesting selective retention in this organ. In addition to interest in polar bear ecotoxicology, the results of this study have relevance for humans, since both eat marine mammal fats. A Japanese woman occupationally exposed to PCBs was shown to have excreted methylsulfone-PCBs in breast milk. The breast milk of mothers eating arctic marine mammals therefore may contain MSF-PCBs and -DDE. The presence, tissue distribution and toxicity of MSF-PCBs and MSF-DDE in the polar bear and other arctic species, and the significance to human health, therefore needs to be investigated. A method for determination of methylsulfone-PCBs and -DDE in biological samples was developed and validated in 1993/94.

Several studies were undertaken using specimens from bears shot as part of a half-life study of the drug used to immobilize polar bears, Telazol. The study was mainly of concern about human health from consumption of Telazol in polar bear flesh. Four bears were shot in 1992/93 by Inuit hunters from Resolute Bay as part of their regular quota, and various samples were taken for analysis. In 1993/94, eight more bears were shot to complete the study. In addition to samples for chemical analysis, liver samples were taken, stored in liquid nitrogen, and analyzed biochemically to characterize hepatic monooxygenase enzymes. Enzyme activities and enzyme protein concentrations were also determined. The methylsulfone and enzyme studies form part of the Ph.D. thesis research of R. Letcher at Carleton University.

Kinetic studies of organochlorines in individual polar bears and their milk in the Hudson Bay area were initiated in 1993/94 as part of the M.Sc. thesis research of S. Polischuk at the

University of Saskatchewan. These studies will allow the determination of the rate of transfer of contaminants to cubs, and seasonal changes in concentrations in adipose tissue.

ACTIVITIES IN 1993/94

There were four main activities in 1993/94: 1) final development and validation of the method for determination of methylsulfone-PCBs and -DDE in biological samples;
2) preliminary analysis of the tissue distribution of methylsulfone metabolites in male polar bears; 3) final collection of liver samples and completion of hepatic monooxygenase enzyme activities and immunoblot determination of enzyme proteins; and 4) initiation of study on seasonal kinetics of organochlorines in polar bears.

Methods

1) The method for determination of methylsulfone-PCBs and -DDE was thoroughly validated using polar bear fat, polar bear liver, fish (smelt) and bird egg (herring gull) substrates from the CWS Specimen Bank. A flow-chart of the final method is given in Fig. 1. Recoveries were determined from contaminant-free lipid extracts and naturally-contaminated substrates spiked with authentic methylsulfone-PCBs and -DDE obtained from the University of Stockholm. Molar response factors (MRF), instrumental detection limits (IDL) and method detection limits (MDL) were determined for gas chromatography/electron capture negative ion mass spectrometry (GC/ECNIMS) and gas chromatography/electron capture detector (ECD) techniques. The method was applied to the determination of geographical distribution of methylsulfone-PCBs and -DDE in pooled polar bear fat from 12 areas, as reported in this volume under the project, "Contaminant Trends in Polar Bears".

2) Preliminary analysis of the tissue distribution of methylsulfone metabolites in testes, adipose tissue, lung, brain and liver of 3 adult male bears was completed using the method developed in 1). The remaining 9 bears and tissues (kidney, muscle and heart) will be analyzed in 1994/95.

3) Microsomes from liquid nitrogen-frozen liver samples from the 12 Resolute Bay bears were prepared for enzyme studies at the University of British Columbia. EROD and PROD activities of microsomal preparations were determined, as were levels of cytochromes P450 1A1, 1A2 and 2B1 immunoreactive protein using immunoblot techniques. Data analysis and potential correlation with levels of PCBs, OCs and their metabolites will be completed in 1994/95.

4) The single-fraction analytical method for determination of OCs and PCBs by GC/MSD was modified to include fully ^{13}C-labelled internal standards of pentachlorobenzene, hexachlorobenzene, PCB-28, PCB-52, PCB-118, PCB-153, PCB-180 and PCB-194. This group of compounds encompasses the whole range of volatility of analytes, allowing determination of recoveries for the whole set of analytes by interpolation of GC retention times. Adipose tissue and milk samples from three solitary females and two family groups (a female with a cub-of-the-year and a female with a yearling) were analyzed for PCBs and organochlorines and samples preserved for later analysis of methylsulfone-PCBs and -DDE. Family groups were sampled at

a one month interval in the Fall, while solitary females, all of whom were pregnant, were sampled prior to denning, and following five months of total fasting, after emerging from the den with cubs.

Quality Assurance

The CWS laboratory participated in the Northern Contaminants Program check sample round-robin. The quality of the results showed very good accuracy. Analysis of recoveries of ^{13}C internal standards in the organochlorine/PCB methodology showed that non-volatile compounds (RT longer than PCB-52) were normally recovered >85%. Because of the extremely small sample size of biopsies, and the necessity for evaporating the final extract under a nitrogen stream, recoveries of chlorobenzenes and lower chlorinated PCBs were frequently lower, but were corrected by the internal standards or could be calculated by interpolation of recoveries by retention time. Levels of methylsulfone-PCBs and -DDE were corrected for recovery of the internal standard.

RESULTS

1) Absolute recoveries of methylsulfone-PCBs and -DDE were in the order of 75% to 85% (Table 1). When corrected for internal standard recovery, the corrected recoveries were in an acceptable range of ca. 90-110%. Subsequent to these studies, it was discovered that some losses of sample occurred in the gel-permeation chromatograph, and the recoveries of the internal standard in recent analyses are generally >85%. Recoveries of methylsulfone-PCBs and -DDE spiked to natural-contaminated samples, minus the natural contamination, ranged from 77% to 83%. MDL for ECD was in the order of 3 pg, whereas it was 0.2 to 0.7 pg for ECNIMS. However, due to significant non-linearity and variability in response at low levels, the practical detection limit for ECNIMS was >30 pg for all congeners using single ion monitoring (SIM), and 10-30 pg for ECD. Total ion current monitoring (TIC) ECNIMS gave a similar practical detection limit as SIM. MRFs were the least variable for ECD followed by TIC and SIM ECNIMS, indicating that chlorine substitution patterns had more influence on electron-capturing ability in the ECNIMS techniques. In all techniques, the MRF was higher for 3-methylsulfone-PCBs than for 4-methylsulfone PCBs.

2) Levels of total methylsulfone-PCBs and -DDE in liver, fat, testes and lung of three male bears, and brain of one bear, are given in Table 2 on a lipid weight basis. Levels in liver were 100 times higher than those in brain, and 10-20 times higher than in the other tissues. The distribution of PCBs was similar to that of methylsulfone-PCBs as indicated by the ratio of the two, which ranged from 0.034 in lung to 0.083 in brain. There was much more selective retention of methylsulfone-DDE in liver, in which average levels were 0.3 ppm (lipid wt. basis), which was nearly half the level of DDE itself. Lower levels of methylsulfone-DDE in other tissues may be due to covalent binding in adrenals.

3) Results of the enzyme activity and immunoblot analyses of the 12 male bear livers have not been tabulated or analyzed in any detail. Preliminary indications are that cytochrome P450 levels determined by quantitative immunoblot analysis will correlate significantly better with

PCB and OC levels than will EROD activity, possibly due to the inability to preserve activity in the tissue samples. No PROD activity was found, in spite of the indication of induced levels of P450 2B1. These results emphasize the importance of not assuming that typical substrates used for enzyme activity determination in laboratory mammals will cross-react among species.

4) The concentration of PCBs and chlordanes in individual bears tended to increase as the fasting period progressed (Fig. 2). Levels in pregnant females approximately doubled during the 5 month fasting period. To a lesser extent chlorobenzene levels also increased, but HCH and dieldrin levels were similar at both time points, indicating a faster equilibration. Cubs had higher levels than their mothers.

DISCUSSION AND CONCLUSIONS

Polar bear data were included in a collaborative study on human exposure to PCBs via a diet of mammals in northern Québec (Dewailly *et al.* 1993). Polar bear fat had 7 times higher levels of PCBs than human milk fat. There is also the potential for humans to be exposed to methylsulfone-PCBs through ingestion of ringed seal blubber.

A paper on the methylsulfone method has been drafted and will be submitted to Analytical Chemistry in 1994/95 (Letcher *et al.* in prep.). The results of this study were presented at the 24th International Symposium on Environmental Analytical Chemistry in Ottawa, May 16-19, 1994. Current research is focusing on adapting the method to analysis of blood plasma using C-18 solid phase extraction cartridges. Research is also underway to investigate the structure-activity relationships for fragmentation of methylsulfone-PCBs in ECNIMS.

A paper on the identification of methylsulfone-PCBs in polar bear and St. Lawrence beluga tissues has been published (Bergman *et al.* 1994). Tissue distribution studies showed that methylsulfones, especially 3-methylsulfone-substituted congeners, are preferentially stored in liver. Distribution among other tissues analyzed to date seems to be controlled more by the lipid content than selective binding, since the pattern of congeners was similar in fat, testes, lung and brain. It has recently been shown that 3-methylsulfone PCBs induce P450 2B monooxygenases in laboratory animals. Selective storage of 3-methylsulfone-PCBs in liver therefore may be an indication of binding to microsomal protein. Preferential storage in stellate cells, which are rich in lipid and specialized in (presumably protective) storage of vitamin A, may also occur. Stellate cells are the suspected cause of the highly selective accumulation of intermediate polarity organochlorine metabolites, such as oxychlordane and dieldrin, in liver. The role of stellate cells in cytochrome P450-mediated metabolism has not been investigated. The preliminary tissue distribution results were presented at the SETAC'93 conference in Houston in November, 1993. Analysis of all remaining samples and tissues will be completed in 1994/95. Further studies will address the possibility of bioaccumulation of MSF-PCBs and -DDEs from the diet. Samples of other species indicative of high trophic level food chains in the Arctic, such as beluga, narwhal and walrus, and lower trophic levels will also be studied.

A publication on the characterization in male polar bears of the hepatic monooxygenase enzymes and activity toward several substrates, including testosterone, was completed (Bandiera *et al.*, submitted). It is interesting that the testosterone metabolite profile was similar to that recently described for ruminants, and different from rats. This research will be carried on for another two years under an NSERC Strategic Grant to S. Bandiera at the University of British Columbia. Controlled storage studies of immunoreactive P450 protein stability in frozen livers are underway. In 1994/95, attempts will be made by M. Ramsay, University of Saskatchewan, to use liver biopsy techniques on tranquillized bears to determine hepatic enzyme levels.

Expected project completion date: End of the Arctic Environmental Strategy in 1997.

REFERENCES

Bandiera, S.M., S.M. Torok, M.A. Ramsay and R.J. Norstrom (in review). Immunological characterization of hepatic and lung cytochromes P450 in polar bears. Submitted to Biochem. Pharmacol.

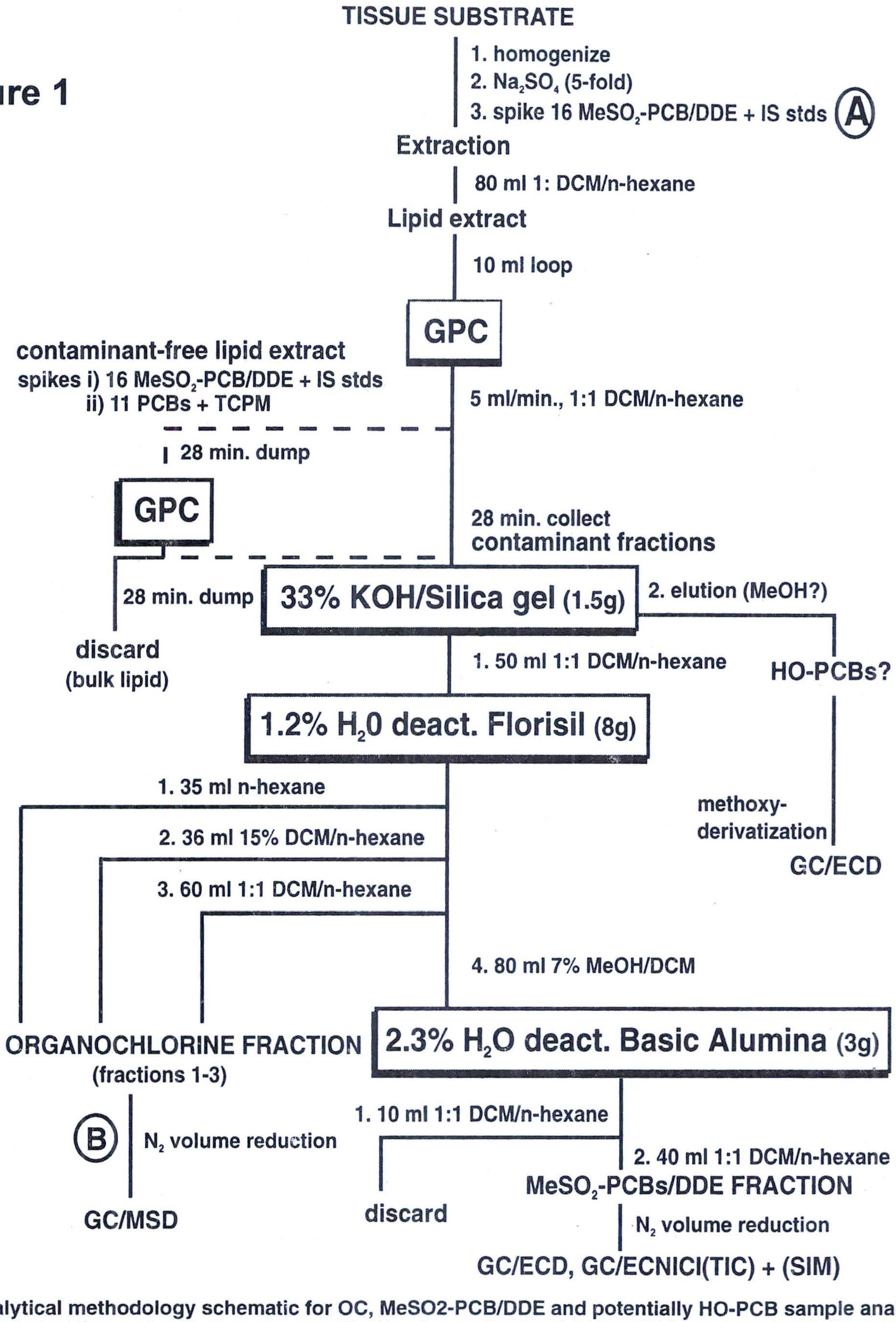
Bergman, A., R.J. Norstrom, K. Haraguchi, H. Kuroki and P. Beland. 1994. PCB and DDE methyl sulphones in mammals from Canada and Sweden. Environ. Toxicol. Chem. 13: 121-128.

Dewailly, E., 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 Quebec. Environmental Health Perspectives 101: 618-620.

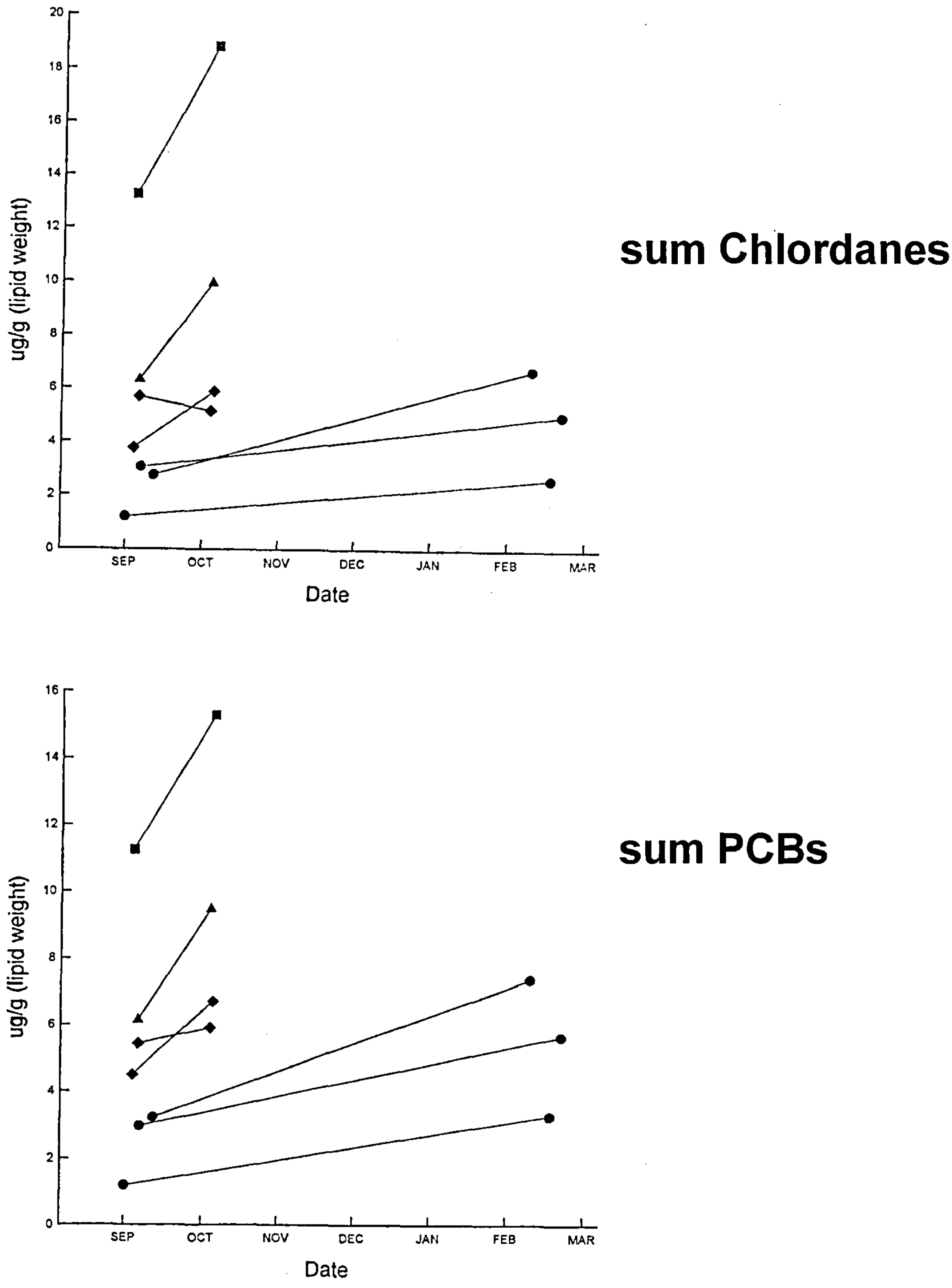
Letcher, R.J., R.J. Norstrom and A. Bergman. (in prep.). Polychlorinated biphenyls (PCBs), DDE and their methylsulfone metabolites: an integrated analytical method for determination in biological matrices.

Polischuk, S.C., R.J. Letcher, R.J. Norstrom and M.A. Ramsay. 1994. Preliminary results on the kinetics of organochlorines in western Hudson Bay polar bear (*Ursus maritimus*) Sci. Total Environ. (in press).

Figure 1



Analytical methodology schematic for OC, MeSO2-PCB/DDE and potentially HO-PCB sample analysis. The dotted line and spikes were a modification for method validation. (A) is replaced with IS and 13C-OC spikes and (B) with PCB-154 performance standard for sample analysis.



sum Chlordanes

sum PCBs

Fig. 2. sum chlordane and sum PCB concentrations in adipose tissue of solitary and pregnant females (circle), females with cubs (diamond), cub-of-the-year (square) and yearling (trangle).

Table 1. MeSO2-PCB and -DDE, PCB and tris(4-chlorophenyl)methanol percent recovery**** from contaminant-free lipid extracts by GC/ECD.

				Herring Gull Egg	Smelt	Polar Bear Liver	Polar Bear Adipose
			% Lipid	10.0	4.4	2.7	65.0
			Lipid Extract Weight (g)	0.18	0.15	0.019	0.65
			Wet Weight (g)	1.0	3.5	0.7	1.0
Peak	Congener Structural Formula *	Abbreviation	Spiking Level*** (pg/ul)				
	MeSO2-PCB and -DDE						
1	3-MeSO2-2,5-2',4'-Cl4CB	**3M-CB49**	312	78±4	75±6	71±1	79±2
2	4-MeSO2-2,5-2',4'-Cl4CB	**4M-CB49**	228	75±6	76±7	74±2	77±2
3	4-MeSO2-2,5,6-4'-Cl4CB	**4M-CB64**	272	81±6	76±8	79±3	77±5
4	3-MeSO2-2,5-2',4',5'-Cl5CB	**3M-CB101**	264	70±7	74±2	72±1	79±1
5	4-MeSO2-2,5-2',4',5'-Cl5CB	**4M-CB101**	220	74±6	78±6	76±4	89±5
6	3-MeSO2-DDE	**3M-DDE**	595	85±5	78±8	71±1	78±2
7	3-MeSO2-2,5-2',3',4'-Cl5CB	**3M-CB87**	368	74±3	72±3	71±2	79±4
8	3-MeSO2-2,5,6-2',4',5'-Cl6CB	**3M-CB149**	472	82±4	77±8	79±4	82±3
9	4-MeSO2-2,5-2',3',4'-Cl5CB	**4M-CB87**	368	83±4	75±8	76±4	79±2
10	4-MeSO2-2,5,6-2',4',5'-Cl6CB	**4M-CB149**	211	83±7	78±7	83±8	87±2
11	3-MeSO2-2,5,6-2',3',4'-Cl6CB	**3M-CB132**	414	80±5	76±9	77±2	78±1
12	4-MeSO2-2,5,6-2',3',4'-Cl6CB	**4M-CB132**	604	81±6	78±9	78±3	79±3
13	3-MeSO2-2,5-2',3',4',5'-Cl6CB	**3M-CB141**	284	77±5	75±9	72±2	78±3
14	4-MeSO2-2,5-2',3',4',5'-Cl6CB	**4M-CB141**	436	80±7	75±8	76±3	79±3
15	3-MeSO2-2-CH3-5-2',3',4',5'-Cl5CB	**IS****	436	74±2	72±1	74±2	79±3
16	3-MeSO2-2,5,6-2',3',4',5'-Cl7CB	**3M-CB174**	440	67±4	69±4	77±2	81±4
17	4-MeSO2-2,5,6-2',3',4',5'-Cl7CB	**4M-CB174**	316	75±2	75±4	79±4	82±2
Tissue/Congener Mean % Recovery*****				78±5	75±3	76±4	80±3
Cumulative Tissue/Congener Mean % Recovery = 77.1±7.1							
	PCB and tris						
	2,5-2'-Cl3CB	**CB-18**	295	71±4	79±.3	75±1	74±1
	2,6-2',6'-Cl4CB	**CB-54**	415	71±6	76±1	79±1	77±1
	2,5-4'-Cl3CB	**CB-31**	165	71±6	77±3	84±3	76±4
	2,5-2',4'-Cl4CB	**CB-49**	190	74±7	78±4	78±3	78±4
	2,3-2',5'-Cl4CB	**CB-44**	148	69±5	80±4	77±2	77±2
	2,3-2',3'-Cl4CB	**CB-40**	122	67±3	79±4	90±7	77±3
	2,4,6-3',5'-Cl5CB	**CB-121**	78	67±5	81±2	90±3	78±3
	2,3,4,5-2'-Cl5CB	**CB-86**	72	77±2	84±.3	81±5	82±1
	2,5-2',3',4'-Cl5CB	**CB-87**	95	69±4	77±4	89±5	80±1
	3,4-3',4'-Cl4CB	**CB-77**	138	74±4	78±.3	83±2	81±2
	2,4,5-2',4',5'-Cl6CB	**CB-153**	52	86±7	77±2	90±3	86±2
	2,3,4,5-3',5'-Cl6CB	**CB-159**	30	84±5	84±2	88±9	80±3
	2,3,4,5-3',4'-Cl6CB	**CB-156**	38	81±6	80±.4	82±3	78±2
	tris(4-chlorophenyl)methanol	***tris***	500	86±5	79±.2	-	78±3
	2,3,4,5,6-2',3',4',5',6'-Cl10CB	**CB-209**	42	84±7	81±.3	-	82±2
Tissue/Congener Mean % Recovery*****				75±7	79±.3	84±5	79±3
Cumulative Tissue/Congener Mean % Recovery = 79.3±9.3							

*see Figure 1

** IS = internal standard

*** corrected by GC/MS(EI), total ion monitoring

**** n=3 replicate spiked matrices with standard deviation

***** standard deviation of mean congener % recovery only

Table 2. Total (s-) MeSO$_2$-PCB and -DDE levels (ng/g lipid) and ratios of the congener sums to total PCBs and p,p'-DDE in polar bear tissues from the Resolute Bay area of the Canadian Arctic.

	LIVER average	SD(+/-)†	FAT average	SD(+/-)†	TESTES average	SD(+/-)†	LUNG average	SD(+/-)†	BRAIN‡
s-MeSO$_2$-PCBs	3059	1290	351	66	207	31	143	35	31
s-PCBs	48304	19268	6210	948	6387	1940	3263	354	377
s-MeSO$_2$/s-PCB	0.0654	0.0089	0.0565	0.0071	0.0341	0.0068	0.0432	0.0067	0.0830
3-MeSO$_2$-DDE	302.6	85.1	2.4	1	2.7	1.4	0.9	0.1	n/d
p,p'-DDE	704.4	99.6	262.4	32.4	89	13.7	48.1	9	224
3-MeSO2/DDE ratio	0.4582	0.203	0.0092	0.0044	0.0331	0.0196	0.0193	0.003	-

† Standard deviation. ‡ Only one sample.

BIOMARKERS AND STRESS EFFECTS IN ARCTIC MARINE MAMMALS

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PROJECT TEAM: D.A. Metner, J. Toews, Freshwater Institute, Fisheries and Oceans Canada

OBJECTIVES

Short-term:

To define levels of biochemical stress responses in marine mammals as functions of contaminant concentrations measured in the same animals, and to define the influences of normal biological and habitat variables (eg. sex, age, size, etc.) on the ranges of bioindicator values.

Long-term:

To understand the implications of contaminants (PCBs, chlorinated dioxins and furans, polycyclic aromatic hydrocarbons, heavy metals) for the health of individual arctic marine mammals, using the liver microsomal mixed function oxidase system.

DESCRIPTION

It is well established that arctic marine mammals contain a range of chemical contaminants. This project asks whether these contaminants matter to the animals by examining them for subtle indicators of biological responses (biomarkers or bioindicators) to contaminants. The bioindicators selected for these animals have established sensitivities (in laboratory animals) to some of the same contaminants measured in arctic marine mammals, notably several PCB congeners, chlorinated dioxins and furans, and polycyclic aromatic hydrocarbons including petroleum oil. Experimental studies directly on seals have also shown that some marine mammals respond. The principal biomarker being used is the microsomal monooxygenase system since it has been associated both with exposures to planar aromatic compounds and with a cascade of other biological responses.

There is currently no evidence, other than that from this project, to support or refute arguments that chemical contaminants are present in sufficient quantities to act biologically on the animals. Changes in natural populations do occur but we cannot establish whether the contaminants are contributing to these changes without knowing some of the steps between exposure and ecological change. Examination of the animals for indicators of subtle responses known to be associated with the contaminants found in them is perhaps the only way to make a convincing case either for or against the hypothesis that trace contaminants are acting biologically on the animals. If the contaminants are affecting the animals, then we should expect to see some correlations between bioindicator values and contaminant measures. Moreover, there is natural biological variation in the bioindicator measurements themselves but this variation has not been established for any arctic population. The objectives therefore are to test for correlations between bioindicator responses and contaminant levels in the same animals, and to assess natural variation. Knowledge of this variation is essential to the interpretation of biomarker responses as within or outside the normal range.

ACTIVITIES IN 1993/94

Early in 1993/94 this project was cancelled because funding was withheld. Late in the fiscal year partial funding was restored, and samples on hand from the previous year were analyzed for additional enzymatic activities. Unlike fish, mammals have two mixed-function oxygenase systems, one inducible by certain aromatic hydrocarbons and planar organochlorines, and one induced by other compounds, notably phenobarbital. The assays reported for this project in the past (ethoxyresorufin-O-deethylase, EROD, and aryl hydrocarbon hydroxylase, AHH) fall into the first of these groups. Among important contaminant groups reported to induce the second group of MFO activities in some mammals are DDT and chlordane. We have analyzed seals from the Arviat collection (Lockhart and Stewart 1993) for one of these latter types of enzymes, aminopyrene-N-demethylase (APND) and then attempted to test for statistical linkages between the enzymatic activity and blubber residues in the same animals.

Results were communicated at scientific and public meetings, notably at open public meetings hosted by the Fisheries Joint Management Committee in Inuvik in March, 1994, public meetings hosted by the Department of Indian Affairs and Northern Development in Yellowknife in March, open meetings hosted by the Yukon Contaminants Committee meeting in Whitehorse in February, and at public meetings in Fort Good Hope. The initial scientific journal publication has just been issued (White *et al.* 1994).

RESULTS

EROD and AHH values for the Arviat seals were reported in Lockhart and Stewart (1993). A subset of those results is shown in Table 1, restricted to those seals for which we have organochlorine residues.

Blubber residues of organochlorines were obtained from D. Muir and tests for pair-by-pair correlations analysis were done using PROC CORR of SAS. With the Arviat seals we now have some 52 seals for which we have one or more enzymatic activities and blubber residues. The four biochemical measurements (EROD, AHH, cytochrome P-450 and APND) were correlated with each other, but correlation analysis also revealed some associations between enzymatic activities and residues, the most consistent of which were with dieldrin (Fig. 1). These correlations were tested further using analysis of covariance with PROC GLM of SAS,

Table 1. Hepatic microsomal enzymatic activities in ringed seals from Arviat (nmol product/mg microsomal protein/min at 37 °C)

Assay	Sex	N	Mean	S.D.	Minimum	Maximum
APND	Males	29	5.61	1.38	1.00	7.75
APND	Females	19	5.39	1.76	2.42	9.10
EROD	Males	30	0.186	0.183	0.002	0.679
EROD	Females	22	0.146	0.150	0.004	0.570
AHH	Males	27	0.092	0.069	0.001	0.270
AHH	Females	17	0.090	0.069	0.001	0.205

incorporating sex, blubber lipid and age as covariates. This analysis indicated that the associations between the biochemical measurements and dieldrin were not accounted for by the other biological measurements on the seals. Probabilities of the associations being the result of chance were 0.004, 0.0065, 0.0083 and 0.0047, respectively, for EROD, AHH, cytochrome-P450 and APND respectively. Dieldrin has not been studied extensively as an inducer of the mixed-function oxygenase system, although there is some evidence of inducing activity in birds. In the previous report (Lockhart and Stewart 1993), it was shown that the EROD and AHH activities in the Arviat seals were often relatively low in seals for which the intervals between death and dissection of the liver were long. Consequently, associations demonstrated with these seals will require confirmation with other animals.

There was no suggestion of the hypothesized associations between DDT or chlordane and APND activity. Considered alone in the analysis of covariance, females showed some association between APND activities and toxaphene residues. There were associations detected between the EROD or AHH activities and the sum of PCB congeners; such an association was reported earlier for starving beluga whales taken from the Eskimo Lakes area of the Mackenzie Delta. (Testing enzymatic activities against specific individual congeners is still underway.)

DISCUSSION/CONCLUSIONS

Correlation analysis demonstrated several associations between enzymatic activities and blubber residues in the same seals; all four biochemical measurements were correlated with dieldrin residues, and these associations were not artifacts due to other biological covariates (age, sex, blubber lipid content). The correlations demonstrated with these seals are different from and weaker than those demonstrated earlier with beluga whales from the Mackenzie Delta (Lockhart and Stewart 1993). They do not provide evidence that dieldrin (or toxaphene) caused the biochemical responses, although they are consistent with such an hypothesis. Additional samples will be needed to test whether these correlations occur with other animals.

Expected project completion date:

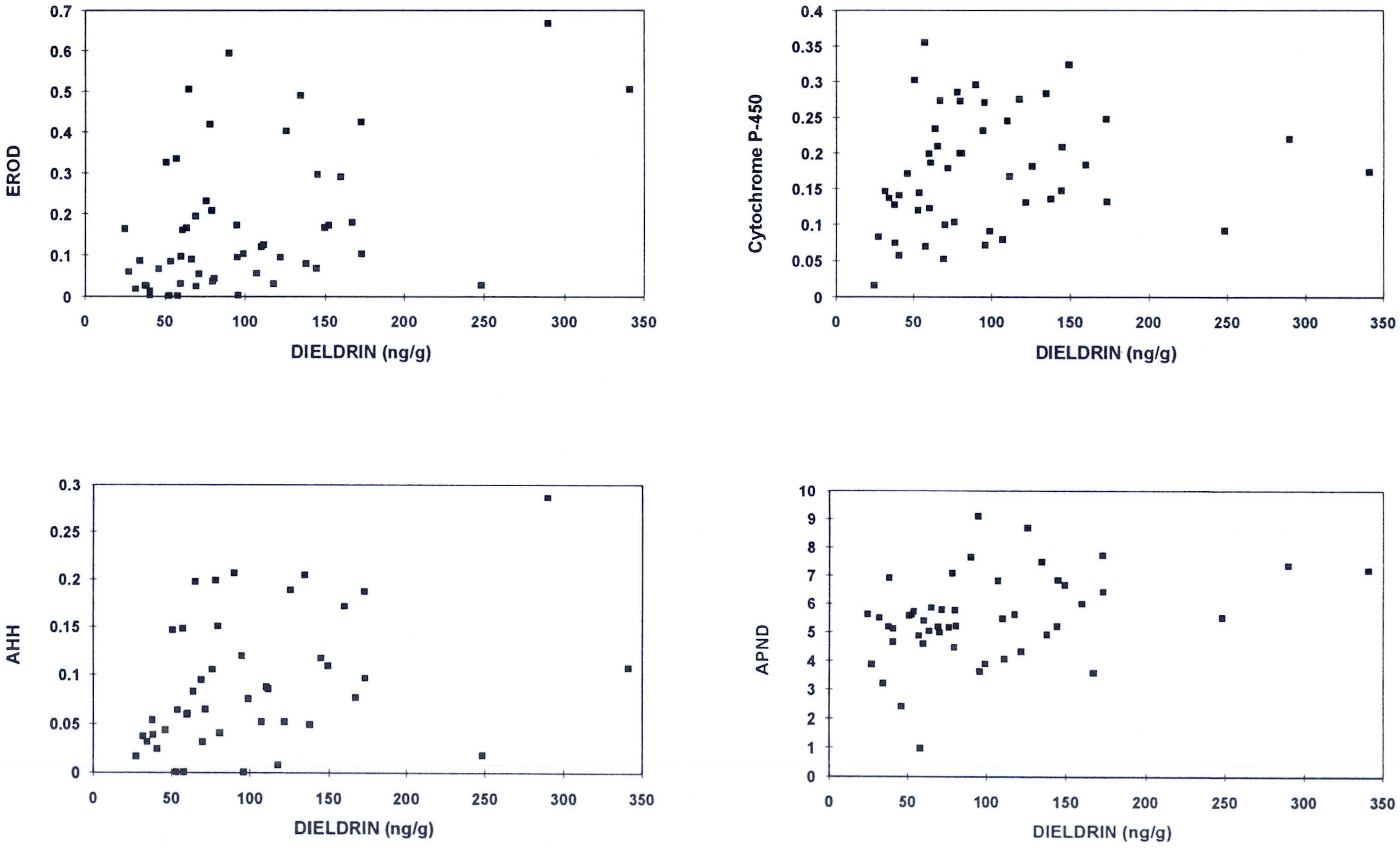
The project will not be completed until samples over a gradient of body residues have been analyzed in sufficient numbers to establish with confidence the presence or absence of correlations between chemical residues and biological responses. Probably the best way to do this is to conduct experimental exposures, however, the legal and logistical approvals for such experiments would be formidable. The question of whether the contaminants in the animals have effects on the animals cannot be ignored, however, and so examination of the animals will have to continue for the foreseeable future.

REFERENCES

Lockhart, W.L. and R.E.A. Stewart. 1993. Biomarkers and stress effects in arctic marine mammals. Pp. 144-152 *in*: Synopsis of Research Conducted Under the 1992/93 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 70. Indian and Northern Affairs Canada, Ottawa. 285 pp.

White, R.D., M.E. Hahn and W.L. Lockhart. 1994. Catalytic and immunochemical characterization of hepatic microsomal cytochrome P450 in beluga whale (*Delphinapterus leucas*). Toxicol. Appl. Pharmacol. 126: 45-57.

Figure 1. Liver microsomal mixed-function oxygenases and cytochrome P-450 as a function of blubber dieldrin concentrations in Arviat ringed seals.



POTENTIAL FOR EFFECTS ON REPRODUCTION, CARCINOGENESIS, MUTAGENESIS AND TERATOGENESIS IN ARCTIC MAMMALS: STATUS OF BIOMARKERS IN ARCTIC SEALS AND WHALES

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PROJECT TEAM: A. Mathieu, S. Ray and L. Fancey, Fisheries and Oceans Canada; R. Santella, Columbia University (contractor); A. Rahimtula and W. Davidson, Memorial University (contractors)

OBJECTIVES

1. To determine if the levels of contaminants in the Arctic are sufficiently high to engender concerns about reproductive failure and carcinogenesis, mutagenesis, and teratogenesis in marine mammals - the species at highest risk.

2. To assess the present situation and provide a baseline on the critical biological indices that will be of paramount importance for a monitoring/assessment strategy for the Arctic.

DESCRIPTION

Sublethal stressors can elicit physiological, immunological and pathological changes in vertebrates - changes which can lead to cancer, impairment of growth and reproductive functions. Responses to stressors are preceded by changes at the biochemical/molecular level and such changes can be used as either biomarkers or early warning indicators of impending problems. Alternatively some biomarkers are bona fide pathological responses.

Is there a cause for concern for contaminant mediated diseases in arctic animals, such as marine mammals which bioaccumulate inordinate amounts of persistent organochlorines? Investigations have revealed a dramatic decrease in reproductive capacity in ring, grey and harbour seals in the Baltic (Helle and Stenman 1991). Also, recent studies have demonstrated a high frequency of cancer and other pathological changes in beluga whales from the Gulf of St. Lawrence (Martineau *et al.* 1988).

It is proposed to investigate the status of three important markers of biological damage in beluga whales, seals and walrus from Arctic and Labrador waters. Where possible, such as for belugas, harbour seals and ringed seals, comparisons will be made in reference to animals from more heavily contaminated areas, namely the Gulf of St. Lawrence and the Baltic and Wadden Seas.

Given the known effects of contaminants on marine mammals from the North and Baltic Seas and the Gulf of St. Lawrence, the biomarkers identified as being important include those for reproduction (e.g. hormone receptor numbers), cancer/mutagenesis (e.g. DNA-adducts, DNA oxidation and ras-oncoproteins) and general pathology (e.g. porphyria).

Reproductive Effect Biomarkers

Steroid receptors

The reproductive effects seen in seals from the North Sea are believed to be caused by the high level of organochlorines in their diet. Basic studies indicate that the molecular basis for reproductive effects may be at the hormone receptor level, which is decreased in animals exposed to organochlorines such as polychlorinated biphenyls (Romkes *et al.* 1987, Korach *et al.* 1988)

Vitamin A

Vitamin A is a critical vitamin for the maintenance of epithelial cells and as such is directly involved in modulating viral and bacterial infections, reproductive disorders, and other pathologies. Exposure of animals to elevated concentrations of chlorinated organics such as PCBs can result in depression of Vitamin A levels. Studies carried out by Dutch scientists suggest that the lethal viral infections and reproductive disorders in seals and other marine mammal populations in the Baltic, North and Wadden Seas are linked to Vitamin A and thyroid hormone imbalances. It is postulated that such imbalances (Brouwer *et al.* 1989) can be affected through consumption of fish having elevated concentrations of chlorinated hydrocarbons.

Cancer/Mutagenesis Biomarkers

Sophisticated techniques are presently available for measuring pollutant mediated DNA damage. DNA damage can occur directly through covalent bonding of contaminants (or contaminant by-products) to selective nucleotides forming so-called DNA adducts. Alternatively, damage can occur indirectly through the formation of powerful oxidizing radicals which degrade nucleotide bases in DNA in a more or less characteristic manner. Organic compounds are primarily involved in DNA adduct formation while both heavy metals and organic compounds can be involved in radical formation.

Both chemical mediated DNA adduction and DNA oxidation are linked with organism carcinogenesis, mutagenesis and teratogenesis. (In this regard it is worth noting that DNA damage is most often emphasized, but a theoretical basis exists for damage to other cellular macromolecules).

Ras-oncoprotein

Many reports have shown that interaction of a variety of chemical carcinogens with DNA can lead to specific mutations resulting in oncogene activation (Zarbl *et al.* 1985). Results obtained with carcinogen-induced tumours and transgenic mice have indicated that ras-oncogenes can participate in the initiation of carcinogenesis (Stowers *et al.* 1987). The overexpression of total proto-oncoproteins such as ras and myc have been implicated in the pathogenesis of a number of neoplastic conditions (Rayter *et al.* 1989).

Porphyria

Porphyrins are building blocks for heme proteins, the most commonly known being oxygen binding hemoglobins, cytochromes and muscle myoglobins. Heme biosynthesis is carefully regulated and levels of porphyrins and their precursors are normally quite low. Disturbances in heme metabolism can lead to the build-up of excessive levels of various porphyrins, a condition clinically defined as porphyria. Porphyria can be hereditary, but is also expressed under various disease conditions or chemical insult. In this regard it is of particular interest that evidence has been obtained for porphyria in some birds in the Great Lakes (Fox *et al.* 1988).

ACTIVITIES IN 1993/94

DNA Adducts

As in 1992/93 considerable effort was directed towards exploring for specific benzo(a)pyrene adducts (released as tetrols and measured by HPLC/fluorometric techniques) in the DNA of beluga from the Arctic and the Gulf of St. Lawrence. Investigators from the Oak Ridge Laboratory have produced evidence for such adducts in beluga from the Gulf of St. Lawrence. We have been unable to find evidence for benzo(a)pyrene adducts in DNA and protein hydrolysates of beluga from either the Arctic or the Gulf. Results employing HPLC/fluorometric techniques being negative, further studies for benzo(a)pyrene adducts were carried out with novel immunochemical techniques (at Columbia University). Preliminary results have been obtained for liver, brain and kidney tissues, but no differences were found for adduct levels in animals from the Gulf of St. Lawrence in comparison with the Arctic.

We previously reported that DNA adduct levels, as measured by the P-32 labelling technique, were also similar in both populations of beluga. During 1993/94 more samples were evaluated with this technique and distinctly higher levels of adducts were found in animals from the Gulf of St. Lawrence (Figure 1a, b). It is not known if the original negative results were due to sample size, but due to the distinct differences observed, we are confident of the 1993/94 results.

Update on Vitamin A and Porphyrins

No further studies were carried out with vitamin A in 1993/94. In 1992/93 we provided evidence that vitamin A status may be an important health effects response to assess in connection with chemical insult in marine mammals.

One of the most interesting observations made in 1992/93 was an apparent elevated level of "total heme" in animals from the Gulf of St. Lawrence. In 1993/94 we determined that this was not due to sample freshness, the animals from the Gulf being dead for longer periods before sample preservation. We postulate that elevated levels of total heme could be an indicator of toxic liver injury.

Exploratory Studies for Other Health Effects Indices - Stress Proteins and the Neurotoxicity Indicator, Acetylcholinesterase

Stress Proteins

Cells from many organisms increase the expression of a class of proteins referred to as heat shock or stress proteins when subject to a wide variety of environmental assaults. Within the past 2-3 years antibodies to these stress proteins have become available commercially in sufficient quantities to permit environmental studies on preserved tissues. Preliminary immunoblotting studies were carried out with various tissues. The HSP70 protein was observed to be present in the brains of whales from both the Gulf and the Arctic, but levels appeared to be similar.

Acetylcholinesterase

The most interesting observation made in 1993/94 was in relation to the neurotoxicity indicator, acetylcholinesterase which was distinctly elevated in the brains of animals from the Gulf (Figure 2a, b). It is postulated that such levels could be due to chronic stress, whereby adrenal glands are releasing elevated levels of epinephrine and stimulating the production of acetylcholinesterase enzymes in brain tissue.

CONCLUSIONS AND FUTURE DIRECTIONS

- In spite of extended studies employing both HPLC/fluorometric and immunochemical techniques, we have been unable to substantiate claims that beluga from the Gulf of St. Lawrence have elevated levels of benzo(a)pyrene related adducts. Accordingly, it seems difficult to implicate benzo(a)pyrene and the aluminum smelting industry (which produces large amounts of benzo(a)pyrene) as the cause of the cancer problem in beluga in the Gulf of St. Lawrence. Given the lack of evidence from the Gulf, it would be even more difficult to implicate sources of benzo(a)pyrene in the Arctic, such as those stemming from arctic haze, to be a significant health risk for beluga.

- Further evidence has been produced indicating that selected biological effects indices have excellent potential for assessing the health of marine mammals. There is a requirement for studies to be carried out on animals from the Arctic to determine if a case can be made for contaminant dose and biological response relationships. This should include studies on "adaptive" type responses, e.g. induction of cytochrome P-450 linked enzymes, as well as studies on more "pathological" type responses, e.g. reduction in levels of vitamin A or steroid hormones. In this regard it is worth noting that the interregional study planned for 1994/95 is going in this direction. The Newfoundland Region will carry out P-32 adduct studies on the "full" complement of tissues from the Arctic. A select number of animals having "low" and "high" levels of contaminants will also be investigated for steroid and vitamin A differences.

REFERENCES

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.

Fox, G.A., S.W. Kennedy, R.J. Norstrom and D.C. Wigfield. 1988. Porphyria in herring gulls: response to chemical contamination of Great Lakes food chains. Environ. Toxicol. Chem. 7: 831-839.

Helle, E. and 0. Stenman. 1991. Present state and future of Baltic seals in the Gulf of Finland. Memoranda Soc. Fauna Flora Fennica 67: 21-25.

Korach, K.S., P. Sarver, K. Chae, J.A. McLachlan and J.D. McKinney. 1987. Estrogen receptorbinding activity of polychlorinated hydroxybiphenyls: conformationally restricted structural probes. Mol. Pharmacol. 33: 120-126.

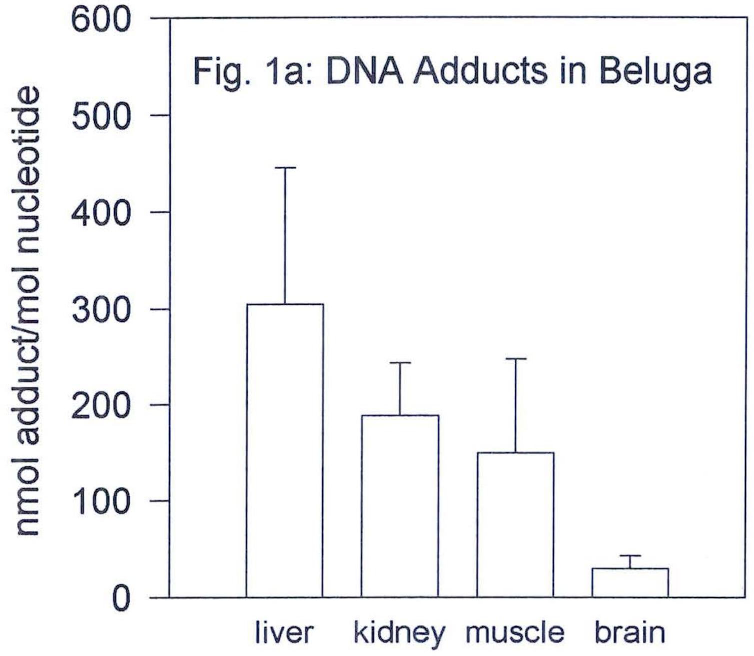
Martineau, D., A. Lagacé, R. Béland, R. Higgins, D. Armstrong and L.R. Shugart. 1988. Pathology of stranded beluga whales *(Delphinapterus leucas)* from the St. Lawrence estuary, Quebec. Canada. J. Comp. Pathol. 98: 287-311.

Rayter, S.I., K.K. Iwata, R.W. Michitsch, J.M. Sorvilla, D.M. Valenzueta and J.G. Foulkes. 1989. Pp. 113-189 *in*: Oncogenes, D.M. Glover and B.D. Hames (eds.). IRL Press, Oxford.

Romkes, M., J. Piskorska-Pliszczynska and S. Safe. 1987. Effects of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin on hepatic and uterine estrogen receptor levels in rats. Toxicol. Appl. Pharmacol. 87: 306-314.

Stowers, S.J., R.R. Maronpot, S.H. Reynolds and M.W. Anderson. 1987. The role of oncogenes in chemical carcinogenesis. Environ. Health Perspect. 75: 81-85.

Zarbl, H., S. Sukumar, A.V. Arthur, D. Martin-Zanca and M. Barbacid. 1985. Direct mutagenesis of Ha-ras-1 oncogenes by N-nitroso-N-methylurea during initiation of mammary carcinogenesis in rats. Nature 315: 382-385.



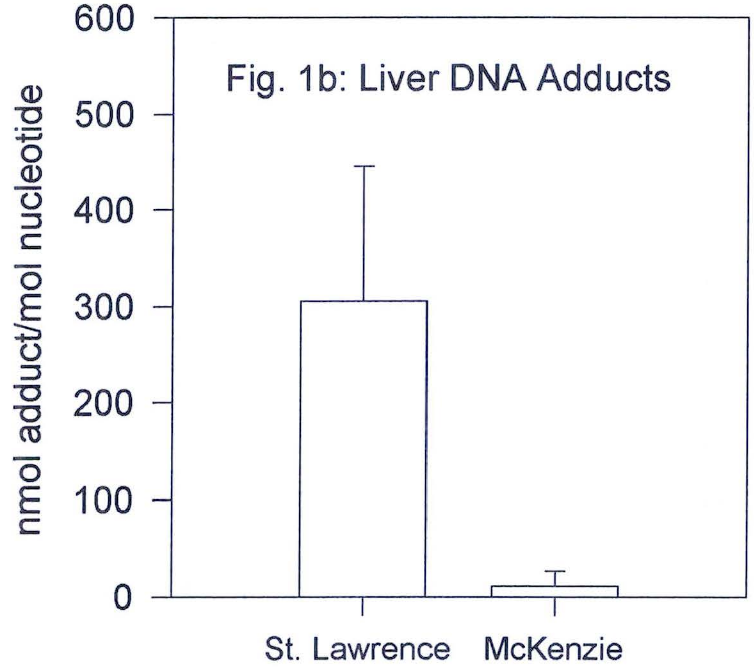
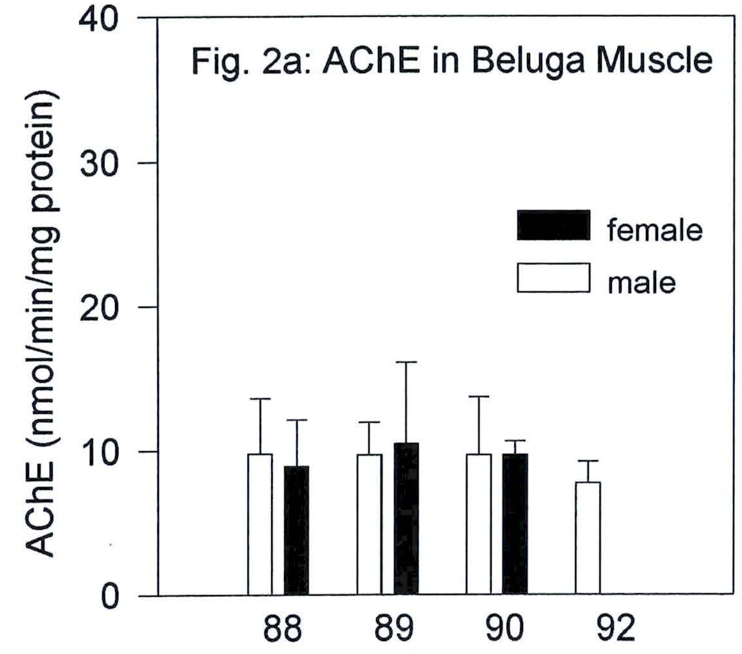


Figure 1a. DNA adducts in beluga from the Gulf of St Lawrence. The number of samples analyzed were as follows: liver, muscle and kidney, n=9; brain, n=11.

Figure 1b. DNA adducts in liver tissues of beluga from the Gulf of St Lawrence (n=9) in comparison with the McKenzie Delta (n=6).



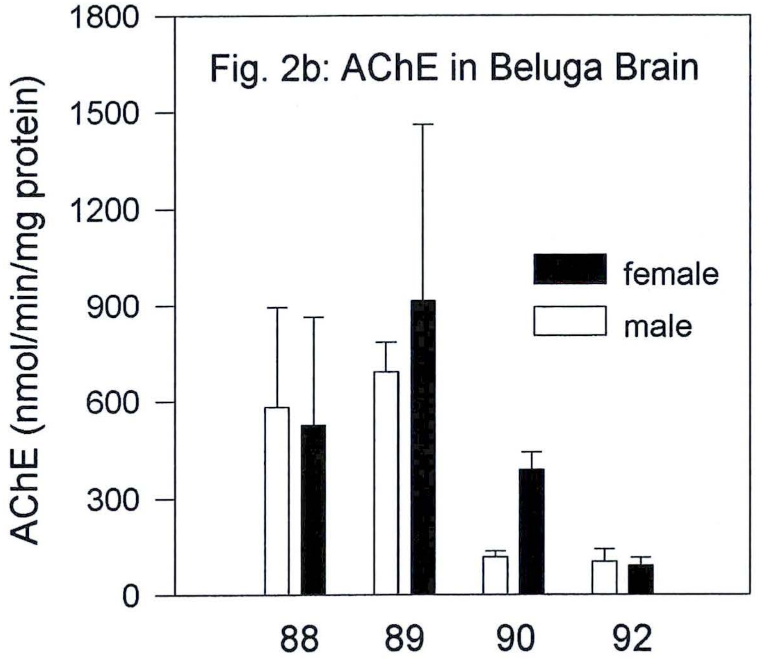


Figure 2a. Acetylcholinesterase (AChE) in muscle tissues of Beluga from the Gulf of St Lawrence (years 88, 89, 90) and the Arctic (year 92). The number of samples analyzed were as follows: 88, 4 males and 7 females; 89, 4 males and 7 females; 90, 5 males and 4 females; and 92, 2 males. Although the number of samples from the Arctic is too small to draw conclusions, the levels of AChE in muscle tissue all appear to be similar.

Figure 2b. Acetylcholinesterase (AChE) in brain tissues of Beluga from the Gulf of St Lawrence (years 88, 89, 90) and the Artic (year 92). The number of samples analyzed were as follows: 88, 3 males and 6 females; 89, 5 males and 4 females; 90, 3 males and 3 females; and 92, 7 males and 2 females. In most cases, AChE levels in animals from the Arctic and the Gulf of St Lawrence were distinctly different.

METALLOTHIONEIN IN ARCTIC MARINE MAMMALS AND FISH

PROGRAM LEADER: R. Wagemann, Freshwater Institute, Fisheries and Oceans Canada, Winnipeg, Manitoba

PROJECT TEAM: R. Wagemann, G. Boila, D. Savoie (contractor), L.W. Lockhart

OBJECTIVES

1. To determine the natural ranges of metallothionein in tissues of marine mammals from the Canadian Arctic.

2. To determine the sub-cellular distribution of metals (Cd, Cu, Zn. Hg) in Arctic marine mammals.

3. To determine the influence of age of animals on metallothionein, and the relationship between metal concentration in tissues and metallothionein.

DESCRIPTION

The most frequent type of measurement made for toxic metals (Hg, Cd, Pb) in tissues is the total concentration of the metal (Wagemann *et al.* 1988). However, metals exist in tissues in different forms (chemical species) which have different toxicities. Mercury, for example, can be present as inorganic mercury and as methylmercury, the latter being much more toxic than inorganic mercury. The total metal concentration alone in a tissue is therefore not a good measure of the potential toxicity of the metal. Similarly, cadmium can be present in tissues in different forms by association with different proteins in the cytosol. The different protein-cadmium compounds have different toxicities. The cadmium associated with a low-molecular weight protein called "metallothionein" is much less toxic to organisms than the cadmium associated with higher-molecular weight proteins. Induction of metallothionein is a protective cellular response to some metals, specifically to cadmium; when this protective capacity is exceeded toxicity occurs. Measurements of cadmium in tissues of wild animals have, to date, been made largely only as total cadmium. As in the case of mercury, the total cadmium concentration alone is not a good measure of its toxicity to organisms. The measurement of metallothionein in conjunction with total cadmium is a much better toxicity indicator than total cadmium alone, and the additional measurement of the fraction of cadmium associated with high-molecular weight proteins is a further requirement for a better estimation of the in-tissue toxicity of cadmium. Metallothionein (MT) is a low-molecular weight, ubiquitous, protein that occurs naturally at background levels in most organisms. It responds integratively to stressors including cadmium, and can be measured polarographically, and by radio-isotope and immunoassay techniques. The aim of this project is to provide information on background concentration ranges of metallothionein in marine mammal tissues, to determine the influence of variables such as age on metallothionein levels in tissues, and to determine the fraction of cadmium associated with high-molecular weight proteins in liver and kidney cytosol. Narwhal in particular have some of the highest cadmium concentrations in liver and kidney of marine mammals. We intend to measure metallothionein in tissues of narwhal and other marine mammals to determine background concentrations, and to establish whether or not the relatively high cadmium burdens carried by some animals are largely in the form of metallothionein and therefore relatively non-toxic.

ACTIVITIES IN 1993/94

Samples

Liver tissue samples from 26 narwhal from three locations (9 from Pond Inlet, 7 from Repulse Bay, 10 from Iqaluit) were used in this project. Procurement of the appropriate hard tissue (tusk) for age determination remains a problem because it is notoriously difficult to age these animals. Ages have therefore not been determined. Tissue samples of narwhal from the 1993 hunt at Pond Inlet were lost in transit from the Arctic to the Freshwater Institute, and previously collected tissue samples from this location were therefore used in this study. Tissue samples of narwhal from the vicinity of Pond Inlet will be obtained from the 1994 hunt for further, more detailed analysis and fractionation.

Methods

Narwhal liver tissue was homogenized in 0.9 % saline solution (containing 5 mM dithiothreitol), centrifuged (100,000 g, 1 h), and the pellet and supernatant (cytosol) and original homogenate were analyzed for total cadmium, mercury, zinc and copper. The cytosol was further fractionated to separate high-molecular weight proteins from metallothionein by heating for 5 min at 95° C and then centrifuging for 20 min at 16,650×g. This supernatant was analyzed for metallothionein by differential pulsed polarography and total metals by direct-current plasma emission spectrometry, flame AA, or Zeeman graphite furnace AA, depending on concentration. Some cytosols were fractionated by gel permeation chromatography to separate high and low molecular weight proteins and these fractions were also analyzed for metals.

Quality Assurance

Purified rabbit liver metallothionein (Sigma Chemical Co.) was used as a reference material for metallothionein determinations. Metallothionein was also measured by the ^{203}Hg saturation method using the same reference material. Certified reference materials (Bovine Liver, NBS; DOLT-1, NRC; DORM-1, NRC) were used to check the accuracy of total metal determinations. High-purity reagents were used. Water for working standards and reagents was triply distilled in a quartz still, and reagent-grade acids were re-distilled in a Teflon still. A previous paper has dealt with the comparative methodology (Wagemann *et al.* 1993).

RESULTS

In a previous report (Wagemann 1992) background concentrations of metallothionein in the liver of harp seals were reported. This report deals with metallothionein in narwhal. Concentrations of metallothionein and metals in liver cytosol of narwhal from three different locations in the eastern Arctic, Pond Inlet, Repulse Bay and Iqaluit were determined. The mean metallothionein concentrations in the liver of narwhal from two of these groups (Resolute Bay, Iqaluit) were similar, 418 and 394 $\mu g/g$, respectively and considered to be normal (Table 1). The metallothionein mean for the two groups combined was 404 $\mu g/g$, and the individual concentrations were all within 1 standard deviation (± 264 $\mu g/g$) of the mean except for one individual from Repulse Bay (Figure 1). However, the mean for the Pond Inlet group was significantly higher, 1021 $\mu g/g$, and the individual values ranged widely and mostly exceeded the upper 1 SD limit of the mean.

Table 1. Mean±1 SD, metallothionein, $\mu g/g$, number of animals, and concentration range in liver of narwhal from three sites (Repulse Bay, Iqaluit, Pond Inlet) in the Arctic.

	Repulse Bay	Iqaluit	Pond Inlet
Mean±SD	418±396	394±140	1021±681
n	7	10	9
Range	164-1295	200-777	154-2314

Some narwhal from Pond Inlet had high metallothionein concentrations in the liver (Figure 1), but these individuals did not necessarily also have the highest concentration of cadmium in liver tissue as a whole or in the cytosol (Figure 1), nor higher than normal liver cytosolic zinc or copper concentrations. The individual from Pond Inlet with the highest metallothionein concentration (2314 $\mu g/g$) (Figure 1), did have a correspondingly high cadmium concentration which was the likely inductor of the high metallothionein concentration in this individual. However, most individuals in the Pond Inlet group and one individual from the Repulse Bay group, although they had relatively high metallothionein concentrations in the liver, did not have abnormally high cadmium, zinc or copper concentrations in the liver cytosol, and vectors other than metals may have been operating in these individuals, possibly disease or other contaminants, to induce these relatively high metallothionein concentrations. However, tissues were not examined histologically for evidence of disease.

The intention was to fractionate liver cytosol from animals in the Pond Inlet area that had a relatively high metallothionein concentration in their tissues but also from animals with normal metallothionein concentrations (from Iqaluit) as a basis for comparison. However, funding for this project was received only late in the year (December 1993), curtailing significantly the available time for more detailed work. One individual of the Iqaluit group (animal # 22) with relatively normal concentrations of metals and metallothionein in liver was chosen initially for more detailed analysis to determine the distribution of cadmium between high and low molecular weight proteins. Liver cytosol was fractionated by high performance liquid chromatography (HPLC) and the individual fractions were analyzed for metallothionein and cadmium (Figure 2) (also copper and zinc, not shown). No significant amount of cadmium was found associated with proteins other than metallothionein in this individual (Figure 2) and therefore the cadmium was considered be relatively nontoxic to this animal. Time did not permit to subject tissues from other animals, particularly those with abnormally high concentrations of metallothionein (Pond Inlet) to a similar analysis, and nothing can be said about the relative toxicity of cadmium in the tissues of these animals. Continued research would include more detailed analysis of tissues from individuals with high cadmium concentrations to determine if any cadmium is associated with higher molecular weight proteins.

CONCLUSIONS AND UTILIZATION OF RESULTS

The normal metallothionein background concentration range in the liver of narwhal was 150-650 μg/g, with an approximate mean of 400 μg/g. The metallothionein concentration in the liver of Pond Inlet narwhal, with a mean of 1021 μg/g, was considerably higher, but cadmium and other metals in the liver were not sufficiently high in these animals, except in one individual, to have induced these relatively high metallothionein concentrations. It is possible that other inductors, such as disease or organochlorine contaminants were present in these individuals and were responsible for these high metallothionein values. However, the number of animals from Pond Inlet, and other locations, was relatively small. It is therefore possible that the sampled individuals represent an abberation in terms of their metallothionein concentration, especially those from Pond Inlet, and do not represent the levels in the larger population. A larger sample of animals should therefore be investigated.

The sub-cellular distribution of metals in liver tissue was determined for one narwhal (Iqaluit) having a normal metallothionein concentration in the liver. Essentially all the cadmium in the liver of this individual was associated with metallothionein, an indication that it was all present in a relatively nontoxic form in this individual. Similar analyses on tissues from individuals at Pond Inlet with higher metallothionein concentrations were not carried out due to time constraints. It is recommended that such analyses be carried out in the future on narwhal and beluga that have higher concentrations of cadmium and other toxic metals to see whether or not some of the cadmium "spills over" to higher molecular weight proteins thereby posing a greater danger to the animals. These results would have implications for the assessment of the toxicity of cadmium to animals, and would provide a better assessment of toxicity than do total metal concentrations alone. Contractual arrangements have been made to obtain samples of narwhal and other marine mammals in 1994.

Expected project completion date: March 31, 1996

CLIENTS/PARTNERS: Indian and Northern Affairs Canada; Fisheries and Oceans Canada; Health Canada, Native Hunters and Trappers Associations; Makivik Research Corp., Kuujjuak, Quebec; Inuit of N.W.T. A private laboratory (Methodologies Consultations Limited, Gloucester, Ontario) was involved in the methods assessment work.

REFERENCES

Wagemann, R. 1992. Metallothionein in Arctic marine mammals and fish. Pp. 91-101 *in*: Synopsis of Research Conducted Under the 1991/92 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 68. Indian and Northern Affairs Canada, Ottawa. 213 pp.

Wagemann, R., R.E.A. Stewart, W.L. Lockhart, and B.E. Stewart. 1988. Trace metals and methyl mercury: associations and transfer in harp seal (*Phoca groenlandica*) mothers and their pups. Mar. Mam. Sci. 4: 339-355.

Wagemann, R., J.G. Dick, and J.F.K. Klaverkamp. 1993. Metallothionein estimates in marine mammal and fish tissues by three methods: ^{203}Hg displacement, polarography and metal-summation. Intern. J. Environ. Anal. Chem. (in press).

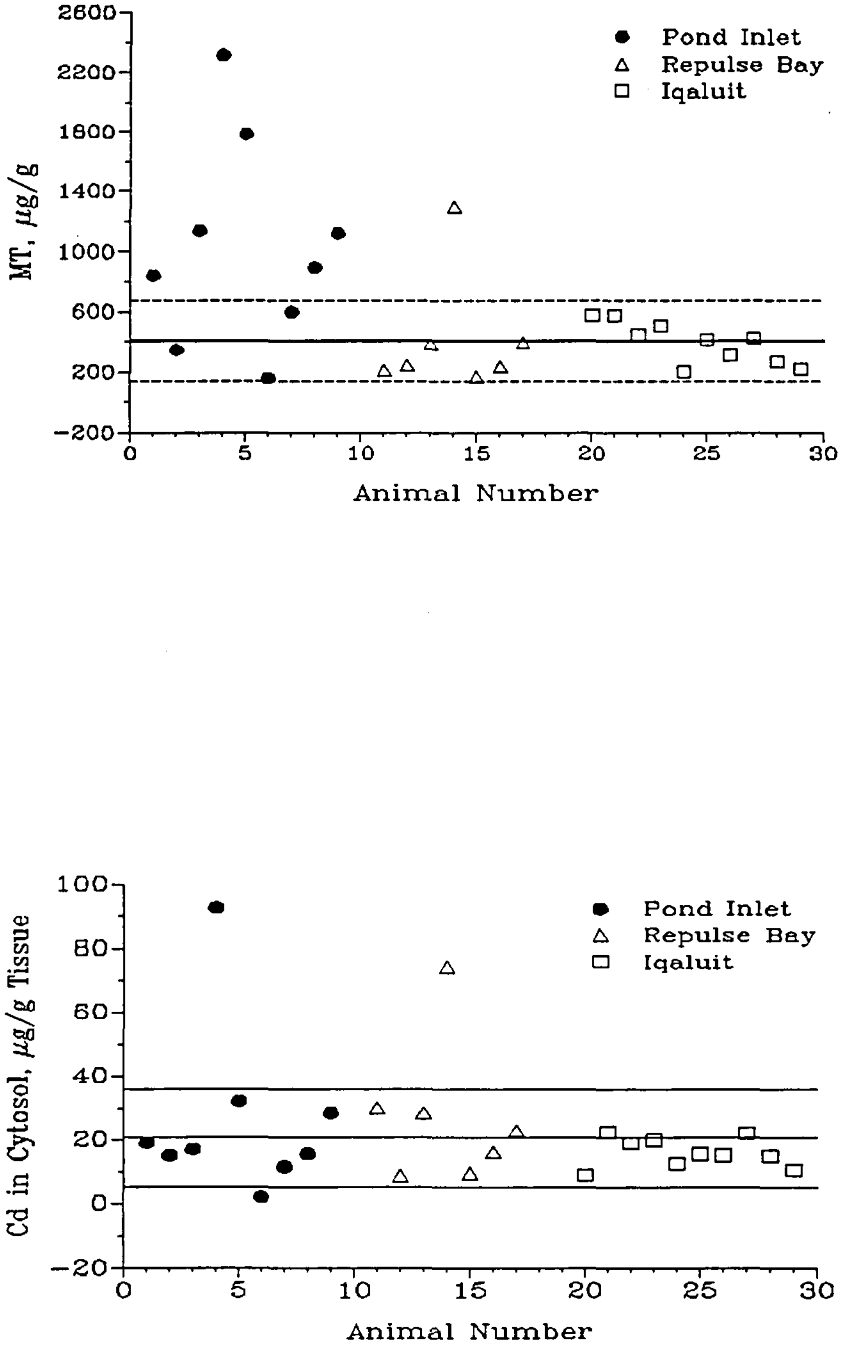


Figure 1. Concentrations of metallothionein (MT) and cadmium (Cd) in the cytosol of narwhal liver from Pond Inlet, Repulse Bay and Iqaluit. Data from the latter two sites only were used to calculate the mean ± SD.

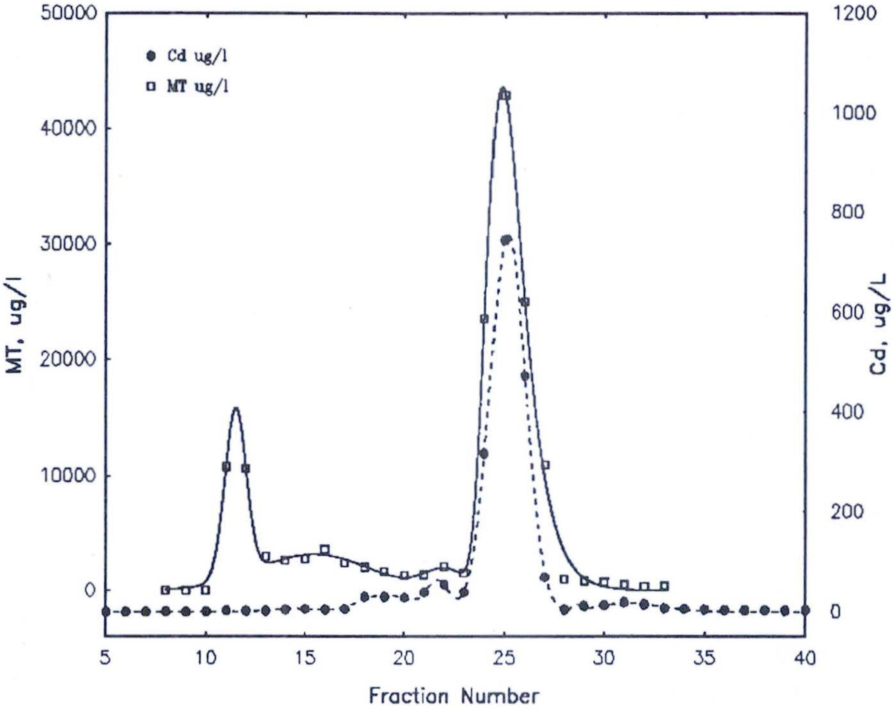


Figure 2. Metallothionein (MT) and cadmium (Cd) concentrations in HPLC fractions of narwhal liver cytosol. The large peak is the MT peak, and the smaller peak is a sulfhydryl peak associated with higher molecular weight proteins.

CONTAMINANT TRENDS IN FRESHWATER AND MARINE FISH

PROGRAM LEADERS: D. Muir and W.L. Lockhart, Freshwater Institute, Fisheries and Oceans Canada (DFO), Winnipeg, Manitoba

PROJECT TEAM: D. Muir, B. Grift, D. Metner, B. Billeck, L. Lockhart, B. Rosenberg, S. Mohammed, R. Hunt

OBJECTIVES

1. To determine temporal and spatial trends in PCBs, organochlorines, PAHs and heavy metals in fish from lakes and rivers in the Northwest Territories and northern Quebec.

2. To provide information on contaminants to evaluate current risks of exposure to PCBs, PAH and chlorophenols via fish consumption.

DESCRIPTION

Reviews of contaminant data in freshwater fish from arctic and subarctic Canada available to 1991 (Muir *et al.* 1990, Lockhart *et al.* 1992) indicated that information on the levels and geographic variation of PCBs and related organochlorines (OCs), polyaromatic hydrocarbons (PAHs) and heavy metals was limited while data on temporal trends is nonexistent. The initial objectives of the project were therefore to: (1) determine levels of organics and metals in fishes from a broad range of remote lakes in northern Quebec and the NWT, (2) revisit locations first monitored in 1970 by Reinke *et al.* (1972) and Riseborough and Berger (1971), in order to examine the general temporal trends in DDT, dieldrin and PCBs, and (3) investigate the presence of additional contaminants not reported in the early work. Most of the emphasis has been placed on organochlorine chemicals such as PCBs and toxaphene as well as mercury (Hg), rather than on PAHs, because the OCs and Hg are known to biomagnify in aquatic food chains. The main focus of the study is on piscivorous fishes such as burbot, lake trout and arctic char, because of their importance in the traditional subsistence fishery and because of interest in biomagnification in top predators. But there has also been a need to examine contamination of fishes feeding at lower trophic levels, such as whitefish, which are also of dietary importance to native people in the NWT, the Yukon and N. Quebec. The long term objective is to provide a baseline for contaminant levels at a level of detail sufficient to give northern residents useful information on contaminant levels in major species and in a wide range of lakes.

ACTIVITIES IN 1993/94

Samples

Fish samples were collected by DFO personnel from Winnipeg (D. Metner, J. Reist, J. Johnson) or Yellowknife (A. Wilson) from locations in the western NWT. Samples of broad whitefish (*Coregonus nasus)* were obtained from the Ob River in Russia by J. Reist (DFO). Samples of char from Sanikiluaq were obtained from M. Hermanson (Academy of Natural Sciences, Philadelphia, PA). Species were the same as those from previous years, broad whitefish, land-locked char (*Salvelinus alpinus*), burbot (*Lota lota*) and lake trout (*Salvelinus namaycush*). Also analysed were Arctic cod (*Boreogadus saida*) at Resolute (collected by H. Welch, DFO) and marine clams (*Mytillus* sp) from southeast Hudson Bay (collected by L. Lockhart). Sampling locations are given in Table 1. Samples of dorsal muscle + skin were analysed with the exception of burbot, for which liver was analysed. Sex, weight and age (by using ootoliths) were determined for all samples except Arctic cod and clams. Generally equal numbers of male and female samples were analysed and samples were selected to give 3 to 6 specimens from similar age classes for each species.

Analysis

Samples of whole fish or muscle were analysed for organochlorines (PCB congeners and other organochlorine contaminants (toxaphene, PCCs), chlordane (CHLOR), and the DDT group). A total of 130 individual OC compounds were determined. A complete list of OC analytes was given in our 1993 report on OCs in marine mammals (Muir and Lockhart 1993). Methods of extraction and GC analysis were identical to those described by Muir *et al.* (1990). In brief: Muscle/skin samples were homogenized by grinding with dry ice. The homogenate (20 g) was Soxhlet extracted with hexane:dichloromethane (1:1). Liver samples were mixed with sodium sulfate and ballmilled with hexane. Internal standards of PCB 30 and octachloronaphthalene (OCN) were added at the extraction step. Lipid was removed by automated gel permeation chromatography. Extracts were then chromatographed on a Florisil column to separate PCBs, *p,p'*-DDE and trans-nonachlor (hexane eluate) from most chlorinated bornanes (toxaphene), chlordanes and DDT-related compounds. Florisil eluates were then analysed by capillary gas chromatography with electron capture detection using a 60 m x 0.25 mm (id) DB-5 column with H_2 carrier gas. Confirmation of PCBs was carried out by GC-mass spectrometry using a HP5971MSD while chlorinated bornanes were confirmed by electron-capture negative ion mass spectrometry.

Heavy metals (Hg, Cd, Pb, As) were determined in fish muscle by atomic absorption (AA) spectrophotometry (Vijan and Wood 1974, Hendzel and Jamieson 1976). Hg was determined by hot block digestion followed by cold vapour AA. Cu, Zn were determined by air-acetylene flame atomic absorption (Varian SpectrAA-20) with deuterium background correction, after nitric acid digestion. Cd and Pb were determined by Zeeman background corrected graphite furnace AA spectrophoto (Hitachi model Z8200) after sulfuric acid digestion.

Quality assurance

Recovery of internal standards was checked in each sample and samples with low recoveries (generally <60%) were reextracted. Blank samples were run approximately every 10 samples to check contamination of reagents and glassware. During 1993 the laboratory participated in the intercomparison on PCB congeners for the Northern Contaminants Program, the toxaphene round robin using a certified cod liver oil (P. Andrews, Health Canada), a check sample program for the analysis of OC pesticides and PCBs (Atmospheric Environment Service, Downsview), and an ICES (International Council for Exploration of the Sea) interlab comparison of PCBs in fish and seal oil.

RESULTS

Fishes from 9 locations in NWT and from the Ob River (Russia) were analysed during 1993/94 for a suite of about 130 individual organochlorines (OCs) (90 PCB congeners, 4 chlorobenzenes, 36 organochlorine pesticides). In addition, five heavy metals were determined in fish muscle from three lakes, and mercury (Hg) was determined in fish from an additional seven lakes.

As has been observed previously, toxaphene was the major OC contaminant in all fish except whitefish from the Ob River (Table 1). Toxaphene/ΣPCB ratios ranged from 1.1 (Colville Lake lake trout) to 8.6 (Peter Lake lake trout). The laboratory participated in the first toxaphene round robin comparison organized by P. Andrews (Health Canada) and obtained results similar to other labs using GC-ECD or GC-MS (negative chemical ionization).

PCBs (sum of 89 congeners) were generally present at 1.5 to 2-fold higher levels than DDT- or chlordane-related compounds. Hexachlorocyclohexanes (sum of α, β and γ-HCH isomers) and chlorobenzenes were present at much lower concentrations than the four major organochlorines.

The wide variation in toxaphene and PCBs in *Salvelinus* species in NWT lakes is illustrated in Figure 1 using vertical bars to represent concentrations. Results include samples analysed in previous years (Muir and Lockhart 1993). Concentrations in Figure 1 are reported on a lipid weight basis to eliminate the effect of different fat content of samples from different locations. Even in lakes of similar size at similar latitude (Peter, Belot and Colville) there were large differences in concentrations of toxaphene and to a lesser extent of PCBs. These differences are probably due to the trophic position of the lake trout. Analyses of muscle nitrogen isotope ratios in lake trout from Peter Lake have shown that they occupy a higher trophic level (as defined by their nitrogen isotope ratios) than those fish from Yukon Lakes (except Lake Laberge) (K. Kidd, University of Alberta, unpublished data). The nitrogen isotope ratios of lake trout from Belot and Colville Lakes have not been determined but stomach contents of the fish we analysed suggest they are mainly insectivorous.

The lowest concentrations of organochlorines among the samples analysed during 1993/94 were in marine clams (*Septentrion* sp.) from Manitounik Sound on the east cost of Hudson Bay. Arctic cod from Resolute also had low concentrations of organochlorines, relative to arctic char (Table 1).

High Hg levels (ranging from 0.26 to 1.85 μg/g fresh wt) were found in muscle of lake trout from Peter Lake (Table 2). These were large, older trout (weight range 1.56 - 13 kg) thus the higher levels were anticipated based on their trophic position. Further samples of lake trout and char from Peter Lake need to be analysed to get a more representative picture of the contaminant burdens in these fishes. A survey of Hg levels in arctic char from lakes on Cornwallis Island was carried out following our observation of high Hg in char from Amituk Lake (Muir and Lockhart 1993). Mean concentrations in char muscle from 5 lakes exceeded the Health Canada guideline of 0.2 μg/g for subsistence fisheries but were well below the 0.5 μg/g level (Table 2).

CONCLUSIONS AND UTILIZATION OF RESULTS

The results further confirm the remarkable lake to lake variation of organochlorines and metals in Arctic lakes. The results from this study, especially from work by Kidd and Schindler (this volume) in the Yukon are confirming that the trophic position of fish influences levels of organochlorines in fish. Further analyses are required to sort out the influence of these variables on organochlorine levels in remote Arctic lakes. In addition to the results reported here, the laboratory collaborated with the project of M. Evans (National Hydrology Research Institute, Saskatoon) on the analysis of 40 fish from Great Slave Lake. High priority for 1994/95 is the collection of additional samples of both lake trout and char from Peter Lake. A trip to the lake was organized for July 1994 in cooperation with R. Tallman (DFO Winnipeg). Further sample collections are planned for other major lakes in NWT in cooperation with DFO Fish Inspection, including Baker Lake and Great Slave Lake. Additional work will be done in the Mackenzie Delta area in cooperation with Fisheries Joint Management Committee. Char and lake trout from lakes in the delta and from Banks Island, obtained from J. Reist (DFO) Winnipeg) will also be analysed. Arctic char muscle samples received from T. Savinova (Murmansk Marine Biology Institute) will also be analysed for organochlorines and metals if time permits.

Expected project completion date: March 31, 1997

PARTNERS

DFO Fish Inspection (M. Hendzel), J. Reist, DFO (Winnipeg), A. Wilson (DFO Yellowknife), B. Ferguson (DFO Inuvik), Fisheries Joint Management (Inuvik), B. Carpenter (Metis Nation, Yellowknife).

REFERENCES

Hendzel, M.R. and D.M. Jamieson. 1976. Determination of mercury in fish. Anal. Chem. 48: 926-928.

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: 165-245.

Muir, D.C.G., C.A. Ford, N.P. Grift, D.A. Metner and W.L. Lockhart. 1990. Geographic variation of chlorinated hydrocarbons in burbot (*Lota lota*) from remote lakes and rivers in Canada. Arch. Environ. Contam. Toxicol. 19: 530-542.

Muir, D.C.G. and W.L. Lockhart. 1993. Contaminant trends in freshwater biota. Pp. 167-173 *in*: Synopsis of Research Conducted Under the 1992/93 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 70. Indian and Northern Affairs Canada, Ottawa. 285 pp.

Rasmussen, J.B., D.J. Rowan, D.R.S. Lean and J.H. Carey. 1990. Food chain structure in Ontario lakes determines PCB levels in lake trout (*Salvelinus namaycush*) and other pelagic fish. Can. J. Fish. Aquat. Sci. 47: 2030-2038.

Reinke, J., J.F. Uthe and D. Jamieson. 1972. Organochlorine pesticide residues in commercially caught fish in Canada - 1970. Pestic. Monit. J. 6: 43-49.

Riseborough, R.W. and D.D. Berger. 1971. Evidence for aerial fallout of polychlorinated biphenyls (PCB) in the eastern Canadian Arctic. Contract report CWS 7071-052. Canadian Wildlife Service, Ottawa.

Vijan, P.N. and G.R. Wood. 1974. An automated submicrogram determination of arsenic in atmospheric particulate matter by flameless atomic absorption spectrophotometry. A.A. Newsletter 13: 33-37.

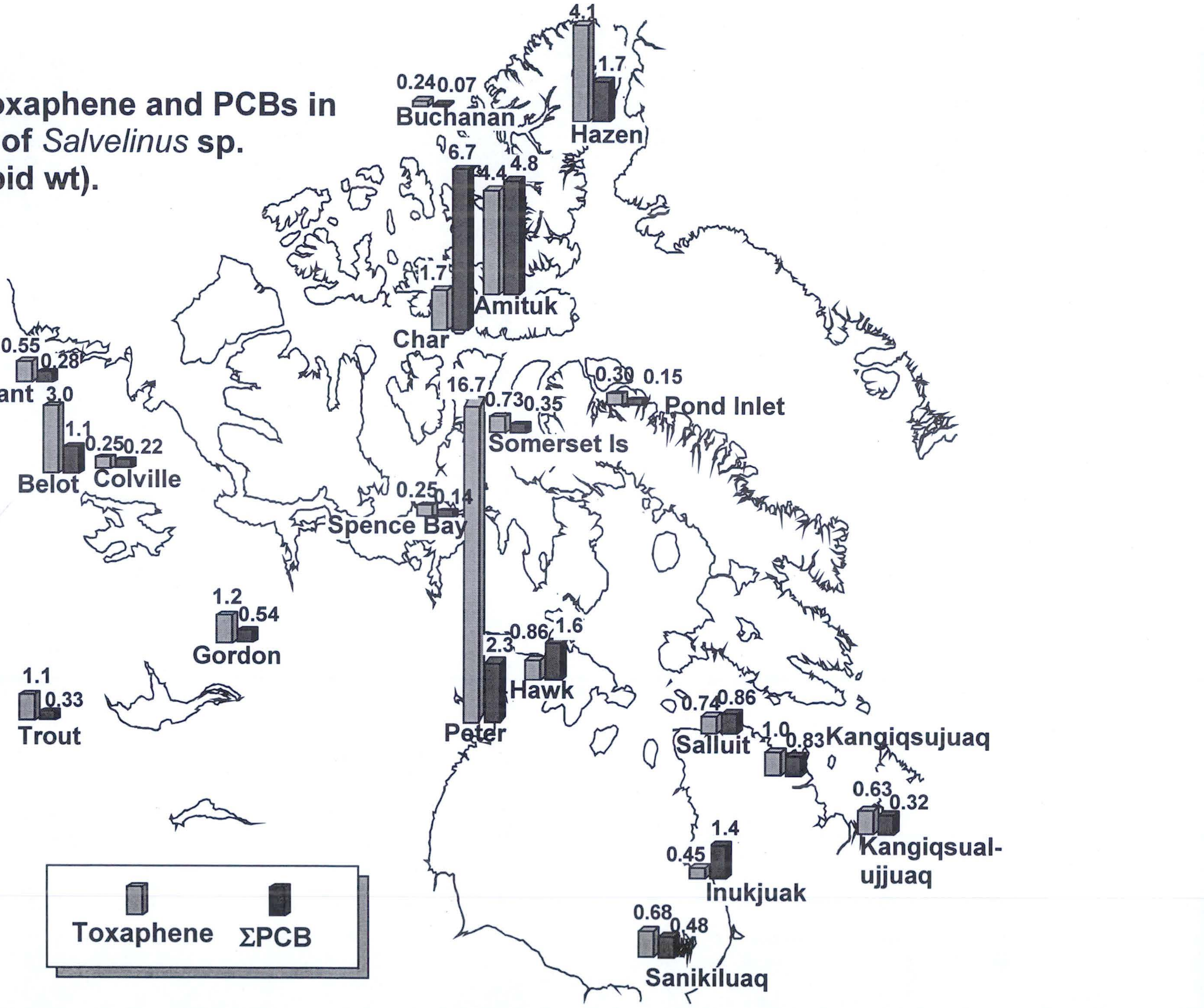
Table 1. Organochlorines (ng/g wet weight) in fish analysed during 1993/94.

Lake	Species	Tissue		N	% lipid	ΣHCH	ΣCHLOR	ΣDDT	ΣPCB	Toxaphene	Tox/PCB
Alexie Lake	burbot	liver	Mean	5	26.3	4.89	14.7	13.6	26.9	40.5	1.5
			SD		12.9	1.62	5.88	7.88	18.0	26.6	
Great Slave Lake	burbot	liver	Mean	7	28.2	7.18	39.6	51.7	103.0	286.7	2.8
			SD		7.2	3.71	20.8	43.0	65.9	134.2	
Peter Lake	Lake trout	muscle	Mean	5	9.3	5.82	145.2	186.7	231.9	1993	8.6
			SD		7.0	7.08	180.2	241.8	289.7	1952	
Ob River (Russia)	Whitefish	muscle	Mean	11	1.5	1.52	1.85	3.74	5.66	3.66	0.6
			SD		0.5	0.62	0.78	1.44	0.93	1.49	
Lake Belot	Lake trout	muscle	Mean	9	4.9	3.76	20.8	24.2	52.4	138.5	2.6
			SD		3.2	1.34	6.12	12.8	36.1	81.8	
Colville Lake	Lake trout	muscle	Mean	7	5.2	0.89	3.27	3.13	10.5	11.9	1.1
			SD		2.6	0.54	1.91	2.13	9.02	7.13	
Colville Lake	Whitefish	muscle	Mean	9	2.6	1.05	1.85	1.71	4.44	11.0	2.5
			SD		0.8	0.71	0.83	1.39	2.10	13.4	
Resolute	Arctic cod	whole	Mean	3	7.3	3.34	5.90	6.53	6.2	39.0	6.3
			SD		0.5	0.58	2.20	2.19	1.5	13.8	
Horseshoe Bend (Mackenzie R. near Inuvik)	Whitefish	muscle	Mean	9	3.1	0.18	1.02	0.15	0.82	3.21	3.9
			SD		0.9	0.11	0.60	0.11	0.42	1.62	
Travalliant Lake	Lake trout	muscle	Mean	6	3.1	1.15	4.25	2.03	8.8	17.1	1.9
			SD		0.9	0.54	1.78	0.95	3.70	7.16	
Sanikiluaq	char	muscle	Mean	8	4.9	2.06	7.79	7.62	23.6	33.7	1.4
			SD		3.2	0.88	4.39	4.39	17.0	29.3	
Manitounik Sound	mussels	whole	pool	9	1.9	0.30	0.24	0.25	2.55	2.99	1.2

Table 2. Mean concentrations of metals in muscle of freshwater fish (ng/g or μg/g wet weight) analysed during 1993/94.

Source	Region	Species	n	Cd ng/g	Cu μg/g	Zn μg/g	Hg μg/g	Se μg/g
Colville Lake	NW NWT	Lake trout	11	0.92	1.21	3.08	0.28	0.17
		Lake whitefish	23	0.96	1.07	3.07	0.02	0.14
Lac Belot	NW NWT	Lake trout	23	1.31	1.43	3.07	0.13	0.10
Hawk Lake	W. Hudson Bay	Lake trout	9	-	-	-	0.24	0.27
Peter Lake	W. Hudson Bay	Lake trout	5	-	-	-	1.04	-
Char Lake	Cornwallis Is.	Arctic char	7	-	-	-	0.26	-
NN Lake	Cornwallis Is.	Arctic char	3	-	-	-	0.26	-
Resolute Lake	Cornwallis Is.	Arctic char	7	-	-	-	0.2	-
Small Lake	Cornwallis Is.	Arctic char	2	-	-	-	0.05	-
Victory Lake	Cornwallis Is.	Arctic char	1	-	-	-	0.42	-

Fig. 1. Toxaphene and PCBs in muscle of *Salvelinus* sp. (µg/g lipid wt).



SOURCES, PATHWAYS AND LEVELS OF CONTAMINANTS IN FISH FROM YUKON WATERS

PROJECT LEADER: Yukon Technical Committee on Contaminants in Northern Ecosystems and Native Diets (Contact: M. Palmer, Chair)

PROJECT TEAM: Government of Yukon Fisheries Department; Fisheries and Oceans Canada; Indian and Northern Affairs Canada; Environmental Protection; Council for Yukon Indians

OBJECTIVES

Short-term:

1. To collect information to complement that gathered in the 1991 and 1992 seasons by sampling fish from additional lakes.
2. To collect further fish contaminant data to confirm that information gathered in the 1991 and 1992 seasons address concerns raised by health advisories based on existing data.
3. To determine spatial variability in fish contaminant loadings, and to assess short-term trends.

Long-term:

1. To investigate the sources, processes and rates of contaminant deposition and transport into and within the waters of the Yukon.
2. To determine levels of contaminants for use in long term trend analysis.
3. To develop additional monitoring on levels of organic contaminants within the Yukon.
4. To provide additional information for use in updating health advisories.

DESCRIPTION

Burbot liver and lake trout flesh samples from headwater lakes in the Yukon River system (Tagish, Laberge, etc.) indicated elevated levels of organochlorine pesticides. In response to elevated toxaphene levels, Health Canada issued a public health advisory on Laberge (1991) and Atlin (1992) Lakes. The advisory recommended that consumption of lake trout flesh be limited on Lake Laberge and that burbot livers not be consumed on Lake Laberge and only limited consumption on Atlin Lake. This has affected the various fisheries on the lakes, and generated considerable concern from residents who used the fisheries resources throughout the Yukon.

As a result of the increased concern over elevated contaminant levels, the monitoring program has expanded to meet the concerns of northeners. Additional lakes are being added to the monitoring program in an attempt to put confidence back in country foods. The program has also been expanded to include new species such as salmon and grayling and will also examine levels in the different body parts consumed.

ACTIVITIES IN 1993/94

The 1993/94 sampling program was dominated by requests from First Nations concerned over the safety of their country foods. The sampling program also focused on filling in data gaps, especially in the area of burbot livers. Listed below are the key components of this year's sampling program:

- Lake trout and whitefish samples were collected from Bennet Lake. The intent was to examine the varying levels of contaminants in body parts consumed. The body parts analyzed were muscle, eggs, stomach walls and liver.
- Burbot were collected from several lakes in an attempt to fill in data gaps. The lakes that were sampled in 1993 were Kusawa, Little Salmon and Wellsly.
- Six large lake trout (larger that 15 pounds) were collected from Atlin Lake. There was some concern that no large fish were sampled from this lake.
- Grayling were collected from three locations as requested by local residents. The locations were Lake Laberge, Bennet Lake and Kusawa Lake.
- Salmon were collected from three locations as requested by local consumers. The locations were Old Crow, Whitehorse and Dalton Post.
- Whitefish, grayling, burbot and inconnu were collected in Old Crow as requested by local consumers.
- Four new lakes were sampled on requests from local consumers. The lakes sampled were Tatlmain, Little Salmon, Dragon and Mayo.

RESULTS

The samples collected in 1993/94 have been sent to Axys Analytical Services Ltd. in British Columbia for analysis. When the results are received and verified they will be sent to Health Canada for a human health hazard assessment.

Figures 1, 2 and 3 summarize the results from the previous two years of sampling.

CONCLUSION AND UTILIZATION OF RESULTS

The results collected during the 1993/94 sampling season will be added to the Yukon fish database. All results will be sent to Health Canada for a human health hazard assessment. The objective is to allow northerners to consume their country foods with confidence.

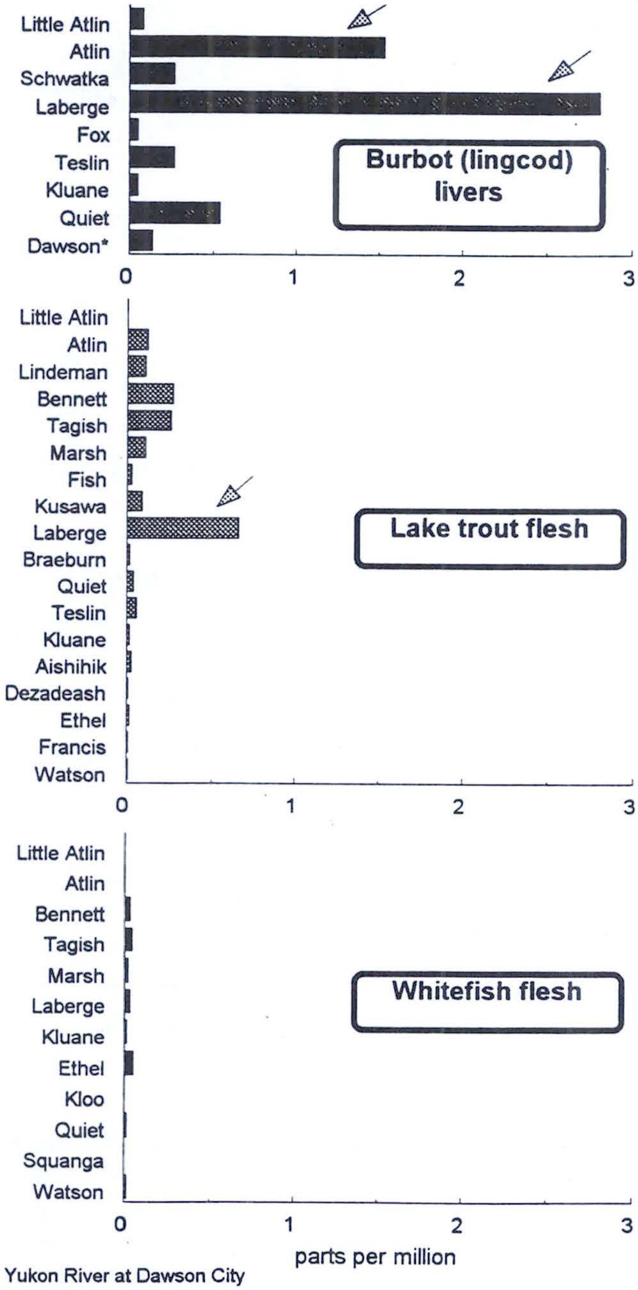
The information will also be used in determining the sources and sinks of a wide range of contaminants in Yukon lakes. All data will be presented at the Contaminants Workshop scheduled to be held in Whitehorse in early 1995.

Expected project completion date: March 31, 1997

Organochlorines in Yukon Fish

All bars represent averages of concentrations of contaminants in wet tissue samples.

Fig. 1
Toxaphene levels in Yukon fish

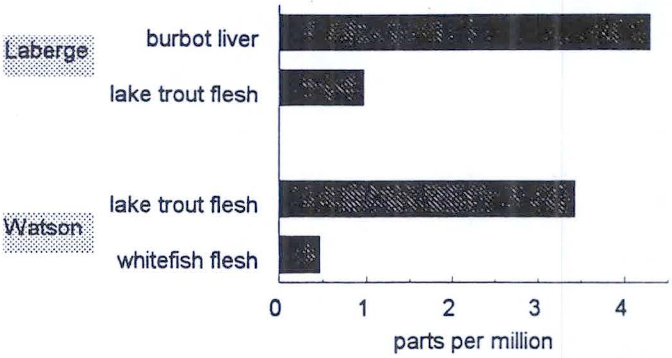


* Yukon River at Dawson City

Toxaphene levels were high enough in the three samples marked with arrows to be considered a possible health concern for people who eat these fish regularly and over a long period. Whitefish samples were all relatively low in toxaphene, as were northern pike samples (not shown). The toxaphene in fish shown in this graph likely enters the Yukon from the atmosphere through rain and snow and directly from the air. Local use of toxaphene was always limited, and no local sources of toxaphene to these lakes have been identified.

Fig. 2
DDT levels in Yukon fish

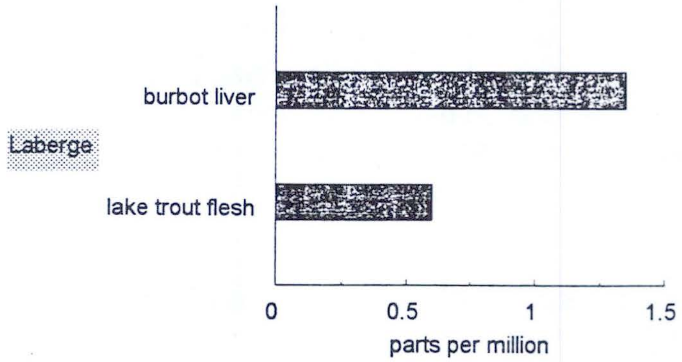
All other fish at all lakes sampled contained very low (< 0.3 ppm) total DDT.



Watson Lake and Lake Laberge had by far the highest levels of DDT in Yukon lakes sampled. DDT at these levels in fish is not considered to be a risk to human health. Higher DDT in fish in these lakes is probably a legacy of DDT spraying for mosquito control from the 1940s to the early 1960s in the Whitehorse and Watson Lake areas. Some DDT still enters Yukon lakes from the atmosphere.

Fig. 3
Total PCB levels in Yukon fish

All other fish at all lakes sampled contained very low (< 0.2 ppm) total PCBs.



Lake Laberge fish had higher levels of PCBs than other Yukon lakes. These levels of PCBs in fish are not considered to be a risk to human health. Sampling of sediment cores from Lake Laberge indicates that a spill of PCB oil may have occurred in the 1950s. PCBs were in common use in the Whitehorse area during that time. Low levels of PCBs continue to enter Yukon lakes from the atmosphere.

FOOD CHAIN ACCUMULATION, BIOLOGICAL EFFECTS AND SEDIMENT CONTAMINATION IN LAKE LABERGE AND OTHER YUKON LAKES

PROGRAM LEADER: D. Muir and W.L. Lockhart, Freshwater Institute, Fisheries and Oceans Canada (DFO), Winnipeg, Manitoba

PROJECT TEAM: D. Muir, L. Lockhart, D. Metner, B. Billeck, P. Wilkinson, R. Danell, B. Grift, C. Ford, B. Rosenberg

OBJECTIVES

1. To measure biochemical stress indicators (e.g. bone hydroxyproline and hepatic mixed function oxidase enzyme activity) and concentrations of organochlorines (PCBs, toxaphene, etc.) in tissues of burbot, lake trout and whitefish of Lake Laberge and other lakes.

2. To determine temporal trends in organochlorines and PAHs via analysis of archived fish and via dated sediment cores.

3. To contribute to studies of food chain contamination of organochlorines in Yukon Lakes.

INTRODUCTION

This project has the general objectives of identifying the biological effects of elevated concentrations of organochlorine pesticides (toxaphene, DDT) and polychlorinated biphenyls (PCBs), first observed in Lake Laberge fish in 1990/91, and examining historical trends in these contaminants in Yukon lakes. The elevated levels of toxaphene, DDT and PCBs in fish from Laberge suggest that there could be biological effects such as reproductive failure, similar to those observed in the Great Lakes. One measure of exposure to toxicants is hepatic mixed function oxidase activity which has been shown, when used as an *in vitro* assay, to be correlated with concentrations of planar PCBs and dioxins in Great Lakes fish. Another is bone hydroxyproline which has been shown to be depressed in fish during exposure to toxaphene.

Lake sediments are being used to examine temporal trends in the deposition of particle reactive contaminants (OCs, PAH, heavy metals) in lakes in the NWT. They are being employed in this study to examine the possibility that Lake Laberge and other lakes have been contaminated by spills of these chemicals as well as by atmospheric deposition. Temporal trend studies are also supplemented by analysis of archived whitefish available from J. Clayton at the Freshwater Institute.

The major emphasis in 1993/94 was the dating and analysis of lake sediments for organochlorines and PAHs and the correlation of bone hydroxyproline with toxaphene concentrations in Lake Laberge lake trout.

MATERIALS AND METHODS

Sample collection

Fish samples were collected from Lake Laberge and Kusawa Lake (control site) by DFO personnel (D. Metner, P. Wilkinson, B. Billeck, R. Danell) in 1992 and by Ph.D. student K. Kidd (University of Alberta) in cooperation with Environment Canada in the Yukon, DFO, and Yukon Government biologists in 1993. Livers were obtained from lake trout, burbot and whitefish, quick frozen on dry ice, and stored at -80 °C in Winnipeg until assayed for MFO activity. Weight, length and sex of the fish were recorded. Otoliths were taken for aging. Samples for OC analysis were stored on ice in the field, frozen in Whitehorse and shipped frozen to Winnipeg where they were stored at -40 °C until analysis.

Sediments were collected from Fox, and Little Atlin Lakes in March 1993 and from Lindeman, Bennet and Marsh Lakes in March 1994. Cores were sliced at 0.5 cm intervals and the sediment placed in "WhirlPak" bags. Further details of sediment sampling are given in Lockhart (1993).

Sample analysis

OCs in fish tissues: Procedures for the analysis of fish muscle and liver samples are described in this volume (see Muir and Lockhart paper on Contaminant Trends in Freshwater and Marine Fish) and by Muir and Lockhart (1993), with further details on the extraction and cleanup steps given by Muir *et al.* (1990). Analysis of planar PCBs and chlorinated dioxins/furans in fish tissues is described by Muir (1993).

Sediments: Sediments were freeze-dried in their sample bags. Dried sediment was assayed for ^{210}Pb,^{226}Ra, ^{137}Cs and ^{7}Be and the profile of radionuclides was used to date each slice. Sediment (10 g) was extracted with dichloromethane (DCM) in a Soxhlet apparatus using glass thimbles with sintered glass frits. Internal standards of deuterated PAHs were added at the extraction step. The DCM extract was split 1:1 for determination of PAHs and OCs. To recover PAHs, the extract was chromatographed on a silica column (topped with 1 cm alumina) and eluted with hexane (to recover alkanes) followed by hexane:DCM (1:1) for 2 to 6 ring PAHs. OCs were isolated by chromatography on Florisil (Muir *et al.* 1990).

Capillary gas chromatographic analysis of PCBs, toxaphene, DDT and other organochlorines was carried out on a 60 m x 0.25 mm DB-5 column (0.25 μm film thickness) under conditions described by Muir *et al.* (1990). Organochlorines were quantified by use of external standards of individual PCB congeners, DDT-group, chlordane-related compounds, and hexachlorocyclohexanes and chlorobenzenes. Toxaphene was quantified using a single response factor based on the area of 19 peaks in the standard. PAHs were quantified by capillary GC-mass spectrometry (HP 5980-5970 MSD) using an internal standard technique. Sixteen unsubstituted "priority pollutant" PAHs, plus alkylated naphthalenes and phenanthrenes, as well as the biogenic compounds, perylene and retene were determined.

Biomarkers: Hydroxyproline, collagen and calcium were determined in lake trout vertebral samples. Approximately 10 vertebrae were removed and thoroughly cleaned of all tissue prior to analysis. The bone was divided into two fractions in the first collagen, was determined by the method of Flanagan and Nichols (1962), and then hydroxyproline was extracted and measured using the method described by Woessner (1961). In the other fraction the sample was hydrolyzed at 115 °C for six hours and then calcium was determined by the method of Gittelman (1967) using Sigma Scientific Kit # 586 (Sigma Scientific, St. Louis MO.)

Quality assurance

The laboratories also participated in interlab check sample programs on PAHs in sediments and on organochlorines in sediments and fish tissues during 1993/94.

RESULTS

PCB and organochlorine pesticide concentration in fish

Twenty four additional samples of burbot liver and whitefish (collected in 1992) were analysed for 130 organochlorines (OCs). Mean concentrations of major OCs (Table 1) were similar to those found in the smaller sample set analysed in 1992/93 (Muir and Lockhart 1993) and in line with those observed in previous studies (Eamer 1991). With results for 16 whitefish collected in 1992 available we were able to make a more valid comparison with (broad) whitefish samples from 1974 (N=10). Lake whitefish collected in 1974 had 3-fold higher concentrations of ΣDDT, 4-fold lower toxaphene and 2-fold lower PCBs than those from 1992 (Figure 1). Lipid content and age could influence the results. Lipid content in samples of 1974 animals was higher (4.5%) than the 1992 group (2.5%) but this would not account for the differences. Both groups (11 fish each) had the same average age (11 years). Minor organochlorines HCH, dieldrin and chlorobenzenes were also significantly higher in 1974 samples than in 1992 while chlordane showed the opposite trend. The higher DDT in 1974 is in agreement with results for sediment which show higher DDT concentrations at that time in sediments than in present day sediments.

Table 1. Organochlorine contaminants in lake whitefish and burbot liver from Lake Laberge determined by DFO Winnipeg during 1993/94.

	burbot liver		Whitefish muscle+skin	
	Mean	SD	Mean	SD
N	10		14	
% lipid	41.0	± 18.3	3.6	± 1.8
ΣHCH (hexachlorocyclohexanes)	23.0	± 5.6	2.2	± 1.3
ΣCHLOR (chlordane-related cmpds)	156	± 54	12.0	± 6.1
ΣDDT (DDT-related compounds)	1578	± 506	101	± 54
ΣPCB (polychlorobiphenyls)	836	± 205	71.0	± 34
ΣToxaphene[1]	1702	± 516	106	± 56
Toxaphene/PCB ratio	2.0		1.5	

[1] Toxaphene quantified with a single response factor.

Lake sediments

The concentration profile of total DDT (ΣDDT) and total PCBs (ΣPCB) in a single dated core from each lake is shown in Figure 2. The scale of the horizontal axis of each graph is the same to allow visual comparison of concentrations between lakes. ΣPCB levels in surface sediments of the four lakes are quite similar (10-30 ng/g dry weight). These concentrations are low compared to Lake Ontario where concentrations of 500 ng/g (dry weight) have been reported in surface sediments and they are similar to concentrations found in sediments of lakes in NWT (Lockhart 1993). Concentrations of ΣDDT in the surface sediments of all four lakes vary over a 20-fold range (from <0.2 ng/g to 3.7 ng/g). The maximum ΣDDT concentrations vary even more widely, from 0.2 ng/g in Kusawa Lake to 20 ng/g, because of higher levels in subsurface slices from Lake Laberge.

The historical profile of ΣDDT differs greatly among the four lakes. Highest concentrations of ΣDDT are seen in slices from the period 1940-1946 in Laberge. A second core from Lake Laberge cores shows a similar profile although the dates are older than expected (not shown). The proportion of *p,p'*-DDD, a dechlorination product of *p,p'*-DDT (the product originally used as an insecticide) increases with age of the slice (Figure 2). This is expected because the loss of the chlorine proceeds slowly under anaerobic conditions and helps to confirm the age of the sediment. The composition of the ΣPCB changes dramatically down the core. At the surface the PCBs consist mainly of di-, tri- and tetrachlorobiphenyls. For slices dated from 1945-1955 there is a much different pattern, dominated by hexachlorobiphenyls. This pattern is characteristic of Aroclor oils, the commercial PCB-containing product used in electrical transformers and other applications requiring flame retardant chemicals. The PCB results suggest that there were inputs of Aroclor oils upstream of Lake Laberge during the period 1945 to 1955. But the results also show that this dumping has now ceased because the recent slices are dominated by a PCB pattern resembling atmospheric sources, i.e. lower molecular di-, tri and tetra-chlorobiphenyls that are also found in snow, rain and air in the Yukon. The PCB congener pattern in Kusawa and Fox Lake sediments does not show the dominant hexachlorobiphenyl pattern indicating that these lakes probably never received the Aroclor oil inputs.

Profiles of total PAHs (minus perylene and retene) and retene in Cores 1 and 3 from Lake Laberge are shown in Figure 3. Total PAH concentrations have fluctuated over a relatively narrow range over the past 60 years. Both cores show highest concentrations of total PAHs in pre 1900 slices. Perhaps the most interesting profile is that of retene which is a product of woodburning. Retene concentrations peak in both cores in slices with the median ages near 1900. These elevated levels may correspond to woodburning during the gold rush. The addition of lampblack to the ice to enhance melting, a practice which was carried out earlier in the century may also have increased PAH levels. Concentrations of PAHs are lower than those found in northwestern Ontario and similar to what we have found in other Arctic lakes (Lockhart 1993).

Bone collagen and hydroxyproline

Lake trout from Laberge have significantly lower levels of hydroxyproline than lake trout from Kusawa or from northwestern Ontario (Lake 260) (Figure 4). Fish in Lake 260 were treated with a single intraperitoneal dose of 7 ug/g toxaphene, tagged and returned to the lake (Delorme 1994). No differences were seen in mean levels of hydroxyproline or calcium between treated and control fish from L260. This is in contrast with results from lake trout from Lake Laberge. The probable reason for this is that the fish from Laberge have been continuously exposed to toxaphene throughout their life, where as the fish in L260 experiment were treated as adults. Mayer *et al.* (1977) found that adult fathead minnows and channel catfish exposed to 54-173 ng/L and 72-630 ng/L, respectively, had no decreases in hydroxyproline levels, but levels in exposed offspring were significantly decreased.

CONCLUSIONS AND UTILIZATION OF RESULTS

The results of the work in 1993/94 have added significantly to our knowledge of temporal trends and effects of toxaphene and other organochlorines in Lake Laberge. The ΣDDT and ΣPCB concentrations in Lake Laberge surface sediments (0.5-1 ng/g) correspond to fluxes of 1.3 $\mu g/m^2$ per year current inputs. This agrees well with results presented at the Yukon Contaminants workshop (January 1994) by D. Gregor which indicated fluxes of 1.7 $\mu g/m^2$ per year in snow at Tagish and provides further confirmation that the current inputs are primarily from the atmosphere by direct deposition to the lake or runoff from the watershed.

Toxaphene, the other major contaminant in fish in Lake Laberge, was not detected in Laberge and other Yukon lake sediments even using highly sensitive electron-capture negative ion MS (<0.01 ng/g). Low levels of toxaphene (10-30 pg/L) were found in lake water from all lakes (See Alaee *et al.* this volume).

These results indicate that DDT, PCBs and toxaphene have been elevated in Lake Laberge whitefish and presumably in lake trout and burbot (which prey on the whitefish) since 1974. Of the three compounds, toxaphene shows the greatest similarity in concentrations between Lake Laberge and other lakes in the Yukon or NWT for all three species that have been studied (lake trout, burbot and whitefish). This suggests that the presence of toxaphene in Laberge fish is almost certainly the result of atmospheric input. In the case of PCBs and DDT, however, their consistently higher levels compared to other locations suggests a local influence as well as atmospheric sources.

The lower bone calcium and hydroxyproline in lake trout from Laberge in comparison with 2 other lakes (and with experimentally treated lake trout) is a significant finding because to the best of our knowledge it has not been reported before in wild fish. The result is consistent with laboratory studies where offspring of exposed fathead minnows (but not exposed adults) also had depressed bone hydroxyproline. The lower bone calcium and hydroxyproline could affect the long term survival of the fish by reducing bone strength.

Future plans include the analysis of additional cores from Lindeman, Bennet and Marsh Lakes collected in March 1994. Additional fish will also be analysed for MFO, hydroxyproline and planar PCBs to determine if a correlation exists in Lake Laberge fish.

Expected project completion date: March 1997

REFERENCES

Delorme, P. 1994. Ph.D. Thesis, University of Manitoba, Winnipeg. R3T 2N2.

Eamer, J. 1991. Report on Organochlorines in Yukon Fish. Environmental Protection, Environment Canada, Whitehorse, Yukon.

Flanagan, B. and G. Nichols. 1962. Metabolic studies of bone *In vitro*. J. Biol. Chem. 237: 3686-3692.

Gittelman, H.J. 1967. An improved automated procedure for the determination of calcium in biological specimens. Anal. Biochem. 18: 521-531.

Lockhart, W.L. 1993. Depositional trends - lake and marine sediments. Pp. 46-56 *in*: Synopsis of Research Conducted Under the 1992/93 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 70. Indian and Northern Affairs Canada, Ottawa. 285 pp.

Mayer, F.L., P.M. Mehrle and W.P. Dwyer. 1977. Toxaphene: Chronic Toxicity to Fathead Minnows and Channel Catfish. EPA-600/3-77-069. 38pp.

Muir, D.C.G. 1993. Co-planar PCBs in Arctic marine mammals and fish. Pp. 99-104 *in*: Synopsis of Research Conducted Under the 1992/93 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 70. Indian and Northern Affairs Canada, Ottawa. 285 pp.

Muir, D.C.G., C.A. Ford, N.P. Grift, D.A. Metner and W.L. Lockhart. 1990. Geographic variation of chlorinated hydrocarbons in burbot *Lota lota* from remote lakes and rivers in Canada. Arch. Environ. Contam. Toxicol. 19: 530-542.

Muir, D.C.G. and W.L. Lockhart. 1993. Contaminant trends in freshwater biota. Pp. 167-173 *in*: Synopsis of Research Conducted Under the 1992/93 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 70. Indian and Northern Affairs Canada, Ottawa. 285 pp.

Woessner, J.F. 1961. The determination of hydroxyproline in tissue and protein samples containing small proportions of this amino acid. Arch. Biochem. Biophys. 93: 440-447.

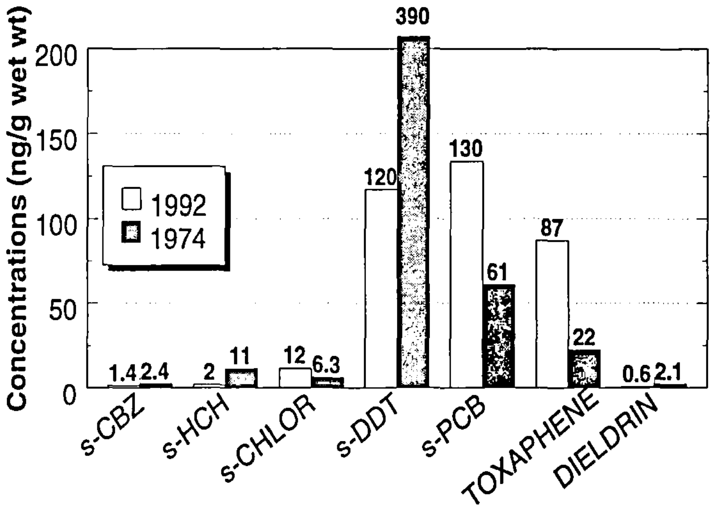


Figure 1. Organochlorine contaminants in lake whitefish and burbot liver from Lake Laberge determined by DFO Winnipeg during 1993/94.

Figure 2. Total DDT and PCBs in dated sediment cores from Yukon lakes.

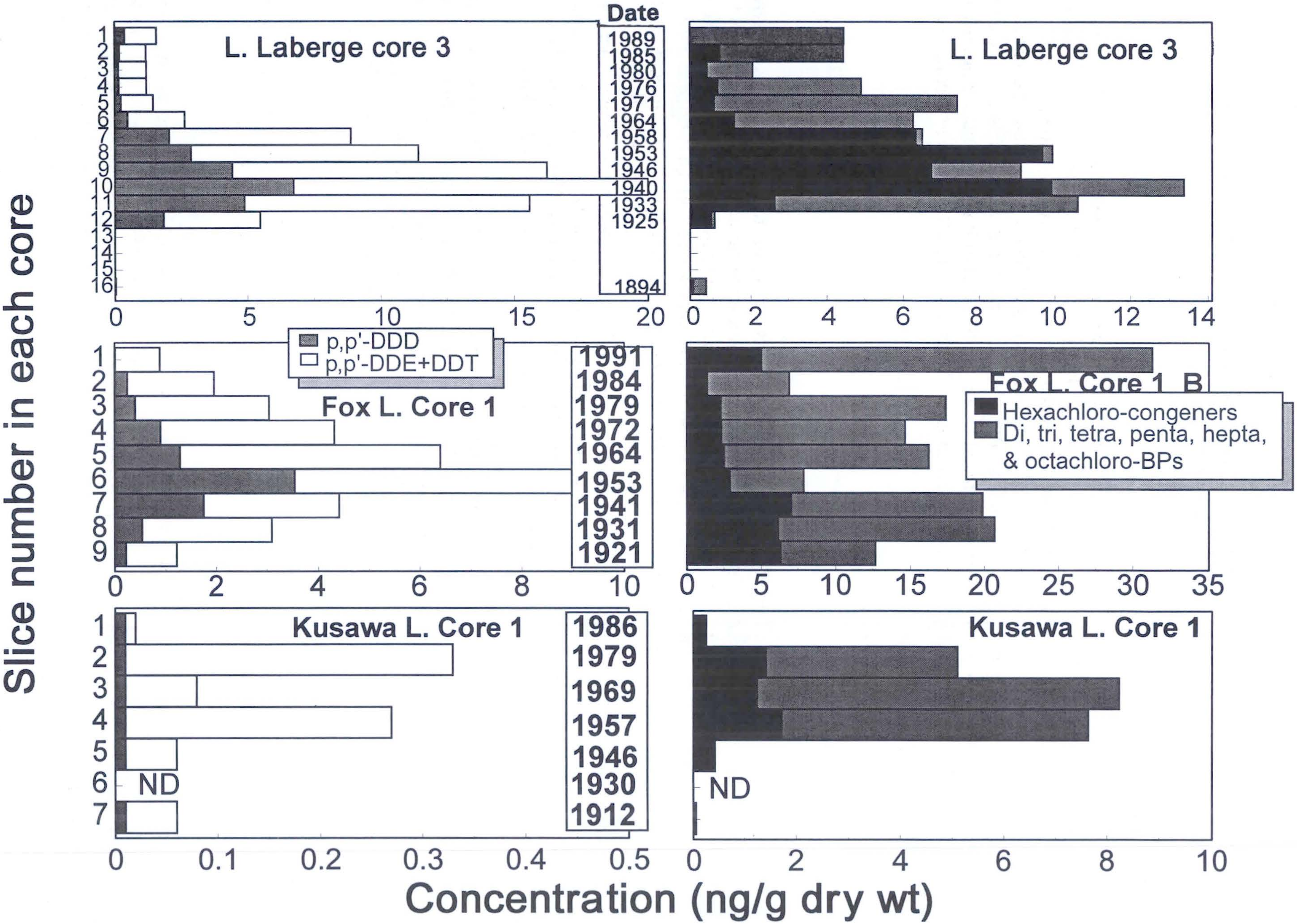


Figure 3. Sum of PAHs (excluding perylene and retene) in slices of Lake Laberge cores 1 and 3 (left) and retene in the same slices (right).

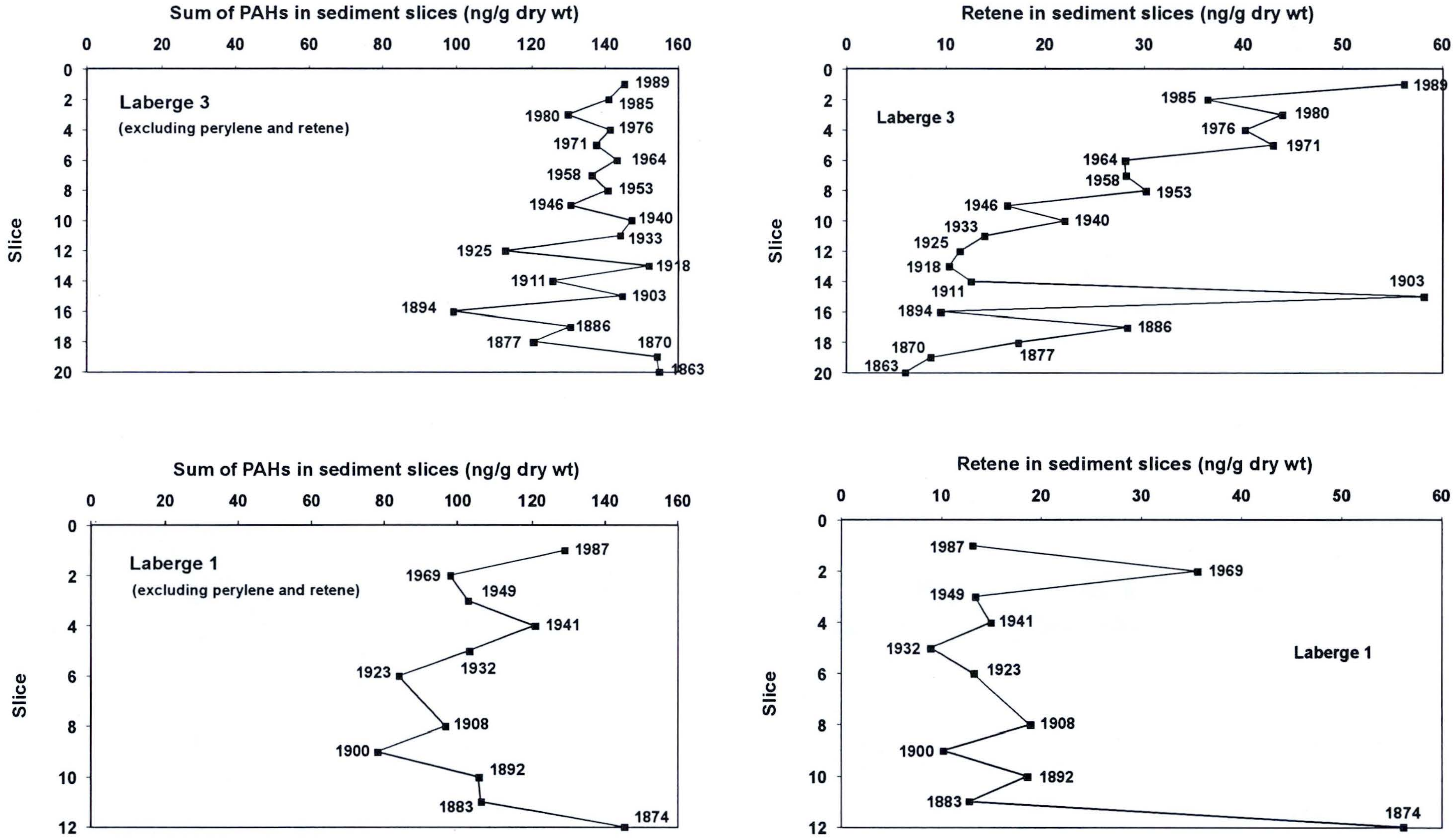
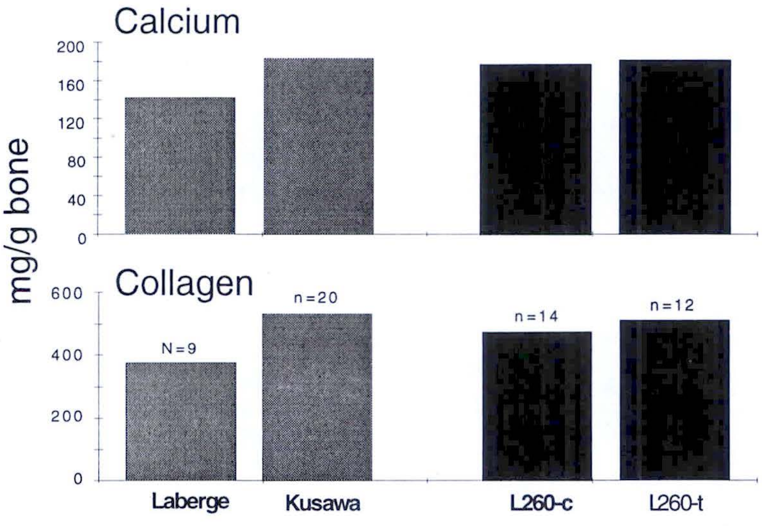


Figure 4. Bone calcium and hydroxyproline in lake trout.



THE BIOMAGNIFICATION OF ORGANOCHLORINES THROUGH THE FOOD WEB OF LAKE LABERGE AND OTHER YUKON LAKES

PROJECT TEAM: K.A. Kidd and D.W. Schindler, University of Alberta; and
D.C.G. Muir and R.H. Hesslein, Fisheries and Oceans Canada

SUPPORTING AGENCIES: Fisheries and Oceans Canada, Indian and Northern Affairs Canada; Environment Canada, Northern Research Institute, Ta'an Kwach'an First Nation, Yukon Contaminants Committee, and Yukon Territorial Government Fisheries Branch (Yukon); Arctic Institute of North America, and Canadian Circumpolar Institute (Alberta)

OBJECTIVES

1. To collect benthic and planktonic invertebrates, and piscivorous and forage fishes from Laberge, Fox and Kusawa Lakes, Yukon Territory (YT) and analyse these samples for organochlorines (including PCBs, DDT and toxaphene).

2. To characterize the food webs of these lakes through the use of stable isotopes of carbon and nitrogen, and fish stomach contents, in order to quantify and qualify the biomagnification of organochlorines through the biota.

3. To understand the among lake differences in organochlorine concentrations in fishes from Yukon lakes.

RATIONALE

Elevated concentrations of the pesticide toxaphene were found in lake trout and burbot from Lake Laberge, YT in 1990/91. Levels were significantly higher in fish from Lake Laberge than those found in the same species from other Yukon lakes (Kidd *et al.* 1993), and resulted in a consumption advisory being issued from Health Canada for burbot liver and lake trout flesh. Other organochlorines, including PCBs and DDT, were also highest in fishes from Lake Laberge (Muir *et al.* 1992a, 1993; Yukon Contaminants Committee, in press). As a result, the commercial, sport and native subsistence fisheries for burbot and lake trout on Lake Laberge have been closed.

Previous studies of Lake Laberge have found that the fish community structure is different from other lakes; the percentages of lake trout and lake whitefish are low while the numbers of burbot and longnose sucker are unusually high. The lake trout are also high in lipid and are solely piscivorous unlike trout populations from other regional lakes. Rasmussen *et al.* (1990) found that lake trout from lakes with longer food webs had higher concentrations of persistent contaminants. We hypothesized that the food web structure of Lake Laberge is different, resulting in elevated concentrations of atmospherically deposited contaminants in the fishes.

To investigate this hypothesis, we are characterizing the food webs of Laberge, Fox and Kusawa lakes, and measuring the concentrations of organochlorines in benthic and planktonic invertebrates, and fishes. Fox and Kusawa lakes were chosen for comparison to Laberge due to their proximity and known low levels of organochlorines in the fishes. Stable isotope ratios of carbon ($^{13}C/^{12}C$) and nitrogen ($^{15}N/^{14}N$) are being used to characterize the food webs of these lakes. Carbon isotope ratios do not change from prey to predator, enabling the original carbon source (pelagic vs. littoral) to be traced through the food web. The heavier isotope of nitrogen (^{15}N) is generally enriched 3 to 5 parts per thousand (‰) in an organism compared to its diet, and is used as an indicator of trophic level (see review by Peterson and Fry 1987). Stable isotope ratios integrate information from an organism's diet over the time period of tissue turnover.

ACTIVITIES IN 1993/94

Field work conducted in 1993/94 was comparable to that done in 1992/93. Throughout the summer, samples of benthic invertebrates (mainly chironomids, snails, tricopterans and oligochaetes), zooplankton, algae and particulate matter were collected from Laberge, Fox and Kusawa Lakes. These samples were collected using benthic grabs, shore sampling, vertical tows, rock scrapings and sediment traps. Fishes were collected from Kusawa and Laberge in conjunction with the YT Renewable Resources Fisheries Branch population survey work and the contaminant monitoring program (this volume). Independent fish collections were done on Laberge and Fox Lakes using gill nets, and seines in all three lakes. Where present, lake trout, burbot, lake whitefish, round whitefish, broad whitefish, longnose sucker, cisco, northern pike and sculpin were collected. Weights, lengths and sex of all fish were recorded, otoliths or cleithra were removed for aging, and stomach contents were identified. All samples were kept on ice, and were frozen shortly after collection.

In the laboratory, fishes were partially thawed and samples of dorsal muscle (skinless) and liver (burbot only) were removed and frozen separately until needed for analyses. Subsamples of muscle and whole invertebrate samples were dried in an oven (50°C) until a constant weight was obtained. These dried samples were ground to a fine powder and used for the stable isotope analyses described below.

Stable Isotope Analyses

Methods for stable isotope analyses followed those found in Hesslein *et al.* (1989). Approximately 15 mg of dried tissue was vacuum sealed in a Vycor tube with 1 g copper wire, 1 g copper oxide wire, and a 1-mm^2 piece of silver foil. The tube was combusted at 850°C for 4 h and at 600°C for 2 h. Nitrogen gas was cryogenically separated from CO_2 and trapped in a molecular sieve. CO_2 and N_2 gases were analysed on a dual inlet isotope ratio mass spectrometer (VG Micromass 602E) and standardized against Peedee Belemnite limestone or air, respectively, as follows:

$$\delta R‰ = [(R_{sample}/R_{air})-1] \times 1000$$

where R = $^{13}C/^{12}C$ or $^{15}N/^{14}N$. Precision of the instrument for carbon and nitrogen isotope analysis over several years of use has been 0.1 and 0.4 ‰ (2 SD), respectively.

Organochlorine Analyses

Organochlorine analyses followed those outlined in Muir *et al.* (1990). Briefly, wet tissues (muscle, liver or whole invertebrates) were homogenized with dry ice. After CO_2 sublimation, 5 - 20 g was mixed with anhydrous sodium sulfate. Internal standards were added to the samples to determine extraction efficiencies. Liver tissues and invertebrates were ball-milled with hexane for 30 min, allowed to sit for 4 h and then centrifuged (4000 rpm). Muscle samples were Soxhlet extracted using hexane:dichloromethane (DCM) 1:1. Lipids were determined gravimetrically with 1/10th of the extract. Remaining lipids were removed from the extract using gel permeation chromatography on SX-3 Biobeads with DCM:hexane (1:1) as the eluant. The eluant was then separated on Florisil (1.2% deactivated with water) into three fractions: hexane (F1), hexane:DCM (85:15)(F2), and hexane:DCM (1:1)(F3) (Norstrom and Won 1985).

All fractions were analyzed for organochlorines using a Varian 6000 with a ^{63}Ni-electron capture detector (GC-ECD) and a 60 m by 0.25 mm i.d. DB-5 column with H_2 carrier gas. Toxaphene was quantified using a single response factor based on the areas of 20 peaks in the standard (Muir *et al.* 1992b).

RESULTS AND DISCUSSION

Measurements of stable nitrogen isotopes have enabled us to distinguish the relative trophic positions of all organisms collected from these lakes (Figure 1). Lake trout and burbot were the top predators in each of the lakes, with mean $\delta^{15}N$ ranging from 8 to 12 ‰ between sites. $\delta^{15}N$ indicated that the lake trout and burbot from Lake Laberge feed at a higher trophic level than the same species from Fox and Kusawa Lakes. Mean $\delta^{15}N$ of lake and round whitefish, cisco and longnose sucker ranged between 6.5 and 8 ‰, a "trophic" level lower than the top predators in each lake. Results obtained from the stable nitrogen isotope measurements were consistent with dietary information acquired from stomach content analyses (Kidd *et al.* 1994), with piscivorous fishes having the highest $\delta^{15}N$, and omnivorous and forage fishes having intermediate and lowest isotope ratios of any fish analysed.

To date, stable carbon isotope ratios have been used for limited interpretation of carbon flow through these food webs. Carbon isotope signals appear to be more useful in determining the direct relationships between predator and prey in lower trophic levels. The top predators in these lakes feed on both littoral and pelagic organisms, and have carbon isotope ratios that are representative of a combined signal from both of these sources. Further interpretation of the carbon isotope results is required to determine its usefulness in contaminant studies.

Total concentrations of HCH, DDT, PCBs and toxaphene (chlorinated bornanes, CHB) in burbot liver, and lake trout and lake whitefish muscle from Laberge, Fox and Kusawa Lakes are presented in Table 1. Mean levels of these persistent contaminants in lake trout muscle, burbot liver and lake whitefish muscle from Laberge are up to 150-, 45- and 43-fold higher, respectively, than found in the same species from Fox Lake. Organochlorine concentrations in lake trout and whitefish muscle are up to 21- and 13-fold higher, respectively, in fish from Laberge than those from Kusawa. The lower concentrations of contaminants in lake trout and burbot from Fox may be a due to the fact that they occupy a lower trophic level (as measured by $\delta^{15}N$) than the same species from either Laberge or Kusawa. Further organochlorine and stable isotope analyses of individual fishes will aid in interpreting these between lake differences. Data from additional invertebrate and fish samples collected in 1992/93 are not yet available to report.

Total log-normalized concentrations of persistent contaminants were found to correlate significantly with the $\delta^{15}N$ of organisms through the food webs of Laberge, Fox and Kusawa Lakes. Results for concentrations of ΣHCH, ΣDDT and ΣCHB in biota from Laberge are shown in Figure 2 along with their respective regression equations. The coefficients of determination (r^2) ranged from 0.67 to 0.81, indicating that $\delta^{15}N$ is a good predictor of contaminant concentrations in biota. Slopes of the regression equations are believed to be related to the lipophilicity of compounds, with the less lipophilic compounds (i.e. HCH) having a lower slope than those for more lipophilic compounds such as DDT or CHB. The slope may represent the biomagnification potential of a compound (Kidd *et al.* 1994).

CONCLUSIONS

Results indicated that differences exist between the food webs of Laberge, Fox and Kusawa Lakes. The top predators in Laberge feed at a higher trophic level than those from the other lakes in this study, a factor which has been previously implicated in higher contaminant concentrations in lake trout. This trophic difference between lakes provides an explanation for the higher concentrations of DDT, PCBs and toxaphene in the fishes from Lake Laberge. Stable isotopes of nitrogen appear to have significant potential for predicting contaminant burdens in biota.

Further field and laboratory work is planned for 1994/95 to improve our understanding of the food web interactions in these lakes, and the effects of food web structure on contaminant burdens in the fishes. The upcoming field season will be used to collect more invertebrate samples for stable isotope and organochlorine analyses. These samples will then be used to examine inter-annual variability in the contaminant burdens of these organisms, and to improve the data available for the lower trophic levels of these lakes. Further analyses of fishes collected over the 1993/94 season will also be done over the upcoming year.

Expected project completion date: September, 1995

ADDITIONAL SOURCES OF FUNDING

Arctic Institute of North America - Lorraine Allison Scholarship
Canadian Circumpolar Institute - Boreal Alberta Research Grant

Indian and Northern Affairs - Northern Scientific Training Program Grant
Northern Research Institute Fellowship
Tri-Council Eco-Research Doctoral Fellowship

REFERENCES

Hesslein, R.H., M.J. Capel, D.E. Fox and K.A. Hallard. 1991. Stable isotopes of sulfur, carbon, and nitrogen as indicators of trophic level in fish migration in the lower Mackenzie River basin, Canada. Can. J. Fish. Aquat. Sci. 48: 2258-2265.

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(10): 1975-1986.

Kidd, K.A., D.W. Schindler, R.H. Hesslein and D.C.G. Muir. 1994. Correlation between stable nitrogen isotope ratios and concentrations of organochlorines in biota from a freshwater food web. Sci. Total Environ. (in press).

Muir, D.C.G., C.A. Ford, N.P. Grift, D.A. Metner and W.L. Lockhart. 1990. Geographic variation of chlorinated hydrocarbons in burbot (*Lota lota*) from remote lakes and rivers in Canada. Arch. Environ. Contam. Toxicol. 19: 530.

Muir, D.C.G., B. Rosenberg and C.A. Ford. 1992a. Interim report on organochlorine contaminants in fish from Lake Laberge. Report to Yukon Contaminants Committee. September 1992.

Muir, D.C.G., C.A. Ford, N.P. Grift, R.E.A. Stewart and T.F. Bidleman. 1992b. Organochlorine contamination in narwhal (*Monodon monoceros*) from the Canadian Arctic. Environ. Pollut. 75: 306-316.

Muir, D.C.G. 1992c. Food chain accumulation and biochemical effects of organochlorine contaminants in fish from Lake Laberge and other Yukon Lakes. Pp. 173-177 *in*: Synopsis of Research Conducted Under the 1991/92 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 68. Indian and Northern Affairs Canada, Ottawa. 213 pp.

Muir, D.C.G 1993. Food chain accumulation and biological effects of organochlorines in fish from Lake Laberge and other Yukon lakes. Pp. 180-188 *in*: Synopsis of Research Conducted Under the 1992/93 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 70. Indian and Northern Affairs Canada, Ottawa. 285 pp.

Norstrom, R.J. and H.J. 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.

Peterson, B.J. and B. Fry. 1987. Stable isotopes in ecosystem studies. Ann. Rev. Ecol. Syst. 18: 293-320.

Rasmussen, J.B., D.J. Rowan, D.R.S. Lean and J.H. Carey. 1990. Food chain structure in Ontario lakes determines PCB levels in lake trout (*Salvelinus namaycush*) and other pelagic fish. Can. J. Fish. Aquat. Sci. 47: 2030-2038.

Schindler, D.W. and K.A. Kidd. 1993. The biomagnification of organochlorines through the food web of Lake Laberge and other Yukon lakes. Pp. 174-179 *in*: Synopsis of Research Conducted Under the 1992/93 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 70. Indian and Northern Affairs Canada, Ottawa. 285 pp.

Yukon Contaminants Committee. Report on contaminants in Yukon fish 1991/92, 1992/93 and 1993/94. Contact: M. Palmer, Indian Affairs and Northern Development, Whitehorse, YT (in press).

Table 1: Total concentrations of chlordane, DDT, PCBs and toxaphene in lake trout muscle, burbot liver and lake whitefish muscle from Laberge, Fox and Kusawa Lakes, YT (mean and range, ng/g wet weight).

Site	Species	N	% Lipid	ΣHCH	ΣDDT	ΣPCB	ΣToxaphene[3]
Laberge							
	Lake Trout[1]	6	8.4	4.3	940	820	560
			(3.2-13)	(2.6-6.1)	(44-3000)	(76-2600)	(140-1400)
	Burbot[1,2]	6	34	31	4100	1800	2900
			(21-47)	(24-38)	(1600-7300)	(560-3600)	(1400-4500)
	Lake Whitefish[1,2]	6	2.5	1.7	155	280	44
			(1.5-3.5)	(1.2-2.7)	(48-530)	(43-1200)	(21-78)
Fox	Lake Trout	9	1.4	1.0	6.1	10	6.2
			(0.5-5.9)	(0.2-2.1)	(1.4-16)	(1.4-15)	(0.8-21)
	Burbot	3	27	15	91	79	90
			(23-30)	(6.1-24)	(47-120)	(29-140)	(71-110)
	Lake Whitefish	5	1.8	0.7	6.1	6.4	5.7
			(1.5-2.4)	(0.4-1.0)	(2.3-14)	(1.1-16)	(2.5-12)
Kusawa							
	Lake Trout[1]	10	1.8	1.2	44	85	120
			(0.3-5.9)	(0.2-4.1)	(9.2-230)	(29-310)	(23-240)
	Lake Whitefish	9	1.1	0.5	15	21	17
			(0.4-2.7)	(0.1-0.7)	(0.4-59)	(2.3-72)	(2.7-55)

[1] Muir *et al.* (1993).

[2] Muir *et al.* (1992c).

[3] Toxaphene concentrations calculated using a single response factor.

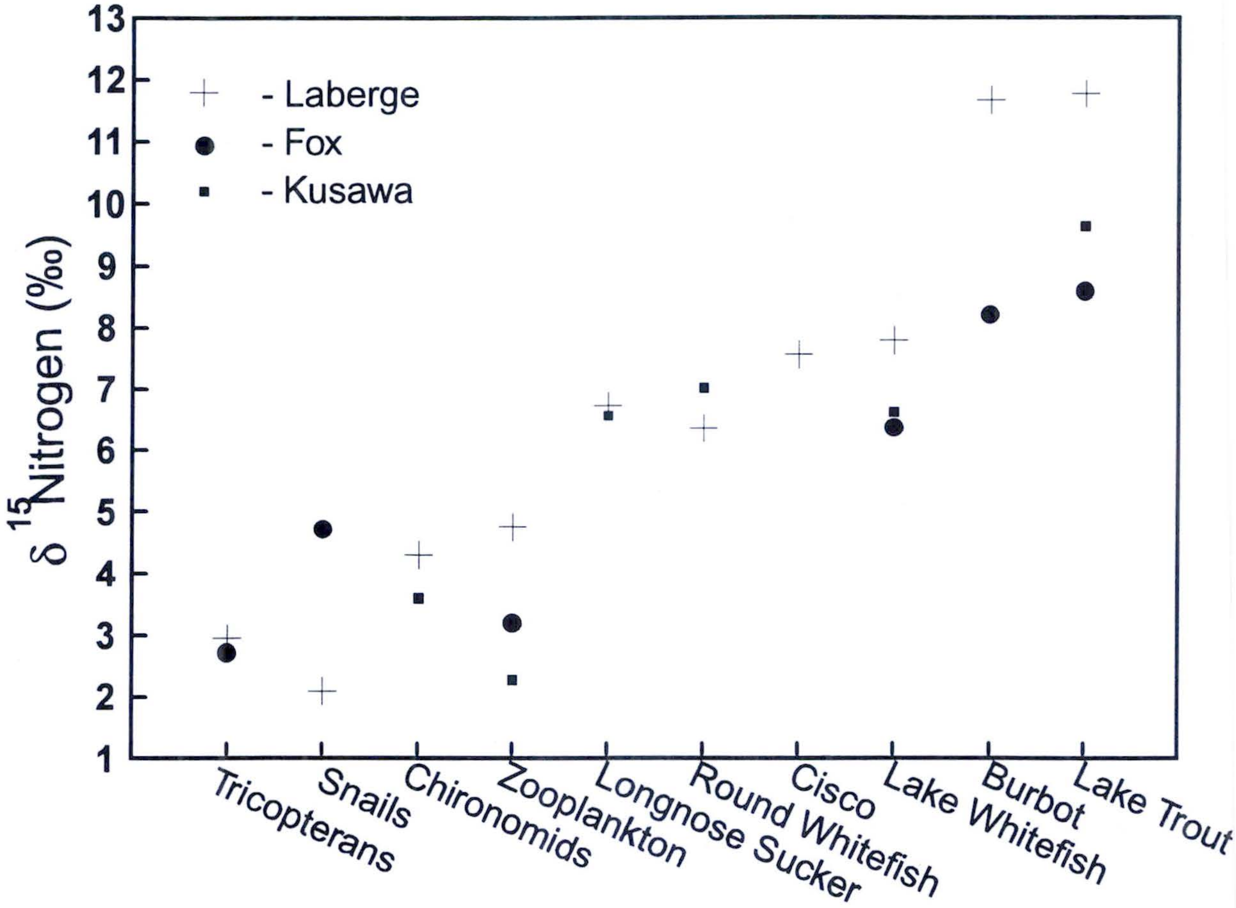


Figure 1: Mean δ^{15}nitrogen (‰) for invertebrates and fishes collected from Laberge, Fox and Kusawa lakes.

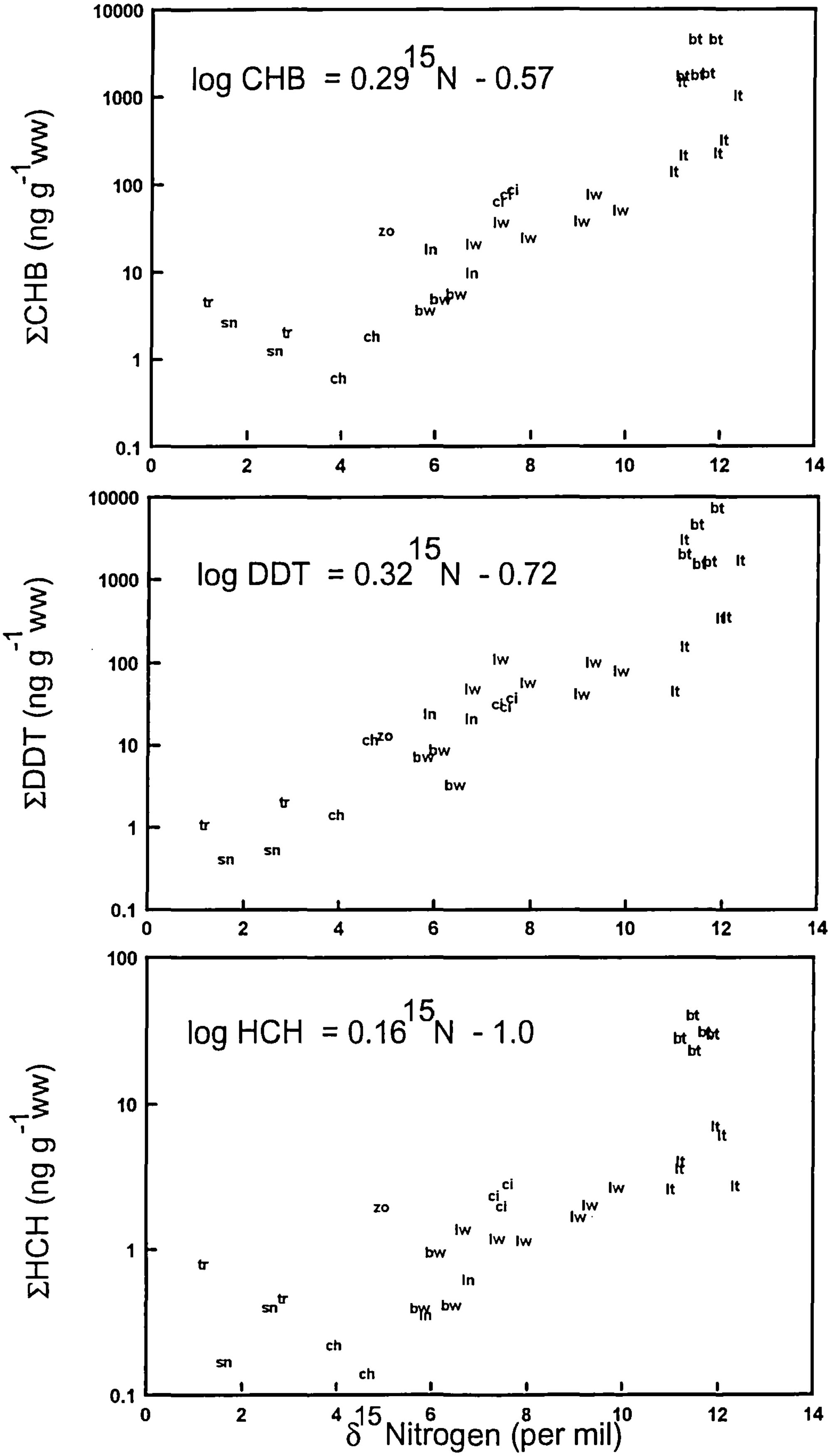


Figure 2: δ^{15}Nitrogen isotope ratios versus ΣCHB (toxaphene), DDT and HCH for fishes and invertebrates from Lake Laberge, Yukon Territory (tr=tricopteran, sn=snail, ch=chironomid and zo=zooplankton (whole); bw=broad whitefish, lw=lake whitefish, ln=longnose sucker, ci=cisco and lt=lake trout (muscle); and bt=burbot (δ^{15}N in muscle, contaminants in liver) (Kidd *et al.* 1994).

BIOMAGNIFICATION OF PERSISTENT ORGANIC CONTAMINANTS IN GREAT SLAVE LAKE

PROGRAM LEADER: M.S. Evans, National Hydrology Research Institute, Environment Canada, Saskatoon

PROJECT TEAM: D. Muir and W.L. Lockhart, Freshwater Institute, Winnipeg

OBJECTIVES

Long-term:

1. To determine the concentrations of persistent organic contaminants in various components of Great Slave Lake food webs.

2. To determine the influence of the Slave River on the contaminant loading to Great Slave Lake.

3. To determine the influence of the Slave River on the biomagnification of persistent organic contaminants in Great Slave Lake food webs.

Short-term:

1. To determine organic contaminant concentrations in whitefish, burbot, and lake trout collected from two regions of Great Slave Lake, i.e., an area strongly influenced by the Slave River and a second, more isolated "control" area. Compare these data with data collected from other subarctic and arctic regions.

2. To conduct preliminary collections of plankton, mysids, and amphipods in the West Basin of Great Slave Lake (i.e., near the Slave River outflow) to determine abundance patterns and to investigate methods for obtaining large numbers of organisms required for organic contaminant determinations (1994/95).

DESCRIPTION

This project is investigating pathways (atmospheric, riverine) by which persistent organic contaminants are transported to and biomagnified in Great Slave Lake food webs. It also is investigating the potential implications of increased development in the Great Slave Lake drainage basin on contaminant loading to the lake. Such implications include an increase in contaminant body burdens in fish with potential economic consequences to the sport and commercial fisheries and to the well-being of humans who consume these fish. Ultimately, down-river transport via the Mackenzie River may result in increased contaminant loading to the Arctic Ocean.

ACTIVITIES IN 1993/94

Two regions were selected for investigating the influence of the Slave River on contaminant loading and biomagnification in Great Slave Lake fish. Resolution Bay, near the Slave River delta in the West Basin, was selected as the general location for investigating organic contaminant concentrations in fish in a region strongly affected by the Slave River. Lutsel K'e (Snowdrift), in the East Arm, was selected as a "control" site for a region under relatively weak Slave River influence.

The communities at Fort Resolution (Slave River delta) and Lutsel K'e were informed of the objectives of the study and their assistance requested in collecting burbot, whitefish, and lake trout. Fifteen lake trout, twenty whitefish, and five burbot were collected from the vicinity of Lutsel K'e in early autumn. Eleven whitefish and nine burbot were collected from Resolution Bay in December. In January 1994, nine lake trout were provided by commercial fishermen (from Hay River) operating in the western West Basin. Lake trout, burbot, and whitefish then were analyzed for persistent organochlorine contaminant concentrations including toxaphene and PCB congeners. Pooled samples were analyzed for PAHs, dioxin and furans. Fish also were aged, weighed, and their sex and length determined.

In August 1993, a 4-day research cruise was conducted in the Slave River delta region using the enforcement vessel operated by Fisheries and Oceans, Hay River. During this cruise, information was obtained on the spatial patterns of plankton, mysid, and amphipod distribution in the vicinity of the Slave River plume. The cruise also allowed for the determination of potential difficulties which might be encountered in collecting the large numbers of invertebrates required for organic contaminant analysis in 1994/95. Limited sampling was conducted of the water column, i.e., temperature, conductivity, turbidity, and plant nutrients.

A series of 10 surficial sediment samples were collected during the 4-day cruise. Samples were collected along two, 4-station transects west and immediately offshore of the Slave River outflow and one, 2-station transect east of the River mouth. These samples were then analyzed for concentrations of persistent organochlorine contaminants (including PCBs and toxaphene), PAHs, dioxins and furans. In addition, two short cores were collected in a shelf region offshore of Resolution Bay. These cores were collected for dating determinations to ascertain whether or not this region of the delta is suitable for historic contaminant deposition studies (i.e., core studies). Funding (18 K) for these analyses was received from the Department of Indian Affairs and Northern Development in Yellowknife (J. Peddle and J. Witteman).

In February 1994, funding (55 K) was received from the Northern River Basin Study (NRBS) to collect a series of sediment core samples in the West Basin of Great Slave Lake. This field sampling was conducted by M. S. Evans and R. Bourbonniere (National Water Research Institute).

RESULTS

The analyses of lake trout, burbot, and whitefish collected in 1993/94 are near completion. A brief summary of the results to date is presented in the following paragraphs. Statistical analyses of the data (for differences in contaminant concentration between species and region) will begin following the completion of all chemical analyses.

Whitefish from Resolution Bay tended to be younger and have a higher lipid content than whitefish from Lutsel K'e. Toxaphene (Table 1) was the predominant organochlorine detected in whitefish muscle followed by total PCBs and chlordane. Data were highly variable and differences in contaminant concentrations between sites, if statistically real, were small.

Lake trout from the West Basin (Table 1) had a higher lipid content than lake trout from Lutsel K'e. Toxaphene was the predominant organochlorine contaminant detected. There was some evidence that West Basin trout had lower toxaphene concentrations than trout from the East Arm. PCB, DDT, and chlordane concentrations also appeared lower in West Basin than Lutsel K'e lake trout. Statistical analyses will be used to test this hypothesis.

Burbot analyses have not been completed. Limited data (Table 1) suggest that toxaphene, PCB, DDT, and chlordane concentrations may be lower in West Basin than Lutsel K'e burbot liver.

Two pools each of the three fish species from the West Basin and East Arm were analyzed for dioxins and furans. Low concentrations (1.00 pg/g) of dichlorodibenzodioxin were detected in burbot liver from Resolution Bay. Whitefish and lake trout muscle from Resolution Bay contained 0.05 and 0.15 pg/g of tetrachlorodibenzodioxin, respectively. The only dioxin detected in fish from Lutsel K'e was hexachlorodibenzodioxin (0.55 pg/g) in burbot liver.

Furans were more readily detected in fish from the West Basin and East Arm. For the West Basin, low concentrations of tetrachlorodibenzofuran were detected in burbot liver (2.65 pg/g), whitefish muscle (0.70 pg/g) and lake trout muscle (0.75 pg/g). Trichlorodibenzofuran (0.05 pg/g) was detected in lake trout muscle and pentachlorodibenzofuran was detected in whitefish (0.15 pg/g) and lake trout (0.10 pg/g) muscle. For the East Arm, tetrachlorodibenzofuran was detected in burbot liver (11.75 pg/g), whitefish muscle (0.55 pg/g), and lake trout muscle (0.55 pg/g). Pentachlorodibenzofuran was detected only in burbot liver (0.80 pg/g) and lake trout muscle (0.10 pg/g).

PAH concentrations were low in burbot liver (2.44 ng/g), whitefish muscle (2.65 ng/g) and lake trout muscle (2.39 ng/g) from Lutsel K'e. Naphthalene, 2-methylnaphthalene, and 1-methylnaphthalene were the primary compounds detected. Fish from the West Basin have yet to be analyzed.

The lake survey provided interesting information on the limnology and aquatic ecology of Great Slave Lake in the vicinity of the Slave River plume. Turbidity decreased markedly with depth suggesting that, during summer stratification, river-borne contaminants are dispersed into the West Basin with the surface river plume. Moreover, some of these river-borne contaminants may be transported with Great Slave Lake outflow via the Mackenzie River. Nutrient data provided evidence that the Slave River is an enriched source of particulate organic carbon, nitrogen and phosphorus to the West Basin of Great Slave Lake. Ultimately this enrichment may affect the lipid content of fish and their contaminant body burdens.

Zooplankton densities were low but the samples relatively free of large, organic debris. Mysids were relatively abundant and readily caught even during daylight hours. Amphipods (benthos) were the most difficult to sample occurring in low densities and in "sticky" sediments. Amphipods were small in comparison to amphipods from Lake Michigan and Ontario.

Analyses of sediment samples (funded by Indian and Northern Affairs Canada in Yellowknife) are continuing. The March 1994 coring trip (supported by NRBS) was successful with a good to excellent series of cores collected at five sites in the West Basin. Following dating of these cores, a series of core sections will be selected for organic contaminant analysis with 1994/95 AES funding.

DISCUSSION/CONCLUSIONS

Initial results of our study indicate that most organochlorine contaminants occur in relatively low concentrations in whitefish, lake trout, and burbot collected from the two regions of Great Slave Lake. Similarly, regional differences in organic contaminant concentrations in fish collected from the two regions are generally small. Notable exceptions are: toxaphene in lake trout, burbot, and whitefish females; PCB in lake trout and burbot; DDT in burbot; and HCH in burbot. Statistical analyses (nonparametric tests) will be performed to determine whether or not such differences are significant.

There were interesting similarities and differences in organochlorine contaminant concentrations in Great Slave Lake and Lake Laberge fish (Muir and Lockhart 1993). Chlorobenzene, chlordane, HCH, and dieldrin concentrations were similar in Great Slave Lake whitefish to levels observed in Lake Laberge whitefish. However, toxaphene concentrations were slightly lower and DDT and PCB concentrations substantially lower in Great Slave Lake than Lake Laberge whitefish. Great Slave Lake lake trout contained lower concentrations of chlordane, DDT, PCB, and toxaphene than Lake Laberge lake trout. Great Slave Lake burbot also contained lower concentrations of DDT and PCB than burbot of Lake Laberge. Toxaphene values were similar for Lake Laberge and Lustel K'e lake trout but higher than lake trout collected from the West Basin. Whitefish, lake trout, and burbot from Great Slave Lake had similar lipid concentrations as the same species from Lake Laberge. Therefore, differences in organic contaminant concentrations in fish inhabiting the two lakes may be related to factors such as fish age, feeding behaviour, and/or genetic differences in their ability to metabolize xenobiotic compounds.

PAH, dioxin, and furan concentrations were relatively low in burbot, whitefish, and lake trout collected from the two regions of Great Slave Lake. Regional differences were subtle. Analysis of surficial sediment samples collected in August 1993 will provide a strong basis for evaluating the influence of the Slave River on contaminant loading to Great Slave Lake. With this information, and the completion of analyses of fish collected in 1993/94, we will continue to investigate regional differences in organic contaminant concentrations in fish tissue. Research in 1994/95 will focus on the further elucidation of these questions.

Expected project completion date: March 1997

REFERENCE

Muir, D. and W.L. Lockhart. 1993. Food chain accumulation and biological effects of organochlorines in fish from Lake Laberge and other Yukon lakes. Pp. 167-173 *in*: Synopsis of Research Conducted Under the 1992/93 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 70. Indian and Northern Affairs Canada, Ottawa. 285 pp.

Table 1. Mean (and standard deviation) concentration of organochlorine contaminants in whitefish muscle, lake trout muscle, and burbot liver from Resolution Bay (Hay River for lake trout) in the West Basin and Lutsel K'e in the East Arm of Great Slave Lake. Concentrations are ng/g wet weight.

Parameter	Whitefish		Lake trout		Burbot	
	Lutsel K'e	Resolut.	Lutsel K'e	Resolut.	Lutsel K'e	Resolut.
Age - M	14.3 ± 4.2	11.4 ± 1.8	13.0 ± 4.1	-	16+	13+
Age - F	17.5 ± 2.1	11.5 ± 5.0	16.0 ± 6.7	-	11.8 ± 2.8	-
%Lipid - M	2.5 ± 1.3	6.7 ± 1.6	7.4 ± 3.7	11.2 ± 1.2	20.9	19.5
%Lipid - F	3.1 ± 1.4	4.4 ± 0.7	7.9 ± 4.7	13.8 ± 3.6	32.3 ± 6.9	-
s-CBZ M	1.2 ± 0.7	2.4 ± 1.4	3.1 ± 1.3	2.4 ± 1.0	23.1	13.2
s-CBZ F	1.6 ± 0.6	1.2 ± 0.4	3.3 ± 3.0	2.7 ± 0.9	14.8 ± 2.4	-
s-HCH M	0.8 ± 0.7	1.8 ± 0.4	2.6 ± 1.2	1.8 ± 0.8	15.2	7.3
s-HCH F	0.9 ± 0.4	1.4 ± 0.2	2.6 ± 1.7	2.1 ± 0.6	9.7 ± 5.3	-
s-CHLOR M	4.2 ± 2.6	6.2 ± 4.8	16.1 ± 7.8	9.2 ± 5.9	152.4	76.9
s-CHLOR F	5.1 ± 2.5	3.1 ± 1.6	17.4±13.0	10.7± 4.6	78.7±12.7	-
s-DDT M	2.1 ± 1.3	1.7 ± 1.3	9.7 ± 4.8	5.3 ± 4.4	95.7	27.8
s-DDT F	2.1 ± 0.9	1.0 ± 0.7	9.5 ± 9.8	6.1 ± 3.1	40.1 ± 7.7	-
s-PCB M	5.9 ± 3.9	5.2 ± 5.6	23.1±10.1	13.1± 9.9	227.5	92.5
s-PCB F	5.1 ± 5.1	1.7 ± 1.2	26.8±26.3	14.3± 6.4	116 ± 18	-
s-TOX M	29.3±20.2	27.0±22.7	140.7±69	41.3±24.1	1266.6	401.3
s-TOX F	38.7±16.8	14.7 ± 8.7	160±140	52.8±24.7	635± 110	-
DIELD. M	0.5 ± 0.3	0.9 ± 0.3	1.0 ± 0.4	0.7 ± 0.3	15.8	7.2
DIELD. F	0.7 ± 0.4	0.6 ± 0.1	1.2 ± 0.8	0.8 ± 0.3	8.1 ± 2.2	-

LAKE TROUT RECOVERY AND CONTAMINANT MANAGEMENT PROGRAM IN LAKE LABERGE, YUKON TERRITORY

PROJECT LEADERS: N. de Graff and L. Mychasiw, Department of Renewable Resources, Government of Yukon

PROJECT TEAM: S. Thompson, P. Sparling, M. Connor, G. Pope

OBJECTIVES

1. To assess temporal changes in organochlorine levels within fish from Lake Laberge and a reference lake.
2. To determine changes in the Lake Laberge fish community in response to the elimination of significant harvests.
3. To examine the expression of toxic effects of organochlorine levels in response to anticipated change in lipid content.

DESCRIPTION

Lake Laberge is one of the headwater lakes of the Yukon River drainage system, located 30 km downstream of Whitehorse, Yukon. Elevated levels of organochlorine contaminants (PCBs, DDT and toxaphene) were discovered in fish in 1991. Concentrations of DDT were equivalent to those found in Lake Ontario and were higher than those found in fish from other parts of the Arctic.

In response to high toxaphene levels, Health Canada issued a public health advisory in 1991, recommending that consumption of lake trout flesh from Lake Laberge be limited and that no burbot (lingcod) livers be eaten. This has essentially eliminated the commercial fishery and curtailed subsistence and domestic use, and consequently the fish community in Lake Laberge is practically unexploited, allowing this study to proceed.

Lake Laberge has low abundance of lake trout, due to high levels of commercial exploitation in the past, and high abundance of prey species such as coregonids and sucker. As a result, lake trout in Lake Laberge have a large forage base and are much fatter (13% muscle lipid) than lake trout from other systems such as Bennett Lake (2% lipid) and Tagish Lake (5% lipid). The anomalous composition of the Lake Laberge fish community is summarized in Table 1.

Accordingly, if the lake trout stock in Lake Laberge could be rehabilitated and a predator:prey balance restored, to a level comparable with other lakes, the body composition of lake trout should shift toward less lipid and, because organochlorines are sequestered in fat, contaminant levels should decline.

Fish community changes of this kind, as well as any associated effects on contaminant levels, are expected to occur over a period of a decade or more. The work completed in 1993/94 is the first of four surveys that are planned to take place at three-year intervals. The fish community in Kusawa Lake is used as a standard of comparison in assessing contaminant changes in Lake Laberge.

ACTIVITIES IN 1993/94

Fish Community Sampling

Twenty sinking gill-net sets were placed in Lake Laberge between July 27 and August 12, 1994. Set locations were selected to yield a representative sample. Each set consisted of seven panels with mesh sizes of: 3.8, 12.7, 6.4, 11.4, 7.6, 10.2 and 8.9 cm. Each panel was 22.9 m long and 2.4 m deep. All sets were placed with the 3.8 cm panel to shoreward and left overnight. The average set time was 23.5 hours.

Contaminant Sampling

Fifteen burbot and 17 lake trout from Lake Laberge were selected for contaminant sampling. Fifteen lake trout were taken for the control sample from the stock assessment survey on Kusawa Lake. Seven burbot from Kusawa Lake, which were previously taken as part of the project to survey Yukon Lakes under the Northern Contaminants Program, were used to complete the control sample. Fish that were kept for contaminant sampling were iced and then, within eight hours of being caught, frozen at -80 °C.

Muscle- and liver-tissue samples were extracted from lake trout and burbot, respectively. Sample contamination was prevented by following rigorous quality control procedures. Contaminant samples were sent to AXYS Analytical Services Ltd. in Sidney, BC for analysis.

RESULTS

Seventy-one lake trout were sampled and described on the basis of external form, condition factor, age, reproductive status and diet. Catch results from the fish community survey are similar to the 1991 survey (Table 1), confirming the low abundance of lake trout relative to the numbers of long-nose sucker and coregonids in the system. Dietary analysis of lake trout showed a strictly piscivorous diet, with cisco as the primary forage species. Stomach content analysis in burbot and northern pike showed no evidence of predation by those species on lake trout.

Laboratory results on contaminant levels and lipid values in muscle and liver tissue have not been received to date. Results are expected by late summer 1994.

DISCUSSION/CONCLUSIONS

Lake Laberge supports a viable fish community, in which lake trout are under represented in relation to the biomass of forage species. It does not appear that the lake trout population is being suppressed on account of predation by other fish-eating species. With no significant harvest of lake trout, a gradual recovery of the lake trout stock is predicted.

Expected project completion date: March 31, 2003

Table 1. Catch composition, presented as percentages of total catch biomass, from index netting programs within Bennett, Frances and Kluane Lakes in 1990 and Lake Laberge 1991 and 1993.

Scientific Name	Species	Waterbody				
		Bennett	Frances	Kluane	Laberge-1991	Laberge-1993
Salvelinus namaycush	lake trout	32.0	31.5	30.3	7.0	7.7
Coregonus clupeaformis	Lake whitefish	27.1	47.5	58.8	19.3	13.4
Coregonus nasus	broad whitefish				.4	3.8
Prosopium cylindraceum	round whitefish	10.5	1.0	.8	.1	1.6
Catostomus catostomus	longnose sucker	29.7	13.3	8.9	50.1	50.2
Lota lota	burbot	.2	.6	.1	16.9	6.7
Esox lucius	northern pike		5.4		.4	14.5
Stenodus leucichthys	inconnu			1.0		1.2
Coregonus sardinella	least ciscoe	.1			5.7	.5
Salvelinus malma	dolly varden		.5			
Thymallus arcticus	arctic grayling	.4	.2		.1	.2

TRENDS AND EFFECTS OF ENVIRONMENTAL CONTAMINANTS IN ARCTIC SEABIRDS, WATERFOWL, AND OTHER WILDLIFE
I. CONTAMINANTS IN WATERFOWL: NATIVE HARVEST IN NWT

PROJECT LEADER: B.M. Braune, National Wildlife Research Centre, Canadian Wildlife Service (CWS), Environment Canada

PROJECT TEAM: B. Wakeford, CWS (Hull); K. McCormick, CWS (Yellowknife); J. Bastedo, contractor (Yellowknife)

OBJECTIVES

1. To determine the levels and geographical distribution of contaminants in arctic wildlife with particular emphasis on avian species.

2. To provide a data set on contaminants in waterfowl and other game birds potentially used as food by native people to Health Canada so that potential health risks to the human consumer may be evaluated.

DESCRIPTION

There is very little information available on contaminants, particularly heavy metals and dioxins/furans, in arctic wildlife potentially consumed by humans. Although a limited number of measurements of contaminants in seabirds, waterfowl, and other wildlife have been obtained, the data base is too limited to derive any conclusions about spatial and temporal trends, or degree of contamination of those species. This study will enable estimates to be made of the contribution of specific contaminants to the native diet, and it will also enable an assessment of effects of contaminants on birds and other wildlife at the top of the Arctic food web. The information gathered will also contribute to the data bases requested by the Terrestrial, Marine, Freshwater and Human Health Subprograms of the Arctic Monitoring and Assessment Programme (AMAP).

Waterfowl, terrestrial game birds, shorebirds and seabirds (and their eggs) are harvested to varying degrees by native people for consumption (Coad 1994). A survey of contaminants in harvested avian species in the Canadian Arctic has been a part of a larger national survey since 1988. Each year, a different arctic region has been subject to intensive study. In 1991/92, the Nunavik Region of northern Quebec was surveyed. Data collected from that survey was submitted to Health Canada in December 1992 for evaluation of risk to human health of consuming harvested waterfowl. The Nunavik survey was followed by a survey in Labrador in 1992/93, and the Northwest Territories was the focus of the 1993/94 intensive study. In 1994/95, the study will move to the Yukon Territory.

The specific objectives for 1993/94 were to collect birds and eggs commonly harvested and consumed by native people across the Northwest Territories for chemical analyses and to submit the resulting data to Health Canada for evaluation of risk to human health of eating those birds or eggs.

ACTIVITIES IN 1993/94

Collections of birds or eggs representative of the hunted/harvested population in NWT were requested. Eggs were collected by hand on the basis of one egg per nest. Adult birds were collected with the use of a shotgun. All samples were collected under permit by local native hunters and enforcement officers. Collection, storage, and analytical protocols as specified by the National Wildlife Research Centre (NWRC), Hull, Quebec, were followed. All tissues are being processed by the Laboratory Services Section of the CWS at NWRC. Breast muscle was chosen as the tissue most representative of the edible portion of the bird.

The last of the samples from NWT was received during March 1994. Processing of samples is proceeding. Where adequate tissue is available, samples of breast muscle will be sent to the Bureau of Radiation and Medical Devices, Health Canada, for radiocesium analyses. The gastro-intestinal tracts and morphometric information are being sent to McGill University for a feeding study and a study on morphology of diving birds, respectively. As well, samples will be sent to the Norwegian Institute for Nature Research in support of an international study on metals in Willow Ptarmigan.

Breast muscle and egg contents will be submitted to the analytical laboratories of the Great Lakes Institute, University of Windsor, for chemical residue analyses for PCBs and organochlorines. Analyses of mercury, cadmium, lead and selenium are being carried out in the CWS laboratories at NWRC. Both of these laboratories have participated in the 1993/94 interlaboratory quality assurance program for analytical data produced for the Northern Contaminants Program of the Arctic Environmental Strategy. All analyses are done on a pooled basis, that is, samples of individuals of the same species from a given location collected within a specified time period are pooled to make a composite sample which is then analyzed. In the case of eggs, 5 pools of 3 eggs each were made from each collection of 15 eggs. Only limited results are available to date.

Additionally, mid-year funding allowed for the analysis of contaminant residues in winter collections (1989-93) of some harvested species of birds which breed in the Yukon Territory and overwinter in contaminated coastal areas of British Columbia. Birds being analyzed include 101 Surf Scoters collected from 14 sites, 10 Common Mergansers from one site, 18 Western Grebe from three sites, 3 Harlequin Ducks from one site, 12 Greater Scaup from two sites, 5 Lesser Scaup from one site, 23 Common Goldeneye from two sites, and 11 Bufflehead from one site. The resulting data will be compared to residue levels in harvested waterfowl being collected in the Yukon Territory during 1994. Results are not yet available.

RESULTS

A total of 9 collections of eggs representing 5 species and 43 collections of birds representing 20 species harvested and consumed by native people were made from 12 sites across the Northwest Territories in 1993 (Table 1). Organochlorine residue analyses for some of the birds collected earlier in the year are complete and presented in Table 2 combined with samples collected from NWT during 1988-91. Mean levels (and standard deviations) of organochlorine residues in harvested eggs are presented in Table 3.

As is to be expected, those species which feed at a lower trophic level, such as grazers (geese), browsers (ptarmigan) and dabbling ducks (Mallard), contain the least amount of contaminants (Table 2). Diving ducks, such as the eiders and Oldsquaw which feed mainly on invertebrates, reflect a higher exposure to organochlorine contaminants. Oldsquaw collected from the Baker Lake area contained the highest contaminant concentrations of birds collected from the NWT to date, although the levels are not much different from levels in other collections of Oldsquaw from Ontario, Quebec and Atlantic Canada (Braune 1993, CWS unpubl. data). The most commonly detected residues were the chlordanes, total DDT and dieldrin, although the chlorobenzenes and PCBs were also prevalent in the diving species.

Of the eggs analyzed thus far, those of Glaucous Gull contained higher levels of organochlorines (except for dieldrin) than those of eiders (Table 3). Residue levels in Glaucous Gull eggs harvested from the Coppermine area are not much different from eggs collected further west near the Anderson River (for comparisons, see Table 1 in following report on Contaminants in Arctic Seabirds). The residue levels in Glaucous Gull eggs collected from the NWT mainland (Coppermine area, Anderson River), however, are considerably lower than those found in eggs collected from the High Arctic (Prince Leopold Island, Browne Island). Residue levels in eider eggs are similar to levels found in eiders collected in northern Quebec and Labrador (Braune 1993).

DISCUSSION/CONCLUSIONS

All chemical data on the birds collected from the NWT in 1993/94 will be submitted to the Bureau of Chemical Safety of Health Canada in late 1994 or early 1995 for evaluation of risk to human health of eating those harvested birds and eggs. Health Canada has recently issued its report with recommendations for earlier residue data (1988-92) for samples collected from the NWT, Yukon, northern Quebec and Labrador. Those recommendations are being forwarded to the appropriate local health authorities.

The data are being submitted on an annual basis to the Arctic Contaminants Database managed by the Département de Santé Communautaire du Centre Hospitalier de l'Université Laval. As well, the data will be submitted as part of the Canadian database to the Arctic Monitoring and Assessment Programme (AMAP).

Expected project completion date: March 31, 1996

REFERENCES

Braune, B.M. 1993. Trends and effects of environmental contaminants in arctic seabirds, waterfowl, and other wildlife. Study I. Contaminants in waterfowl: Native harvest in Labrador. Pp. 203-221 *in*: Synopsis of Research Conducted Under the 1992/93 Northern Contaminants Program, J.L. Murray and R.G Shearer (eds.). Environmental Studies No. 70. Indian and Northern Affairs Canada, Ottawa. 285 pp.

Coad, S. 1994. Consumption of fish and wildlife by Canadian native peoples: a quantitative assessment from the published and unpublished literature. Unpublished Report, Health Canada.

TABLE 1. HARVESTED BIRDS AND EGGS SAMPLED IN NWT DURING 1993

	SPECIES SAMPLED	
LOCATION	BIRDS	EGGS
Yellowknife	Mallard	
	Northern Pintail	
	Canvasback	
	American Wigeon	
	Bufflehead	
	Green-winged Teal	
	Greater Scaup	
	Ring-necked Duck	
Fort Good Hope	Canada Goose	
	Rock Ptarmigan	
	Willow Ptarmigan	
	Spruce Grouse	
	Sharp-tailed Grouse	
	Surf Scoter	
	White-winged Scoter	
	Oldsquaw	
Inuvik	Oldsquaw	
Holman I	Oldsquaw	Glaucous Gull *
Coppermine area	Willow Ptarmigan	Glaucous Gull *
	Oldsquaw	Common Eider *
	Yellow-billed Loon	
	Arctic Loon	
Grise Fiord	Common Eider	
	Rock Ptarmigan	
Hall Beach	Snow Goose	King Eider *
	Oldsquaw	
	Common Eider	
Cape Dorset	Snow Goose	Common Eider *
	Oldsquaw	
	Common Eider	
Coral Harbour	Snow Goose	Snow Goose
	Canada Goose	Canada Goose
	Common Eider	
	Oldsquaw	
Arviat	Snow Goose	Snow Goose
	Canada Goose	Canada Goose
	Common Eider	
	Oldsquaw	
Baker Lake	Oldsquaw	
	Willow Ptarmigan	
	Canada Goose	
Sanikiluaq	Oldsquaw	
	Rock Ptarmigan	

* collections also used in study of arctic seabirds

TABLE 2. LEVELS OF ORGANOCHLORINES IN BREAST MUSCLE OF BIRDS HARVESTED IN NWT

Wet Wt. (mg/kg or ppm)

I.D.	Species	Age	Sex	N	Date mo yr	Location	% Lipid	SUM CBz	SUM HCH	OCS	SUM CHLOR	SUM DDT	SUM MIREX	DIELDRIN	SUM PCB
49246	Canada Goose	1Ad,1Im	1F,1M	2	5/6 91	Arviat	3.00	ND	ND	ND	0.003	0.001	ND	ND	0.003
46654	Canada Goose	9Im,1U	9F,1M	10	Spr 90	Sanikiluaq	1.55	ND	ND	ND	ND	ND	ND	ND	ND
44791	Canada Goose	10Ad	3F,6M,1U	10	5/6 90	Spence Bay	4.93	ND	ND	ND	0.003	ND	ND	ND	ND
60490	Canada Goose	10Ad	3F,7M	10	6 93	Baker Lake area	3.12	ND	ND	ND	ND	0.001	ND	ND	ND
49331	Lesser Snow Goose	1Im	1F	1	5/6 91	Arviat	5.09	ND	ND	ND	ND	0.002	ND	ND	ND
49333	Lesser Snow Goose	7Ad	7F	7	5/6 91	Arviat	5.25	ND	ND	ND	ND	ND	ND	0.001	ND
49332	Lesser Snow Goose	7Ad	7M	7	5/6 91	Arviat	5.16	ND	ND	ND	ND	0.001	ND	0.001	ND
43107	Lesser Snow Goose	4Ad	4F	4	6 89	Eskimo Point	4.58	ND	ND	ND	0.001	ND	ND	0.001	ND
43108	Lesser Snow Goose	6Ad	6M	6	6 89	Eskimo Point	3.86	ND	ND	ND	0.001	0.001	ND	0.001	ND
43109	Lesser Snow Goose	4Ad	2F,2M	4	5 89	Tuktoyaktuk	4.12	ND	ND	ND	0.001	ND	ND	ND	ND
43110	Lesser Snow Goose	6Im	2F,3M,1U	6	5 89	Tuktoyaktuk	4.36	ND	ND	ND	0.005	0.001	ND	0.001	ND
39916	Mallard	7Im,1Ad,2U	6F,4M	10	9/10 88	Stagg River	1.94	ND	ND	ND	ND	ND	ND	ND	0.002
43279	Common Eider	5Im	3F,2M	5	1 90	Cumberland Sound area	3.47	0.005	ND	ND	0.004	0.001	ND	ND	0.007
43280	Common Eider	3Ad	3F	3	1 90	Cumberland Sound area	3.28	0.003	ND	ND	0.001	0.003	ND	0.002	0.006
40634	Common Eider	2Ad	2F	2	11 88	Sanikiluaq	3.31	0.006	ND	ND	0.012	0.017	0.001	0.004	0.019
40870	Common Eider	5Ad	5M	5	11 88	Sanikiluaq	3.35	0.002	ND	ND	0.003	0.005	ND	0.001	0.005
40871	Common Eider	5Im	1F,4M	5	11 88	Sanikiluaq	3.07	0.001	ND	ND	0.001	0.003	ND	0.002	0.003
43111	King Eider	3Ad	3F	3	5 89	Holman Island	4.32	0.002	0.001	ND	0.003	0.004	ND	0.001	0.005
43112	King Eider	8Ad	8M	8	5 89	Holman Island	4.30	0.003	0.001	ND	0.002	0.003	ND	0.001	0.005
60488	Oldsquaw	9Ad,1U	4F,5M,1U	10	6 93	Baker Lake area	3.84	0.006	0.027	ND	0.048	0.142	ND	0.090	0.173
62171	Oldsquaw	10Ad	2F,8M	10	7 93	Holman	3.81	0.004	0.013	ND	0.003	0.004	ND	0.001	0.008
60489	Willow Ptarmigan	5Ad	3F,2M	5	5/6 93	Baker Lake area	3.23	ND	ND	ND	ND	ND	ND	ND	ND

ND < 0.001 mg/kg wet wt.

Im - Immature; Ad - Adult; F - Female; M - Male; U - Unknown
N = number of birds in pooled sample
SUM CBz = Sum of 1,2,3,5- & 1,2,3,4-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene
SUM HCH = Sum of alpha-, beta- & gamma-hexachlorocyclohexane
OCS = Octachlorostyrene
SUM CHLOR = Sum of oxy-, trans & cis-chlordane, trans- & cis-nonachlor and heptachlor epoxide
SUM DDT = Sum of p,p'-DDE, p,p'-DDD & p,p'-DDT
SUM MIREX = Sum of photo-mirex and mirex
SUM PCB = Sum of PCB congeners: 1988 - 17 congeners = 28, 31, 52, 66/95, 87, 99, 101, 105, 110, 118, 138, 153, 170/190, 174, 180, 182/187, 194
1989 - 24 congeners = 1988 congeners & 44, 172, 183, 195, 201, 203, 206
1990 - 29 congeners = 1989 congeners & 60, 97, 141, 146, 171
1991 - 38 congeners = 1990 congeners & 42, 64, 70, 74, 129, 149, 151, 185, 200
1993 - 42 congeners = 1991 congeners & 49, 128, 137, 158

TABLE 3. MEAN LEVELS OF ORGANOCHLORINES IN HARVESTED EGGS OF ARCTIC BIRDS

Wet Wt. (mg/kg or ppm)

	#	# Eggs/	Date	Location					SUM	SUM		SUM	SUM	SUM		SUM
Species	Pools	Pool	mo yr	Lat	Long	Place Name		% Lipid	CBz	HCH	OCS	CHLOR	DDT	MIREX	DIELDRIN	PCB
Glaucous Gull	5	3*	6 93	6749	11505	Coppermine area	Mean	8.64	0.052	0.020	0.003	0.078	0.339	0.015	0.008	0.462
							S.D.	1.15	0.023	0.008	0.001	0.029	0.123	0.006	0.006	0.050
Common Eider	5	3	7 93	6820	11425	Coppermine area	Mean	16.06	0.019	0.013	ND	0.025	0.017	ND	0.008	0.031
							S.D.	1.57	0.002	0.009	---	0.004	0.004	---	0.006	0.005
Common Eider	5	3	6 93	6410	07629	Cape Dorset	Mean	17.30	0.010	0.001	ND	0.014	0.014	ND	0.007	0.030
							S.D.	0.96	0.001	0.001	---	0.002	0.001	---	0.004	0.001
King Eider	5	3	6 93	6847	08113	Hall Beach	Mean	14.18	0.012	0.003	ND	0.021	0.012	ND	0.010	0.042
							S.D.	0.46	0.003	0.003	---	0.006	0.003	---	0.001	0.028

ND < 0.001 mg/kg wet wt.

* one of the 5 pools contained only 2 eggs

SUM CBz = Sum of 1,2,3,5- & 1,2,3,4-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene
SUM HCH = Sum of alpha-, beta- & gamma-hexachlorocyclohexane
OCS = Octachlorostyrene
SUM CHLOR = Sum of oxy-, trans & cis-chlordane, trans- & cis-nonachlor and heptachlor epoxide
SUM DDT = Sum of p,p'-DDE, p,p'-DDD & p,p'-DDT
SUM MIREX = Sum of photo-mirex and mirex
SUM PCB = Sum of PCB congeners: 1993 - 42 congeners (see Table 2)

TRENDS AND EFFECTS OF ENVIRONMENTAL CONTAMINANTS IN ARCTIC SEABIRDS, WATERFOWL, AND OTHER WILDLIFE

II. CONTAMINANTS IN ARCTIC SEABIRDS

PROJECT LEADER: B.M. Braune, National Wildlife Research Centre, Canadian Wildlife Service (CWS), Environment Canada

PROJECT TEAM: B. Wakeford, A. Gaston, A. Scheuhammer, CWS (Hull);
D. Nettleship, CWS (Atlantic); K. McCormick, CWS (Yellowknife)

OBJECTIVES

Part 1. Contaminants in seabird eggs: To determine if levels of contaminants in eggs of arctic seabirds, as representative of the marine environment, are declining.

Part 2. Contaminant loading in seabirds: To determine whether or not seabirds are picking up contaminants locally in the Canadian Arctic, and whether the contaminant levels found are indicative of possible wildlife health concerns.

DESCRIPTION

During the mid-1970s, the Canadian Wildlife Service (CWS) conducted surveys to determine organochlorine levels in eggs and tissues of a number of arctic seabirds (Thick-billed Murres, Black-legged Kittiwakes, Northern Fulmars, Ivory Gulls). Seabirds breeding in the High Arctic were shown to be contaminated with a similar suite of organic contaminants as those breeding in temperate regions (Noble and Elliott 1986). Subsequent surveys conducted in the late 1980s showed that organochlorine levels had generally decreased in migrant species (probably reflecting overall lower contamination of the food chain in oceanic wintering areas), but organochlorine levels in eggs of a resident arctic species (Ivory Gull) had remained stable or increased (Noble 1990). Very limited data has been collected on heavy metals in arctic seabirds despite evidence showing that seabirds elsewhere accumulate very high levels, particularly of cadmium and mercury.

Part 1. Survey of contaminants in seabird eggs

The seabird egg contaminant monitoring program was established by CWS to provide an index to contamination of the marine ecosystem. Collection of eggs was chosen as a non-intrusive way of obtaining information. The program is divided into three components: Atlantic, Pacific and Arctic. This study is part of an ongoing survey to provide an indication of trends in organochlorine contamination in the marine environment of the Canadian Arctic.

In order to continue historical trends, 1993 collections were proposed for the Northern Fulmar, Black-legged Kittiwake and Thick-billed Murre. Continued collection of the Ivory Gull was dropped because this species, although not endangered, is not particularly common. It is also known to frequently scavenge at garbage dumps which compromises its usefulness as a monitor of the marine environment.

In order to include a greater variety of habitats and trophic levels, several species were added. The Black Guillemot was added since it is distributed throughout Canadian waters, appears to be a benthic feeder everywhere, and is resident in the Arctic. The Glaucous Gull was also added because of its designation as an essential species for monitoring of contaminants under the Arctic Monitoring and Assessment Programme (AMAP). Eggs of Common/King Eiders were collected as well to represent benthic invertebrate feeders.

Part 2. Contaminant loading in seabirds

In order to investigate the local contaminant situation in selected areas of the Canadian Arctic, seabird species representing different habitats and trophic levels were studied. The first component of Part 2 of this study looks at whether or not chicks are taking up contaminants from the local marine environment by calculating the difference between total contaminant load in the egg contents and contaminant body burden in the whole chick. The resulting difference in contaminant load will be used as an indication of whether or not a given contaminant is being taken up via food from the local environment. The second component looks at the results of organochlorine as well as of metal and metallothionein analyses for tissues of the adult birds as an indication of the health of the adult seabird population with respect to contamination.

ACTIVITIES IN 1993/94

In 1993, eggs were collected for seven species: Northern Fulmar, Thick-billed Murre, Black-legged Kittiwake, Black Guillemot, Glaucous Gull, and Common and King Eider. A total of 17 collections were made from colonies in the eastern Low Arctic (Digges Island, Nuvuk Islands, Coats Island, Walrus Island, Cape Dorset, Hall Beach), the western Low Arctic (Anderson River, Coppermine) and the High Arctic (Coburg Island, Prince Leopold Island, Browne Island). Not all species were collected from all sites.

A collection of 15 eggs per species per site was made where possible. Eggs were collected by hand on the basis of one egg per nest. Eggs were analyzed for metals (lead, cadmium, mercury, selenium) and organochlorines including PCBs. The eggs were analyzed in 5 pools of 3 eggs each (except where noted).

Chicks and adults of five species were analyzed: Black-legged Kittiwake, Black Guillemot, Thick-billed Murre, Northern Fulmar, and Glaucous Gull. Egg-chick collections were available for contaminant burden comparisons for all five species although the collections were not paired from the same nests. Chicks were collected by hand and dispatched by cervical dislocation. The adult birds were either shot, or noosed and dispatched by cervical dislocation.

A collection of 10 chicks and 10 adult birds per species per site was requested although not always obtained. Samples were analyzed for organochlorines and PCBs, mercury, lead, cadmium and selenium on a pooled basis, that is, samples of individuals of the same species from a given location collected within a specified time period are pooled to make a composite sample. Chicks were analyzed on a whole body basis (feathers were analyzed separately for metals only) to allow calculation of total body burden for a given contaminant. For the adults, liver samples were analyzed. A 1992 collection of Glaucous Gulls from Coats Island and a 1983 collection of Glaucous Gulls from Akpatok Island, which have been stored in the CWS Specimen Bank, were also analyzed in order to obtain historical information for that species.

Metallothionein, primarily a biomarker of cadmium accumulation, was also measured in kidney samples from the adult birds. This requires analyses of cadmium, zinc and copper in addition to metallothionein in kidney on an individual basis.

A. Gaston arranged collections from the eastern Low Arctic, eggs and adult birds from Prince Leopold and Browne Islands were collected by B. Braune, Coburg Island samples and Prince Leopold chicks were collected by D. Nettleship, and collections from the western Low Arctic were arranged through the CWS in Yellowknife.

Collection, storage and analytical protocols specified by the National Wildlife Research Centre (NWRC), Hull, Quebec, were followed. All tissues were processed at NWRC. Egg samples were sent to the analytical laboratories of the Great Lakes Institute, University of Windsor, for chemical residue analyses for PCBs and organochlorines. Metal analyses for eggs, chicks and adult livers as well as organochlorine analyses for the chicks and adult livers were carried out in the CWS laboratories at NWRC. All of these laboratories have participated in the 1993/94 interlaboratory quality assurance program for analytical data produced for the Northern Contaminants Program of the Arctic Environmental Strategy. Analyses of metallothionein and the associated cadmium, copper and zinc analyses were done for kidneys of the individual adult birds in the laboratory of A. Scheuhammer at NWRC.

RESULTS

Mean residue levels (and standard deviations) given in Table 1 show that Glaucous Gull eggs collected from the High Arctic (Prince Leopold and Browne Islands) generally contained the highest concentrations of organochlorine residues whereas the eiders followed by the Black-legged Kittiwakes contained the lowest levels. Glaucous Gull chicks (Table 2A) and livers of adult Glaucous Gulls (Table 3) also contained the highest residue concentrations of organochlorine residues. This is to be expected since this species is highly predatory, often feeding on the eggs and chicks of other birds or scavenging on carcasses.

Preliminary comparison of 1993 egg residue data from Prince Leopold Island with data for the same location from the 1970s and mid-1980s (Nettleship and Peakall 1987; Noble 1990) shows a stabilization of PCB (as Aroclor 1254:1260) and DDT residues for Thick-billed Murres (TBMU), a continuing decline in levels for Black-legged Kittiwakes (BLKI), and possibly an increase in DDE levels in Northern Fulmars (NOFU) (Figure 1).

Comparisons of total body burdens of organochlorine residues between eggs and chicks shows the largest difference in Glaucous Gulls from Prince Leopold Island (Table 2B). This may be due to the fact that the eggs were close to hatch when collected so the chicks were being fed for a longer period of time than the other species and their predatory parents probably brought their chicks the eggs and chicks of other species on which to feed.

Lead and cadmium were virtually not detected in the eggs (Table 4) and lead was only minimally detected in the chicks (Table 5) and livers of adult birds (Table 7). The highest levels of total mercury were found in eggs of Glaucous Gulls from Prince Leopold Island whereas the highest selenium levels were found in eggs of Black-legged Kittiwakes (Table 4). Although burdens of total mercury increase from egg to chick for all species (Table 6), much of the mercury is concentrated in the feathers (Table 5). Cadmium and, to a lesser extent, lead are taken up by the chick after hatch (Table 6) indicating that transfer of these elements from parent to egg is minimal. Of the species collected from Prince Leopold Island, adult Northern Fulmars contained the highest total mercury and cadmium levels and, along with Black-legged Kittiwakes, the highest selenium levels (Table 7). There is evidence that mercury and cadmium are atmospherically transported to the Arctic (Barrie *et al.* 1992) and since both species are surface feeders, they are likely obtaining these contaminants through their prey.

Regression analyses of metallothionein levels in kidney against cadmium, copper and zinc concentrations were run on data for 71 individuals (collections listed in Table 3). The highest correlation was with cadmium ($r=0.81$, $P<0.001$) followed by zinc ($r=0.63$, $P<0.001$). The relationship between metallothionein and copper was not significant ($r=0.23$, $P>0.05$).

DISCUSSION/CONCLUSIONS

Results from this study will contribute to the historical time trend data as well as adding needed new information on other species. The metal residue data will add substantially to what little is known about metals in Canadian arctic seabirds.

The data will be submitted to the Arctic Contaminants Database managed by the Département de Santé Communautaire du Centre Hospitalier de l'Université Laval. As well, the data will be submitted as part of the Canadian database to the Arctic Monitoring and Assessment Programme.

Expected project completion date: March 31, 1995

REFERENCES

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. 122: 1-74.

Nettleship, D.N. and D.B. Peakall. 1987. Organochlorine residue levels in three high arctic species of colonially-breeding seabirds from Prince Leopold Island. Mar. Pollut. Bull. 18: 434-438.

Noble, D.G. 1990. Contaminants in Canadian seabirds. SOE Report No. 90-2.

Noble, D.G. and J.E. Elliott. 1986. Environmental contaminants in Canadian seabirds 1968-1985: trends and effects. Technical Report Series No. 13, Canadian Wildlife Service, Ottawa.

TABLE 1. MEAN LEVELS OF ORGANOCHLORINES IN EGGS OF ARCTIC BIRDS

Wet Wt. (mg/kg or ppm)

Species	# Pools	# Eggs/ Pool	Date mo yr	Location Lat	Long	Place Name		% Lipid	SUM CBz	SUM HCH	OCS	SUM CHLOR	SUM DDT	SUM MIREX	DIELDRIN	SUM PCB
Thick-billed Murre	5	1	7 91	6235	07750	Digges I	Mean	13.81	0.069	0.012	0.007	0.053	0.200	0.002	0.022	0.156
							S.D.	1.81	0.007	0.004	0.002	0.010	0.052	0.002	0.007	0.029
Thick-billed Murre	5	3	7 93	6235	07750	Digges I	Mean	12.52	0.129	0.018	0.013	0.063	0.311	0.011	0.026	0.434
							S.D.	0.27	0.015	0.004	0.001	0.013	0.064	0.002	0.007	0.086
Thick-billed Murre	5	3	7 93	6250	08300	Coats I	Mean	14.50	0.124	0.023	0.012	0.058	0.326	0.006	0.021	0.360
							S.D.	0.75	0.021	0.003	0.001	0.010	0.078	0.002	0.002	0.088
Thick-billed Murre	5	3	7 93	7402	09005	Prince Leopold I	Mean	12.23	0.054	0.020	0.004	0.042	0.201	0.033	0.013	0.233
							S.D.	0.48	0.019	0.010	0.001	0.046	0.130	0.040	0.002	0.150
Thick-billed Murre	5	3	8 93	7550	07925	Coburg I	Mean	13.46	0.078	0.018	0.016	0.039	0.309	0.008	0.014	0.420
							S.D.	1.09	0.018	0.003	0.002	0.003	0.083	0.001	0.002	0.040
Black Guillemot	4	3	7 93	6235	07803	Nuvuk Is	Mean	9.40	0.106	0.019	0.013	0.141	0.150	0.017	0.019	0.577
							S.D.	0.75	0.010	0.003	0.002	0.026	0.034	0.005	0.004	0.109
Black Guillemot	5	3	7 93	6316	08340	Walrus I	Mean	11.71	0.092	0.018	0.011	0.111	0.144	0.007	0.012	0.300
							S.D.	0.86	0.013	0.002	0.002	0.029	0.027	0.001	0.006	0.056
Black Guillemot	4	3	7 93	7402	09005	Prince Leopold I	Mean	10.08	0.079	0.025	0.011	0.068	0.162	0.004	0.015	0.317
							S.D.	0.22	0.010	0.006	0.001	0.019	0.061	0.001	0.009	0.054
Northern Fulmar	5	3	6 93	7402	09005	Prince Leopold I	Mean	11.88	0.069	0.005	0.004	0.136	0.490	0.036	0.013	0.563
							S.D.	1.86	0.015	0.002	0.001	0.015	0.081	0.031	0.002	0.100
Black-legged Kittiwake	5	1	8 93	7550	07925	Coburg I	Mean	10.00	0.045	0.005	0.008	0.061	0.124	0.021	0.016	0.602
							S.D.	2.54	0.009	0.002	0.002	0.011	0.051	0.009	0.004	0.196
Black-legged Kittiwake	5	3	7 93	7402	09005	Prince Leopold I	Mean	8.54	0.043	0.005	0.004	0.024	0.122	0.013	0.008	0.470
							S.D.	1.27	0.013	0.002	0.001	0.007	0.024	0.005	0.002	0.138

TABLE 1. cont'd

Wet Wt. (mg/kg or ppm)

Species	# Pools	# Eggs/ Pool	Date mo yr	Location Lat	Long	Place Name		% Lipid	SUM CBz	SUM HCH	OCS	SUM CHLOR	SUM DDT	SUM MIREX	DIELDRIN	SUM PCB
Glaucous Gull	5	3	6 93	6944	12858	Anderson R area	Mean	8.36	0.062	0.022	0.003	0.048	0.144	0.009	0.008	0.316
							S.D.	0.59	0.023	0.010	0.001	0.013	0.070	0.003	0.003	0.117
Glaucous Gull	5	3*	6 93	6749	11505	Coppermine area	Mean	8.64	0.052	0.020	0.003	0.078	0.339	0.015	0.008	0.462
							S.D.	1.15	0.023	0.008	0.001	0.029	0.123	0.006	0.006	0.050
Glaucous Gull	5	2	6 93	7402	09005	Prince Leopold I	Mean	8.85	0.235	0.066	0.021	0.388	2.367	0.095	0.028	3.326
							S.D.	0.74	0.065	0.034	0.007	0.120	0.188	0.031	0.017	0.423
Glaucous Gull	5	2	7 93	7449	09621	Browne I	Mean	8.42	0.143	0.070	0.010	0.295	0.831	0.030	0.023	1.262
							S.D.	0.49	0.050	0.021	0.003	0.082	0.250	0.013	0.029	0.437
Common Eider	5	3	7 93	6820	11425	Coppermine area	Mean	16.06	0.019	0.013	ND	0.025	0.017	ND	0.008	0.031
							S.D.	1.57	0.002	0.009	---	0.004	0.004	---	0.006	0.005
Common Eider	5	3	6 93	6410	07629	Cape Dorset	Mean	17.30	0.010	0.001	ND	0.014	0.014	ND	0.007	0.030
							S.D.	0.96	0.001	0.001	---	0.002	0.001	---	0.004	0.001
King Eider	5	3	6 93	6847	08113	Hall Beach	Mean	14.18	0.012	0.003	0.000	0.021	0.012	ND	0.010	0.042
							S.D.	0.46	0.003	0.003	0.000	0.006	0.003	---	0.001	0.028

ND < 0.001 mg/kg wet wt.

* one of the 5 pools contained only 2 eggs

SUM CBz = Sum of 1,2,3,5- & 1,2,3,4-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene
SUM HCH = Sum of alpha-, beta- & gamma-hexachlorocyclohexane
OCS = Octachlorostyrene
SUM CHLOR = Sum of oxy-, trans & cis-chlordane, trans- & cis-nonachlor and heptachlor epoxide
SUM DDT = Sum of p,p'-DDE, p,p'-DDD & p,p'-DDT
SUM MIREX = Sum of photo-mirex and mirex
SUM PCB = Sum of PCB congeners: 1991 - 38 congeners = 28, 31, 42, 44, 52, 60, 64, 66/95, 70, 74, 87, 97, 99, 101, 105, 110, 118, 129, 138, 141, 146,
149, 151, 153, 170/190, 171, 172, 174, 180, 182/187, 183, 185, 194, 195, 200, 201, 203, 206
1993 - 42 congeners = 1991 congeners & 49, 128, 137, 158

TABLE 2A. LEVELS OF ORGANOCHLORINES IN EGGS AND CHICKS OF ARCTIC SEABIRDS

Wet Wt. (mg/kg or ppm)

Species	Sample	# Pools	# Eggs or Chicks/Pool	Date mo yr	Location Lat	Long	Place Name	% Lipid	SUM CBz	SUM HCH	OCS	SUM CHLOR	SUM DDT	SUM MIREX	DIELDRIN	SUM PCB
Thick-billed Murre	Egg	5	3	8 93	7550	07925	Coburg I	13.46	0.078	0.018	0.016	0.039	0.309	0.008	0.014	0.420
Thick-billed Murre	Chick	1	6	8 93	7550	07925	Coburg I	9.40	0.060	0.008	0.006	0.024	0.237	0.005	0.012	0.263
Thick-billed Murre	Egg	5	3	7 93	7402	09005	Prince Leopold I	12.23	0.054	0.020	0.004	0.042	0.201	0.033	0.013	0.233
Thick-billed Murre	Chick	1	10	8 93	7402	09005	Prince Leopold I	7.50	0.051	0.008	0.004	0.019	0.095	0.004	0.008	0.127
Thick-billed Murre	Egg	5	3	7 93	6250	08300	Coats I	14.50	0.124	0.023	0.012	0.058	0.326	0.006	0.021	0.360
Thick-billed Murre	Chick	1	10	8 93	6250	08300	Coats I	10.00	0.069	0.006	0.007	0.038	0.192	0.006	0.014	0.192
Black Guillemot	Egg	4	3	7 93	7402	09005	Prince Leopold I	10.08	0.079	0.025	0.011	0.068	0.162	0.004	0.015	0.317
Black Guillemot	Chick	1	10	8 93	7402	09005	Prince Leopold I	14.70	0.042	0.013	0.004	0.039	0.040	0.003	0.011	0.141
Black Guillemot	Egg	4	3	7 93	6235	07803	Nuvuk Is	9.40	0.106	0.019	0.013	0.141	0.150	0.017	0.019	0.577
Black Guillemot	Chick	1	10	8 93	6235	07803	Nuvuk Is	11.50	0.018	0.005	0.002	0.024	0.020	0.002	0.009	0.059
Northern Fulmar	Egg	5	3	6 93	7402	09005	Prince Leopold I	11.88	0.069	0.005	0.004	0.136	0.490	0.036	0.013	0.563
Northern Fulmar	Chick	1	10	8 93	7402	09005	Prince Leopold I	12.70	0.030	0.008	0.001	0.064	0.248	0.013	0.006	0.302
Black-legged Kittiwake	Egg	5	3	7 93	7402	09005	Prince Leopold I	8.54	0.043	0.005	0.004	0.024	0.122	0.013	0.008	0.470
Black-legged Kittiwake	Chick	1	1	8 93	7402	09005	Prince Leopold I	7.70	0.018	0.004	0.003	0.020	0.038	0.006	0.005	0.179
Glaucous Gull	Egg	5	2	6 93	7402	09005	Prince Leopold I	8.85	0.235	0.066	0.021	0.388	2.367	0.095	0.028	3.326
Glaucous Gull	Chick	1	4	8 93	7402	09005	Prince Leopold I	12.70	0.190	0.030	0.020	0.161	1.139	0.050	0.027	1.635

Detection Limit = 0.001 mg/kg wet wt.

Results for eggs are calculated means for 4-5 pools of 2-3 eggs each per collection (see Table 1)
Results for chicks are for the single pooled analysis per collection

SUM CBz = Sum of 1,2,3,5- & 1,2,3,4-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene
SUM HCH = Sum of alpha-, beta- & gamma-hexachlorocyclohexane
OCS = Octachlorostyrene
SUM CHLOR = Sum of oxy-, trans & cis-chlordane, trans- & cis-nonachlor and heptachlor epoxide
SUM DDT = Sum of p,p'-DDE, p,p'-DDD & p,p'-DDT
SUM MIREX = Sum of photo-mirex and mirex
SUM PCB = Sum of PCB congeners: 1993 - 42 congeners = 28, 31, 42, 44, 49, 52, 60, 64, 66/95, 70, 74, 87, 97, 99, 101, 105, 110, 118, 128, 129, 137, 138, 141, 146, 149, 151, 153, 158, 170/190, 171, 172, 174, 180, 182/187, 183, 185, 194, 195, 200, 201, 203, 206

TABLE 2B. TOTAL BURDENS OF ORGANOCHLORINES IN EGGS AND CHICKS OF ARCTIC SEABIRDS

Mean Residue Burdens (ug)

Species	Sample	# Pools	# Eggs or Chicks/Pool	Date mo yr	Place Name	Mean Wt. (g)	% Lipid	SUM CBz	SUM HCH	OCS	SUM CHLOR	SUM DDT	SUM MIREX	DIELDRIN	SUM PCB
Thick-billed Murre	Egg	5	3	8 93	Coburg I	72.1	13.5	5.63	1.33	1.14	2.81	22.26	0.57	1.03	30.30
Thick-billed Murre	Chick	1	6	8 93	Coburg I	88.0	9.4	5.31	0.67	0.51	2.12	20.83	0.42	1.09	23.16
Thick-billed Murre	Egg	5	3	7 93	Prince Leopold I	75.1	12.2	4.05	1.48	0.30	3.14	15.07	2.51	0.94	17.52
Thick-billed Murre	Chick	1	10	8 93	Prince Leopold I	115.8	7.5	5.88	0.90	0.43	2.25	10.97	0.43	0.90	14.66
Thick-billed Murre	Egg	5	3	7 93	Coats I	75.9	14.5	9.37	1.72	0.88	4.41	24.72	0.46	1.61	27.28
Thick-billed Murre	Chick	1	10	8 93	Coats I	185.1	10.0	12.70	1.09	1.20	7.02	35.59	1.13	2.55	35.51
Black Guillemot	Egg	4	3	7 93	Prince Leopold I	42.4	10.1	3.35	1.04	0.46	2.87	6.90	0.17	0.65	13.47
Black Guillemot	Chick	1	10	8 93	Prince Leopold I	207.0	14.7	8.78	2.69	0.83	8.09	8.20	0.58	2.26	29.26
Black Guillemot	Egg	4	3	7 93	Nuvuk Is	36.8	9.4	3.89	0.70	0.49	5.17	5.51	0.63	0.72	21.20
Black Guillemot	Chick	1	10	8 93	Nuvuk Is	253.8	11.5	4.54	1.24	0.43	6.19	5.13	0.53	2.39	14.90
Northern Fulmar	Egg	5	3	6 93	Prince Leopold I	79.7	11.9	5.51	0.38	0.35	10.84	39.06	2.84	1.03	44.84
Northern Fulmar	Chick	1	10	8 93	Prince Leopold I	142.2	12.7	4.27	1.07	0.16	9.06	35.28	1.86	0.82	42.95
Black-legged Kittiwake	Egg	5	3	7 93	Prince Leopold I	37.8	8.5	1.62	0.19	0.14	0.92	4.62	0.47	0.30	17.76
Black-legged Kittiwake	Chick	1	1	8 93	Prince Leopold I	97.4	7.7	1.77	0.39	0.26	1.93	3.70	0.62	0.46	17.47
Glaucous Gull	Egg	5	2	6 93	Prince Leopold I	98.5	8.9	23.17	6.49	2.04	38.27	233.17	9.36	2.74	327.64
Glaucous Gull	Chick	1	4	8 93	Prince Leopold I	730.2	12.7	138.66	21.69	14.38	117.78	831.33	36.29	19.50	1193.69

Mean egg weight refers to egg contents
Mean chick weight refers to plucked carcass

SUM CBz = Sum of 1,2,3,5- & 1,2,3,4-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene
SUM HCH = Sum of alpha-, beta- & gamma-hexachlorocyclohexane
OCS = Octachlorostyrene
SUM CHLOR = Sum of oxy-, trans & cis-chlordane, trans- & cis-nonachlor and heptachlor epoxide
SUM DDT = Sum of p,p'-DDE, p,p'-DDD & p,p'-DDT
SUM MIREX = Sum of photo-mirex and mirex
SUM PCB = Sum of PCB congeners: 1993 - 42 congeners = 28, 31, 42, 44, 49, 52, 60, 64, 66/95, 70, 74, 87, 97, 99, 101, 105, 110, 118, 128, 129, 137, 138, 141, 146, 149, 151, 153, 158, 170/190, 171, 172, 174, 180, 182/187, 183, 185, 194, 195, 200, 201, 203, 206

TABLE 3. LEVELS OF ORGANOCHLORINES IN LIVERS OF ADULT ARCTIC SEABIRDS

Wet Wt. (mg/kg or ppm)

			Date	Location				SUM	SUM		SUM	SUM	SUM		SUM
Species	N	Sex	mo yr	Lat	Long	Place Name	% Lipid	CBz	HCH	OCS	CHLOR	DDT	MIREX	DIELDRIN	PCB
Thick-billed Murre	4	1F,3M	6/8 91	6214	07538	Salluit	5.00	0.042	0.003	0.005	0.020	0.125	0.004	0.008	0.143
Thick-billed Murre	5	3F,2M	7 91	6224	07755	Ivujivik	3.90	0.048	0.004	0.004	0.022	0.156	0.005	0.007	0.176
Thick-billed Murre	10	1F,9M	8 93	6250	08300	Coats I	3.00	0.033	0.003	0.003	0.020	0.073	0.020	0.005	0.930
Thick-billed Murre	10	5F,5M	7 93	7402	09005	Prince Leopold I	4.90	0.038	0.006	0.005	0.019	0.114	0.005	0.008	0.168
Black Guillemot	10	6F,4M	8 93	6235	07803	Nuvuk Is	3.30	0.016	0.002	0.002	0.028	0.047	0.005	0.006	0.102
Black Guillemot	5	4F,1M	7 93	7402	09005	Prince Leopold I	3.30	0.029	0.005	0.003	0.032	0.059	0.003	0.010	0.082
Northern Fulmar	10	8F,2M	6 93	7402	09005	Prince Leopold I	3.30	0.029	ND	0.004	0.104	0.178	0.009	0.012	0.196
Black-legged Kittiwake	10	3F,7M	6 93	7402	09005	Prince Leopold I	4.20	0.028	0.002	0.003	0.029	0.071	0.014	0.008	0.359
Glaucous Gull	5	3F,2M	8 83	6025	06808	Akpatok I	4.60	0.246	0.011	0.017	0.217	2.238	0.079	0.030	2.301
Glaucous Gull	2	1F,1M	8 92	6250	08300	Coats I	3.60	0.086	0.010	0.010	0.457	1.965	0.111	0.041	2.506

ND < 0.001 mg/kg wet wt.

F - Female; M - Male
N = number of birds in pooled sample

SUM CBz = Sum of 1,2,3,5- & 1,2,3,4-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene
SUM HCH = Sum of alpha-, beta- & gamma-hexachlorocyclohexane
OCS = Octachlorostyrene
SUM CHLOR = Sum of oxy-, trans & cis-chlordane, trans- & cis-nonachlor and heptachlor epoxide
SUM DDT = Sum of p,p'-DDE, p,p'-DDD & p,p'-DDT
SUM MIREX = Sum of photo-mirex and mirex
SUM PCB = Sum of PCB congeners: 42 congeners = 28, 31, 42, 44, 49, 52, 60, 64, 66/95, 70, 74, 87, 97, 99, 101, 105, 110, 118, 128, 129, 137, 138, 141, 146, 149, 151, 153, 158, 170/190, 171, 172, 174, 180, 182/187, 183, 185, 194, 195, 200, 201, 203, 206

TABLE 4. MEAN METAL LEVELS IN EGGS OF ARCTIC SEABIRDS

Dry Wt. (mg/kg or ppm)

Species	# Pools	# Eggs/ Pool	Date mo yr	Location		% H2O	Total Hg	Pb	Cd	Se
Northern Fulmar	5	3	6 93	Prince Leopold I	Mean	73	1.19	<0.13	<0.25	4.01
					S.D.	3.3	0.21	---	---	0.58
Thick-billed Murre	5	3	7 93	Prince Leopold I	Mean	73	1.13	<0.13	<0.25	2.57
					S.D.	1.1	0.22	---	---	0.30
Thick-billed Murre	5	3	7 93	Coats I	Mean	70	0.76	<0.13	<0.25	2.36
					S.D.	0.5	0.08	---	---	0.33
Black Guillemot	4	3	7 93	Prince Leopold I	Mean	74	2.32	<0.13	<0.25	2.19
					S.D.	0.0	0.22	---	---	0.22
Black Guillemot	5	3	7 93	Walrus I	Mean	73	1.52	<0.13	<0.25	2.67
					S.D.	1.0	0.17	---	---	0.22
Black-legged Kittiwake	5	3	7 93	Prince Leopold I	Mean	77	0.62	<0.13	<0.25	4.38
					S.D.	0.4	0.10	---	---	0.81
Glaucous Gull	5	2	7 93	Prince Leopold I	Mean	76	4.89	<0.13	<0.25	2.72
					S.D.	1.5	1.33	---	---	0.28
Glaucous Gull	5	2	7 93	Browne I	Mean	77	2.68	0.05	<0.25	2.19
					S.D.	1.2	0.80	0.11	---	0.15

TABLE 5. METAL RESIDUE LEVELS IN CHICKS OF ARCTIC SEABIRDS

Dry Wt. (mg/kg or ppm)

Species	Sample	N	Date mo yr	Location	% H_2O	Total Hg	Pb	Cd	Se
Thick-billed Murre	Carcass	6	8 93	Coburg I	74	1.10	0.10	0.54	1.54
Thick-billed Murre	Feathers	6	8 93	Coburg I		3.03	1.16	2.37	2.68
Thick-billed Murre	Carcass	10	8 93	Prince Leopold I	75	0.34	<0.12	0.24	1.39
Thick-billed Murre	Feathers	10	8 93	Prince Leopold I		2.58	<0.07	0.43	1.11
Thick-billed Murre	Carcass	10	8 93	Coats I	72	0.21	<0.07	0.13	0.99
Thick-billed Murre	Feathers	10	8 93	Coats I		1.82	<0.07	0.74	1.53
Black Guillemot	Carcass	10	8 93	Prince Leopold I	67	0.32	<0.10	0.32	1.16
Black Guillemot	Feathers	10	8 93	Prince Leopold I		4.51	0.23	0.38	1.31
Northern Fulmar	Carcass	10	8 93	Prince Leopold I	76	0.53	<0.10	0.84	2.79
Northern Fulmar	Feathers	10	8 93	Prince Leopold I		4.57	0.19	0.49	3.27
Black-legged Kittiwake	Carcass	1	8 93	Prince Leopold I	73	0.37	0.21	0.23	1.51
Black-legged Kittiwake	Feathers	1	8 93	Prince Leopold I		1.65	0.78	0.84	2.07
Glaucous Gull	Carcass	4	8 93	Prince Leopold I	72	0.84	<0.10	<0.13	3.41
Glaucous Gull	Feathers	4	8 93	Prince Leopold I		9.37	<0.07	0.17	1.69

N = number of birds in pooled sample

TABLE 6. TOTAL RESIDUE BURDENS OF METALS IN EGGS AND CHICKS OF ARCTIC SEABIRDS

Mean Residue Burdens (ug)

Species	Sample	# Pools	# Eggs or Chicks/Pool	Date mo yr	Location	Mean Wt. (g)	Total Hg	Pb	Cd	Se
Thick-billed Murre	Egg	5	3	7 93	Prince Leopold I	75.1	22.7	---	---	51.6
Thick-billed Murre	Chick	1	10	8 93	Prince Leopold I	129.3	44.8	---	12.7	55.2
Thick-billed Murre	Egg	5	3	7 93	Coats I	75.9	17.0	---	---	53.1
Thick-billed Murre	Chick	1	10	8 93	Coats I	200.8	39.3	---	18.3	75.3
Black Guillemot	Egg	4	3	7 93	Prince Leopold I	42.4	25.6	---	---	24.1
Black Guillemot	Chick	1	10	8 93	Prince Leopold I	225.6	105.5	4.2	29.0	103.5
Northern Fulmar	Egg	5	3	6 93	Prince Leopold I	79.7	25.5	---	---	86.9
Northern Fulmar	Chick	1	10	8 93	Prince Leopold I	155.8	80.2	2.6	35.3	139.8
Black-legged Kittiwake	Egg	5	3	7 93	Prince Leopold I	37.8	5.3	---	---	37.6
Black-legged Kittiwake	Chick	1	1	8 93	Prince Leopold I	101.5	16.5	8.7	9.5	48.2
Glaucous Gull	Egg	5	2	6 93	Prince Leopold I	98.5	112.8	---	---	63.3
Glaucous Gull	Chick	1	4	8 93	Prince Leopold I	838.3	1183.6	---	18.4	880.2

Mean egg weight refers to egg contents

Mean chick weight includes carcass + feathers

TABLE 7. METAL RESIDUE LEVELS IN LIVERS OF ADULT ARCTIC SEABIRDS

Dry Wt. (mg/kg or ppm)

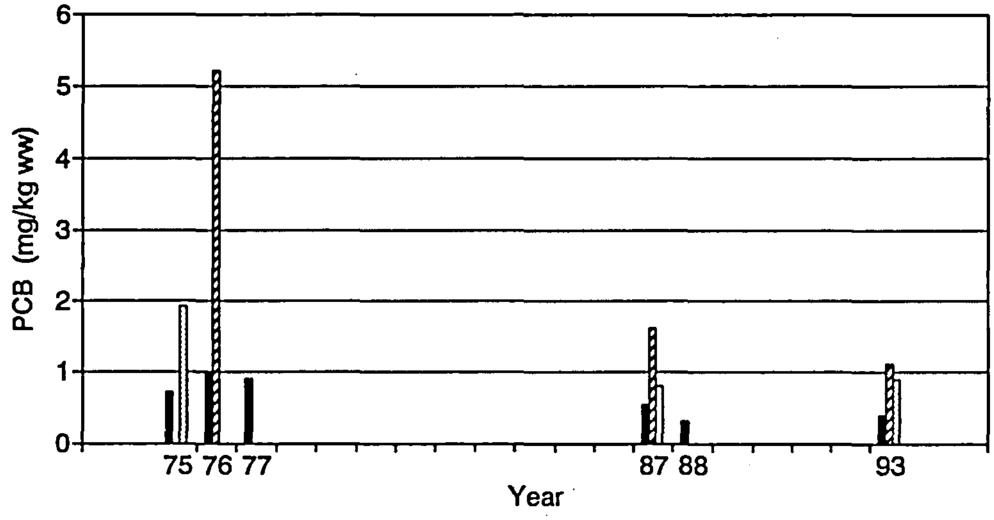
Species	N	Sex	Date mo yr	Location	% H2O	Total Hg	Pb	Cd	Se
Thick-billed Murre	4	1F,3M	6/8 91	Salluit	71	2.93	0.11	15.10	5.66
Thick-billed Murre	5	3F,2M	7 91	Ivujivik	67	3.17	0.26	35.41	5.34
Thick-billed Murre	10	1F,9M	8 93	Coats I	74	2.64	<0.12	26.04	5.57
Thick-billed Murre	10	5F,5M	7 93	Prince Leopold I	71	3.61	<0.09	23.45	6.11
Black Guillemot	5	4F,1M	7 93	Prince Leopold I	71	3.97	<0.07	25.44	10.81
Northern Fulmar	10	8F,2M	6 93	Prince Leopold I	70	8.12	<0.08	39.44	34.40
Black-legged Kittiwake	10	3F,7M	6 93	Prince Leopold I	68	3.05	<0.14	24.24	36.16
Glaucous Gull	5	3F,2M	8 83	Akpatok I	70	9.44	<0.09	17.44	19.57
Glaucous Gull	2	1F,1M	8 92	Coats I	69	6.78	<0.08	8.54	9.20

F = Female; M = Male

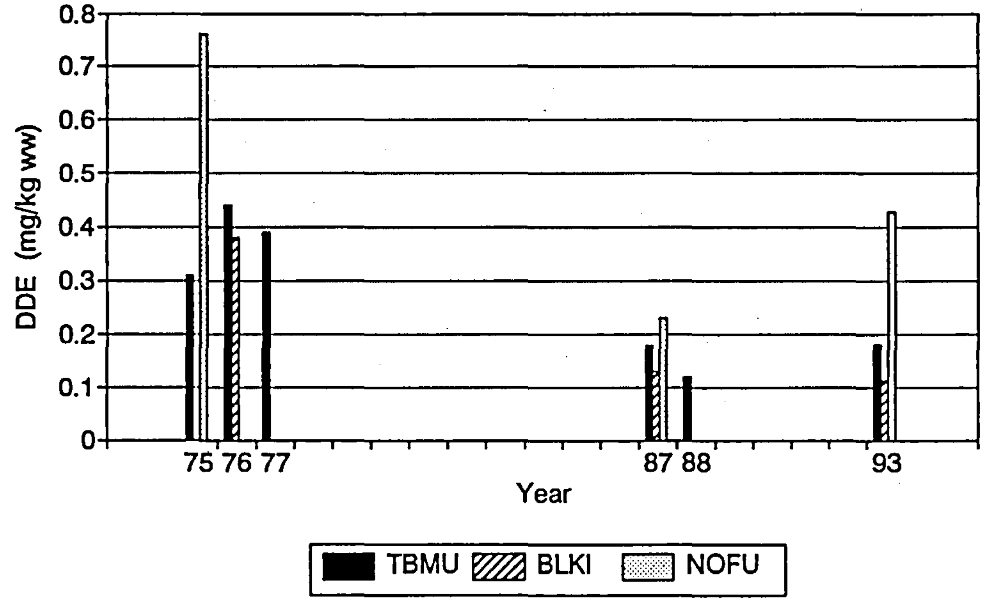
N = number of birds in pool

Figure 1. Contaminants in Seabird Eggs

a. PCBs



b. DDE



TEMPORAL TRENDS IN CONTAMINANT LEVELS OF THE PEREGRINE FALCON AND ITS PREY IN THE KEEWATIN DISTRICT OF THE NORTHWEST TERRITORIES

PROJECT LEADER: R.M. Johnstone, Department of Veterinary Anatomy, Western College of Veterinary Anatomy, University of Saskatchewan

PROJECT TEAM: G.S. Court, D.M. Bradley, J.D. MacNeil (Contractor), A.C. Fesser (Contractor), L.W. Oliphant.

OBJECTIVES

1. To establish the level of organochlorine contamination for the avian component of an Arctic terrestrial ecosystem.

2. To assess the impact of organochlorine contamination on the reproductive success of an arctic population of Peregrine Falcons.

3. To establish the temporal trends of these contaminants in a single ecosystem over a 10 year interval.

4. To assess the value of the Peregrine Falcon as an indicator of ecosystem health.

DESCRIPTION

Data on the contamination of Arctic terrestrial ecosystems is very limited (Thomas *et al.* 1992). Instead work has mainly focused on the contamination of marine mammals, fish, and marine and freshwater food webs. Studies regarding contamination of the avian component of terrestrial ecosystems in the North are even more limited (Thomas *et al.* 1992).

This study aims to establish the present level of organochlorine contamination of the avian component of an Arctic ecosystem. Some 14 common avian species will be sampled around the hamlet of Rankin Inlet and analyzed for selected organochlorine contaminants.

This study aims to establish the biological significance of the presence of these contaminants. Due to bio-accumulation, it is the top carnivores in an ecosystem that are most likely to show toxic effects. Is the level of organochlorine contamination within the avian component of the ecosystem to be studied within the range known to affect reproductive success for species at the top of the food chain (Peakall *et al.* 1990)? The present impact of organochlorine contaminants on the reproductive success of a population of Peregrine Falcons (*Falco peregrinus tundrius*) will be assessed. Eggshell fragments from successful and unsuccessful nests, whole eggs, blood plasma from adults and nestling, and whole bodies of nestling and adults found dead within the study site will be used.

Court *et al.* (1990) assessed the contamination of 14 avian species breeding around Rankin Inlet in the Keewatin District of the NWT. He concluded that significant amounts of organochlorine pesticides and PCB residues had accumulated in some of these species. Furthermore, the levels detected were of biological significance. Contamination was concluded to be interfering with the reproductive performance of the local population of Peregrine Falcons. Eggshell thinning, levels of DDE residues in eggs, and the levels of contaminants found in prey items were all close to the critical levels considered to result in decreased production for the Peregrine Falcon (Peakall and Kiff 1988, Court *et al.* 1990, Peakall *et al.* 1990).

This study is based on the same population as Court *et al.* (1990). We have been collecting and analyzing a similar data set using the same protocol as Court *et al.* (1990) around Rankin Inlet. Temporal trends may then be quantified by comparing contaminant levels between 1991-1994 with the data set of Court *et al.* (1990) covering the period 1982-1986. Previously published comparisons are severely restricted by data sets that frequently lack sufficient samples for meaningful conclusions, have been collected in a haphazard manner both temporally and spatially, or interpret results from different tissue samples (Baril *et al.* 1990, Peakall *et al.* 1990, Thomas *et al.* 1992).

Temporal changes in the effects of contamination on the breeding success of the local Peregrine Falcon population will also be assessed. In a report for the Committee on the Status of Endangered Wildlife in Canada (COSEWIC), Bromley (1991) concluded that "it is not known how critical these factors [pollutant levels] are to the long term survival of populations, or whether the trend toward declining levels of contamination is likely to continue, or be reversed as peregrines continue to be exposed to foreign sources of organochlorines as well as other pollutants in North America". The present study will provide data to test this statement.

This study aims to assess whether the Peregrine Falcon is a useful single species indicator of ecosystem health (Rapport 1989). This will be achieved by comparing trends in the contamination of Peregrine Falcons (using eggshell thickness, residue levels in the eggs, plasma, and body tissue) with the trends of contamination in their prey species. If peregrines are to be considered a reliable indicator species then changes in contaminant levels should be correlated between prey species and peregrines. If contaminant levels in both prey and peregrines decrease then there should be a decrease in the number of breeding attempts by Peregrine Falcons that fail due to pesticide contamination. Few, if any, studies to date have assessed contamination levels of both prey and predators, and the reproductive success of the predator in a single ecosystem.

ACTIVITIES IN 1993/94

Data necessary for achieving the aims of the project were collected between May 10 and September 1 of 1991-1993 around the Inuit hamlet of Rankin Inlet in the Keewatin District of the NWT.

Twenty whole peregrine eggs, plasma samples from 95 peregrines, tissue samples from nine adult peregrines, and whole body homogenates from 57 individuals representing 11 prey species were collected during this time. Production of the Rankin Inlet peregrine population and other standard population parameters were also measured. Analysis of the samples was initiated at the Health of Animals Laboratory, Agriculture and Agri-Food Canada, Saskatoon.

Fragments of shells from hatched eggs, and whole eggs which did not hatch were also collected during the 1991-1993 field seasons. The thickness of eggshell fragments was measured using an optical micrometer at the Engineering Dept., University of Alberta, Edmonton in late September 1993.

RESULTS

Peregrine eggshell fragments collected since 1991 are still thinner than those laid in the Nearctic prior to the introduction of pesticides (Figure 1). A comparison of eggshell thickness, with fragments representing 109 clutches of peregrine falcons indicates that, contrary to predictions, there has not been an increase in eggshell thickness since the early 1980s. The average eggshell thickness remains close to critical levels associated with reproductive failure and population decline in this species (Peakall and Kiff 1988).

Preliminary residue data (still subject to confirmation by mass spectrometry) available to date is presented in Tables 1, 2 and 3.

Our analysis shows measurable levels of contaminants in tissue samples of peregrine falcons (Table 1). The highest level of DDE found was 4.71 ppm wet wt. in a nestling some 3 weeks old.

There is evidence that organochlorine contamination of peregrine eggs (Table 2) has decreased since the sample taken by Court *et al.* (1991) in the early 1980s. Also, the mean levels are under the levels considered critical. Peakall *et al.* (1975) concluded that reproductive failures in peregrine eggs would be associated with DDE residues averaging 15 to 20 ppm. None of the eggs in this sample had levels approaching this. A final sample will be collected in the summer of 1994 to conclude this work.

Residues from whole body analyses of prey species of the peregrine (Bradley 1989) are summarised in Table 3. All species contained measurable levels of organochlorine pesticides and PCB contaminants. The exception to this were lemmings which showed no detectable residues but for a single individual which recorded elevated levels of PCBs. Water Pipits contained the highest DDE level (9.49 ppm ww) for any species including peregrines.

DISCUSSION/CONCLUSIONS

Results from data collected from 1991 to 1993 indicate a continued presence of organochlorines in arctic peregrine falcons and their prey. In addition, the levels are within ranges known to be of biological significance.

Sampling during the summer of 1994 will complete the collection of data. Analysis of the complete set will be finished by February 1995 and final conclusions regarding contaminant levels and temporal trends based on this.

Expected project completion date: March 1995

REFERENCES

Baril, A., J.E. Elliott, J.D. Somers and G. Erickson. 1990. Residue levels of environmental contaminants in prey species of the Peregrine Falcon, *Falco peregrinus*, in Canada. Can. Field-Nat. 104: 273-284.

Bradley, D.M. 1989. Factors affecting the reproductive success of Peregrine Falcons in Rankin Inlet, N.W.T. M.Sc. thesis. University of Saskatchewan, Saskatoon, Saskatchewan.

Court, G.S., C.C. Gates, D.A. Boag, J.D. MacNeil, D.M. Bradley, A.C. Fesser, J.R. Patterson, G.B. Stenhouse and L.W. Oliphant. 1990. A toxicological assessment of Peregrine Falcons, *Falco peregrinus tundrius*, breeding the Keewatin District of the Northwest Territories, Canada. Can. Field-Nat. 104(2): 255-272.

Hickey, J.J. and D.W. Anderson. 1968. Chlorinated hydrocarbons and eggshell changes in raptorial and fish eating birds. Science 165: 271-273.

Peakall, D.B. 1990. Prospects for the Peregrine Falcon, *Falco peregrinus*, in the nineties. Can. Field-Nat. 104: 168-173.

Peakall, D.B., T.J. Cade, C.M. White and J.R. Haugh. 1975. Organochlorine residues in Alaskan Peregrines. Pesticides Monitoring Journal 8: 255-260.

Peakall, D.B. and L.F. Kiff. 1988. DDE contamination in Peregrines and American Kestrels and its effect on reproduction. Pp. 337-350 *in*: Peregrine Falcon populations: their management and recovery. Proceedings of the 1985 International Peregrine Conference, Sacramento, T.J. Cade, C.G. Thelander and C.M. White (eds.). Braun-Brumfeld, San Francisco.

Peakall, D.B., D.G. Noble, J.E. Elliott, J.D. Somers and G. Erickson. 1990. Environmental contaminants in Canadian Peregrine Falcons, *Falco peregrinus*: a toxicological assessment. Can. Field-Nat. 104: 244-254.

Thomas, D.J., B. Tracey, H. Marshall and R.J. Norstrom. 1992. Arctic terrestrial ecosystem contamination. Sci. Total Environ. 122: 135-164.

Table 1. Levels of selected organochlorine contaminants of five nestling Peregrine Falcons found dead within the Rankin Inlet study area (ppm or mg/kg wet wt.).

ID	Tissue	HCB	Oxychlor	BHC	HCE	DDE	DDD	DDT	DIEL	Mirex	PCB
P18	Liver	0.023	0.096	ND	0.109	1.439	ND	ND	0.045	0.181	3.789
	Breast	ND	ND	ND	0.026	0.511	ND	ND	ND	ND	1.496
P53	Liver	0.174	0.695	ND	0.338	4.710	ND	ND	0.144	0.461	14.863
	Breast	0.059	0.377	ND	0.083	1.695	ND	ND	0.012	0.131	5.729
P4	Liver	ND	0.107	ND	0.111	0.747	ND	ND	0.079	0	1.880
	Breast	ND	ND	ND	0.017	0.748	ND	ND	0.019	ND	2.410
P80	Liver	ND	0.077	ND	0.057	0.490	ND	ND	0.012	0.096	2.714
	Breast	ND	ND	ND	ND	0.231	ND	ND	ND	0.096	0.738
P88	Liver	0.020	ND	ND	0.034	1.830	0.033	0.040	0.023	0.082	3.061
	Breast	ND	ND	ND	ND	0.570	0.944	0.079	ND	ND	0.748

Table 2. Levels of selected organochlorine contaminants in Peregrine Falcon eggs from 14 different nesting attempts[1] at Rankin Inlet (ppm or mg/kg wet wt.).

Compound	Geometric mean	Range
HCB	0.016	0.000 - 0.052
Oxychlordane	0.052	0.000 - 0.238
HCE	0.112	0.050 - 0.287
DDE	1.618	0.156 - 6.707
DDD	0.002	0.000 - 0.020
DDT	0.002	0.000 - 0.032
Dieldrin	0.140	0.004 - 0.697
Mirex	0.197	0.017 - 0.667
PCB	2.381	0.179 - 10.175

[1] Includes residues from 9 single eggs and 5 clutch means.

Table 3. Levels of selected organochlorine contaminants in representative prey species of Peregrine Falcons nesting at Rankin Inlet (ppm or mg/kg wet wt.).

		Residues[1]				
Species	N	Oxychlor	HCE	DDE	DIEL	PCB
Black Guillemot	8	0.023 (0-0.077)	0.009 (0-0.025)	0.084 (0.01-0.239)	0.002 (0-0.021)	0.180 (0-0.645)
Horned Lark	7	.002 (0-0.008)	ND	0.006 (0-0.017)	ND	ND
Oldsquaw	5	0.091 (0.015-0.256)	0.089 (0-0.284)	0.845 (0.104-3.478)	0.178 (0-0.290)	2.856 (0.569-8.517)
Pintail	4	0.023 (0-0.055)	0.0139 (0-0.053)	0.337 (0.055-0.910)	0.081 (0.005-0.261)	1.312 (0-5.395)
Semipalmated Plover	5	0.021 (0-0.035)	0.005 (0-0.021)	0.500 (0.102-1.067)	0.112[2]	0.303 (0-2.059)
Lapland Longspur	10	.002 (0-0.015)	ND	0.004 (0-0.037)	ND	0.024[2]
Semipalmated Sandpiper	3	0.054 (0.035-0.069)	0.027[2]	0.211 (0-0.700)	ND	0.102[2]
Water Pipit	5	0.0617 (0-0.306)	0.114[2]	0.694 (0.004-9.498)	ND	0.143 (0-0.787)
Collared lemming	8	0.004[2]	ND	0.414[2]	0.003[2]	4.168[2]

[1] Geometric mean and range

[2] Detected in only one individual

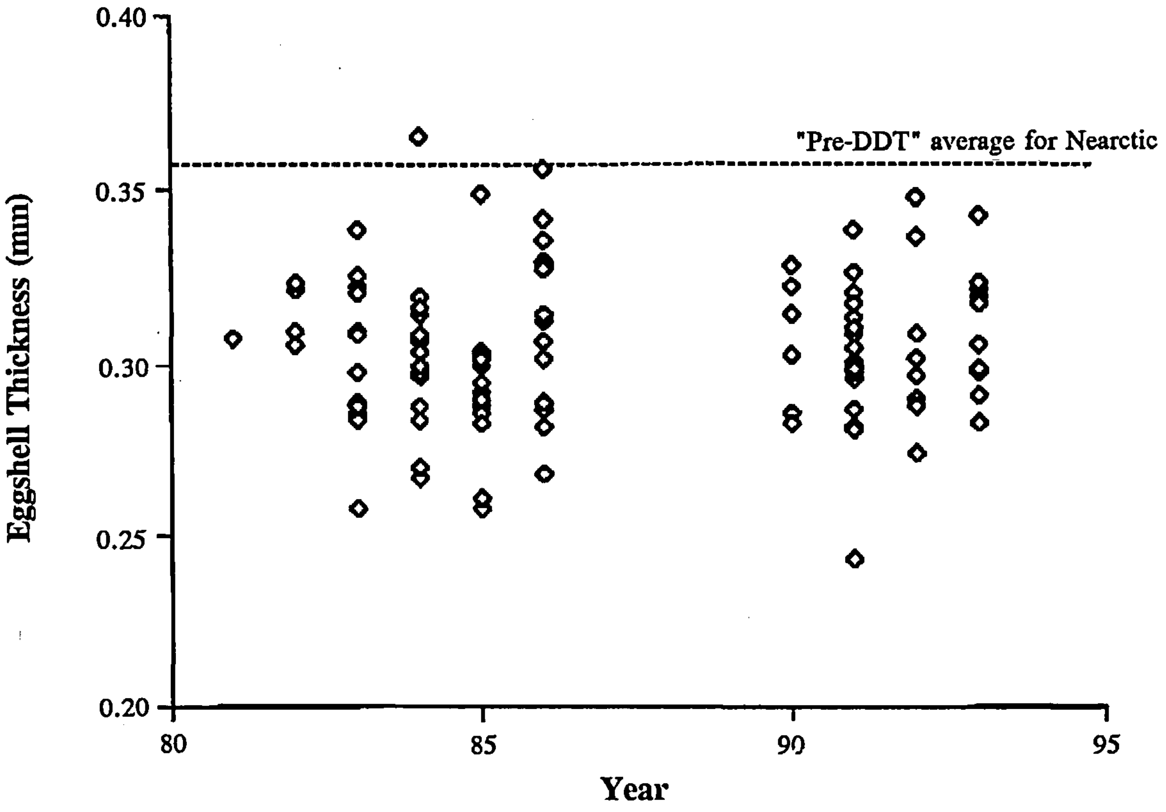


Figure 1. Shell thickness (mm) of peregrine falcon eggs representing 109 clutches produced in Rankin Inlet, NWT between 1981 to 1986 and 1990 to 1993.

IDENTIFICATION OF BASELINE LEVELS AND SPATIAL TRENDS OF ORGANOCHLORINE, HEAVY METAL AND RADIONUCLIDE CONTAMINANTS IN CARIBOU (*Rangifer tarandus*)

PROJECT LEADER: B. Elkin, Department of Renewable Resources, Government of Northwest Territories

PROJECT TEAM: R. Bethke, S. Bohnet, Local Hunters and Trappers Associations

OBJECTIVES

1. To assess the exposure of free-ranging caribou in the Northwest Territories (NWT) to organochlorine, heavy metal and radionuclide contaminants.

2. To establish baseline levels and spatial trends of organochlorine, heavy metal and radionuclide contaminants in several caribou tissues.

3. To identify specific contaminants or geographical locations that warrant further study in caribou.

4. To provide data for use in surveys of contaminants in country food species and for use by the Arctic Monitoring and Assessment Programme (AMAP).

DESCRIPTION

Information on contaminant exposure in caribou in Canadian arctic and subarctic regions is extremely limited, and data on temporal trends are nonexistent. The scarcity of metal or organic residue data for terrestrial mammals has been identified as a data gap in Arctic contaminant research. The few analyses that have been conducted on terrestrial species have indicated that a wide range of organochlorine, heavy metal and radionuclide contaminants are present, and warrant more comprehensive studies to establish baseline levels. Caribou are a major component of the traditional diet in communities across the NWT, highlighting the need for baseline data in this important country food species.

Caribou are strict herbivores that have a winter diet consisting primarily of lichen. Lichens have a long-lived surface and accumulate atmospheric contaminants in a non-selective manner, resulting in a contaminant load similar to atmospheric input through long-range transport. This simple food chain makes caribou a good species for monitoring changes and spatial trends in terrestrial ecosystem contamination. The defined ranges and distribution of caribou herds across the NWT also make it an ideal species for the examination of spatial trends of contaminant deposition in the terrestrial ecosystem.

This study will provide important baseline levels and spatial trends of organochlorine, heavy metal and radionuclide contaminants in caribou from 10 major herds across the NWT. Spatial trends in contaminant residues will contribute to the understanding of contaminant deposition within the terrestrial ecosystem. The specific objectives for 1993/94 were (1) to conduct caribou collections from four additional herds, (2) to determine organochlorine, heavy metal and radionuclide residues in several caribou tissues, and (3) to evaluate the results from the first five herds tested.

ACTIVITIES IN 1993/94

Field Sampling

In 1993/94, field collections of caribou were conducted in cooperation with local Hunters and Trappers Associations at Cambridge Bay, Inuvik, Pond Inlet and Taloyoak. Collections had been conducted in previous years at Arviat, Cape Dorset, Lake Harbour, Southampton Island, and on the Bathurst herd (Fig. 1). Ten male and 10 female caribou were collected at each site, and samples were collected from each animal for contaminant analysis. Teeth were collected for aging by tooth cementum analysis, and a variety of reproductive, biological and morphometric measurements were taken.

Contaminant Analysis

Tissue samples from 10 caribou collected at each of the 4 sites were analyzed in 1993/94 for organochlorine and metal contaminants at the Great Lakes Institute in Windsor, Ontario. The suite of contaminants assessed comprised a spectrum of 63 organochlorines, including 43 PCB congeners and 20 pesticides, and 10 metals. Fat, liver, and muscle samples were analyzed for organochlorine residues, and metal analysis was conducted on kidney and liver samples. Muscle samples from 10 caribou at each location were also analyzed for radionuclides at AECL Whiteshell Laboratories in Pinawa, Manitoba. Samples from the remaining 10 caribou from each site were banked for future use.

RESULTS

The contaminant residue data set from the first 5 caribou herds sampled was completed in 1992/93, and the data has been analyzed and evaluated. Results of data from Arviat, Cape Dorset, Lake Harbour, Southampton Island and the Bathurst herd are presented here (Figure 1); results from the 4 most recent collections are still being evaluated.

Almost all of the 63 organochlorine compounds could be detected in caribou from all five sites. Mean residue levels of the predominant organochlorine compounds found are given by community in Table 1. In general, organochlorine concentrations were significantly higher in caribou from Lake Harbour and Cape Dorset on south Baffin Island than in caribou from Southampton Island and the mainland Bathurst and Qamanirjuaq herds. The levels and patterns of organochlorine residues detected were similar to those from limited analyses previously conducted on Baffin Island and Ft. Good Hope caribou.

Hexachlorobenzene (HCB), hexachlorocyclohexane (HCH), chlordane, and DDT were the predominant organochlorine compounds detected at all five study sites. HCB residues ranged from a lipid corrected mean of 32.83 ng/g in fat of Bathurst caribou to 129.41 ng/g in Lake Harbour animals. α-HCH was the predominant hexachlorocyclohexane, with levels ranging from 8.11 ng/g in Bathurst animals to 37.9 ng/g in Cape Dorset caribou. Total chlordane levels ranged from 0.81 ng/g in Bathurst caribou to 5.01 ng/g at Cape Dorset, with oxychlordane the dominant chlordane compound. The levels of total DDT ranged from 0.46 ng/g at Arviat to 2.58 ng/g at Cape Dorset, consisting largely of *p,p'*-DDE. Total polychlorinated biphenyl (ΣPCB) residues ranged from 6.24 ng/g in fat of Arviat caribou to 31.68 ng/g at Cape Dorset, with congeners 153 and 138 most dominant of the 43 congeners tested. The concentration of individual PCB congeners relative to PCB-153 are given by site in Figure 2. The patterns of PCB congener distribution were generally similar at all sites, although the levels of lower chlorinated PCB congeners were generally higher in the Bathurst and Arviat caribou than in those at the other three sites.

The mean levels of trace and heavy metals by location are listed for kidney in Table 2 and for liver in Table 3. Moderately elevated levels of Cd and Hg were detected in caribou from all five sites. Cd levels in kidney tissue ranged from 9.68 μg/g dry weight in Bathurst animals to 33.87 μg/g in Arviat caribou. Hg levels in kidney tissue ranged from 0.52 μg/g wet weight in Bathurst caribou to 2.93 μg/g in Arviat animals. Although there were significant among group differences in levels of the 10 metals tested, there was no general geographical trend to the pattern of concentrations. Cadmium levels detected in this study were similar to recent findings in caribou in the NWT and Yukon, and comparable to those found in caribou from Norway and northern Quebec.

The mean levels of radionuclide activity from each site are listed in Table 4. Radionuclide levels were generally low or non-detectable, with the exception of ^{137}Cs, ^{40}K, and ^{134}Cs. ^{137}Cs was the most predominant nuclide, with activity ranging from 34.86 Bq/kg in the Bathurst herd to 184.10 Bq/kg in Lake Harbour caribou. ^{40}K was also consistently found in all samples. Levels ranged from 115.20 Bq/kg in Bathurst caribou to 123.80 Bq/kg in Lake Harbour animals. Levels of ^{134}Cs ranged from <0.37 Bq/kg in Bathurst caribou to <1.50 Bq/kg in Lake Harbour animals. Trace levels of ^{232}Th, ^{235}U, and ^{226}Ra were also observed. ^{60}Co was only observed in three caribou samples, and was found at very low levels.

DISCUSSION

Long-range atmospheric transport appears to be the primary source of the contaminants detected in this study, and the air-plant-animal contaminant pathway is the most likely route of contaminant deposition into the terrestrial food chain. Overall, organochlorine residue levels in NWT caribou were substantially lower than levels found in arctic marine mammal tissues, and similar to limited analyses previously conducted on terrestrial herbivores in the Canadian Arctic. Moderately elevated levels of Cd in caribou from the NWT are comparable with findings in other big game species in Canada, and are most consistent with long-range atmospheric transport. The levels of ^{137}Cs, the predominant radionuclide in this study, supports the conclusion that levels of ^{137}Cs are steadily declining in the Canadian Arctic.

The comparatively low levels of contaminants detected, coupled with stable or expanding populations in the herds tested, suggest little or no effects on caribou population health as a result of these contaminants. Health Canada and Government of Northwest Territories Department of Health have conducted a human health risk assessment on the complete organochlorine and heavy metal data set from the first 4 herds tested. The results of this assessment have been published in the October/November 1993 issue of EPINORTH. Spatial trends in contaminant exposure in caribou herds across the NWT will be further defined with the completion of sample collection and analyses from the remaining herds.

Expected project completion date: Field caribou collections and contaminant analysis will be completed in 1994/95. Data evaluation and interpretation, human health risk assessment, and community consultation will occur in 1994/95 and continue in 1995/96.

Table 1. Arithmetic means (ng/g, lipid corrected (SE)) of selected organochlorine residues in fat of caribou collected from five sites in the NWT. For each compound, site means having the same superscript were not significantly different ($p < 0.05$).

Compound	Collection Sites				
	Bathurst Herd	Arviat	Southampton Island	Cape Dorset	Lake Harbour
n	20	10	10	8	10
% Lipid	45.52 (4.95)	78.58 (3.44)	85.62 (5.72)	54.52 (3.02)	83.52 (1.78)
HCB	32.93^{c} (8.24)	56.19^{b} (2.75)	39.07^{b} (2.42)	$108.28^{a,b}$ (15.61)	129.41^{a} (6.47)
Dieldrin	0.07^{c} (0.03)	$0.44^{a,b}$ (0.20)	0.26^{b} (0.09)	0.65^{a} (0.12)	0.50^{a} (0.11)
ΣHCH[1]	9.65^{b} (1.06)	26.91^{a} (2.55)	26.71^{a} (2.36)	39.78^{a} (6.73)	27.84^{a} (2.95)
ΣChlordane[2]	0.81^{a} (0.17)	$1.62^{b,c}$ (0.29)	1.29^{c} (0.23)	5.01^{a} (0.80)	2.35^{b} (0.38)
ΣDDT[3]	1.94^{a} (0.57)	0.46^{b} (0.13)	$0.87^{a,b}$ (0.18)	2.58^{a} (1.48)	1.78^{a} (0.39)
ΣPCB[4]	10.71^{b} (1.95)	6.24^{b} (0.71)	8.79^{b} (0.77)	31.68^{a} (4.35)	25.23^{a} (2.23)

[1] ΣHCH = Sum of α-HCH, ß-HCH and γ-HCH.

[2] ΣChlordane = Sum of *oxy*-, *cis*- and *trans*-chlordane, *cis*- and *trans*-nonachlor, and heptachlor epoxide.

[3] ΣDDT = Sum of *pp*'-DDT, *pp*'-DDE and *pp*'-DDD.

[4] ΣPCB = Sum of 43 individual congeners.

Table 2. Arithmetic means of metal concentrations in kidney of caribou collected from five sites in the NWT. All concentrations (µg/g, (SE)) are given in dry weight except for mercury (Hg) where wet weight is given. For each metal, site means having the same superscript were not significantly different ($p < 0.05$).

Metal	Collection Sites				
	Bathurst Herd	Arviat	Southampton Island	Cape Dorset	Lake Harbour
n	20	10	10	10	10
% Water	81.13 (0.79)	79.28 (0.88)	79.70 (0.26)	81.04 (0.95)	80.52 (1.11)
Al	5.64^{b} (1.23)	9.43^{a} (3.61)	6.36^{b} (0.61)	$6.58^{a,b}$ (0.46)	11.72^{a} (2.30)
Cd	9.68^{c} (1.27)	33.87^{a} (6.06)	18.79^{b} (3.29)	$14.06^{b,c}$ (2.27)	31.98^{a} (5.89)
Cr	1.15^{a} (0.12)	1.67^{a} (0.30)	0.43^{b} (0.06)	1.23^{a} (0.19)	2.06^{a} (0.56)
Cu	49.73^{a} (5.82)	$40.10^{a,b}$ (11.46)	27.76^{b} (1.81)	43.65^{a} (5.90)	29.57^{b} (2.80)
Fe	237.26^{b} (17.74)	217.67^{b} (19.90)	194.94^{b} (24.39)	440.85^{a} (51.59)	342.99^{a} (34.21)
Mn	8.96^{b} (0.63)	12.03^{b} (1.01)	9.73^{b} (1.24)	11.66^{b} (0.67)	18.62^{a} (1.27)
Ni	0.44^{b} (0.08)	0.24^{b} (0.06)	0.30^{b} (0.16)	0.90^{a} (0.30)	1.33^{a} (0.65)
Pb	0.11^{b} (0.02)	0.10^{b} (0.02)	$0.33^{a,b}$ (0.06)	0.42^{a} (0.07)	0.47^{a} (0.10)
Zn	123.49^{a} (4.51)	120.86^{a} (6.46)	$111.87^{a,b}$ (4.13)	106.73^{b} (10.22)	96.75^{b} (4.23)
Hg	0.52^{d} (0.04)	2.93^{a} (0.21)	2.22^{b} (0.13)	1.25^{c} (0.05)	$2.56^{a,b}$ (0.25)

Table 3. Arithmetic means of metal concentrations in liver of caribou collected from four sites in the NWT. Southampton Island liver samples were not available for analysis. All concentrations (μg/g, (SE)) are given in dry weight except for mercury (Hg) where wet weight is given.

Metal	Collection Sites			
	Bathurst Herd	Arviat	Cape Dorset	Lake Harbour
n	20	10	10	10
% Water	70.67 (0.37)	70.71 (1.31)	75.10 (0.92)	73.52 (1.47)
Al	4.44 (9.10)	16.18 (4.82)	8.25 (5.50)	14.12 (6.15)
Cd	1.96 (0.14)	3.69 (0.62)	2.24 (0.47)	4.39 (0.71)
Cr	0.68 (0.05)	0.90 (0.10)	0.62 (0.08)	0.40 (0.12)
Cu	83.63 (5.82)	51.85 (11.83)	120.76 (20.24)	105.36 (22.80)
Fe	1594.97 (315.71)	701.84 (53.01)	3627.66 (802.22)	3956.18 (575.53)
Mn	12.62 (0.82)	10.84 (0.91)	8.60 (0.27)	15.85 (0.74)
Ni	0.45 (0.13)	0.49 (0.32)	0.45 (0.13)	0.13 (0.04)
Pb	0.38 (0.07)	0.25 (0.08)	2.64 (0.27)	3.38 (0.73)
Zn	114.11 (4.95)	92.27 (7.82)	75.84 (4.77)	76.27 (3.93)
Hg	0.16 (0.03)	0.92 (0.08)	0.38 (0.11)	0.58 (0.08)

Table 4. Arithmetic means of radionuclide activities (Bq/kg wet weight, (SE)) in muscle of caribou collected from three sites in the NWT. Values indicated by " < " are reported as the minimum detectable limit.

Radionuclide	Collection Sites		
	Bathurst Herd	Cape Dorset	Lake Harbour
n	20	10	10
% Dry Weight	25.80 (0.09)	24.70 (0.09	27.70 (0.08)
Cesium-137	34.86 (0.37)	38.58 (0.69)	184.10 (7.67)
Cesium-134	<0.37 .	0.48 (0.02)	<1.50 .
Potassium-40	115.20 (0.59)	115.70 (1.44)	123.80 (00.57)
Thorium-232	<0.84 .	<0.68 .	<0.90 .
Uranium-235	<1.46 .	<1.11 .	<1.36 .
Radium-226	<0.62 .	<0.49 .	<0.65 .
Cobalt-60	<0.45 .	<0.34 .	<0.34 .

Figure 1. Sites in the Northwest Territories where caribou collections were made in 1991 and 1992. All collections were made within 100 km of the site.

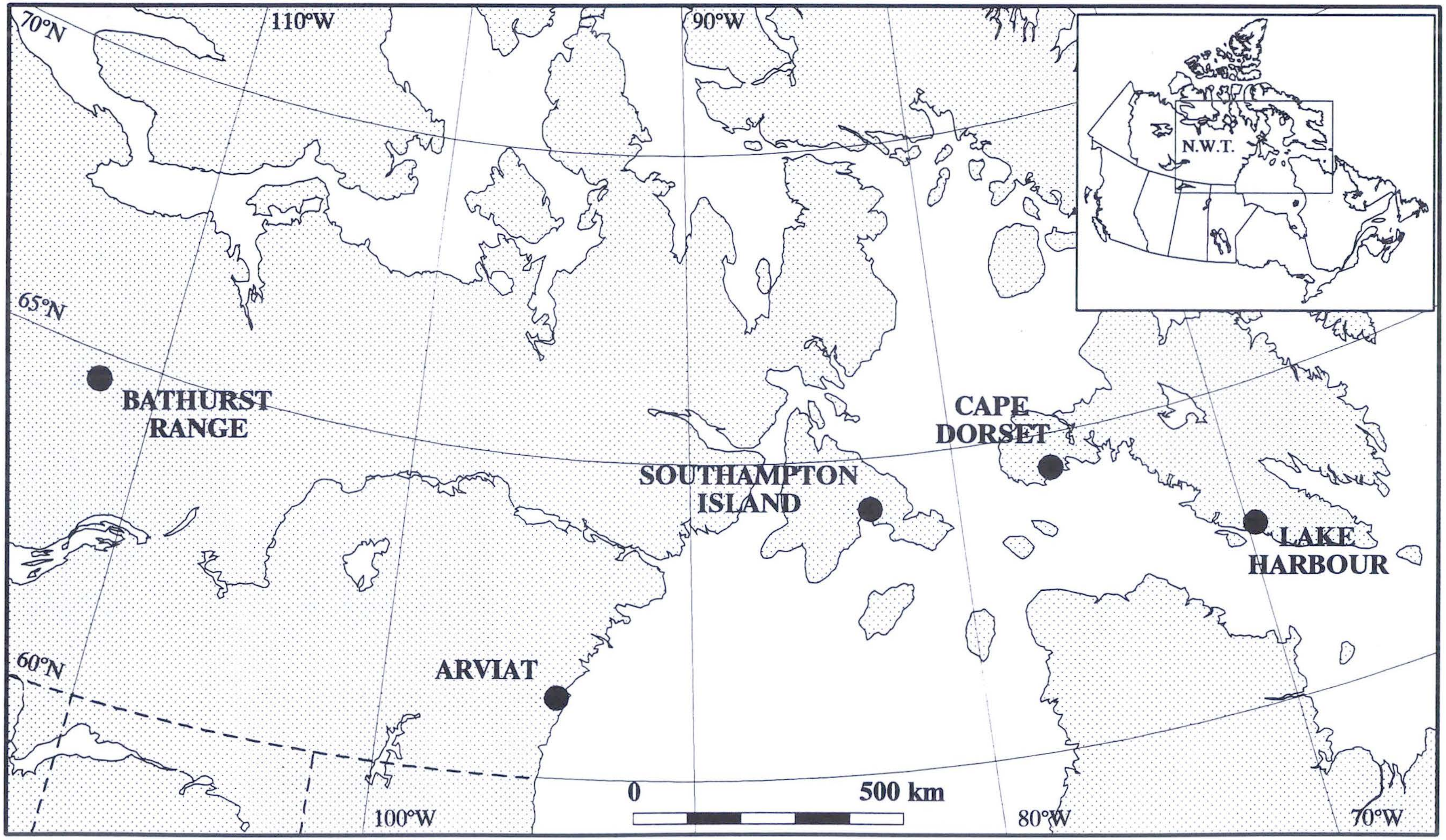
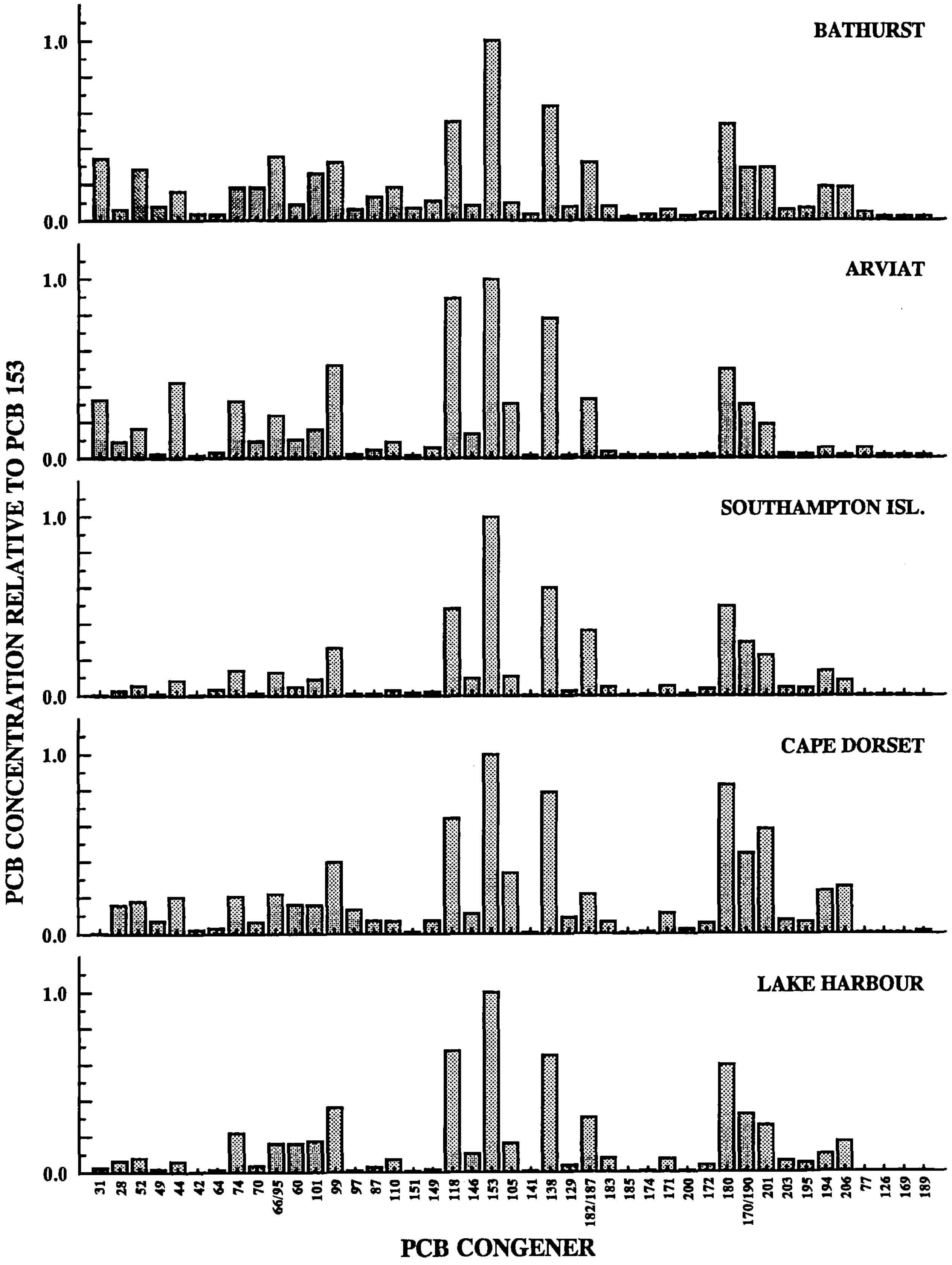


Figure 2. Pattern of PCB congeners (relative to PCB-153) in fat of caribou collected in the Northwest Territories, 1991-92.



CONTAMINANTS IN WOODLAND CARIBOU

PROJECT LEADERS: M. Gamberg, Gamberg Consulting, Yukon; and L. Mychasiw, Department of Renewable Resources, Government of Yukon

PROJECT TEAM: R. Florkiewicz, D. Bakica, D. Cooley, T. Hunter, C. Hebert and A. Scheuhammer

OBJECTIVES

1. To confirm contaminant levels found in the Finlayson Caribou Herd in 1992/93, and to determine the source of cadmium contamination.

2. To determine contaminant levels in two additional woodland caribou herds -the Tay and the Bonnet Plume.

3. To determine whether cadmium is affecting the health of individual caribou in the three caribou herds.

DESCRIPTION

The Finlayson Caribou Herd is a woodland herd in the Ross River area, used by people of the Kaska First Nation as a food source. A 1992/93 survey of contaminants in these caribou indicated high levels of cadmium, mercury, and some dioxins and furans (Gamberg 1993). Natives consuming these caribou are concerned about health risks from eating contaminated animals. The Ross River Dena Council has passed a resolution acknowledging a partnership with the Government of the Yukon (Renewable Resources) with respect to contaminant testing of caribou in the Kaska Nation homelands.

The specific objectives for 1993/94 were: (1) to confirm cadmium levels found in the Finlayson Caribou herd in the previous year, (2) to determine the source of cadmium in the caribou by measuring absolute levels in lichens, soil, ore and air, and also by attempting to use cadmium isotope ratios to identify a source, (3) to further explore the unusual pattern of dioxin and furan contamination found in the Finlayson Caribou in the previous year, by analyzing several different tissues for specific congeners, (4) to determine the geographical extent of the contamination in caribou, by surveying two additional woodland caribou herds, one geographically near the Finlayson herd, and one distant, and (5) to determine whether the cadmium contamination is affecting the health of the caribou by analyzing kidney sections histopathologically.

ACTIVITIES IN 1993/94

Sampling

Kidney and liver samples taken from 20 adult female caribou from each of the Finlayson, Tay and Bonnet Plume caribou herds were analyzed for a suite of inorganic elements. Liver, muscle and fat samples from the same animals were analyzed for organic contaminants (polychlorinated dibenzodioxins, dibenzofurans and non-ortho polychlorinated biphenyls) as part of another AES project (C. Hebert, Canadian Wildlife Service). Kidney sections from each animal were examined histopathologically for proximal tubule damage (T. Bollinger, Canadian Cooperative Wildlife Health Centre). Liver and muscle samples from all three herds were also used as part of another study on radionuclides in caribou (C. Macdonald, AECL Research), and liver samples from the Finlayson herd were used to study DNA sequencing in caribou (J. Eger, ROM). All sampling was done by R. Florkiewicz (Yukon Territorial Government) with the assistance of Yukon Territorial Government conservation officers and members of the Kaska and Na Cho N'yukdun First Nations. Lichens and humus sampled from the winter range of each herd and a control area (R. Florkiewicz), and lake overflow from the Finlayson winter range were analyzed for a suite of inorganic elements. Those lichens, as well as ore samples from the mine near the Finlayson range, and air samples taken at two points distant from the Finlayson range were analyzed for cadmium and lead isotope ratios.

Methods and Results

Caribou were aged using the tooth cementum technique. Methods for and results of the organic analyses are fully described by Hebert *et al.* (1994). Results from inorganic and isotope ratio analyses are not yet available.

Renal histopathology

Kidney sections were fixed in 10% formalin as soon as possible after the death of the animal. Time between death and tissue fixing was recorded, and the sections were examined histologically for renal damage, specifically to the proximal tubules. Results are currently available for the Finlayson herd only.

All kidneys appeared relatively normal with no evidence of clinically significant renal pathology. However, lipofuscin deposition was seen in varying degrees in proximal tubules in approximately half the kidneys.

CONCLUSIONS AND UTILIZATION OF RESULTS

Unfortunately, little of the data from this project is available yet, so few conclusions can be drawn. The organic portion of the project has been completed and is reported in Hebert *et al.* (1994). Results indicate that PCDDs, PCDFs and NOPCBs do not pose a threat to the caribou herds sampled in the study. Although a greater variety of PCDDs/PCDFs were detected in the Tay herd as compared to the Finlayson and Bonnet Plume herds, all levels were extremely low.

The high levels reported from the previous year were probably the result of sample contamination.

The lipofuscin found in some kidneys from the Finlayson herd represents the indigestible residues of intracellular breakdown caused by free radical injury. This accumulation can occur with aging or malnutrition, but may also be related to mild cellular injury by heavy metals. There is, however, no correlation between the presence of the lipofuscin and age. The relationship between the presence of lipofuscin and the concentration of cadmium will be assessed once cadmium levels are available.

Data from the current study that suggest a potential health risk for humans will be submitted to Health Canada for a health risk assessment. That assessment will be communicated to First Nations and other people of the Yukon by the Yukon Contaminants Committee.

Expected project completion date: December 31, 1994

PARTNERS

Environmental Protection Service (J. Eamer), Indian and Northern Affairs Canada (M. Palmer), Fisheries and Oceans Canada (A. von Finster), Yukon Health (D. Schiller), Health Canada (F. O'Brien), Council for Yukon Indians (N. Kassi), Ross River Dena Council (N. Sterriah), Canadian Wildlife Service (C. Hebert, A. Scheuhammer)

REFERENCES

Gamberg, M. 1993. Survey of contaminants in the Finlayson caribou herd, Ross River, Yukon Territory. Technical report TRC-93-2 prepared for Fish and Wildlife Branch, Dept. of Renewable Resources, Yukon Territorial Government, Whitehorse, Yukon.

Hebert, C., M. Simon, R. Norstrom, J. Moisey, M. Mulvihill, and A. Idrissi. 1994. Polychlorinated dibenzodioxins, dibenzofurans and non-ortho polychlorinated biphenyls in caribou from the Canadian Arctic. Internal Report. Canadian Wildlife Service, National Wildlife Research Centre, Hull, Quebec.

PCDD/PCDF RESIDUES IN CARIBOU FROM THE CANADIAN ARCTIC

PROJECT LEADER: C. Hebert, National Wildlife Research Centre, Canadian Wildlife Service, Environment Canada

PROJECT TEAM: M. Gamberg, L. Mychasiw, B. Elkin, M. Simon, R. Norstrom, J. Moisey, M. Mulvihill, A. Idrissi

OBJECTIVES

1. To determine the levels of PCDDs, PCDFs and non-ortho PCBs in caribou samples from seven herds across the Canadian Arctic.
2. To compare the distribution of PCDDs and PCDFs in muscle, liver and fat tissue from Finlayson caribou.
3. To determine the sources and inputs of PCDDs and PCDFs to the arctic terrestrial ecosystem.

DESCRIPTION

In February/March 1992 near Ross River in the Yukon, adult female caribou were collected from the Finlayson herd by the Yukon Department of Renewable Resources. These samples were analyzed by a commercial laboratory. Results from this study indicated that the caribou contained relatively high levels of PCDDs and PCDFs (Gamberg 1993). In addition, the pattern of congener accumulation was unusual. In fish, birds and mammals the congeners which usually contribute the most to overall dioxin levels are the 2,3,7,8-substituted congeners (Kuehl *et al.* 1986, van den Berg *et al.* 1987a, 1987b). In the 1992 caribou samples, these congeners contributed only slightly to total concentrations of hexachlorodibenzodioxin (H_6CDD), heptachlorodibenzodioxin (H_7CDD), pentachlorodibenzofuran (P_5CDF), hexachlorodibenzofuran (H_6CDF) and heptachlorodibenzofuran (H_7CDF). Initial hypotheses proposed to explain these results were that: 1) the samples had been contaminated in the field or laboratory or 2) that the flux of PCDDs and PCDFs into the caribou was so great that a steady state between intake rate and metabolism had not been established. It was thought that perhaps a local mining operation at Faro, near Ross River, might have been the potential source of PCDDs/PCDFs. In 1993, co-operation among the Canadian Wildlife Service, the Yukon Department of Renewable Resources and the Northwest Territories Department of Renewable Resources resulted in the chemical analysis of additional caribou samples from the Yukon and Northwest Territories. In addition to PCDDs and PCDFs, levels of non-ortho substituted PCB congeners (NOPCBs) were measured in most of the samples.

ACTIVITIES IN 1993/94

Sample Collection

In March 1993, twenty female caribou were shot from each of the Finlayson, Tay and Bonnet Plume herds. Liver, muscle and subcutaneous back or kidney fat samples were taken from each animal within one hour of death. Kidney fat was collected only when the animals did not have sufficient subcutaneous fat reserves for a sample to be obtained. Approximately 500 g of liver, gastrocnemius muscle and fat were stored in individual hexane and acetone-rinsed glass jars sealed with teflon caps. Age determinations were made for each animal by examining an incisor using the tooth cementum technique. From the four Northwest Territories herds, subcutaneous back fat samples had been collected previously as part of a study examining levels of other contaminants in caribou (Elkin and Bethke 1994). These collections had been made on the following dates: Southampton Island (November 1991), Cape Dorset and Lake Harbour (April 1992), and Bathurst (July and September 1992). Only females were analyzed to facilitate comparison with the Yukon caribou.

METHODS

Sample Processing

Only subcutaneous fat samples were analyzed in this study so that comparisons could be made among the Yukon and NWT herds. Fat samples were analyzed first because hydrophobic compounds such as PCDDs, PCDFs and non-ortho PCBs are stored in lipid. If these contaminants are not found in fat tissue then they should not be present in liver or muscle tissue which contains a much lower proportion of lipid. Fat samples from the Finlayson herd were analyzed first to determine if there was a relationship between age and PCDD/PCDF levels. Individual samples were pooled according to age and five separate age pools resulted: Age 2 (N=3), Age 3 (N=2), Age 4 (N=6), Age 5 (N=6) and Age 6 (N=2). One caribou, aged 10, was not included in the pools and was, therefore, not analyzed. As levels of all compounds were extremely low in the Finlayson fat samples, only one liver and one muscle sample were analyzed. The sample analyzed (Age 3 pool) was selected at random. No relationship was observed between age and PCDD/PCDF levels in fat tissue from the Finlayson caribou, therefore, all female caribou over the age of one were included in the pools for the other six herds. The number of animals and the mean (±1 std error) age of the caribou included in each of the pooled samples were as follows: Bonnet Plume (N=14, 6.6±0.6 yrs), Tay (N=13, 5.3±0.8 yrs), Bathurst (N=7, 4.1±0.6 yrs), Southampton Island (N=5, 3.6±0.5 yrs), Cape Dorset (N=3, 3.7±0.9 yrs) and Lake Harbour (N=4, 4.3±0.9 yrs). Six of the caribou from the Bonnet Plume herd were omitted because there were no subcutaneous fat samples available. For the Tay herd, seven caribou were not included because for four of the caribou there were no subcutaneous fat samples available. The other three caribou were not included because after collection the samples had thawed or their containers had broken and the samples were potentially contaminated.

Chemical Analysis

Most of the samples were analyzed using high resolution gas chromatography/mass spectrometry. However, three of the samples were analyzed using only low resolution GC/MS. These were three of the age pools from the Finlayson herd (Age 2, Age 5 and Age 6). The Age 3 and Age 4 pools from the Finlayson herd were analyzed using both high and low GC/MS and the PCDD/PCDF results were comparable. For the samples analyzed using low resolution GC/MS, non-2,3,7,8 substituted PCDD/PCDF congeners and non-ortho PCBs were not measured.

Quality Assurance

Recoveries for $^{13}C_{12}$-PCDDs/PCDFs and -non-ortho PCBs were calculated by comparing the integrated areas of the labelled internal standards and areas of the recovery standards to the areas of these compounds measured in the external standard mixture analyzed along with the samples. Internal standard recoveries are given in Tables 1, 2 and 3. Recoveries for PCDDs and PCDFs were usually greater than 70%. Recoveries for non-ortho PCBs were usually less because of problems occurring during the Alumina column clean-up. Nevertheless, because all calculations were based on internal standard quantitation, reported levels should be accurate within ±15%.

Minimum Detection Limits (MDL, signal/noise = 3) were calculated for every congener detected. PCDD/PCDF and NOPCB analysis of a quality control sample (1989 Herring Gull egg pool from Lake Ontario) was performed along with the samples. Method blanks ($^{13}C_{12}$-PCDDs/PCDFs/non-ortho PCBs) were subjected to the entire clean-up procedure and analyzed along with the caribou samples. No PCDDs, PCDFs or non-ortho PCBs were detected in the blanks.

RESULTS

Concentrations (ng/kg, wet weight) of individual PCDD, PCDF and NOPCB congeners are reported in Tables 1, 2 and 3. Minimum detection limits (MDL) for each compound, in each sample, are also reported. Levels of PCDDs, PCDFs and non-ortho PCBs were low in all samples.

In the Finlayson caribou, results from the low and high resolution analyses were generally similar (Tables 1 and 2). However, there were differences between the two methods regarding the levels of octachlorodibenzofuran (OCDF) found in the samples. Low resolution analysis indicated that OCDF was present in the Finlayson caribou, whereas no OCDF was detected using high resolution analysis. The latter results are correct. The OCDF concentrations reported by low resolution analysis probably represent interference from other compounds, as indicated by incorrect ion ratios for OCDF. Only octachlorodibenzodioxin (OCDD) was found on a regular basis and only at negligible concentrations (<7 ng/kg or parts per trillion). Levels of OCDD in liver and muscle were lower than those observed in fat tissue from the same age pool (Table 1). All of the more highly toxic PCDD/PCDF congeners were below detection limits and no non-2,3,7,8-substituted PCDD/PCDF congeners were detected. PCDD, PCDF and NOPCB levels in the Tay and Bonnet Plume herds were similar to the Finlayson herd.

In the Tay, Bathurst, Southampton, Cape Dorset and Lake Harbour herds a greater variety of PCDDs/PCDFs were detected but levels of these congeners were also extremely low (Tables 2 and 3). Non-ortho PCBs were also present at low concentrations.

CONCLUSIONS

Analysis of all samples indicated that levels of PCDDs, PCDFs and non-ortho substituted PCBs were extremely low. The highest levels found were 2.0 and 6.8 ng/kg of octachlorodibenzo-dioxin, however, these values were probably the result of sample contamination because lower levels were found in replicate analyses. In all other samples, levels of PCDDs and PCDFs were less than 1 ng/kg and were frequently not detected at 0.1 ng/kg or lower. Non-ortho PCBs were detected in most samples, but did not exceed 25 ng/kg. PCB congeners #126 and #169 showed some spatial variability with higher levels in the eastern Arctic. Higher levels of these PCBs in the eastern Arctic may be the result of differences in atmospheric circulation patterns between the eastern and western Arctic, thereby affecting the deposition of these contaminants via long-range atmospheric transport.

The results reported in this study indicate that PCDDs, PCDFs and non-ortho PCBs do not pose a threat to the caribou herds sampled in this study. The levels observed are among the lowest ever reported in wildlife. PCDDs, PCDFs and PCBs are globally distributed and long-range atmospheric transport, with some minor local inputs, can probably account for the PCDD/PCDF and non-ortho PCB levels found in the caribou. The high levels reported earlier (Gamberg 1993) were probably the result of sample contamination either in the field or the laboratory. We recommend that sample collection, handling, storage, processing and analysis procedures be carefully scrutinized if meaningful results are to be obtained from ultra-sensitive chemical analysis.

Expected project completion date: September 30, 1994

REFERENCES

Elkin, B.T. and R.W. Bethke. 1994. Environmental contaminants in caribou in the Northwest Territories, Canada. Sci. Tot. Environ. in press.

Gamberg, M. 1993. Survey of contaminants in the Finlayson caribou herd. Ross River, Yukon Territory. Technical report TRC-93-2 prepared for Fish and Wildlife Branch, Yukon Department of Renewable Resources. Whitehorse, Yukon.

Kuehl, D.W., P.M. Cook, and A.R. Batterman. 1986. Uptake and depuration studies of PCDDs and PCDFs in freshwater fish. Chemosphere 15: 2023-2026.

van den Berg, M., F. Blank, C. Heeremans, H. Wagenaar, and K. Olie. 1987a. Presence of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in fish-eating birds and fish from the Netherlands. Arch. Environ. Contam. Toxicol. 16: 149-158.

van den Berg M., M. Sinke, and H. Wever. 1987b. Vehicle-dependent bioavailability of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in the rat. Chemosphere 16: 1193-1203.

Table 1. Low resolution GC/MS analysis of PCDDs, PCDFs and NOPCBs in Finlayson caribou. Levels are ng/kg (wet wt.).

Low Resolution GC/MS										
Sample #	L93-63599-02		L93-63600-02		L93-63601-02		L93-63602-02		L93-63603-02	
Location	Finlayson		Finlayson		Finlayson		Finlayson		Finlayson	
Territory	Yukon		Yukon		Yukon		Yukon		Yukon	
Pool	Age 2		Age 3		Age 4		Age 5		Age 6	
Sample Type	Fat		Fat		Fat		Fat		Fat	
No. in pool	3		2		6		6		2	
% Lipid	90.78		85.45		87.24		88.10		76.10	
PCDDs	**Levels**	**MDL**	**Levels**	**MDL**	**Levels**	**MDL**	**Levels**	**MDL**	**Levels**	**MDL**
2378-T4D	ND	3.4	ND	3.6	ND	3.6	ND	2.9	ND	2.7
TotalT4D										
12378-P5D	ND	3.1	ND	3.4	ND	3.3	ND	3.8	ND	3.5
Total P5D										
123679-H6D										
123478-H6D	ND	2.6	ND	2.2	ND	2.2	ND	2.7	ND	2.0
123678-H6D	ND	2.4	ND	2.0	ND	2.0	ND	2.5	ND	1.9
123789-H6D	ND	2.4	ND	2.0	ND	2.0	ND	2.5	ND	1.9
Total H6D										
1234679-H7D										
1234678-H7D	ND	2.3	ND	1.9	ND	1.9	ND	2.5	ND	2.3
Total H7D										
12346789-OD	1.7i	3.7	0.4i	2.9	6.8	3.8	0.1	2.9	ND	2.7
PCDFs	**Levels**	**MDL**	**Levels**	**MDL**	**Levels**	**MDL**	**Levels**	**MDL**	**Levels**	**MDL**
2368-T4F										
2378-T4F	ND	2.1	ND	1.8	ND	2.2	ND	1.8	ND	1.7
2367-T4F										
Total T4F										
12468-P5F										
12478-P5F										
12378-P5F	ND	2.4	ND	1.7	ND	1.8	ND	1.7	ND	2.1
23478-P5F	ND	2.4	ND	1.7	ND	1.8	ND	1.7	ND	2.1
23467-P5F										
Total P5F										
123468-H6F										
124678-H6F										
124689-H6F										
123478-H6F	ND	2.3	ND	1.3	ND	1.1	ND	1.3	ND	1.4
123678-H6F	ND	2.3	ND	1.3	ND	1.1	ND	1.3	ND	1.4
123789-H6F	ND	2.3	ND	1.3	ND	1.1	ND	1.3	ND	1.4
234678-H6F	ND	2.3	ND	1.3	ND	1.1	ND	1.3	ND	1.4
Total H6F										
1234678-H7F	ND	3.0	ND	2.5	ND	2.7	ND	2.5	ND	2.0
1234689-H7F										
1234789-H7F	ND	3.0	ND	2.5	ND	2.7	ND	2.5	ND	2.0
Total H7F										
12346789-OF	11.7i	0.9	12.4i	0.7	17.9i	0.7	8.3i	0.7	5.8i	0.6
Recoveries	% Recoveries for 13-C-12									
2378-T4D	38.2		52.0		53.0		74.8		76.6	
12378-P5D	51.0		50.0		53.2		73.6		76.8	
123478-H6D	61.0		50.7		54.9		74.1		77.4	
123678-H6D	63.9		52.3		54.3		75.3		80.5	
1234678-H7D	70.7		50.2		53.5		77.4		86.4	
12346789-OD	87.7		54.7		56.3		77.9		73.6	

i - Incorrect ion ratio, interference by other compounds likely

MDL -Minimum Detection Limit

Table 2. High resolution GC/MS analysis of PCDDs, PCDFs and NOPCBs in Yukon caribou. Levels are ng/kg (wet wt.).

High Resolution GC/MS												
Sample #	L93-63600-02		L93-63600-02		L93-63600-02		L93-63601-02		L94-64249		L94-64250	
Location	Finlayson		Finlayson		Finlayson		Finlayson		Tay		Bonnet Plume	
Territory	Yukon		Yukon		Yukon		Yukon		Yukon		Yukon	
Pool	Age 3		Age 3		Age 3		Age 4		Age 5.3		Age 6.6	
Sample Type	Fat		Liver		Muscle		Fat		Fat		Fat	
No. in pool	2		2		2		6		13		14	
% Lipid	85.45		4.12		1.79		87.24		84.21		83.79	
PCDDs	**Levels**	**MDL**	**Levels**	**MDL**	**Levels**	**MDL**	**Levels**	**MDL**	**Levels**	**MDL**	**Levels**	**MDL**
2378-T4D	ND	0.14	ND	0.33	ND	0.33	ND	0.03	ND	0.04	ND	0.09
TotalT4D	ND		ND		ND		ND		ND		ND	
12378-P5D	ND	0.04	0.33	0.11	ND	0.13	ND	0.08	0.10	0.02	ND	0.11
Total P5D	ND		0.33		ND		ND		0.10		ND	
123679-H6D	ND	0.02	ND	0.14	ND	0.17	ND	0.14	ND	0.02	ND	0.05
123478-H6D	ND	0.02	ND	0.14	ND	0.17	ND	0.14	0.05	0.02	ND	0.05
123678-H6D	ND	0.02	ND	0.14	ND	0.17	ND	0.14	ND	0.02	ND	0.06
123789-H6D	ND	0.02	ND	0.14	ND	0.17	ND	0.14	0.02	0.02	ND	0.06
Total H6D	ND		ND		ND		ND		0.07		ND	
1234679-H7D	ND	0.11	ND	0.09	ND	0.22	ND	0.11	ND	0.02	ND	0.08
1234678-H7D	ND	0.11	ND	0.09	ND	0.22	ND	0.11	0.21	0.02	ND	0.08
Total H7D	ND		ND		ND		ND		0.21		ND	
12346789-OD	2.02	0.04	0.44	0.07	ND	0.15	0.94	0.06	0.92	0.03	0.55	0.01
PCDFs	**Levels**	**MDL**	**Levels**	**MDL**	**Levels**	**MDL**	**Levels**	**MDL**	**Levels**	**MDL**	**Levels**	**MDL**
2368-T4F									0.05	0.03	ND	0.13
2378-T4F	ND	0.05	ND	0.42	ND	0.27	ND	0.03	0.12	0.02	ND	0.13
2367-T4F									ND	0.02	ND	0.13
Total T4F	ND		ND		ND		ND		0.17		ND	
12468-P5F									0.04	0.03	ND	0.09
12478-P5F	ND	0.10	ND	0.10	ND	0.12	ND	0.11	0.20	0.03	0.21	0.09
12378-P5F	ND	0.10	ND	0.10	ND	0.12	ND	0.11	0.05	0.03	ND	0.09
23478-P5F	ND	0.10	ND	0.10	ND	0.12	ND	0.11	0.14	0.03	ND	0.09
23467-P5F	ND	0.10	ND	0.10	ND	0.12	ND	0.11	ND	0.03	ND	0.09
Total P5F	ND		ND		ND		ND		0.43		0.21	
123468-H6F	ND	0.08	ND	0.17	ND	0.09	ND	0.08	ND	0.03	ND	0.08
124678-H6F	ND	0.08	ND	0.17	ND	0.09	ND	0.08	ND	0.03	ND	0.08
124689-H6F	ND	0.08	ND	0.17	ND	0.09	ND	0.08	ND	0.03	ND	0.08
123478-H6F	ND	0.08	ND	0.17	ND	0.09	ND	0.08	ND	0.03	ND	0.08
123678-H6F	ND	0.07	ND	0.17	ND	0.09	ND	0.08	0.05	0.02	ND	0.08
123789-H6F	ND	0.09	ND	0.17	ND	0.09	ND	0.08	0.09	0.03	ND	0.08
234678-H6F	ND	0.10	ND	0.17	ND	0.09	ND	0.08	0.16	0.03	ND	0.08
Total H6F	ND		ND		ND		ND		0.30		ND	
1234678-H7F	ND	0.11	ND		ND	0.03	ND	0.14	0.13	0.01	ND	0.03
1234689-H7F	ND	0.11	ND	0.09	ND	0.03	ND	0.14	0.00	0.01	ND	0.03
1234789-H7F	ND	0.11	ND	0.09	ND	0.04	ND	0.14	0.07	0.01	ND	0.04
Total H7F	ND		ND		ND		ND		0.20		ND	
12346789-OF	ND	0.15	ND	0.07	ND	0.22	ND	0.06	0.21	0.03	ND	0.05
NOPCBs												
IUPAC #37	10.51	1.06	7.23	0.70	3.83	0.38	9.10	0.23	3.35	0.59	3.29	1.32
IUPAC #77	5.85	0.26	1.80	0.21	1.45	0.17	3.23	0.08	2.56	0.50	2.45	0.30
IUPAC #81	0.62	0.26	ND	0.21	ND	0.17	0.47	0.08	ND	0.50	0.30	0.30
IUPAC #126	6.05	0.49	2.05	0.32	ND	0.26	6.20	0.06	4.83	0.15	8.08	0.21
IUPAC #169	0.87	0.20	ND	0.28	ND	0.32	0.69	0.05	0.49	0.22	0.63	0.36
IUPAC #189	ND	0.20	ND	0.28	ND	0.32	ND	0.05	ND	0.22	ND	0.36
Recoveries	% Recoveries for 13-C-12											
2378-T4D	87		91		91		82		92		100	
12378-P5D	92		83		85		77		87		83	
123678-H6D	83		87		83		81		87		91	
1234678-H7D	91		90		89		97		89		93	
12346789-OD	68		69		70		93		84		76	
2378-T4F	91		80		82		79		89		80	
12378-P5F	88		80		83		81		86		72	
123478-H6F	71		82		93		75		84		81	
1234678-H7F	82		83		80		96		80		78	
PCB #77	61		52		49		109		66		38	
PCB #126	65		65		64		111		77		44	
PCB #169	66		67		67		108		75		43	

MDL -Minimum Detection Limit

Table 3. High resolution GC/MS analysis of PCDDs, PCDFs and NOPCBs in NWT caribou. Levels are ng/kg (wet wt.).

High Resolution GC/MS								
Sample #	L94-64252		L94-64253		L94-64255		L94-64254	
Location	Bathurst		Southhampton Is.		Cape Dorset		Lake Harbour	
Territory	NWT		NWT		NWT		NWT	
Pool	Age 4.1		Age 3.6		Age 3.7		Age 4.3	
Sample Type	Fat		Fat		Fat		Fat	
No. in pool	7		5		3		4	
% Lipid	43.02		92.26		19.21		80.37	
PCDDs	Levels	MDL	Levels	MDL	Levels	MDL	Levels	MDL
2378-T4D	ND	0.08	ND	0.14	0.14	0.06	0.11	0.02
TotalT4D	ND		ND		0.14		0.11	
12378-P5D	ND	0.17	0.28	0.17	0.32	0.15	0.25	0.02
Total P5D	ND		0.28		0.32		0.25	
123679-H6D	ND	0.07	ND	0.08	ND	0.02	ND	0.02
123478-H6D	ND	0.07	0.09	0.08	0.20	0.02	0.13	0.02
123678-H6D	ND	0.07	ND	0.09	0.14	0.02	0.26	0.02
123789-H6D	ND	0.07	ND	0.09	ND	0.02	0.07	0.02
Total H6D	ND		0.09		0.34		0.46	
1234679-H7D	ND	0.04	ND	0.15	ND	0.06	ND	0.02
1234678-H7D	0.14	0.04	ND	0.15	0.14	0.06	0.31	0.02
Total H7D	0.14		ND		0.14		0.31	
12346789-OD	0.92	0.01	1.52	0.04	0.90	0.01	0.91	0.01
PCDFs	Levels	MDL	Levels	MDL	Levels	MDL	Levels	MDL
2368-T4F	ND	0.13	ND	0.14	ND	0.19	0.07	0.02
2378-T4F	ND	0.13	0.15	0.14	0.19	0.19	0.17	0.02
2367-T4F	ND	0.13	ND	0.14	ND	0.19	0.04	0.02
Total T4F	ND		0.15		0.19		0.28	
12468-P5F	ND	0.08	ND	0.05	ND	0.02	0.04	0.02
12478-P5F	0.32	0.08	0.37	0.05	0.10	0.02	0.22	0.02
12378-P5F	ND	0.08	ND	0.05	ND	0.02	0.03	0.02
23478-P5F	ND	0.08	0.21	0.08	0.15	0.02	0.33	0.02
23467-P5F	ND	0.08	ND	0.08	0.09	0.02	ND	0.02
Total P5F	0.32		0.58		0.34		0.62	
123468-H6F	ND	0.07	ND	0.04	ND	0.03	ND	0.01
124678-H6F	ND	0.07	ND	0.04	ND	0.03	0.03	0.01
124689-H6F	ND	0.07	ND	0.04	ND	0.03	0.02	0.01
123478-H6F	ND	0.07	ND	0.04	0.08	0.03	0.12	0.01
123678-H6F	ND	0.07	ND	0.04	0.14	0.02	0.09	0.01
123789-H6F	ND	0.07	0.21	0.06	ND	0.03	0.12	0.01
234678-H6F	ND	0.07	ND	0.06	0.16	0.04	0.11	0.01
Total H6F	ND		0.21		0.38		0.49	
1234678-H7F	ND	0.03	ND	0.15	ND	0.06	0.13	0.01
1234689-H7F	ND	0.03	ND	0.15	ND	0.06	ND	0.01
1234789-H7F	ND	0.04	ND	0.15	ND	0.06	0.05	0.01
Total H7F	ND		ND		ND		0.18	
12346789-OF	ND	0.11	ND	0.12	ND	0.04	0.20	0.03
NOPCBs								
IUPAC #37	3.31	0.64	2.40	1.20	2.90	1.05	2.12	0.76
IUPAC #77	2.21	0.10	5.95	0.78	1.98	0.17	4.44	0.60
IUPAC #81	0.25	0.10	0.84	0.78	0.47	0.17	1.40	0.60
IUPAC #126	3.08	0.04	24.67	0.49	14.35	0.04	24.71	0.10
IUPAC #169	0.38	0.11	2.10	0.60	2.26	0.13	2.75	0.24
IUPAC #189	ND	0.11	ND	0.60	ND	0.13	ND	0.24
Recoveries	% Recoveries for 13-C-12							
2378-T4D	103		81		90		96	
12378-P5D	88		60		76		93	
123678-H6D	98		83		76		92	
1234678-H7D	101		58		82		92	
12346789-OD	82		54		75		88	
2378-T4F	91		70		79		92	
12378-P5F	79		65		75		91	
123478-H6F	85		59		69		89	
1234678-H7F	83		48		72		84	
PCB #77	70		24		58		52	
PCB #126	75		28		73		68	
PCB #169	75		27		97		68	

MDL -Minimum Detection Limit

ORGANOCHLORINE, HEAVY METAL AND RADIONUCLIDE CONTAMINANT TRANSFER THROUGH THE LICHEN-CARIBOU-WOLF FOOD CHAIN

PROJECT LEADER: B. Elkin, Department of Renewable Resources, Government of Northwest Territories

PROJECT TEAM: R. Bethke, S. Bohnet, Local Hunters and Trappers

OBJECTIVES

1. To assess the exposure of the lichen-caribou-wolf food chain in the Northwest Territories (NWT) to organochlorine, heavy metal and radionuclide contaminants.
2. To establish baseline levels of organochlorine, heavy metal and radionuclide contaminants in lichen, several caribou tissues, and several wolf tissues.
3. To model the transfer of these contaminants through the lichen-caribou-wolf food chain.
4. To determine spatial variation of contaminant levels in the lichen-caribou-wolf food chain among three locations in the NWT.

DESCRIPTION

Information on contaminant exposure in caribou (*Rangifer tarandus*) and other terrestrial wildlife species in Canadian arctic and subarctic regions are extremely limited. The scarcity of metal or organic residue data for terrestrial mammals has been identified as a data gap in arctic contaminant research. The limited work that has been done has indicated the presence of a number of contaminants of concern, including cadmium, HCH, HCB, toxaphene, PCBs, DDT, chlordane-related compounds, cesium-137 and polonium-210. These findings warrant more comprehensive studies to establish baseline levels in terrestrial species.

All indications suggest a direct air-plant-animal pathway of contaminant transfer in the terrestrial food chain. Lichens are an important component of the arctic ecosystem, and accumulate contaminants more readily than other vascular plants because of their large surface area, longevity, and ability to bind heavy metals. Upon deposition, airborne contaminants are accumulated and retained by lichens, thereby entering the food chain and potentially accumulating in herbivores and their predators. Caribou are strict herbivores that have a winter diet made up primarily of lichen. In arctic areas of the NWT, caribou has been shown to be the predominant food item of wolves (*Canis lupus*). This short and simple food chain provides an excellent opportunity to model and quantify the transfer of contaminants through three trophic levels to the top of the chain.

This study will provide baseline data on organochlorine, heavy metal and radionuclide contaminant levels in several tissues at all three trophic levels of the food chain. This data will be used to evaluate the transfer and biomagnification of specific contaminants through the lichen-caribou-wolf food chain. The defined ranges and distribution of caribou herds across the NWT also allows for an examination of spatial variation in contaminant exposure or food chain dynamics. Samples will be collected near Yellowknife (Bathurst herd), Cambridge Bay (Victoria Island herd), and Inuvik (Bluenose herd).

ACTIVITIES IN 1993/94

Field Sampling

This study was initiated in 1992/93, and lichen, caribou and wolf collections were completed on the Bathurst caribou herd range. In 1993/94, field collections of caribou were conducted in conjunction with local Hunters and Trappers Associations/Committees at Cambridge Bay and Inuvik. Wolf carcasses were collected by local hunters at Cambridge Bay, and submitted frozen for processing and sampling. For both caribou and wolves, samples were collected from 10 male and 10 female animals. Stomach contents were collected from the caribou and wolves for diet analysis. Teeth were collected for aging purposes, and a variety of biological and morphometric measurements were taken. Samples of three common lichen species (*Cladina mitis*, *Cladina rangiferina*, *Cetraria nivalis*) that are important in the caribou diet were selected for analysis. Lichen samples were collected at three different locations on each caribou range, with four subsites sampled at each location.

Contaminant Analysis

Lichen, caribou and wolf samples from the Bathurst herd range were analyzed in 1993/94 for organochlorine and heavy metal contaminants at the Great Lakes Institute in Windsor, Ontario. The suite of contaminants assessed comprised a spectrum of 63 organochlorines, including 43 PCB congeners and 20 pesticides, and 10 metals. Organochlorine analyses were conducted on individual fat, liver and muscle samples to evaluate tissue distribution. Metal analysis was conducted on kidney and liver samples. Whole lichen and muscle samples from caribou and wolves were also analyzed for radionuclides at AECL Whiteshell Laboratories in Pinawa, Manitoba.

RESULTS AND DISCUSSION

The tissue residue analyses from the Bathurst range samples were completed in 1993/94. Analysis of lichen, caribou and wolf samples from Cambridge Bay and Inuvik will be completed in 1994/95. Data on the Bathurst caribou has been included in the paper entitled "Identification of baseline levels and spatial trends of organochlorine, heavy metal and radionuclide contaminants in caribou in the Northwest Territories" (this volume). Mean tissue concentrations of the predominant organochlorine contaminants detected in lichen, caribou and wolf are given in Figure 1. Residue levels in caribou and wolf are for adipose tissue. Mean levels of metals in lichen, caribou kidney and wolf kidney are given in Figure 2. Concentrations of individual PCB congeners in lichen, caribou fat and wolf fat are given in Figure 3. The Bathurst data set is currently being evaluated to assess and model contaminant transfer between the three trophic levels, and this analysis will be completed in 1994/95.

Expected project completion date: Field collections of lichen, caribou and wolves were completed from all 3 sites in 1993/94. Contaminant analysis on the Cambridge Bay and Inuvik samples will be conducted in 1994/95. Data evaluation and interpretation, food chain modelling, human health risk assessment, and community consultation will occur until 1995/96.

Figure 1. Arithmetic mean concentrations (ng • g^{-1}, lipid corrected) of selected organochlorine residues in lichen, caribou fat and wolf fat, collected on the Bathurst caribou range in the NWT.

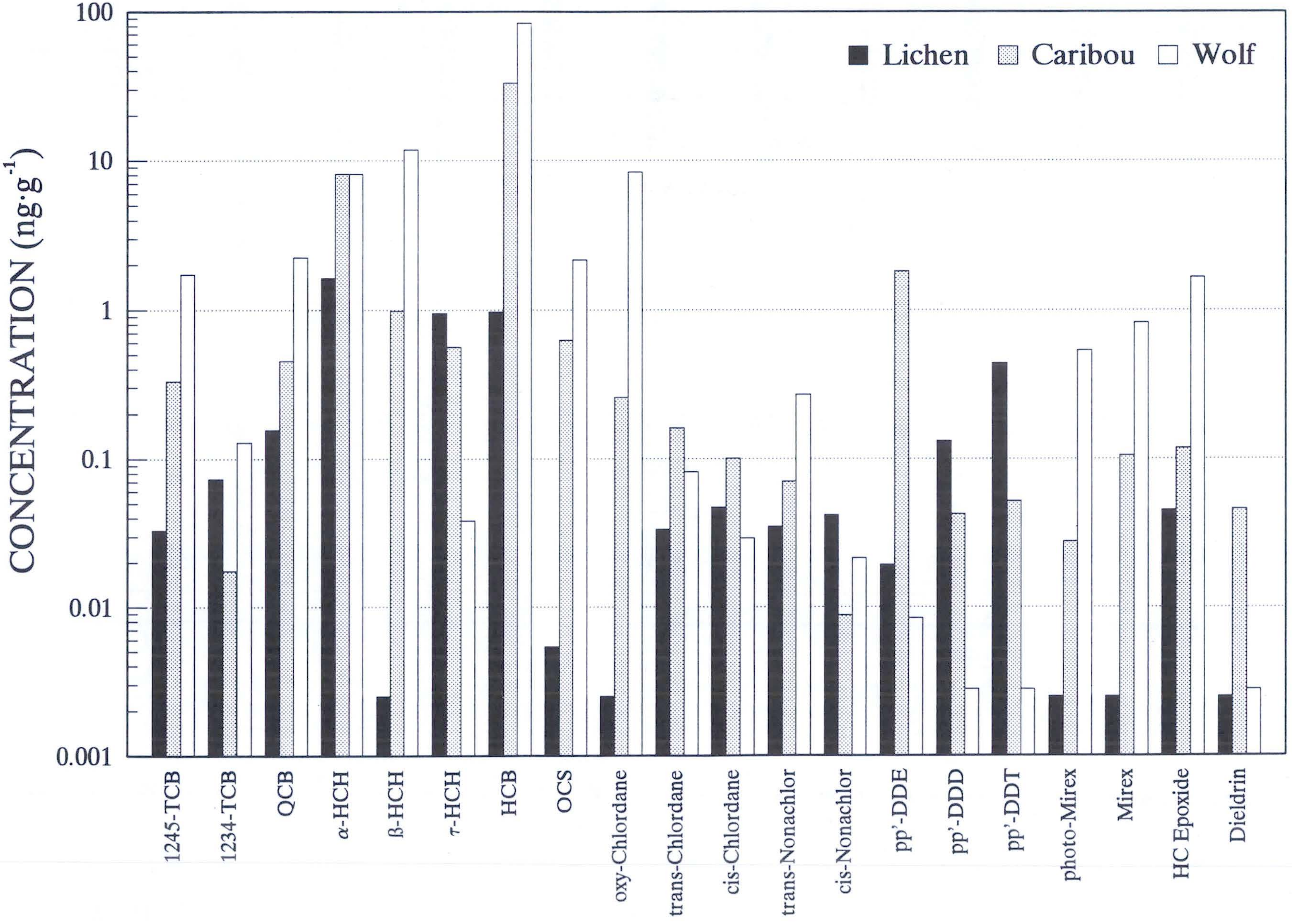


Figure 2. Arithmetic mean concentrations ($\mu g \cdot g^{-1}$) of selected metals in lichen, caribou kidney and wolf kidney, collected on the Bathurst caribou range in the NWT. All concentrations are given in dry weight except for mercury (Hg) where wet weight is given.

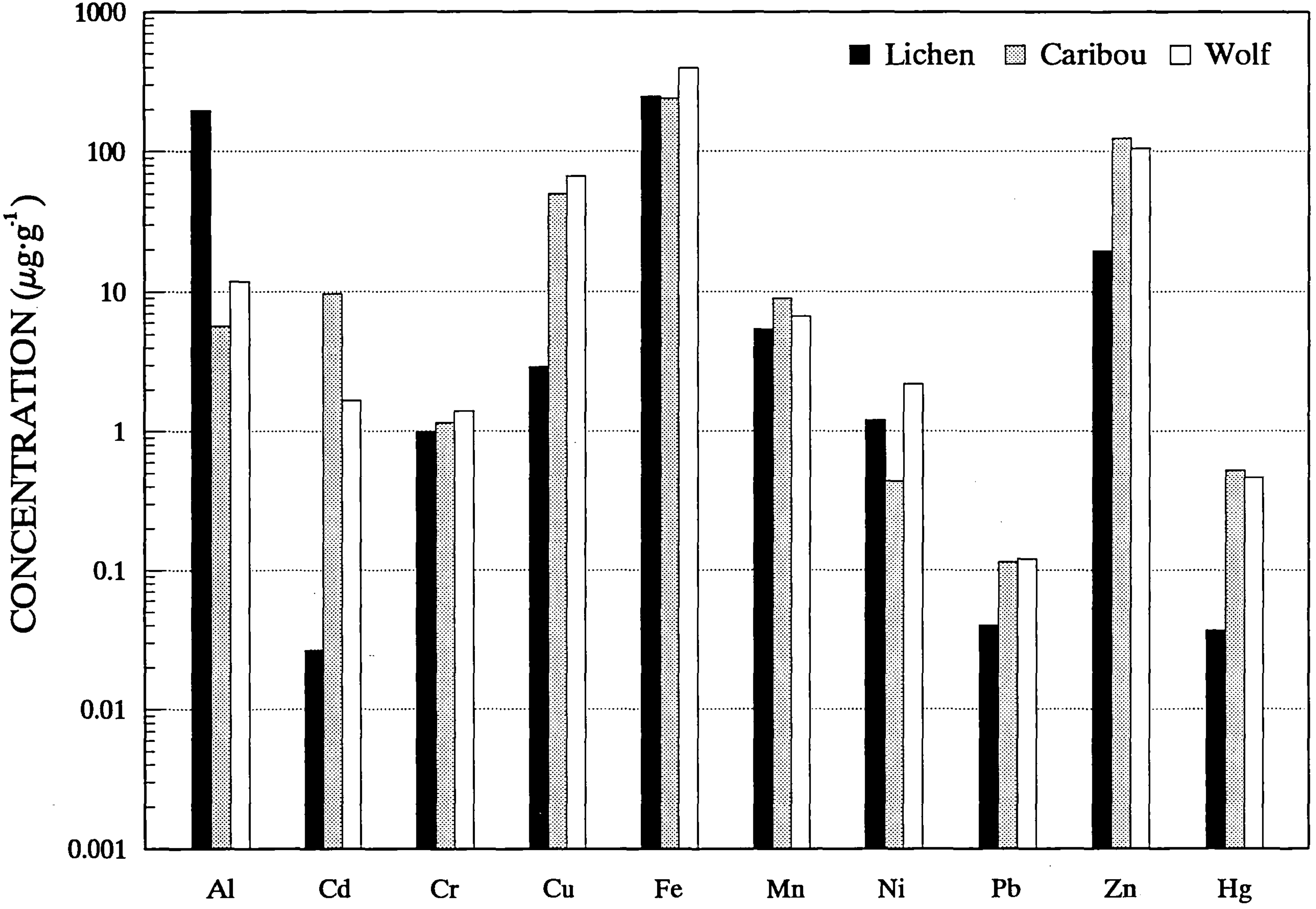
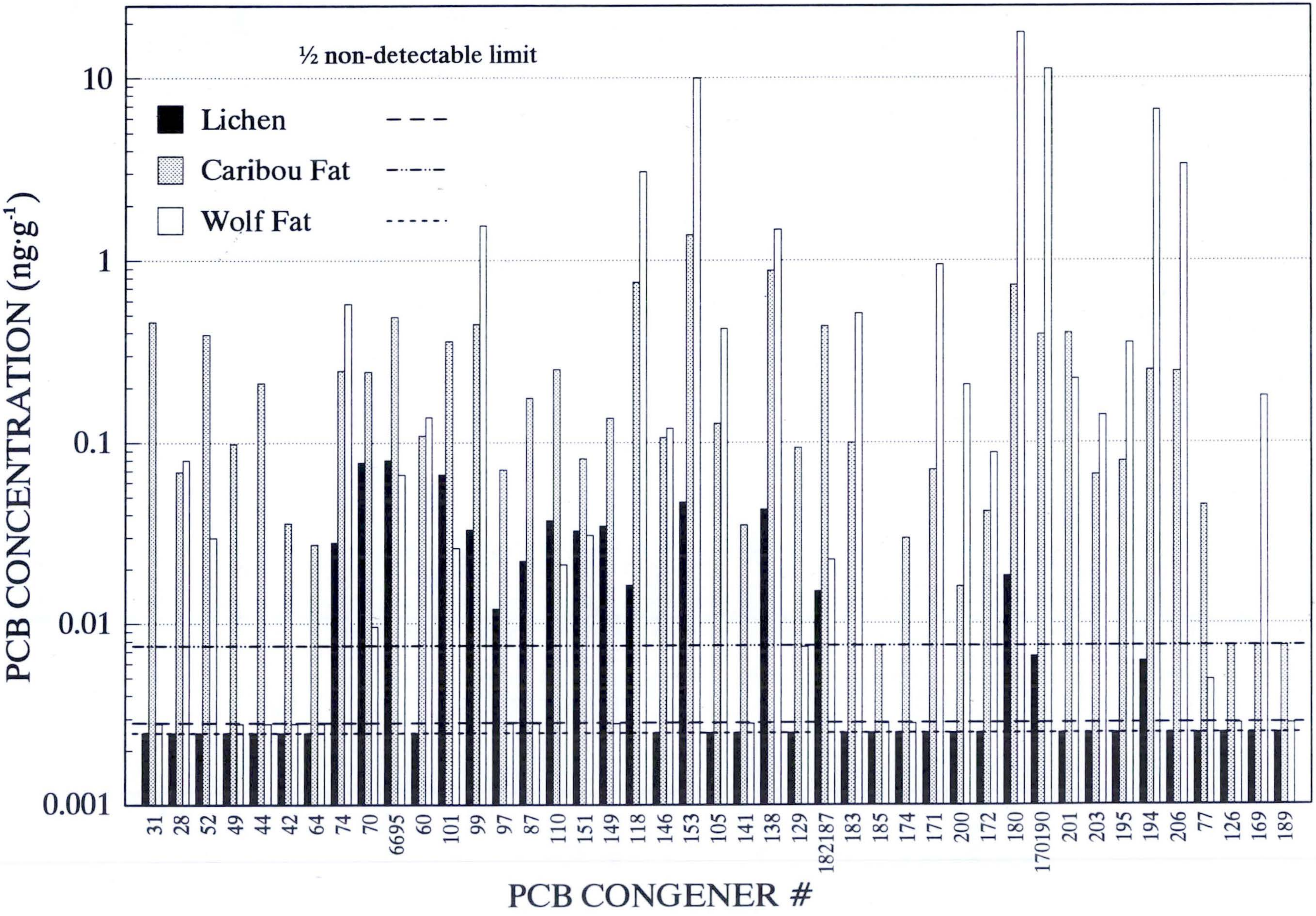


Figure 3. Arithmetic mean concentrations (ng • g^{-1}, lipid corrected) for residues of 43 PCB congeners in lichen, caribou fat and wolf fat, collected on the Bathurst caribou range in the NWT.



IDENTIFICATION OF LEVELS AND REPRODUCTIVE EFFECTS OF ORGANOCHLORINE AND HEAVY METAL CONTAMINANTS IN MINK (*Mustela vison*)

PROJECT LEADERS: K.G. Poole and B.T. Elkin, Department of Renewable Resources, Government of Northwest Territories

PROJECT TEAM: Local Trappers, Renewable Resource Officers

OBJECTIVES

1. To determine levels and spatial and temporal trends of organochlorine and heavy metal contaminants in mink along the Mackenzie, Slave and Liard drainage systems in the western Northwest Territories.
2. To evaluate the potential biological effects of contaminants on mink reproduction.
3. To determine the potential sources (via the prey base) of contaminants found in mink.

DESCRIPTION

Mink (*Mustela vison*) is a top trophic level species that readily bioaccumulates environmental pollutants such as polychlorinated biphenyls (PCBs), DDT and methylmercury. Small mammals and fish form the greatest component of mink diet in most areas (Eagle and Whitman 1987), thus the species is exposed to contaminants from both the aquatic and the terrestrial food webs. Mink are extremely vulnerable to organochlorine contaminants, and are known to experience reproductive failure as a result of eating fish contaminated with relatively low levels of PCBs (reviewed in Ringer 1981, Eisler 1986). This unique sensitivity can result in population effects at low levels of environmental contaminants (Wren 1991). As such, mink may provide a sensitive indicator to assess short and long term trends in environmental contaminants and ecosystem health.

A number of organochlorine and heavy metal contaminants have been identified in freshwater fish in the Mackenzie River, providing a potential source of contaminants for mink (Muir *et al.* 1989a, 1989b). Studies on fish at Ft. Good Hope and Colville Lake have detected the presence of PCBs, toxaphene and chlordane, as well as HCH, chlorobenzene, dieldrin and DDT (Kuhnlein 1991). The heavy metals copper, nickel, cadmium, mercury, selenium and zinc have also been identified. This study was initiated to examine spatial and temporal trends in levels of organochlorine and heavy metal contaminants in harvested mink along the Mackenzie River drainage basin in western NWT. Contaminant levels were also assessed in harvested marten (*Martes americana*) taken in one of the mink sampling sites. Examination of contaminant burdens in this sympatric Mustelid, which has a diet similar to mink with the exception of fish (K. Poole, unpubl. data), may help explain the source of the contaminants detected in mink.

ACTIVITIES IN 1993/94

In 1993/94, 187 mink carcasses were collected from 21 trappers from the Mackenzie Delta near Inuvik, from Ft. Smith and Ft. Resolution near the Slave River, and from Ft. Providence west of Great Slave Lake. This represented the third and final year of carcass collections in the Mackenzie Delta area, and brings to 804 the number of mink carcasses collected to date from NWT trappers. To further examine where mink may be picking up their contaminant burdens, northern red-backed voles (*Clethrionomys rutilus*), a primary prey of both marten and mink, were collected from five areas of the western NWT corresponding to mink collection sites.

Liver and kidney samples from up to 22 mink collected at each site were analyzed for organochlorine and heavy metal contaminants at the Great Lakes Institute in Windsor, Ontario. A subsample of tissues were examined for heavy metals at the DIAND Northern Laboratory in Yellowknife. The suite of contaminants assessed were a spectrum of 63 organic chemicals, including 43 PCB congeners, toxaphene, and dioxins/furans, and 10 metals. Stomach contents were collected for diet analysis, teeth were collected for aging purposes, and a variety of biological and morphometric measurements were taken. The complete contaminant residue data set from the 1991/92 and 1992/93 sampling programs were analyzed and evaluated during 1993/94. A paper detailing the results to date was presented at the October 1993 conference in Iceland, and will be published in fall 1994 in a special issue of STOTEN (Poole *et al.* in press). Analyses of samples collected in 1993/94 is currently in progress.

RESULTS

A total of 617 mink carcasses were collected in 1991/92 and 1992/93, and contaminant analyses were conducted on 90 mink and 20 martens. Organochlorine levels are reported below for livers only. Overall, contaminant levels in NWT mink were low in comparison with other mink studied in North America. Many of the pesticides and PCB congeners detected were found at very low levels, with less toxic compounds predominating. ΣPCB residues (sum of 43 congeners) in mink ranged from a mean of 5.32 ng/g wet weight in the livers of Inuvik mink (the most northerly collection site) to 27.67 ng/g in mink from Fort Smith (the most southerly collection site), and averaged 32.58 ng/g in the Fort Good Hope marten sample (Table 1). There was a doubling of mean ΣPCB levels in Inuvik mink from 5.32 ng/g in 1991/92 to 10.69 ng/g in 1992/93. In all but two mink (n = 90) and two marten samples (n = 20), DDT was below detection limits. Of the more toxic non-ortho substituted PCB congeners, PCB-77 was detected in no mink samples (n = 90) and only two marten samples (n = 20), PCB-169 was only detected in one Fort Smith mink, and residues of PCB-126 were found in two mink and six marten samples.

Eight replicate liver samples were examined for six dioxin/furan compounds. Dioxins/furans were not detected in any mink liver samples, and were detected in only three cases in Fort Good Hope marten liver samples. Two pooled liver samples were examined for total toxaphene. Total toxaphene was 1.42 and 7.85 ng/g (wet weight) for mink from Ft. Good Hope and Ft. Rae, respectively. There appeared to be no differences in organochlorine burden between sexes.

Heavy metal residues were also comparatively low, with the exception of total mercury, which was at moderate levels (community means of 1.16-3.30 μg/g wet weight in liver samples) (Table 2). Mercury levels were highest in Fort Rae, Fort Smith, and Fort Good Hope mink livers. Cadmium was highest in the Fort Liard mink kidneys.

DISCUSSION/CONCLUSIONS

While organochlorine residues were present in mink in the NWT, the observed burdens were generally low in comparison with wild mink from other areas of North America. Overall PCB levels observed in NWT mink were considerably lower than levels shown to cause reproductive impairment. Population indices derived from age and sex ratios of the harvest, coupled with the comparatively low levels of contaminants, suggest little or no effects on mink reproduction or population health as a result of these contaminants.

There was a distinct trend of decreasing organochlorine contaminant burdens with increasing latitude, but no trend in heavy metal burdens was evident. At present, long-range atmospheric transport appears to be the primary source of the contaminants detected. Local point sources for contaminants are not suspected. Inuvik mink, trapped in the Mackenzie Delta, were the only animals in the collections in direct contact with the Mackenzie River and potential water-borne pollutants being flushed down-stream from the South. Burdens in Inuvik mink were lower than levels found in mink collected away from the river in the other communities. Thus, long-range aquatic transport from southern sources of pollution is not likely a major source of the contaminants found in mink.

Collections and analyses for 1994/95 will be limited to increasing sample sizes of mink from the Liard drainage (Ft. Liard and Ft. Simpson). Examination of contaminant levels in terrestrial prey species collected to date (snowshoe hares [*Lepus americanus*] and red-backed voles) will be concluded.

Expected project completion date: March 31, 1996.

REFERENCES

Eagle, T.C. and J.S.D. Whitman. 1987. Mink. Pp. 615-624 *in*: Wild Furbearer Management and Conservation in North America, M. Novak, J.A. Baker, M.E. Obbard and B. Malloch (eds.). Ontario Ministry of Natural Resources, Toronto, Ontario. 1168 pp.

Eisler, R. 1986. Polychlorinated biphenyl hazards to fish, wildlife, and invertebrates: a synoptic review. U.S. Fish and Wildl. Serv. Biol. Rep. 85(1.7). 72 pp.

Kuhnlein, H.V. 1991. Dietary evaluation of food, nutrition, and contaminants in Fort Good Hope and Colville Lake, Northwest Territories. McGill University. Health and Welfare Canada - Medical Services Branch Report HQ88-8901650.

Muir, D.C.G., C.A. Ford, N.P. Grift, D.A. Metner, and W.L. Lockhart. 1989a. Geographic variation of chlorinated hydrocarbon in burbot (*Lota lota*) from remote lakes and rivers in Canada. Arch. Environ. Contam. Toxicol. 19: 1191-1204.

Muir, D., B. Rosenberg, and C.Ford. 1989b. Analysis of dietary samples from Fort Good Hope (N.W.T.) for toxaphene, PCB's and other organochlorine contaminants. Interim Report, Fisheries and Oceans Canada, Central Arctic Region.

Poole, K.G., B.T. Elkin, and R.W. Bethke. In press. Environmental contaminants in wild mink in the Northwest Territories, Canada. The Science of the Total Environment.

Ringer, R.K. 1981. The effects of environmental contaminants on reproduction in the mink (*Mustela vison*). Pp. 232-237 *in* Environmental Factors in Mammal Reproduction, D. Gilmore and B. Cook (eds.). MacMillan Publ. Ltd., London. 330 pp.

Wren, C.D. 1991. Cause-effect linkages between chemicals and populations of mink (*Mustela vison*) and otter (*Lutra lutra*) in the Great Lakes Basin. J. Toxic. Environ. Health 33: 549-585.

Table 1. Arithmetic means (ng/g wet weight (SE)) of selected organochlorine residues in livers of mink and marten trapped in the NWT, 1991/92 and 1992/93.

Species/community	n	% lipid	ΣDDT[a]	ΣHCH[b]	HCB	ΣChlordane[c]	Dieldrin	ΣPCB[d]
Mink Inuvik92	21	5.7	0.77 (0.13)	0.10 (0.02)	0.31 (0.05)	1.46 (0.22)	0.15 (0.04)	5.32 (0.99)
Mink Inuvik93	17	6.2	1.24 (0.29)	0.18 (0.03)	0.44 (0.07)	1.51 (0.16)	0.15 (0.05)	10.69 (1.53)
Mink Fort Good Hope	18	7.5	3.35 (0.62)	0.16 (0.04)	0.67 (0.10)	2.30 (0.36)	0.45 (0.11)	15.31 (2.28)
Mink Fort Rae	14	5.9	4.73 (0.91)	0.20 (0.04)	0.48 (0.06)	2.97 (0.60)	0.22 (0.09)	21.76 (4.05)
Mink Fort Liard	4	5.7	13.66 (5.68)	0.26 (0.14)	0.83 (0.45)	1.67 (0.90)	0.22 (0.08)	19.85 (5.29)
Mink Fort Smith	6	4.4	5.24 (1.09)	0.16 (0.04)	0.70 (0.15)	4.64 (1.67)	0.19 (0.09)	27.67 (4.54)
Marten Fort Good Hope	16	4.5	2.41 (1.23)	0.31 (0.07)	3.47 (0.89)	5.02 (1.10)	0.46 (0.10)	32.58 (4.78)

[a] ΣDDT = Sum of *p,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD.

[b] ΣHCH = Sum of α-HCH, β-HCH and γ-HCH.

[c] ΣChlordane = Sum of *oxy*-, *cis*-, *trans*-chlordane, heptachlor epoxide and *cis*-, *trans*-nonachlor.

[d] ΣPCB = Sum of individual congeners.

Table 2. Metal concentrations from mink and marten trapped in the NWT, 1991/92 and 1992/93. All metals given in dry weight in kidneys, except for total mercury (Hg) given in wet weight in livers. ** denotes significant difference (ANOVA, $p < 0.05$) among mink groups. Significantly higher groups means (LSM) given in bold.

Species/ community	n	Metal concentration (μg/g (SE))									
		Al**	Cd**	Cr**	Cu	Fe	Mn**	Ni**	Pb**	Zn**	Hg**
Mink Inuvik92	23	**9.81** (1.21)	0.84 (0.24)	0.49 (0.08)	24.74 (3.42)	813.9 (51.9)	3.67 (0.39)	**1.18** (0.24)	**1.07** (0.36)	76.21 (6.15)	1.16 (0.13)
Mink Inuvik93	20	2.22 (0.41)	0.50 (0.12)	1.33 (0.10)	12.41 (0.68)	840.1 (45.9)	2.33 (0.24)	0.48 (0.04)	0.10 (0.02)	82.37 (3.25)	1.84 (0.20)
Mink Fort Good Hope	20	**8.41** (0.75)	0.90 (0.19)	0.45 (0.03)	19.89 (1.04)	964.6 (53.4)	**11.18** (2.96)	**1.89** (0.33)	0.27 (0.11)	67.91 (6.00)	**2.17** (0.29)
Mink Fort Rae	16	**9.49** (1.47)	1.12 (0.45)	0.44 (0.05)	20.82 (1.27)	957.9 (45.8)	**4.95** (0.30)	**1.32** (0.22)	**0.99** (0.18)	**104.37** (5.34)	**3.30** (0.65)
Mink Fort Liard	4	2.33 (0.32)	**3.62** (1.94)	**1.09** (0.25)	15.74 (1.06)	965.7 (92.2)	4.02 (0.72)	0.61 (0.12)	0.17 (0.10)	**121.80** (13.5)	1.45 (0.53)
Mink Fort Smith	6	3.61 (1.26)	0.14 (0.05)	**1.17** (0.11)	17.77 (0.88)	852.4 (85.2)	3.08 (0.37)	0.45 (0.05)	0.09 (0.03)	84.38 (7.48)	**2.44** (0.37)
Marten Fort Good Hope	20	3.51 (0.47)	3.21 (0.34)	0.51 (0.04)	14.03 (0.93)	573.9 (46.0)	2.16 (0.15)	0.37 (0.03)	0.23 (0.04)	75.25 (3.92)	0.28 (0.03)

SURVEY OF CONTAMINANTS IN YUKON COUNTRY FOODS

PROJECT LEADERS: M. Gamberg, Gamberg Consulting, Yukon; and L. Mychasiw, Department of Renewable Resources, Government of Yukon

PROJECT TEAM: R. Florkiewicz, D. Bakica, D. Anderson, K. Knutson

OBJECTIVES

1. To determine the presence and quantity of organic and inorganic contaminants in country foods used in southeastern Yukon.
2. To identify potential health risks to First Nations People and others consuming country foods.
3. To develop baseline data on levels of organic and inorganic contaminants in wildlife in southeastern Yukon.

DESCRIPTION

Environmental contamination of food sources is an issue of major concern across Canada, and is being closely monitored in many areas, particularly in the north where country foods constitute a large portion of native diets. In the past, little work has been done on wild mammals used as food sources by natives and other hunters. The recent discovery of high levels of cadmium in caribou from the Porcupine and Finlayson Caribou Herds in the Yukon has raised concern that other contaminants may be present in local wildlife.

This study was intended to be a pilot project in the southeast region of the Yukon, encompassing the Kaska and Teslin Tlingit First Nations. However, as more funding became available, it was extended to include the Dawson and Champagne/Aishihik traditional areas.

This study was designed to address concerns of First Nations and other hunters with regard to contaminants in country foods. The specific objectives were to: (1) identify any contaminants of concern in wild mammals used as country foods, (2) assess the health risk of such contaminants to humans and to the animal population, (3) to provide information necessary to design a viable territory-wide survey of contaminants in country foods for 1994/95, and (4) to assess temporal and geographical trends of contaminants in wildlife in the Yukon.

ACTIVITIES IN 1993/94

Sampling

Tissue samples and carcasses for contaminant analysis were solicited from outfitters, hunters and trappers in selected areas of the Yukon (including Watson Lake, Ross River, Teslin, Dawson and Haines Junction). A nominal fee was offered to trappers for lynx, beaver and muskrat carcasses, and to hunters for bone, liver, kidney, muscle and fat samples from moose, caribou, Dall sheep, mountain goats and black bear, and whole carcasses of snowshoe hare, Arctic ground squirrels and porcupine.

Analysis

Two bone samples from each area from each species were randomly selected for analysis, and muscle and fat tissues were each pooled by species and area. All livers and kidneys were analyzed individually. Bone, liver, kidney and muscle were analyzed for a suite of inorganic contaminants using inductively coupled plasma with ultrasonic nebulization, and, in addition, mercury was measured in kidneys using cold vapour atomic absorption spectrometry. Fat tissue was analyzed for dioxins, furans, PCBs as Aroclors, and pesticides using high resolution gas chromatography with mass spectrometry detection. Animals were aged using tooth cementum where possible, or other physiological indices (e.g. epiphyseal closure, pelage characteristics).

Results

Samples were obtained from a total of 77 animals from the five communities. Sampling success was variable among communities and species. No samples were obtained from Haines Junction, and very few from Dawson and Teslin. No bear samples were obtained from any community, and only one lynx was sampled. Analytical results from the contaminant analysis are not yet available.

CONCLUSIONS AND UTILIZATION OF RESULTS

Few conclusions may be drawn from this project at this point, because analytical results are not yet available. However, the experience gained in sampling designs and protocols will prove invaluable in planning the next phase of this project to be carried out in 1994-96. The study will be expanded to encompass the entire Yukon Territory, and to include plants as well as mammals used as country foods. It will also be streamlined to include only those wild foods that are used in a particular community (as determined by dietary surveys), and each species will be sampled at the time of year it is traditionally taken.

Data from the current study that suggest a potential health risk for humans will be submitted to Health Canada for a health risk assessment. That assessment will be communicated to First Nations and other people of the Yukon by the Yukon Contaminants Committee.

Expected project completion date: December 31, 1994

PARTNERS

Environmental Protection Service (J. Eamer), Indian and Northern Affairs Canada (M. Palmer), Fisheries and Oceans Canada (A. von Finster), Yukon Health (D. Schiller), Health Canada (F. O'Brien), Council for Yukon Indians (N. Kassi), Kaska Tribal Council (H. Dick), Teslin Tlingit Council (R.L. Jackson), Dawson First Nation (E. Kormendy), Champagne/Aishihik First Nation (L. Joe).

HUMAN HEALTH
NEW FINDINGS

1) PCB levels in cord blood of newborns in Nunavik (1101 μg/kg lipid basis) were four times greater than samples collected in the Quebec City area (248 μg/kg).

2) Blood mercury concentrations exceeded the acceptable daily intake (ADI) level in 14 newborns (24%) in Nunavik. By comparison, no newborn from the Québec City area has reached this level.

3) In Nunavik, only 3 newborns (5%) had a blood lead concentration above the intervention level of 0.48 μmol/L, determined by the U.S. Center for Disease Control (US-CDC).

4) Preliminary analysis has revealed the presence of two major chlorobornanes (nonachlorobornane and octachlorobornane) in human milk samples from northern Quebec, which have also been found in marine mammals.

HUMAN CONTAMINANT TRENDS IN ARCTIC CANADA: A CORD BLOOD STUDY IN NUNAVIK

PROJECT LEADER: E. Dewailly, Environmental Health Service, Public Health, Centre Hospitalier de l'Université Laval (CHUL)

PROJECT TEAM: S. Bruneau, P. Ayotte, M. Rhainds, J.-P. Weber, G. Lebel, A. Corriveau

COLLABORATORS: J. Walker (Health Department, Government of Northwest Territories)

OBJECTIVES

1. To assess the exposure of Northern neonates to selected organochlorines and heavy metals in Nunavik (northern Quebec).
2. To compare the levels measured in Nunavik to groups from Southern Canada; identify communities where additional research should be implemented.
3. To evaluate temporal trends during a five-year program.
4. To determine a public health level of action according to blood concentrations found in these populations and the known toxicological properties of the contaminants identified from the scientific literature.

BACKGROUND

Early work conducted on Baffin Island and in Arctic Québec has demonstrated that because of their traditional dietary habits, Inuit people are exposed to an unusually high quantity of contaminants, mainly heavy metals and organochlorines.

This human exposure could be responsible for chronic health effects principally in the most sensitive groups: fetus and breast-fed babies. A study in the Great Lakes area indicated that newborns of women who had eaten large quantities of contaminated fish had smaller birth size, a delay in maturation of motor abilities, and poorer cognitive function and visual recognition memory at age one (Jacobson *et al.* 1985). Researchers reported that at age four, deficits in body size persisted and indicators of poorer cognitive performance continued to be present and were associated with *in utero* exposure, as measured by cord blood PCB levels (Jacobson *et al.* 1990). For these reasons, a routine screening program was started to determine newborn exposure to the contaminants present in the food chain. This project is also part of the Canadian study for the AMAP subprogramme on human health.

Every mother delivering in Kuujjuaq and Povungnituk is asked, after receiving proper information, to participate in the program. After signing the consent form, blood is collected at birth from the umbilical cord. Since the beginning of January 1994, 62 umbilical cord blood samples have been analyzed for heavy metals and organochlorines. Furthermore, in order to adjust organochlorines on a lipid basis, total lipid content of plasma was determined.

Concentrations are compared with a reference group from the Québec City area where 250 cord blood samples were collected in two hospitals in June-July 1993. Samples were analyzed for mercury, lead and organochlorines by the same laboratory (Québec Toxicology Centre). Data are presented Figure 1.

Heavy metals (lead, mercury) and selenium are measured in whole blood. For blood samples containing more than 100 nmol/L of total mercury, inorganic mercury is also measured. Organochlorines include 14 PCB congeners (IUPAC 28, 52, 99, 101, 105, 118, 128, 138, 153, 156, 170, 180, 183, 187) and pesticides (aldrin, β-BHC, α and δ-chlordane, *cis*-nonachlor, *p,p*'-DDE, *p,p*'-DDT, hexachlorobenzene, mirex, oxychlordane and trans-nonachlor). Detection limits are 0.03 μg/L for *p,p*'-DDT and β-BHC, 0.1 μg/L for heptachlor epoxide and dieldrin and 0.02 μg/L for other toxicants. For all organochlorines, if results are lower than detection limits, ½ detection limits were considered in analysis.

Total blood lipid is also measured in order to adjust the organochlorine concentration on a lipid basis (total lipids are usually 50% lower in fetal blood than in maternal blood).

RESULTS

1. Heavy metals

1.1 Lead

The arithmetic mean concentration of lead in the whole cord blood was 0.248 μmol/L with a range of 0.04 to 1.28 μmol/L (geometric mean: 0.206 μmol/L, CI 95%: 0.177-0.240). By comparison, in 1993, the average concentration (geometric mean) of blood lead among 266 newborns from the Québec City area was 0.076 (CI 95%: 0.071-0.081) (Rhainds *et al.* 1994). In Toronto in 1990, the mean concentration was 0.08 μmol/L (Koren *et al.* 1990) (n=95) and in Québec City it was 0.09 μmol/L (n=430) (Rhainds and Levallois 1993). In Toronto no newborn had a blood lead concentration above the intervention level of 0.48 μmol/L, determined by the Center for Disease Control (US-CDC). In 1993, in the Québec City area, among the 266 newborns tested only one had a blood lead concentration above 0.48 μmol/L. In Nunavik only 3 newborns (5%) had a blood concentration above this limit.

1.2 Mercury

The arithmetic mean concentration of total mercury in the whole cord blood was 76.0 nmol/L (n=62) with a range between 16 and 235 nmol/L. The geometric mean was 60.3 nmol/L (CI 95%: 50.4-72.0 nmol/L). In comparison, in 1993 in the Québec City area, the geometric mean concentration was 3.4 nmol/L (CI 95%: 3.0-3.7) (Rhainds *et al.* 1994). Blood mercury concentrations in Nunavik are slightly lower than those reported in the Faroe Islands among a fishing population that regularly eats pilot whale (121 nmol/L, n=997) (Granjean *et al.* 1992). 100 nmol/L (20 μg/L) is the safe biological concentration proposed by FAO/WHO (Lowest Observed Adverse Effects Level (LOAEL) of 200 μg/L divided by a safety factor of 10). This corresponds to an Acceptable Daily Intake (ADI) of 0.47 μg/kg/day. If we use these guidelines (100 nmol/L), no newborn from the Québec City area has reached this concentration. In Nunavik, 14 newborns (24%) had a blood mercury concentration above this safe biological concentration.

1.3 Selenium

The geometric mean concentration of selenium in whole blood was 3.41 μmol/L (CI 95%: 3.13-3.71). In comparison, 72 cord blood samples were analyzed this year in Southern Québec. The geometric mean was 2.45 μmol/L (CI 95% 2.36-2.54) (Rhainds *et al.* 1994). In the Faroe Islands, the median concentration in 1020 cord blood samples was 1.4 μmol/L, in West Greenland it was 3.1 μmol/L and 1.86 μmol/L in East Greenland (Hansen 1988). However, in these studies, selenium concentrations were measured in plasma, so any comparison should be made with caution.

2. Organochlorines

2.1 PCBs

The arithmetic mean concentration of PCBs (Aroclor 1260) in the plasma in the 62 umbilical cord samples was 2.87 μg/L (Geometric mean 2.21 μg/L (CI 95%: 1.81-2.67).

On a lipid basis, total PCBs averaged 1101 μg/kg (geometric mean 862 μg/kg) (CI 95%: 713-1042) which is less than half of the concentration previously found in breast milk lipids (2900 μg/kg) (Dewailly *et al.* 1993). The mean total lipid content in the plasma of the 60 newborns was 2.58 g/L compared to 5-7 g/L in adults. PCB congeners (IUPAC NO.) 138 and 153 represented more than 50% of the sum of the 14 congeners. Low chlorinated congeners (28, 52) were detected in only 4.8 and 25.8% of the samples, respectively. The PCB profile is presented in Figure 2a. In comparison, 126 cord blood samples from the Québec City area were analyzed this year. The total PCB concentration was 0.63 μg/L (CI 95%: 0.57-0.69). On a fat basis, it was 248 μg/kg (CI 95%: 228-271), 4 times less than in Nunavik (Figures 1 and 3).

In Southern Québec, no newborn had a whole plasma PCB concentration above 5 μg/L. However in Nunavik, 13% of the newborns exceeded this limit. For chlorinated pesticides, plasma concentrations are presented Figure 2b. *p,p*'-DDE is the main pesticide found in the plasma followed by hexachlorobenzene and transnonachlor. The very high *p,p*'-DDE/*p,p*'-DDT ratio (> 25) is typical of what is to be expected at the top of the food chain.

2.2 Association between contaminants

Because most of contaminants were log-normally distributed, correlation coefficients were calculated using log transformed variables. All contaminants were associated together indicating that lead, mercury and organochlorines in blood come from the same food source. Examples of such correlations are presented Figure 3. Selenium was slightly correlated with mercury (r=0.25, p=0.08).

3. Polyunsaturated fatty acids (PUFA)

Eicosapentanoic acid (EPA, 20:5n3) and docasahexanoic acid (DHA, 22:6n3) are the major n-3 fatty acids. EPA represents 0.33% and DHA 4.25% of total phospholipids in cord plasma.

Although the proportion of DHA is similar to that found among adults (Santé Québec), EPA is much lower than in adults (3.1%), consequently, the ratio EPA/AA (Arachidonic Acid) is low (0.03) compared to adults (0.53). Interestingly, the ratio DHA/AA is high (0.36) and this is of particular importance, given the fact that effects of PUFA on both brain development and visual acuity of newborns have been reported for DHA only.

The correlation between PUFA and PCB presented in Figure 3c illustrates the common dietary origin (seal blubber). Mercury was not correlated to PUFA.

ON-GOING WORK

In 1993/94 we will continue this program in the Kativik region. Northwest Territories and Labrador results will probably be available during 1994. It will then be possible to evaluate the spatial trends of human contamination throughout the Canadian Arctic. Collaborative work is also on-going with Greenland. Thyroid function tests are on-going.

REFERENCES

Dewailly, E., 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. Environ. Health Perspect. 101(7): 617-620.

Granjean, P., P. Weihe, P.I.J. Jorgensen, T. Clarkson, E. Cernichiari and T. Videro. 1992. Impact of maternal seafood diet on fetal exposure to mercury, selenium and lead. Arch. Env. Health. 47: 185-185.

Hansen, J. 1988. Exposure to Heavy Metals (Hg, Se, Cd and Pb) in Greenlanders. Aarhus Denmark. 78 pp.

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 Development 56: 853-860.

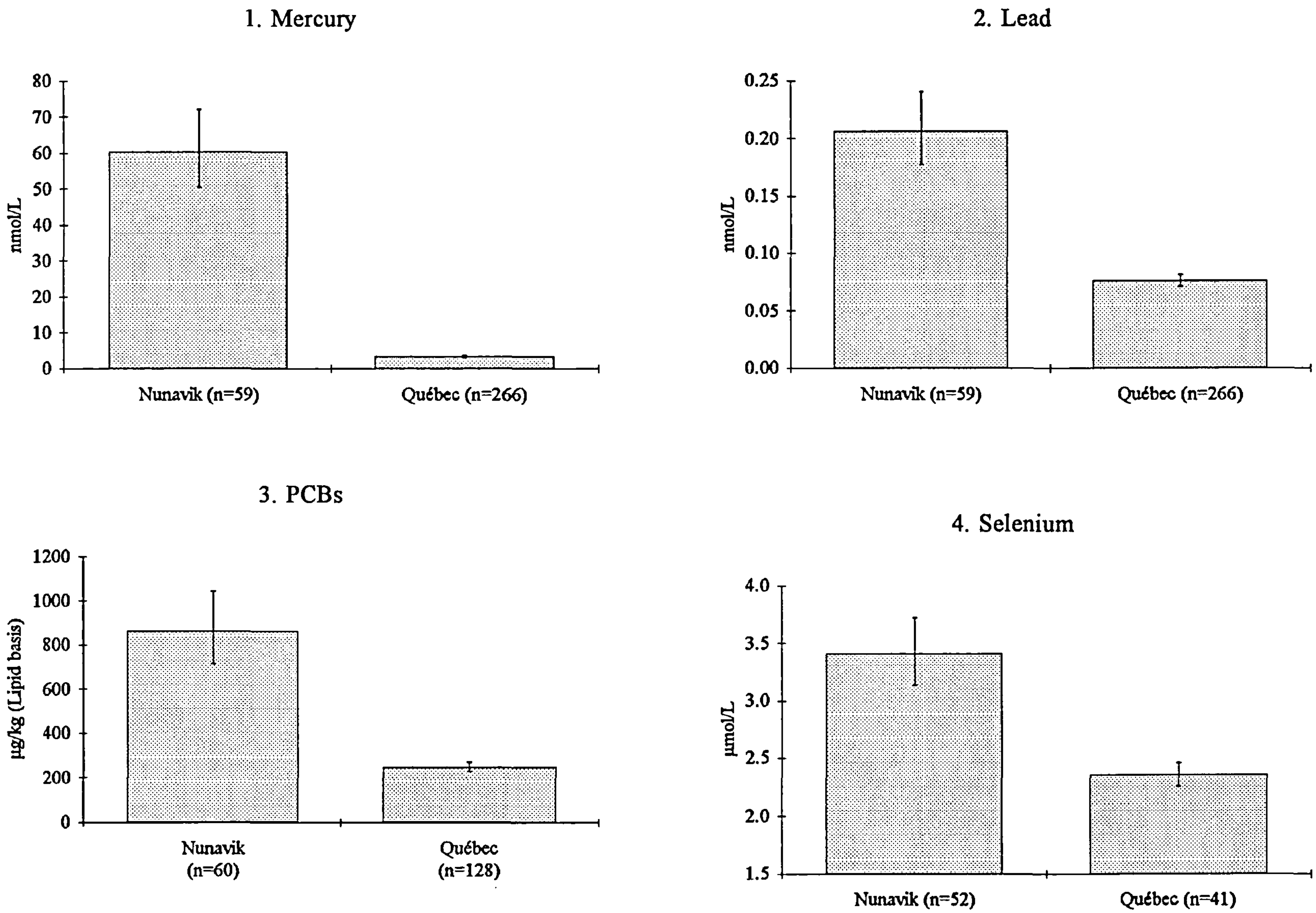
Jacobson, J.L. S.W. Jacobson, and H.E.B. Humphrey. 1990. Effects of *in utero* exposure to polychlorinated biphenyls and related contaminants on cognitive functioning in young children. The Journal of Pediatrics 116: 38-45.

Koren, G., C. Nelson, R. Gonen, J. Klein, L. Weiner, H. Demshar, *et al.* 1990. Lead exposure among mothers and their newborns in Toronto. Can. Med. Assoc. J. 142: 1241-1244.

Rhainds, M. and P. Levallois. 1993. Umbilical cord blood lead levels in the Québec City Area. Arch. Env. Health. 48: 421-427.

Rhainds, M., É. Dewailly, P. Levallois, G. Lebel, C. Laliberté and J.P. Weber. Heavy metals and organochlorine concentrations in the umbilical cord blood in the Province of Québec-Canada (unpublished data-1994).

Figure 1. Heavy metals and PCBs in the umbilical cord plasma of newborns from Nunavik and the Quebec City area, 1994 (geometric means).



1. Mercury

2. Lead

3. PCBs

4. Selenium

Figure 2a PCB congener concentrations in cord blood in Nunavik (n=62)

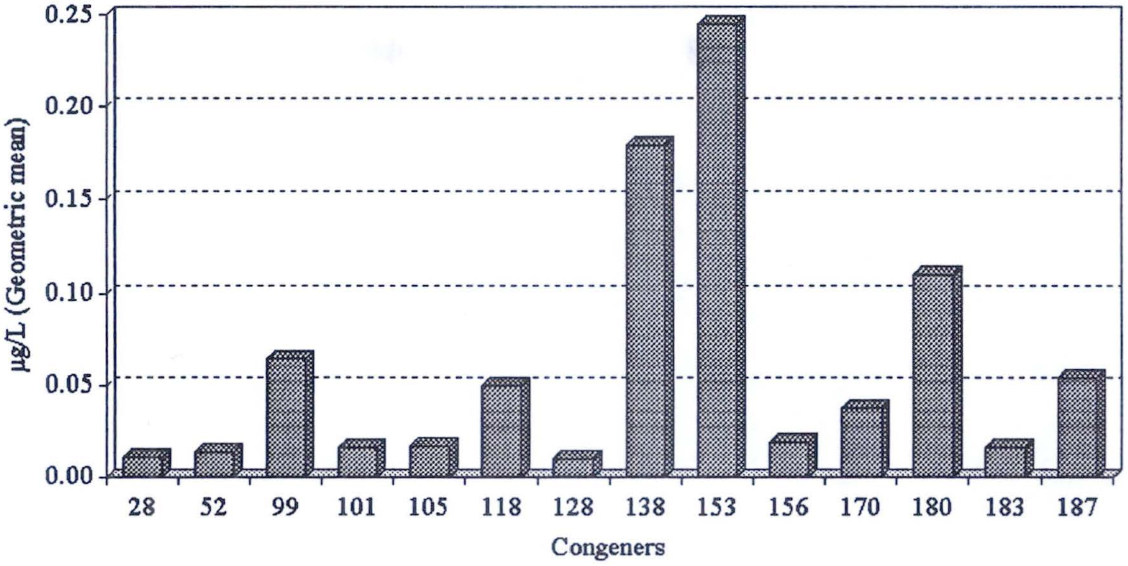


Figure 2b Pesticide concentrations in cord blood in Nunavik (n=62)

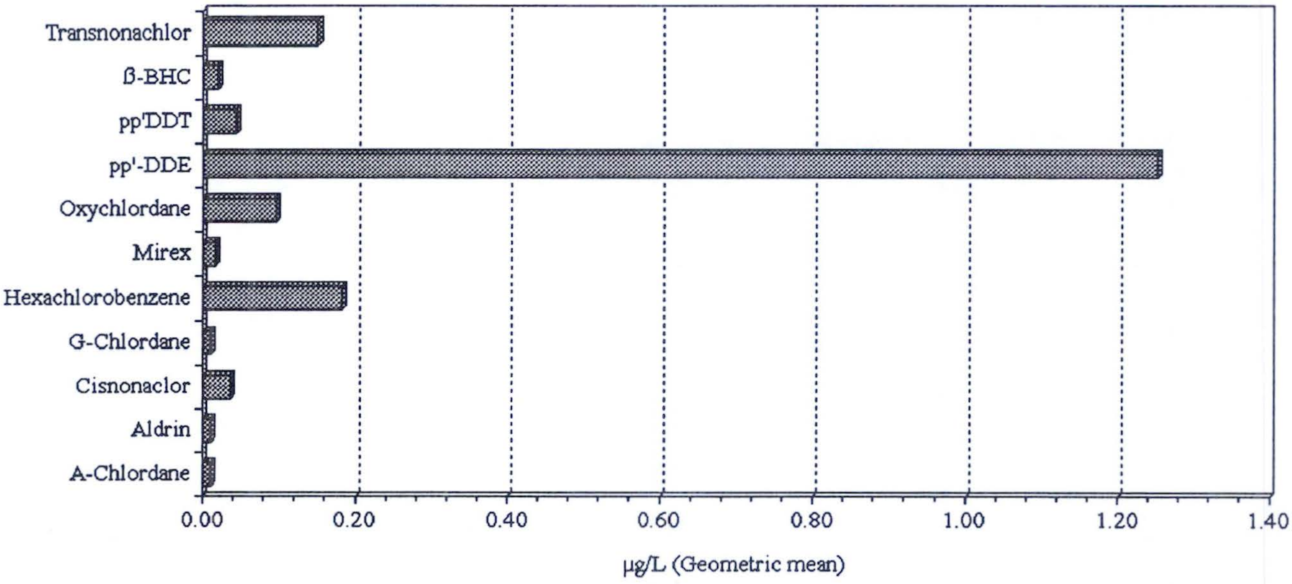


Figure 3a Correlation between lead and mercury in the cord blood in Nunavik (n=59)

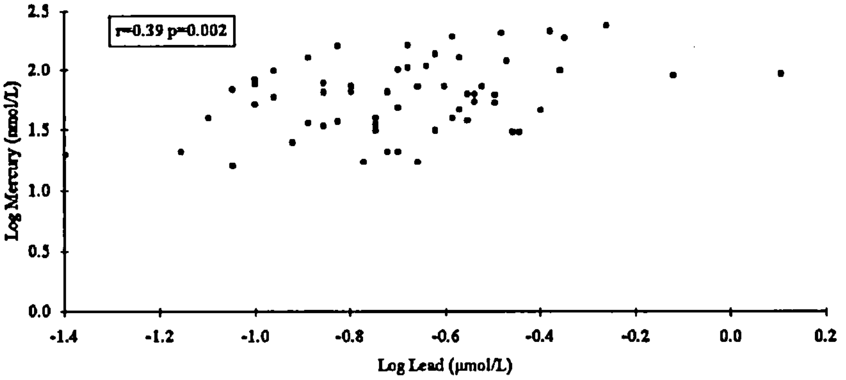


Figure 3b Correlation between PCBs and Mercury in the cord blood in Nunavik (n=56)

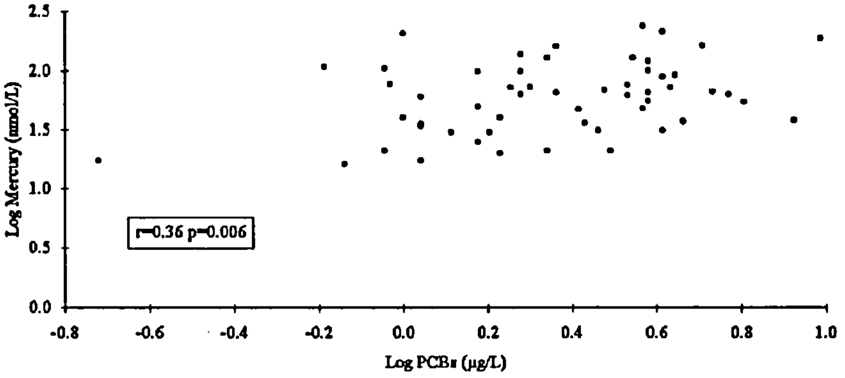
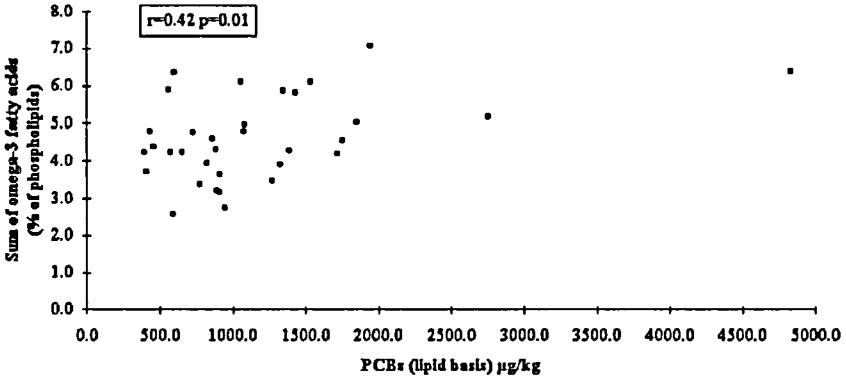


Figure 3c Correlation between PCBs and omega-3 fatty acids in the cord blood in Nunavik (n=33)



HUMAN CONTAMINANT TRENDS IN ARCTIC CANADA

PROJECT LEADER: J.B. Walker and F.I. Gilchrist, Health Department, Government of the Northwest Territories (GNWT)

PROJECT TEAM: C. Mills, Mackenzie and Kitikmeot Health Regions; R. Nuttall, Mackenzie and Kitikmeot Health Regions; Regional Health Boards/Services and Health Centres; Regional Contaminants Working Groups (including Dene Nation, Métis Nation - NWT, and regional Inuit Organizations); É. Dewailly, Laval University (CHUL); A. Gilman, Health Canada

OBJECTIVES

1. To establish a contaminants baseline for NWT populations, including levels of specific organochlorines and metals in maternal and cord blood of NWT mothers and neonates and to compare these to other regions.

2. To develop sampling protocol and risk communication strategies for the assessment and advisement of selected NWT populations on contaminant intake and effects.

ACTIVITIES/RESULTS 1993/94

Consultations

Considerable time, effort and resources have been, and will continue to be focused on consultations and information exchanges with the development of an environmental contaminants baseline for NWT populations. The need for community involvement continues to be a priority of this monitoring activity.

Working Groups

Two Consultation Working Groups on Environmental Contaminants have been established (one for each region involved) with membership from communities, Aboriginal organizations, health boards, and health workers. The purpose of the Consultation Working Groups is to provide direction on planning and implementation of human health baseline monitoring activities, to serve as liaisons with communities and to provide recommendations for future monitoring activities.

The Consultation Working Groups held regular meetings/conference calls, with much effort focusing on protocol development and issues resolution. Other workshops and meetings during the 1993/94 season, notably those held in Fort Simpson, Lac La Martre and Cambridge Bay, which bring together technical and community interests, were important in contaminants issue identification. This is a necessary and important precursor to establishing a human contaminants baseline with informed consent. It is also a necessary step to the ongoing exchange of contaminants information. Environmental contaminants were discussed as well as the maternal and cord blood monitoring activity.

Information sessions have also been held with health workers including Nurses-In-Charge, Community Health Workers, Physicians, Obstetrical staff and Laboratory staff at the Stanton Yellowknife Hospital.

Protocol Development

Consent forms, questionnaires, information packages, communications flowcharts and the protocol outline were developed jointly with the Consultation Working Groups, regional health workers and GNWT Health, with assistance from Health Canada (A. Gilman's group) and Laval University (E. Dewailly's group). It was recognized that all communications concerning the activities themselves and the results, must be geared to three different levels of participation -the health workers, the participants and the communities through the regional health agency.

The Consultation Working Groups have clearly stated that participants should know, prior to consenting their involvement in the monitoring, what type of advisory they will receive for the contaminant levels found in their blood. This information is particularly lacking. Presently, health advisories are based primarily on estimated intake alone and not on body burden levels.

Protocol Implementation

Implementation of the monitoring activity was delayed due to requests from the Consultation Working Groups for greater clarification of processes, including means to informed consent, communication of monitoring objectives, data management, and culturally appropriate interpretation and communication of results. Monitoring began in May 1994.

UTILIZATION OF RESULTS

In the Mackenzie and Kitikmeot Regions, regional and community collaboration will continue as monitoring activities are implemented. The work in these regions will benefit other regions in the NWT as the monitoring protocol is refined. Also, the extensive consultations which continue to take place are important for other monitoring activities and regional involvement in environmental contaminants issues. Other regions are working towards expanding their human health baselines.

Expected project completion date: March 31, 1997

ESTIMATION OF THE RISK TO THE INHABITANTS OF FORT RESOLUTION OF RENAL IMPAIRMENT RELATED TO THE LONG-TERM CONSUMPTION OF TRADITIONAL FOOD CONTAMINATED BY ENVIRONMENTAL CADMIUM

PROJECT LEADER: Centre for Nutrition and the Environment of Indigenous Peoples (CINE), McGill University

PROJECT TEAM: L.H.M. Chan, O. Receveur, CINE; B. Masuzumi, Dene Nation

OBJECTIVES

1. To establish the total external dose of cadmium as a result of traditional food consumption.
2. To determine the proportion of cadmium bound to the metal-binding protein, metallothionein (MT), in the traditional food, particularly, liver and kidney of caribou and moose.
3. To assess the effects of food preparation on the binding of cadmium to metallothionein.
4. To assess the risk of consumption of traditional food in terms of cadmium.

DESCRIPTION

Cadmium (Cd) is a by-product of zinc and lead mining and smelting, which are important sources of environmental pollution. Chronic exposure via food is the main concern in the assessment of the health risks of cadmium in the environment. Average daily intakes of cadmium in Europe and the U.S. are usually about 10—25 μg and range from 150 to 250 μg in known polluted areas in Japan (WHO 1992). Results of a recent study undertaken by the Canadian Wildlife Service showed that elevated levels of cadmium were found in caribou and muskoxen caught between 1985—1990 from locations across the Yukon and the Northwest Territories (Gamberg and Scheuhammer 1993). The highest Cd concentration observed was 166 μg/g dry tissue weight in the kidney of a caribou. It was estimated that the regular weekly consumption of kidney tissue from Arctic caribou of any age, and from muskoxen older than 1 year, will probably cause the World Health Organization Provisional Weekly Tolerable Intake of Cd to be exceeded. Due to its close proximity to the Pine Point Mine, and because traditional food constitutes a major component of the diet of Indigenous People in Fort Resolution, chronic cadmium toxicity in a major concern.

Cadmium has a long biological half-life of 40 years in humans, and the kidney is the major organ affected in chronic exposures (Lauwerys 1983). When the level of cadmium reaches a critical level of about 200 μg/g wet weight of kidney cortex, tubular damage occurs. Therefore, the risk of cadmium toxicity increases with the length of time of exposure and hence with age. About five percent of cadmium in food or water ingested is absorbed and accumulated primarily in the liver and kidney of caribou and may be bound to metallothionein. Metallothionein in the kidney cells sequesters the cadmium to form cadmium-metallothionein and decreases the cadmium toxicity (Goyer and Cherian 1989) in the animal. However, Cd bound to MT (Cd-MT), when absorbed from food, such as caribou liver and kidney, is selectively accumulated in the proximal convoluted tubules of the kidney causing renal injury (Chan and Cherian 1992). Cellular injury and necrosis occur in the nephron at much lower doses of cadmium in the form of Cd-MT than in the ionic form (40—50 μg/g as compared to 200 μg/g). Therefore, Cd-MT is more toxic than Cd and chronic Cd toxicity is dependent on both the total oral dose of Cd and its biological form. In order to assess the risk of renal impairment resulting from chronic cadmium exposure, it is important to assess the cadmium concentrations and the proportion of cadmium-binding to metallothionein in foods which are ready to be served.

ACTIVITIES IN 1993/94

Sample Collection

A local resident in Fort Resolution, Frank Mckay, was trained to undertake the dietary survey and food sample collection in February 1994. Phase 1 of the dietary survey and sample collection was completed in May 1994. A total of 51 dietary interviews which comprised of 26 males and 25 females were conducted. Fifty-five food samples (both raw and cooked) were collected and shipped to CINE. Analyses for cadmium and metallothionein are being undertaken by a graduate student, Christine Kim. Preliminary results for Phase 1 will be available at the end of August 1994. Phase 2 of the project which comprises a second dietary survey and the collection and analysis of more food samples will be conducted in November 1994.

Analytical Methods

Food samples were digested with nitric acid at 100°C and the metal contents were determined by atomic absorption spectroscopy (Hitachi Z8200, Nissei Sangyo Co., Rexdale, Ontario) using either flame (air-acetylene) or graphite furnace for low Cd concentrations (less than 0.1 μg/g).

To study the binding of metals to metallothionein, about 1 g of food samples were homogenized in 0.25 M sucrose solution, and centrifuged at 8000 g for 10 min. Levels of MT in the supernatant were measured using the silver saturation method (Scheuhammer and Cherian 1986). An aliquot (0.3 ml) of the supernatant was fractionated on a calibrated Sephadex G-75 column (0.9 x 60 cm). Cadmium, copper and zinc concentrations of each 1-ml fraction collected were measured.

Statistical Analysis

The dietary data and metal concentrations will be analyzed by SAS program and the total oral intake of cadmium will be estimated.

Quality Assurance

Standard reference materials — Apple leaves (SRM-1515), Bovine liver (SRM-1577b) and Oyster tissue (SRM-1566a) from the National Institute of Standards and Testing (NIST) (Gaithersburg, MD) were used as a laboratory control for all metal analyses.

Expected project completion date: March 31, 1995

PARTNERS

Deninu Kue First Nation, Metis Local #53, Dene Nation, Metis Nation

REFERENCES

Chan, H.M. and M.G. Cherian. 1992. Protective roles of metallothionein and glutathione in hepatotoxicity of cadmium. Toxicology 72: 281-290.

Gamberg, M. and A.M. Scheuhammer. 1993. Cadmium in caribou and muskoxen from the Canadian Yukon and Northwest Territories. Sci. Tot. Environ. in press.

Goyer, R.A. and Cherian, M.G. 1989. Cadmium Toxicity. Comments Toxicology 3: 191-206.

Lauwerys, R.R. 1983. Industrial Chemical Exposure: Guidelines for Biological Monitoring, Biomedical Publications, Davis, California.

Scheuhammer, A.M. and M.G. Cherian. 1986. Quantification of metallothionein by a silver-saturation method. Toxicol. Appl. Pharmacol. 82: 417-425.

WHO. 1992. Environmental Health Criteria 135: Cadmium, Geneva, World Health Organization.

THE EFFECTS OF *IN UTERO* ORGANOCHLORINE AND HEAVY METAL EXPOSURE ON THE NEUROBEHAVIOURAL AND PSYCHOMOTOR DEVELOPMENT OF INUIT INFANTS: PREPARATORY WORK

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Environmental Health Service, Public Health Centre of Quebec

COLLABORATORS: J.L. Jacobson, S.W. Jacobson
Department of Psychology, Wayne State University

OBJECTIVE

To carry out preparatory work in order to structure a research project which will examine the consequences of *in utero* exposure to organochlorines and heavy metals on the development of Inuit children residing in Northern Canada.

DESCRIPTION

It has been demonstrated that over the last ten years, there has been a bioaccumulation of organochlorines and mercury in Arctic fauna. Because these environmental pollutants are present in the arctic food chain, they may generate health problems for Inuit groups whose diet includes significant quantities of food obtained from hunting and fishing. Furthermore, since these toxic substances are transferred prenatally by the placenta and postnatally via breastfeeding, infants in these groups are vulnerable to exposure.

In humans, postnatal exposure to PCBs does not appear to be related to cognitive functioning. However, prenatal exposure to organochlorines, as measured in the umbilical cord, blood or breast milk, is associated with many health and development indicators in newborns and young children. In male newborns, prenatal exposure is negatively associated with height (Dewailly *et al.* 1993). In both sexes, the same exposure is negatively related to weight and head circumference (Fein *et al.* 1984, Jacobson *et al.* 1990a, 1990b), tonus and reflexes (Rogan *et al.* 1987, Weis and Cameron 1991). The relationship still stands in 4-year-old children (Jacobson *et al.* 1990b). At 6, 12 and 24 months, *in utero* exposure to organochlorines is negatively associated with psychomotor development (Gladen *et al.* 1988, Yu *et al.* 1991, Chen *et al.* 1992). Cognitive functions, related to the ability to process information, also seem affected. These include visual recognition memory (Jacobson *et al.* 1985) and short-term verbal and numerical memory in 4-year-old children (Jacobson *et al.* 1990a, Jacobson *et al.* 1992).

The specific objectives for 1993/94 were:

- to review the literature;
- to identify the best measures for assessing outcome variables;

- to specify potential confounding variables that will have to be controlled and to select a measure for each confounding variable;
- in collaboration with anthropologists, to obtain informed consent from Inuit mothers to participate in the research project and the most appropriate measures within the context of Inuit culture;
- to take part in consultations with native representatives; and
- to evaluate the feasibility of the research project and establish the infrastructure necessary for recruiting subjects.

ACTIVITIES IN 1993/94

1. Literature review of the effects of *in utero* organochlorine and heavy metal exposure on the developmental outcome of infants

The first level of analysis of the literature review documented exposure by Canadian Inuit to organochlorine compounds as well as effects observed on previous cohorts (Michigan, North Carolina, and Japan). The review compares Inuit exposure to exposure in other populations for which effects have been observed on infant development. The second level of analysis consisted of comparing methods used in earlier studies, notably the design, independent, dependent and confounding variables, as well as the measures used. The last step in the literature review involved an examination of the results, discussion, alternative explanations, and criticisms of earlier studies.

The comparative analysis of earlier studies enabled us to devise a research protocol for the Inuit. The methodological choices made were based on four criteria: 1) to enable comparison with earlier studies; 2) to reduce the number of alternative explanations for the results (this indicates a better control of confounding factors); 3) to choose sensitive measures to qualify the degree of exposure, the effects of exposure, and confounding factors; 4) to consider the Inuit cultural context in selecting measures and in defining procedures.

2. Identification of potential confounding variables to be controlled

A variable is a potential confounder when it is related to the independent variable and to the dependent variable. Adequate control for confounders is particularly important when subjects cannot be randomly assigned to exposed and non-exposed groups. In the current research, the population under study is determined by living in a geographical region. The groups have already been formed naturally and consequently subjects have not been randomly assigned to exposed or non-exposed groups. For this reason a large part of the preliminary work consisted of identifying potential confounding variables.

The strategy adopted consisted of, as an initial step, identifying potential confounding variables. This was achieved by the study of 1) earlier studies, 2) the psychological literature on the determinants of child development, and 3) reports describing the social situation and mental health method for each of the variables considered to be a potential confounding factor. In this particular project, the choice of instrument must also take cultural factors into account.

Biological, economic and psychosocial factors have all been identified as potential confounding variables. At a biological level, the following variables have been identified: 1) prenatal exposure to toxic products that are likely to have a negative influence on health and development. These teratogenic agents are principally mercury, alcohol, tobacco, drugs, DDE, dioxins, and lead. 2) Omega-3 fatty acids are studied as protective factors. They are the result of a diet rich in fat from fish and marine mammals. 3) Characteristics associated with delivery and perinatal complications represent the third category of biological variables.

Several economic and psychosocial variables are recognized as sources of influence on infant development. They are said to be indirect sources of influence because they influence the capacity of the parent to stimulate the child, which in turn is associated with child development. The traditionally used socioeconomic indicators were retained: mother's age and education, mean family income, employment and marital status, number of children, number of people in the residence, etc. The following psychosocial variables have been retained: 1) quality of cognitive and emotional stimulation provided by the mother, 2) maternal IQ, 3) maternal depression, 4) maternal alcohol and drug consumption after delivery, 5) family stressors, 6) family violence, and 7) mother's social support.

In the final study, the relationship of each confounding variable to exposure and to outcome will be studied during exploratory data analysis. Any confounding variable significantly related ($p < 0.1$) to both exposure and outcome will be retained in all subsequent confirmatory analyses. The confirmatory analysis will use covariance analysis and multiple regression because these allow the testing of whether the effect of exposure remains significant or disappears once the effect of the confounding variable has been partialled out. These analyses will thus enable the conclusion that any effects present are really and uniquely attributable to exposure.

3. General information on the design for the final study

This will be a cohort study starting in the first trimester of pregnancy and finishing 12 months postpartum. The mothers will be met during the first, second, and third trimesters of pregnancy and at 6.5 and 12 months postpartum. The children will be assessed at birth, 6.5 and 12 months. Exposure and numerous confounding variables with a biological origin will be measured through analysis of an umbilical cord blood sample. The study begins during pregnancy because it is the most valid procedure for measuring prenatal exposure to alcohol, drugs and tobacco, whether by physiological measurements or self-report. The postnatal interviews with the mother will enable the psychosocial confounding variables to be measured on two different occasions. The economic variables will be measured at each interview. The child outcome indicators will be measured at birth, 6.5 months and 12 months.

4. Consultation process

The consultation process used to determine the method for the final study involved three phases:

A) The principal researcher of this study is completing post-doctoral studies with Drs. Sandra W. Jacobson and Joseph L. Jacobson. They are the authors of the Michigan cohort study on the effects of prenatal organochlorine exposure on infant development. Numerous meetings between these researchers resulted in a proposal for the method of the final study.

B) The method was presented to professionals at the Centre de Santé Publique de Québec with experience in intervention or research among the inhabitants of the coast of Hudson Bay and Ungava. The working group involved anthropologists, doctors, nurses, epidemiologists, and psychologists specialized in child development. The group met for two days to study and comment on the method proposed. The working sessions had a number of objectives: 1) to determine the most appropriate measures for assessing confounding variables within the context of Inuit culture; 2) to obtain informed consent from Inuit mothers to participate in the research project; 3) to determine the number of Inuit infants who could potentially participate in the research program; 4) to determine the number of settlements in which the recruitment of subjects would take place in order to have an adequate sample size; and 5) to determine the amount of time needed to recruit the necessary number of infants.

C) The second working group was convened at the hospital in Povungnituk in February 1994. It was composed of Inuit midwives from the village and two nurses from the maternity department. These people were chosen because of their experience in conducting prenatal interviews with Inuit women. The working group received all the measures chosen by the first working group at the Centre de Santé Publique de Québec. For each question the members of the second working group were asked to comment on : 1) the clarity of the questions for the target population (Inuit women); and 2) the acceptability of the questions in terms of the Inuit culture. This working session resulted in modifications to the measures and the decision to group the measures into three interviews for the pilot study: a prenatal interview and two postnatal interviews. These versions were translated into Inuktituk.

5. Translation of material into Inuktituk

The consent forms for the pilot study were drafted to respect ethical considerations and translated into Inuktituk. The translation process for the maternal interviews involve five steps:
1) each interview is translated from English to Inuktituk by a professional Inuit translator;
2) the Inuktituk translations will then be given to a second professional Inuit translator who will translate the interview from Inuktituk to English; 3) the English translation will be compared to the original English interview; 4) the two translators will meet with the principal researcher. During this meeting, any differences between the English translation and the original interview will be discussed because they represent a change in meaning introduced by translation. The real meaning of the difficult questions will be explained to the translators who must reach agreement on an adequate Inuktituk formulation; and 5) the final version of the three interviews will be produced. This procedure will ensure that questions or measures that do not retain their original meaning when translated into Inuktituk are identified.

6. Training the experimenter in the administration of all infant measures

The principal researcher was trained at Wayne State University by S. Jacobson. Further, she will be able to train new experimenters for the final study and will be able to control the quality of the data collected throughout the study by periodic inter-judge agreement checks.

7. Submission of the pilot study to the ethics committee

The protocol and the consent forms for the pilot study were submitted to the "Comité d'Éthique et de Déontologie de L'Université Laval. The committee's final approval for the pilot study was obtained in February 1994.

8. Planning for the pilot study

The pilot study will be conducted at the "Centre de Santé Inuulitsivik" in Povungnituk. A. Corriveau, the Director of Professional Services at the hospital, has authorized the pilot study. In order to plan the execution of the study, we met last February with the community service coordination team at the hospital at the request of A. Corriveau. At the request of S. Hodgin, Directeur de la Santé Publique, the study has also been presented to Brian Snarch at CRESS in Kuujjuaq.

CONCLUSION

All activities necessary for the execution of the pilot study as planned in the grant proposal submitted to the 1993/94 Northern Contaminants Program are now completed. The next step in the project is the execution of the pilot study. The specific activities to be carried out in this pilot study concern the collection of data from 15 mother-infant dyads.

REFERENCES

Chen, Y.C-J., Y-L. Guo, C-C. Hsu, and W.J. Rogan. 1992. Cognitive development of Yu-Cheng ('Oil Disease') children prenatally exposed to heat-degraded PCBs. JAMA 268: 3213-3218.

Dewailly, É, S. Bruneau, P. Ayotte, C. Laliberté, S. Gingras, D. Bélanger, and L. Ferron. 1993. Health status at birth of Inuit newborn prenatally exposed to organochlorines. Chemosphere 27: 359-366.

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. The Journal of Pediatrics 105: 315-320.

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. The Journal of Pediatrics 113: 991-995.

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 Development 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. The Journal of Pediatrics 116: 38-45.

Jacobson, J.L., S.W. Jacobson, and H.E.B. Humphrey. 1990b. Effects of exposure to PCBs and related compounds on growth and activity in children. Neurotoxicology and Teratology 12: 319-326.

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. Developmental Psychology 28: 297-306.

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

Tilson, H.A., J.L. Jacobson and W.R. Rogan. 1990. Polychlorinated biphenyls and the developing nervous system: cross-species comparisons. Neurotoxicology and Teratology 12: 239-248.

Weis, M.I. and M. Cameron. 1991. Organic contamination in the arctic food chain: the Inuit diet and contamination levels of important country foods at the Belcher Islands, N.W.T., Canada. Department of Biological Sciences and Great Lakes Institute, University of Windsor, Ms.

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. Neurotoxicology and Teratology 13: 195-202.

BIOMARKERS OF EARLY BIOLOGICAL RESPONSES INDUCED BY ORGANOCHLORINE EXPOSURE IN WOMEN GIVING BIRTH IN ARCTIC QUEBEC

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PROJECT TEAM: P. Ayotte, É. Dewailly, S. Bruneau, G. Poirier, J.-P. Weber, R.M. Tanguay, R. Gagné, R. Roy, M. Feeley, F. Iverson

OBJECTIVES

1. To determine in Inuit women giving birth in Arctic Québec and a control group of women from southern Québec early biological effects possibly induced by contaminants present in country foods.

2. To compare these responses to those previously measured in Yu-Cheng mothers exposed to PCDF/PCBs.

3. To evaluate the feasibility and usefulness of these biomarkers to assess the health risk for the newborn in the Inuit population.

DESCRIPTION

In 1988, the Community Health Department of the "Centre Hospitalier de l'Université Laval" initiated a research program investigating the health status of the Inuit population living in Arctic Québec, in relation to their exposure to various xenobiotics present in country foods. Between July 1989 and July 1990, mothers breast-feeding their babies were asked to submit a milk sample for organochlorine compound analysis. Results for 105 human milk analyses showed high PCB levels, as previously reported (Dewailly *et al.* 1989). The average PCB (Aroclor 1260) concentration measured in this population, 2.9 mg/kg lipid, was 6 times greater than that measured in 550 human milk samples from women living in the southern part of the province (0.52 mg/kg) (Dewailly *et al.* 1992). For chlorinated pesticides, milk levels found among Inuit women were up to ten times greater than those of the reference population. Inuit mothers exhibit the greatest exposure known to occur from organochlorine residues present in the environment, by virtue of their location at the highest trophic level of the arctic food web (Dewailly *et al.* 1993).

Organochlorines (OCs) found in relatively high concentrations in milk samples from lactating Inuit women belong to four chemical families: chlorinated diphenyl ethane (DDT and metabolites), chlorinated cyclodiene and related compounds (dieldrin, mirex), planar (2,3,7,8-TCDD-like) halogenated polycyclic aromatic hydrocarbons (PCDD, PCDF and coplanar PCB), halogenated benzene (hexachlorobenzene) and other halogenated polycyclic aromatic hydrocarbons (non-coplanar PCB).

In view of the adverse effects which could be induced by OCs, the following biological markers were proposed in order to improve health risk assessments:

a. **P450 enzyme induction**. This early response integrates the contribution of all dioxin-like compounds and will reflect possible interaction with other compounds present in the mixture. It will be determined by assessing the ethoxyresorufin-O-deethylase activity (EROD) in placental tissue and also by immunodetection of cytochrome P-4501A1. Enzyme induction is a primary event in the Ah-mediated pathogenic sequence leading to nearly all adverse effects induced by dioxin-like substances. Placental homogenates of Taiwanese mothers, who developed an "oil disease" (called Yu-Cheng in Chinese) from consuming rice oil contaminated with PCDFs and PCBs, had levels of AHH activities 100-fold greater than those measured in homogenates of non-exposed mothers. Accordingly, a specific isozyme (P450IA1) was detected exclusively in the "Yu-Cheng group" and not in the non exposed control group (Lucier *et al.* 1987). The enzyme induction was significantly associated with low birth weight in this population. Hence, this biomarker is validated and can be used to assess the risk of adverse developmental effects in the Inuit population exposed to dioxin-like PCBs. Non-planar PCBs, DDT and chlordane induce a different P450 isoenzyme, P4502B1, which will also be measured by Western blotting. The associated activity, pentoxyresorufin-O-deethylase (PROD) will be determined in placental microsomes (Harris *et al.* 1993).

b. **Ah receptor density and affinity**. The initial step in enzyme induction by polycyclic aromatic hydrocarbons appears to involve specific binding of the inducer to a receptor protein: the Ah receptor. The receptor ligand complex binds to a regulatory region of the structural gene of P4501A1, leading to the characteristic change in protein synthesis. According to receptor theory, both the number of Ah receptor and their affinity for the inducers will modulate the response. Hence, these parameters of the Ah receptor represent potential biomarkers of individual susceptibility to toxicity induced by dioxin-like substances.

c. **Stress protein induction**. Assays for some of the stress proteins (formerly referred to as heat shock proteins) may be useful for determining the extent to which the cells are attempting to protect themselves from environmental damage. They may serve as biomarkers of contaminant exposure and effect. Heat, metals, UV, xenobiotics, steroid hormones to name a few can induce stress proteins. These will be measured in placental tissue and cord blood lymphocytes by Western blotting. This biomarker is by no means validated. However, we believe it is of interest since a protein from this group, hsp 90, is known to interact with the Ah receptor to alter its affinity for ligands (Denis *et al.* 1988).

d. **Biomarkers of immunotoxicity**. A number of biomarkers have been proposed to detect immune system suppression, an adverse effect possibly induced by OC exposure. Three responses will be measured in cord blood samples: a) antibody production by cord blood lymphocytes following antigen (sheep red blood cell/pokeweed mitogen) stimulation; b) enumeration of T-cell populations and subsets by flow cytometry; and c) Natural cell killer assay. These responses are well understood in humans and represent validated biomarkers of immune system function.

e. **Sister chromatid exchange.** This biomarker of genotoxicity will be performed on cord blood lymphocytes. Although genotoxicity is not a main feature of the contaminants present in the arctic food web, clastogenic effects have been reported in various populations exposed to organochlorines or heavy metals: workers occupationally exposed to PCBs (Kalina *et al.* 1991), Eskimos from Greenland consuming large amounts of seal (Wulf *et al.* 1986), and subsistence fishermen from the Lower-North-Shore (Quebec) which consume contaminated sea-bird eggs (Dewailly *et al* 1991).

This biomarker study is integrated into the on-going cord blood surveillance program (already funded). Mothers not on continuous medication are asked for the permission to use their placenta and a cord blood sample for biomarker analysis. They are also being asked to provide a urine sample for cotinine analysis, since smoking is known to influence several of these early responses. One control woman delivering in Québec City is selected for each Inuit mother entering the study. Control women are chosen from the southern Québec cohort started in 1993/94 (already funded) to match the age and the smoking status of the Inuit mothers. Placenta samples are frozen on site at -80°C and sent in dry ice to the laboratories involved in the measurement of cytochrome P450 induction, Ah receptor and stress proteins. Cord blood samples for the measurement of immunotoxicity biomarkers, sister chromatid exchange assay and the determination of stress proteins are kept at 20°C and sent within 2 days to the laboratories.

Placental tissue concentration of the following OCs will be measured: 1) PCBs: IUPAC no. 28, 52, 99, 105, 118, 128, 138, 153, 156, 170, 180, 183, 187; and 2) Chlorinated pesticides: DDE, dieldrin, hexachlorobenzene, mirex. The necessity to determine PCDD/PCDF and coplanar PCBs (IUPAC no. 77, 126 and 169) in placental tissue will be evaluated following an initial analysis of the data.

ACTIVITIES IN 1993/94

Tissue collection is just underway and no results are available at this time. Evaluation of the technical feasibility of all biomarker measurements was conducted. Methods for P450 activities and protein expression determination have been developed in G. Poirier's laboratory at CHUL. No technical problems are expected with these measurements. Heat shock protein measurements are also readily available in R. Tanguay's laboratory at CHUL.

Ah receptor quantification does not appear feasible at this point, according to results of Dr. Okey (University of Toronto) from studies conducted in the United States trying to link intrauterine growth retardation and Ah receptor affinity and density in placental tissue. The receptor is very labile and any delay encountered before freezing the tissue compromises the validity of the results. This includes long labour encountered during a natural birth, with Cesarian section being the most favourable situation to obtain valid measurements. Considering the low rate of Cesarian section in Northern Québec, collecting a sufficient number of placenta from Cesarian section is not feasible. Ah receptor measurements will be replaced by DNA-adduct quantification in placental DNA. This biomarker is of interest since genotoxicity arising from exposure to xenobiotics such as polycyclic aromatic hydrocarbons (PAHs) may be enhanced through bioactivation, secondary to induction of biotransformation enzymes. The adducts are determined by ^{32}P-post labelling, a method which has been developed in G. Poirier's laboratory.

Cord blood measurements (immunotoxicity parameters, SCE) require that blood samples be shipped to the laboratory within 48 hours. We have conducted these assays in other projects, namely those of Lower-North-Shore fishermen and the newborn Inuit cohort in Northern Québec.

OC analysis in placental tissue is also being validated at the Québec Toxicology Center. Freezers (-80°C) were purchased and sent to Povungnituk and Kuujjuaq regional hospitals and personnel have been hired for tissue collection, handling and shipping.

CONCLUSION AND UTILIZATION OF RESULTS

The results from this pilot study will be used to prepare a report to AES on the feasibility/usefulness of measuring biomarkers in the health risk assessment process in the Arctic. The most promising biomarkers will be selected for a larger study investigating possible adverse neurodevelopmental effects induced by organochlorine exposure in newborns from this Inuit population (funded by an Eco-research grant from the Tri-Council Green Plan Program).

Expected project completion date: March 31, 1995

PARTNERS

J. Hansen/U. Aarhus (Denmark)
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REFERENCES

Denis, M., S. Cuthill, A.C. Wikstrom, L. Poellinger, and J.I. Gustafsson. 1988. Association of the dioxin receptor with M_r 90,000 heat shock protein: a structural kinship with the glucocorticoid receptor. Biochemical and Biophysical Research Communications 155: 801-807.

Dewailly, É., A. Nantel, J.P. Weber, and F. Meyer. 1989. High levels of PCBs in breast milk of Inuit women from Arctic Quebec. Bulletin of Environmental Contamination and Toxicology 43: 641-646.

Dewailly, É., C. Laliberté, L. Sauvé, S. Gingras and P. Ayotte. 1991. La consomation des produits de la mer sur la Basse-Côte-Nord du Golfe du Saint-Laurent: risques et bénéfices pour la santé. Service Santé et Environnement, Département de Santé Communautaire, Centre Hospitalier de l'Université Laval, 150 pp. + annexes.

Dewailly, É., A. Nantel, S. Bruneau, C. Laliberte, L. Ferron, and S. Gingras. 1992. Breast milk contamination by PCDDs, PCDFs and PCBs in Arctic Quebec: a preliminary assessment. Chemosphere 25: 1245-1249.

Dewailly, É., P. Ayotte, S. Bruneau, C. Laliberté, D.C.G. Muir and R. Norstrom. 1993. Inuit exposure to organochlorines through the aquatic food chain in Arctic Québec. Environ. Health Perspect. 10: 618-620.

Harris, M., T. Zacharewski, and S. Safe. 1993. Comparative potencies of Aroclors 1232, 1242, 1248, 1254, and 1260 in male wistar rats - assessment of the toxic equivalency factor (TEF) approach for polychlorinated biphenyls (PCBs). Fundamental and Applied Toxicology 20: 456-463.

Kalina, I. R.J. Sram, H. Konecna, and A. Ondrussekova. 1991. Cytogenetic analysis of peripheral blood lymphocytes in workers occupationally exposed to polychlorinated biphenyls. Teratogenesis, Carcinogenesis, and Mutagenesis 11: 77-82.

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.

Wulf, H.C., N. Kromann, N. Kousgaard, J.C. Hansen, E. Nieburh, and K. Alboge. 1986. Sister chromatid exchange (SCE) in Greenlandic Eskimos. Dose-response relationship between SCE and seal diet, smoking, and blood cadmium and mercury concentrations. The Science of the Total Environment 48: 81-94.

CONTAMINANTS IN PLANTS USED AS TRADITIONAL FOOD AND MEDICINE BY KASKA FIRST NATIONS IN THE YUKON

PROJECT LEADER: Yukon Technical Committee on Contaminants in Northern Ecosystems and Native Diets (Contact: M. Palmer, Chair)

PROJECT TEAM: Kaska First Nation; Government of Yukon; Fisheries and Oceans Canada; Indian and Northern Affairs Canada; Environmental Protection, Environment Canada; Council for Yukon Indians; M. Gamberg (Consultant)

OBJECTIVE

To investigate contaminant levels found in plants used as traditional foods and medicines.

DESCRIPTION

This paper is one step in a larger program of contaminant monitoring in terrestrial ecosystems that started in the southeast Yukon in 1992. This study was initiated at the request of the Liard First Nation and the Kaska Tribal Council, following a public meeting and discussion of results from the analysis of contaminants in the organs of caribou from the Finlayson caribou herd.

There can be little doubt that First Nations are among people most concerned about contaminant levels in the environment because of their continued, almost daily, dependence on traditional sources of food and medicine. While the study of contaminant levels in traditional foods is relatively new in North America, it is in its infancy in the Yukon. Something that was but a rumour or news report to many Yukon native elders, quickly became an issue of tremendous local concern. When news of contaminants in the Porcupine and Finlayson caribou herds was presented, naturally concern over contaminant levels in other traditional foods was expressed. This investigation into contaminant levels in plants used as traditional food and medicine was developed cooperatively between the Kaska Tribal Council and the Yukon Department of Renewable Resources. It was also recognized as an important opportunity for training in renewable resources and for information exchange. Under land claim agreements, there are recognized obligations to increase the use of traditional knowledge in the management of renewable resources and for the transfer of technology and experience to First Nations.

ACTIVITIES IN 1993/94

This study has five components, including information gathering, sample collection, sample and data analyses, interpretation and reporting. This summary deals only with the initial components of information gathering and sample collections and perhaps some limited discussion of these components since the samples are just now being sent out for analysis.

Training opportunities were provided for two Kaska First Nation students looking at careers in renewable resource management. These students were hired to undertake the field components of this project. Interviews with community elders were arranged to identify important plant species, plant parts normally used, purpose and frequency of use, and other aspects such as typical locations and collection periods. In both communities, the objective was to interview a sample of 20 individuals to determine the important species and to undertake collections at 3 sites within each traditional territory.

Following interviews, the students worked with local elders and published field guides for local plants, to become competent in species identification. Students were also accompanied by an elder in the field to locate typical sampling sites and become proficient at field identification of plants.

Samples were collected with latex gloved hands and placed into new plastic ziploc and garbage bags, tagged and identified. Samples were made from a composite of 10 individual plants or sampled plant parts from each site. Samples were frozen as soon after collection as possible but ranged from a few hours to 2 days. Samples were identified with unique identification numbers, placed in chest coolers and shipped frozen to a contract laboratory for preparation and analysis.

RESULTS

Nineteen interviews were conducted in Watson Lake, distributed among 8 elders and 11 other band members. Eighteen interviews were similarly conducted in Ross River. Most plant species were used similarly by community members and generally for the same purposes. Plant species that were used by most interviewees, and most frequently, were determined. Collections were made from areas that were similar, and in some cases, in close proximity to collection sites identified in the interviews.

Overall, 41 different species were identified as having food or medicinal value (Table 1). These included 18 shrubs, 14 herbs, 6 trees, 2 lichens and 1 fungus. The parts used varied from foliage, berries, twigs, cones, bark and roots, and uses varied from direct consumption or application to moderate levels of preparation.

CONCLUSION AND UTILIZATION OF RESULTS

The results from the summer sampling season have not been received from the laboratory. When the information has been verified it will be communicated to the affected First Nations and sent to Health Canada for an assessment.

Expected project completion date: March 31, 1995

Table 1. Plants used by Kaska people in Ross River and Watson Lake.

Plant	Latin name	Kaska name	Plant part	Use	Use by Community	
					Watson Lake (N=19)	Ross River (N=18)
Alder	Alnus incana	t'is, k'es	twigs, bark	medicine	9	14
Balsam (fir)	Abies lasiocarpa	tsustsè	bark	medicine	19	17
Balsam poplar	Populus balsamifera	cheba, shoba	bark, cambium	food, medicine	7	3
Bearberries	Arctostaphylos uva-ursi	dzidzé eslone	berries	medicine, food	4	2
Bear root	Hedysarum alpinum	tsus	roots,	food	13	17
Birch	Betula papyrifera	k'i	bark, cambium pith, fungus	medicine, food	6	6
Blueberry	Vaccinium uliginosum	?	berries	food	14	6
Crowberry	Empetrum nigrum	dziz st'è	berry, twigs leaves	medicine, food	17	10
Caribou horn	Coelocaulon aculeatum	gudzih dé	entire	medicine	14	15
Caribou leaves	Artemisia tilesii	gudzih tāné	entire	medicine	13	6
Cloudberry	Rubus chamaemorus	dechenestle-gi	entire	food	11	3
Cranberry	Viburnum edule	gahfé	berries, twigs	food, medicine	15	8
Cranberry	Vaccinium vitis-ideae	itl'át, itl'ét	berries	food	16	7
Current, red	Ribes triste	?	berries	food	2	1
Current, black	Ribes hudsonianium	?	berries	food	5	2
Dandelion	Taraxacum officinale	?	stem	food	3	2
Fireweed	Epilobium angustifolium	egús	stem, leaves	food, medicine	5	5
Gooseberry	Ribes oxyacanthoides	há'yo, dzidzé, háyu	berries	food	11	3
Juniper	Juniperis communis	mesgâ elé	berries, twigs	medicine	14	8
Labrador tea	Ledum groenlandicum	ti mesgé, kehsese	stem, leaves	medicine, food	15	17
Mint	Mentha arvensis	no name	stem	medicine, food	2	0
Mountain ash	Sorbus scopulina	keda dzidzé	stem, berries	medicine	4	0
Nagoon berry	Rubus arcticus	tehk'ede dzidzé, ts'ale	berries	food	8	2
Pine	Pinus contorta	gadze	cambium, cones	food, medicine	3	4
Pineapple weed	Matricaria matricarioides	?	whole	medicine	4	2
Puffball mushroom	Lycoperdon calvatia	nahteni, tl'edzé, nahtene	whole	food, medicine	10	9
Raspberry	Rubus idaeus	tahkadle', dech'ue	berries	food	15	11
Red willow	Cornus stolonifera	gule det'ele	twigs	medicine	11	6
Reindeer moss	Cladina rangiferina	ejú	all	medicine	1	0
Wild rose	Rosa acicularis	esshul, dechene'	hips	food	5	6
Shrubby cinqefoil	Potentilla fruticosa	kustle'eze tsestl'eze	twigs	food	8	3
Soapberry	Sheperdia canadensis	esghushe, gusghosh(e)	berries, stem	medicine, food	10	13
Spruce	Picea mariana (glauca)	ts'u	cones, bark, sap	medicine	8	7
Sage	Artemisia frigida	tlutsén	stem, leaves	medicine	8	9
Strawberry	Fragaria virginiana	ges dzidzé	berry	food	13	9
Tamarack	Larix laricina	tehdúdze	twigs, bark	medicine	12	10
Wild Rhubarb	Polygonum alaskanum	atsok, etsok	stem, leaves	food, medicine	10	8
Wild onion	Allium Schoenoprasum	?	whole	food	11	5
Willow	Salix spp.	gule	leaves, bark	medicine	0	6
Yarrow	Achillea millifolium	non cho	lvs, flrs, stem	medicine	8	3
Yellow water lily	Nuphar polysepalum	taht'adzé	roots	medicine	6	0

VARIANCE IN FOOD USE IN DENE/METIS COMMUNITIES

PROGRAM LEADER: Centre for Nutrition and the Environment of Indigenous Peoples (CINE), McGill University

PROJECT TEAM: H.V. Kuhnlein, O. Receveur (CINE), B. Erasmus, B. Masuzumi (Dene Nation), W. Carpenter (Metis Nation)

OBJECTIVES

1. To define the levels of consumption of traditional food by maximum users in Dene/Métis communities.
2. To understand the extent of traditional food use in order to define contaminant and nutrient intake so that timely advice regarding benefits and risks of food consumption can be made.

DESCRIPTION

This study builds on the experiences and food use data recently completed in Fort Good Hope/Colville Lake and aims at providing the information necessary to evaluate the benefits/risks of consuming various types and quantities of traditional and market foods in Dene/Métis communities in the Northwest Territories (NWT).

This study was initiated by Dene Nation and Métis Nation (NWT) and is being administered in all 28 Dene/Métis communities.

After an exploratory phase during which the study protocol was designed to incorporate community concerns and suggestions, individual interviews are administered in all participating Dene/Métis communities. Each interview includes (1) frequency of traditional food use, (2) 24 hour diet recall, and (3) sociocultural questionnaire. The interviews are administered to random samples of adult males and females during two seasons: Winter and Fall.

ACTIVITIES IN 1993/94

1. Initial planning meeting (May 1993)

In a meeting with Dene Nation, Métis Nation (NWT), and Mackenzie Regional Health Services, CINE reviewed the study plans and developed a framework for collaboration under the leadership of the Dene Nation and Métis Nation, NWT.

2. Development Meeting (June 1993)

A working group consisting of five regional delegates from Dene Nation, five regional delegates from Métis Nation (NWT), as well as two staff from CINE, developed the methodologies and defined the exact timeline of the studies. The survey plans were presented to the Assembly of Dene Chiefs.

3. Community Meetings (July/August 1993)

Community meetings further defined the most appropriate methodology to be used, and contributed much needed information related to community concerns on dietary benefits/risks as well as food practices particular to each community. CINE staff visited a total of 15 Dene/Métis communities in the Northwest Territories; the format of each visit varied by community: presentations to formal meetings, focus group discussions, and individual exchanges.

4. Pilot Projects

Two pilot projects were conducted in September 1993.

One was in Fort Good Hope, a fairly large community close to the Arctic Circle where previous dietary data had been collected. This pilot project was conducted by a local interviewer with extensive experience in dietary surveys.

The other was conducted by CINE staff with the help of a translator in a very small community close to the Alberta border, Trout Lake. The final study design was modified accordingly.

5. Training Workshop

Interviewers selected by each of the nine communities participating in the winter interviews met for a three day training workshop.

6. Community Survey (Winter)

Interviews were administered to 417 adult men and women in the communities of Aklavik, Tsiigehtchic, Colville lake, Fort Good Hope, Deliné, Fort Rae, Liidli Koe, Lutsel K'e, and Fort Resolution.

RESULTS

Data analysis is proceeding at CINE. Results of the spring survey are expected to be presented in the communities at the beginning of the fall Survey (September 1994).

DISCUSSION/CONCLUSION

The research was successful in incorporating community concerns and suggestions, and the use of research agreements facilitated this process.

The data collected are of the required quality to meet study objectives, and the project is proceeding as scheduled.

After completion of the fall interviews, a series of workshops will be conducted with participating communities. This will be followed by a final report to be prepared in April 1995.

Expected project completion date: April 1995

SANIKILUAQ TRADITIONAL FOOD STUDY

PROJECT LEADERS: B. Fleming, Environmental Committee of Sanikiluaq; and
E.E. Wein, Canadian Circumpolar Institute, University of Alberta

PROJECT TEAM: B. Fleming, E.E. Wein, M.M.R. Freeman, M. Inuktaluk, M. Meeko

OBJECTIVES

1. To document the annual frequency of consumption of fish and wildlife species among a representative sample of Inuit households in Sanikiluaq.

2. To demonstrate the variety of traditional food products prepared and consumed from these species.

3. To examine the degree of preference for selected traditional and store-bought foods, among adults and children.

4. To examine the daily diet of a representative sample of adults, once in each of two seasons.

5. To provide insight into the continuing cultural and social importance of traditional foods to Inuit living in the Belcher Islands.

DESCRIPTION

A relatively limited variety of traditional food species occurs in the Belcher Islands, yet these species have nourished the Inuit here for generations, and continue to sustain the community today. Indeed, food from fish and wildlife form the basis of the local non-cash economy (Quigley and McBride 1987). A wide range of food products is consumed from these species. Furthermore, procuring, preparing and consuming traditional Inuits foods have important social and cultural significance, and are integral to community identity.

The community recognizes that impacts from proposed hydroelectric and other developments in southeast Hudson Bay may adversely affect their traditional food resources. Developments within and outside the region may cause physical and biological changes in the environment that could threaten the food species upon which the community depends. Moreover, development within the region may also disrupt harvesting patterns among other Inuit communities in the region. As such, any disruption to harvesting may have negative consequences throughout the region in general, and for the Belcher Island Inuit in particular.

While some information exists on the contamination of arctic ecosystems and food chains, less is known on the benefits and potential risks of consuming these species. It is important, therefore, to document the extent of consumption of and degree of preference for traditional food species, and to examine their continuing social and cultural importance, so that future impacts on human health can be assessed and monitored before further changes occur.

ACTIVITIES IN 1993/94

In December 1993, two weeks of intensive training in household food frequency interviewing and in data entry were provided by E. Wein in the community of Sanikiluaq for the two community interviewers. Questionnaires and details of the methodology were finalized and approved by the Environmental Committee of Sanikiluaq. Household food frequency interviewing was started. Food preference data were collected from school children, and entered onto disk.

Household food frequency interviews were conducted by community interviewers from December 1993 through April 1994. All household food frequency data were entered onto disk and checked.

In February 1994, several days of training were provided in Edmonton for one community interviewer, on the 24-hour recall method of daily food consumption. The sample of 48 randomly selected adults for this part of the study was drawn at this time.

Since April 1994, interviewing has been underway for the first season of 24-hour recalls of daily food consumption.

RESULTS

Household traditional food frequency data were obtained for 102 households. This represents 98% of all Inuit households in Sanikiluaq. Food preference data were obtained for 66 school children (87% participation rate) and 102 adults (household heads).

DISCUSSION/CONCLUSIONS - WORK REMAINING FOR 1994/95

The high participation rate in the household food frequency portion indicates strong community support for this project.

Collection of the 24-hour recall data is still in progress. The second season will be September-November 1994. This data requires extensive coding (each food item) and conversion into gram units prior to entry onto disk. Nutrient computations, statistical analysis and report writing also remain to be done.

Since the data have not yet been analyzed, conclusions cannot be drawn at this point.

Expected project completion data: June 1995

REFERENCE

Quigley, N.C. and N.J. McBride. 1987. The structure of an arctic microeconomy: the traditional sector in community economic development. Arctic 40: 203-210.

CENTRE FOR NUTRITION AND THE ENVIRONMENT OF INDIGENOUS PEOPLES

H.V. Kuhnlein, McGill University

TEAM: T.A. Johns, L. Chan, O. Receveur (McGill University); B. Erasmus (Dene Nation); R. Kuptana, P. Usher, M. Demmer (Inuit Tapirisat of Canada); M. Grey, C. Reimer (Inuit Circumpolar Conference); J. Gingell, E. Schultz, B. Jackson, N. Kassi (Council for Yukon Indians); W. Carpenter (Metis Nation, NWT); A. Kewayosh, B. Thomas (Assembly of First Nations); L. Leborgne (Mohawk Council of Kahnawake Representative); Maroun el Khoury, Rula Soueida, Lori Bell, Kobi Yeboah, Angela Deer, Coreen Delormier, Nicole Legault (McGill University)

OBJECTIVES AND ACTIVITIES

1. The objectives and activities reported in the mid-year report have continued throughout the year. In particular, we have fully occupied the newly renovated building, and the laboratories are completely functional.

2. Recruitment of support staff continued and was finalized. Maroun el Khoury , M.Sc. was hired for work with Laurie Chan on organochlorine and heavy metal contaminants. Kobi Yeboah, M.Sc. was employed on a part-time basis. Lori Bell has been recruited to work on a part-time basis with statistics and computer data bases, and she works with Olivier Receveur and Rula Soueida. Angela Deer left our employment in December, and we recruited Nicole Legault. Regular staff/student meetings are held. Graduate students are now an important component of CINE activities.

3. CINE staff and Governing Board Members held one conference call meeting during this period. Our activities have included a) revising the terms of reference for the Board; b) preparing a CINE Response Strategy for community concerns that are addressed to CINE; c) preparing a draft 6-year plan for the goals and activities of CINE; d) completing and making operational a bi-monthly reporting of activities to the Board; and e) preparation of proposals for the AES program.

4. CINE now has four projects that are funded by the AES:
   a) Variance in Food Use in Dene/Metis communities
   b) Estimation of Risk in Fort Resolution from Cadmium in Traditional Food
   c) Effects of Preparation on Organochlorines in Inuit Traditional Food
   d) Preliminary Dietary Studies in Yukon Communities.

5. The process of approval for CINE within McGill University is now complete. Senate gave approval on November 17, 1993 and the Board of Governors gave approval on December 13, 1993. Vice-Principal Roger Buckland has subsequently initiated his advisory committee for CINE activities within the University.

6. A meeting was held of McGill's CINE Founding Members / Professoriate on February ll, 1994, to discuss potential interdisciplinary activities of CINE with the university community.

7. The CINE laboratories participated in the inter-laboratory comparison exercise on PCBs and metal analyses as part of the AES QA/QC program.

8. The four CINE professors have been active in seeking additional research support.

9. Presentations about CINE and training workshops on dietary survey methodology were given in Whitehorse and Yellowknife. CINE staff presented to the Health Commissioners from communities represented in the Council for Yukon Indians on December 3-4, 1993, and to community members attending the AES workshop in Whitehorse on January 28-February 3, 1994. Workshop sessions were held for representatives from Dene/Metis communities in Yellowknife on February 23-26, 1994.

10. As a result of the CINE Response Strategy, several requests have been received from communities in Yukon, Northwest Territories and British Columbia to assist with their concerns about contaminants and their traditional food systems.

11. Public presentations and discussions on research topics and promotion of CINE, in addition to those noted above, were given to:
    (a) the University of Victoria, (b) the Society of Ethnobiology, (c) the International Development and Research Corporation meeting on Traditional Health Systems and Public Policy (Ottawa), (d) CBC-BC radio, (e) the National Health Research and Development Program (Ottawa), (e) Health Canada (Ottawa), and (f) Global Change Program of the Royal Society of Canada (Yellowknife). Tours of the CINE facilities and presentations about CINE have been given to several groups of McGill students, as well as to classes in Aboriginal Studies at John Abbott College, students from Kahnawake enroled in McGill's B.Ed. program, the McGill Extension Service, and several visitors from various parts of the world.

12. Work on outreach activities continued. CINE's posters and pamphlets have been widely distributed. Work on the video describing the creation of CINE, and its functions is now nearing completion. The first issue of "CINE's Newsletter" was released; it contains discussion on questions about contaminants and traditional food systems in the Yukon.

EDUCATION, COMMUNICATIONS, NATIONAL COORDINATION AND INTERNATIONAL INITIATIVES

EDUCATION AND COMMUNICATIONS
NEW INITIATIVES

1) A Workshop on Guidelines for Responsible Research was held in September 1993 to better enable Arctic Environmental Strategy - Northern Contaminants Program researchers to effectively involve northern communities in research activities from project design to communication of results. The guidelines are intended to assist scientists in initiating community contacts and developing research agreements with communities. Communications/participation planning has since become an integral part of the research proposal development and selection criteria for funding approval.

2) Five Regional Contaminants Workshops were held throughout the Northwest Territories in 1993/94, which were organized by the Government of NWT Department of Health. The workshops were conducted as part of ongoing consultations and communications with NWT residents about contaminants, and enabled discussions to proceed concerning human contaminant monitoring:

i) Taloyoak (Kitikmeot Region) Workshop - June 8-9, 1993
ii) Fort Simpson (MacKenzie Region) Workshop - October 6-7, 1993
iii) Rankin Inlet (Keewatin Region) Workshop - March 10-11, 1994
iv) Wha Ti (Lac La Martre - MacKenzie Region) Workshop - March 16-17, 1994
v) Iqaluit (Baffin Region) Workshop - April 12-13, 1994.

Recommendations for further education, communications, community action and follow-up workshops were made.

3) A public workshop on contaminants, hosted by the Yukon Contaminants Committee (YCC), was held in Whitehorse, Yukon in January 1994. Over 175 people attended the workshop, at which contaminants issues and research results were communicated, and the public was encouraged to provide their input and express their concerns. The information gathered during the workshop allowed the YCC to design a more effective communications and monitoring strategy for the remaining years of the program.

4) As part of an ongoing effort in collaborative information exchange with communities throughout the NWT, an audio-visual production titled *Environmental Contaminants in the North* has been produced by the Government of NWT (GNWT) Health Department. This video provides a general overview of environmental contaminants issues in the north while also providing information on the cultural and nutritional values of traditional foods, and the influence that lifestyle choices such as smoking can have on individual contaminant exposure. The video has been made available to regional and community health agencies, Aboriginal organizations, and other government and community agencies.

5) A travelling display unit has been designed by GNWT Health to visually present information regarding the long-range transport of atmospheric pollutants, movement of contaminants through the ecosystem, pathways for intake by people, impacts of lifestyle choices on individual

contaminant burdens, nutritional benefits of traditional foods, and opportunities for participation in wildlife and human health monitoring. The unit is available for community workshops, public open houses, and other relevant community information and education meetings.

6) The Métis Nation is currently developing an environmental contaminants program to be integrated with the existing NWT school curriculum for grades 6 to 9, and with adult education courses offered through Arctic College. This program is intended to provide Northerners with some of the necessary information and tools to make informed decisions regarding health risks associated with contaminants in the northern food chain.

7) Facts sheets on cadmium and on heavy metals are being completed through the Yukon Contaminants Committee.

WORKSHOP ON GUIDELINES FOR RESPONSIBLE RESEARCH
SEPTEMBER 22-23, 1993
YELLOWKNIFE, NWT

PROJECT LEADER: Indian and Northern Affairs Canada (Contacts: S.L. Han and M. Maki)

PROJECT TEAM: Inuit Tapirisat of Canada; Dene Nation; Metis Nation; Council for Yukon Indians

INTRODUCTION

A workshop on the subject of community-researcher relationships under the AES Northern Contaminants Program (AES-NCP) was conducted in Yellowknife, NWT on September 22 and 23, 1993. It was prompted by interest from the aboriginal organizations and recognition of the issue at the Northern Contaminants Program Review meeting held in Burlington, Ontario in February 1993.

A discussion paper on 'Negotiating Research Relationships in the North' was prepared by the Inuit Tapirisat of Canada (drafted under the earlier title of Research Guidelines for the North in April 1993). It posed questions and presented concerns relevant to the subject, and acted as a catalyst for planning of a workshop which would attempt to develop a practical approach for incorporation of these principles into Contaminants Program project planning and implementation.

Participants at the workshop included contaminants program researchers, representatives from the five northern aboriginal organizations at the local and national level, federal and territorial governments, the Science Institute of the Northwest Territories, and other AES programs. A list of participants is attached.

The goal of the workshop was to develop generic guidelines to better enable AES-NCP researchers to effectively involve northern communities in research activities from project design to communication of results. Ultimately, the objective is that communications/participation planning will become integral to research proposal development.

In October 1993, the Science Managers Committee on Contaminants in Northern Ecosystems and Native Diets approved the attached document and indicated that it would accompany the call for project proposals, starting with the 1994/95 proposals. It represents a proposed guideline to communications planning which would assist scientists in initiating community contacts and developing research agreements with communities. Workshop participants reviewed and commented on a first draft of this paper, and this document reflects that input.

KEY POINTS FROM THE WORKSHOP

- It is necessary to ensure that all AES-NCP projects incorporate some form of communications planning into proposal development (including estimated costs). It is acknowledged that the nature and degree of northern community involvement in contaminants research may vary according to project type and community interest, and that this may itself alter over time as experience is gained.
- AES-NCP researchers who do not personally conduct field work are nonetheless responsible for ensuring that communications requirements for their projects are fulfilled, whether this be through another member of the research team, a third-party intermediary or through their own personal efforts. In the NWT, the role of the Science Institute as "interface" between researchers and communities or "pipeline" to appropriate contacts, may present an opportunity.
- Details of "level of consultation" and "mutual obligations" will be determined through establishment of community-researcher relationships early on in the project planning process - thereby allowing for meaningful two-way exchange of information. The need for and value of feedback of information to the scientists from the community was stressed. The concept of 'partnership' between researchers and communities was emphasized, with communities needing support from researchers in identifying/evaluating contaminants issues and priorities and researchers benefiting from community input and traditional knowledge.
- The existing protocol for reporting of results from human health risk assessments (from analysis of fish/wildlife contaminants burdens) must be adhered to. It is noted that the decision to conduct such assessments is made as part of this process.
- From the program perspective, development of researcher-community relationships is a dynamic and evolving process. As research projects progress, common elements ("models") will emerge regarding the perceptions, needs, and resource/capacity strengths and shortcomings of individual communities, including their criteria and preferred form for participation in scientific research projects.
- Researchers and communities may wish to set out the parameters of their agreements and understandings in a 'memorandum of understanding'. A number of good examples are available for reference (e.g. Dene Nation model for participatory research and model research agreement, ICC model research agreement, the Yellowknife-Back Bay agreement with Mackenzie Regional Health Services is a working example of a Dene research model).
- The right to refuse participation, right to "veto" always rests with the individual at any point in any study.
- It was noted that the obligation to include community participation in project planning and implementation goes beyond the 'moral' with legal/constitutional requirements associated with land claims. In addition, accountability is a factor since research results may influence decisions and policy that can directly affect individuals and communities.
- The importance of developing approaches to research that are responsive to local or regional needs was noted, with the Yukon Contaminants Committee being referenced as a good mechanism for achieving this.

RELATED ISSUES OR TASKS FOR FUTURE CONSIDERATION

- There is a need for preparation of contingency plans if results are reported which require some form of intervention or action. This was emphasized in relation to reporting of individual human results.
- Protocol for reporting of results from retrospective analyses should be developed.
- Translation of documents and summary reports is recognized as critical yet raises issues which are difficult to resolve: appropriate languages/dialects, accuracy and appropriateness of translation (cultural, technical as well as linguistic), costs, and responsibility. An approach is needed. A point was made about presence of translators as 'monitors' during project discussions/negotiations, even those conducted in English or French.
- It was suggested that a 'Guide to government' to assist local/community aboriginal representatives in identifying AES researcher affiliations might be useful.
- Development of 'Layperson's summary' companion report to AES-NCP annual synopsis of scientific research results publication was suggested. The issue of translation was raised here as well.
- Compilation of examples or case studies of previous research project communications plans and community-researcher agreements to assist researchers was suggested.
- It was suggested that the 'Who's who' handbook of community profiles, which was proposed as a result of the Burlington (February 1993) meetings, is no longer necessary. The documents produced by the NWT Science Institute (*Doing Research in the NWT*, which is being updated) and by the Yukon Territorial Government (*Guidebook on Scientific Research in the Yukon)*, and the coordinating role played by the Yukon Contaminants Committee, preclude the need for AES to produce such a handbook.
- Communication of results should include consideration of media other than printed reports. Examples include videos which might present highlights of several projects or categories of research activity over several years. Use of local or regional radio is another effective method for information dissemination.
- The extent to which the non-native community should be consulted and included in AES contaminants activities was also debated and remains unclear.

AES-CONTAMINANTS PROGRAM
Researcher Guidelines for Planning Communications and Community Participation

ALL PROJECTS

It will continue to be the responsibility of individual researchers to determine the institutional requirements (external to the AES-NCP) relevant to their specific projects. These may include federal, territorial and land claims permitting and regulatory conditions.

The document published by the Science Institute of the Northwest Territories (*Doing Research in the NWT*, August 1993) provides a good guide to the legislation and land claims settlement areas in the NWT. It also provides a number of relevant contact names/addresses. A similar document, *Guidebook on Scientific Research in the Yukon* is also available from the Yukon Territorial Government. In the Yukon, contaminants research is overseen by the Yukon Contaminants Committee, and it is expected that project leaders consult with this committee at an early stage in project planning.

A. PROJECTS INVOLVING DATA ON HUMANS

(Medical or Social Information)

Prior to AES funding application

Contact: preliminary discussions with aboriginal organizations (via AES representatives)
YUKON: contact Yukon Contaminants Committee
Purpose: initial troubleshooting and planning of project, project approach

Contact: letter to leaders of communities in which research is intended to occur
(e.g. Hamlet or Band Council, Metis Local)
Purpose: Indicate that a proposal is being submitted
Describe general nature of project, purpose and background, etc.
Describe other contacts within the community that are being made as part of proposal preparation (e.g. health centre, community health committee)
Explain timing of AES funding application process (funding approval, need for community endorsement)

Contact: Regional Health Board
Community health centre/representative (health committee if applicable)
It is expected that contact would be initiated by letter with follow-up by telephone required.
Purpose: Describe project, background/context, purpose, general methodology, etc.
Explain what/how/why/when project results will be used
Receive general input on project proposal/method and planning
Receive general input on plan for dissemination of information about the study
(to community, to study participants, to health workers)
Clarify existing protocols for results reporting/release
Briefly describe and receive general input on plan for results reporting
(to individuals, to community, etc.)
It may be helpful to provide information which provides 'context' for project in terms of the contaminants program as a whole, thus contributing an educational function to the process. If it is determined (by the Science Managers) that a document such as a 'layperson's summary synopsis report' should be produced, this may serve the intended purpose.

It is expected that all of the three above-noted levels of contact will be necessary.

Following Funding Approval

Contact: Based on contacts and information received above
Purpose: Inform that project has received funding approval, indicate schedule/timeline
Identify training/employment opportunities
Finalize details of project planning, recalling three different 'levels' of information recipient: 1) community at large, 2) individual participants, and 3) health workers.
Allow for meetings with community representatives, as requested.

> Community input (obtained from leaders, health workers, etc. prior to proposal submission as well as in the 'fine-tuning' of methodology once funding is committed) will indicate the researcher's required commitment to public meetings, preparation of information packages, one-on-one meetings with participants, etc. This allows planning to be responsive to individual community needs. The need for obtaining **informed consent** from individual participants is a given.

Finalize details of plan and protocol for delivery/communications of results **prior** to commencing sampling. This includes provision for anonymity and confidentiality (at the community level as well) as agreed upon during project planning.
Explain and clarify use of the project results (peer reviewed scientific literature, education - graduate and post-graduate degrees, contribution to decision-making processes, etc.).
Reporting: Will be based upon plan and protocol for delivery as agreed upon with community. This may include interim progress reports at specified intervals.

B. PROJECTS DIRECTLY INVOLVING THE ARCTIC ECOSYSTEM

(Not including human data)

e.g. all biotic sampling (terrestrial, marine or freshwater)
all physical/chemical field studies (air, snow/ice, water, sediment)

Prior to AES funding application

Contact: **YUKON: contact Yukon Contaminants Committee**
Letter to regional organization(s) in which work will be conducted
e.g. Regional Inuit Association - Keewatin, Baffin, Kitikmeot, etc.
Land administrator (e.g. in Inuvialuit)
Regional or Tribal Councils (Gwich'in, Sahtu, Dogrib, etc.)
c.c. nearby communities - selection based on researcher's knowledge and judgment of where the project and all associated activities may be visible to northern residents. This is not restricted to 'on-site' methodology, but may include activities such as repeated overflights, cruises, camp set-up, etc. Community/regional/national contacts should provide researchers

with input if the communication plan (list of contacted communities) requires adjustment.

c.c. in the NWT, Renewable Resource officers or DIAND district offices in nearby communities (in initial stages of planning project communications, may be a good local spokesperson and resource on behalf of the researcher)

Initial contact letter could indicate final response date beyond which researcher will assume no major concerns/comments/suggestions from community. It must be emphasized that follow-up by phone remains essential.

It is recognized that the rapidly changing political face of the north and the various organizations/claimant groups/settlement areas will result in changes to the specific contacts. It is recommended that researchers contact the Science Institute of the Northwest Territories to obtain up-to-date contact names, etc.

Purpose: Inform that project is being proposed.

Describe project, background/context, purpose, general methodology, etc.

(include general description of field activities, including camp set-up, cruises, etc.)

Provide researcher contacts

Explain what/how/why/when project results will be used and reported

Request general input on project proposal, sampling plan, plan for reporting results to community

Explain timing of AES funding application process (funding approval, need for community endorsement)

Following funding approval

Contact: As above and/or as determined from contacts made above.

e.g. recommendations for contacts with Band Councils, Hunters and Trappers Associations or Committees (Inuvialuit), wildlife management boards, fish and/or game councils, etc.

Purpose: Inform that project has received funding approval and can proceed.

Provide schedule and description of intended field activities, etc.

Identify local training/employment opportunities

Inform of all intended or potential future uses of collected samples (i.e. archiving)

Where interest is expressed, receive input on sampling plan

N.B. some researchers, especially those conducting fish and wildlife studies, may wish to plan for meetings with community representatives to discuss details (as requested by the community) and should inform community that this option exists.

Where applicable, request permission for access to lands, wildlife (e.g. exclusive or preferential harvest rights under land claims)

Reporting: Review existing protocols for information dissemination.

Inform of timing for data availability and options for reporting of project-specific results.

Inform community of available general information (summary reports, etc.) and option to receive copies if requested.

Identify community requirements/desires for results reporting.

C. PROJECTS WITH NO DIRECT NORTHERN CONTACT OR SAMPLING

e.g. modelling, inventories, laboratory-based physical/chemical studies (such as volatilization studies), databases

Contact: as part of regular Technical/Science Managers review of project proposals, AES representatives of aboriginal organizations

Purpose: awareness of projects and nature/purpose of research, availability/accessibility of general information related to this kind of research

Reporting: Layman's summary of project results/activities to date, with contact names and explanation of project purpose (general as well as relative to contaminants program goals). Availability or distribution of layman's companion to synopsis could be to regional organizations and upon request from interested parties.

Other media such as an AES newsletter, a 'state of the environment' video, etc. should be considered to present the overall highlights of this category research, rather than (or in addition to) reporting on details from individual projects.

CONTAMINANT MONITORING AND COOPERATIVE RISK MANAGEMENT IN THE NORTHWEST TERRITORIES

PROJECT LEADERS: J.B. Walker and J.A. MacKinnon, Health Department, Government of the Northwest Territories; and
B. Elkin and S. Matthews, Renewable Resources Department, Government of the Northwest Territories

PROJECT TEAM: C. Mills (Regional Contaminants Coordinator); Regional Environmental Health Officers; Renewable Resource Officers; Regional Contaminants Consultation Working Groups; Regional Health Boards/Services and Health Centres

OBJECTIVES

1. To develop the regional capacity for cooperative risk management through the development of appropriate communication and education tools.

2. To foster the development of local information resources and communications networks through the mutual exchange of northern contaminants information/issues on a regional basis.

ACTIVITIES/RESULTS

Empowering communities and individuals with the capacity for informed decision-making regarding environmental contaminants and related monitoring activities is an exponential process, with each previous understanding building on the next. This project continues to be instrumental in providing a variety of written and audio-visual materials which further community education and dialogue about environmental contaminants.

Communication/Education Tools

Video

As part of an ongoing effort in collaborative information exchange with communities throughout the NWT an audio-visual production titled *Environmental Contaminants in the North* has been produced. This video is geared to provide a general overview of environmental contaminants issues in the north while also providing information on the cultural and nutritional values of traditional foods, and the influence that lifestyle choices such as smoking can have on individual contaminant exposure. The video has been made available to regional and community health agencies, Aboriginal organizations, and other government and community agencies.

Posters

Community involvement in contaminants communications has resulted in a number of initiatives. Both the Mackenzie and Kitikmeot Regions have commissioned local artists to produce poster-sized works which convey the commitment of people and governments to maintaining healthy communities and environments.

Display unit

A travelling display unit was designed to visually present information regarding the long-range transport of atmospheric pollutants, movement of contaminants through the ecosystem, pathways for intake by people, impacts of lifestyle choices on individual contaminant burdens, nutritional benefits of traditional foods, and opportunities for participation in wildlife and human health monitoring.

The display unit is available for community workshops, public open houses, and other relevant community information and education meetings.

Education package for health workers

A series of fact sheets addressing the health and environmental aspects of contaminants has been drafted. These overviews are meant to provide information to health workers and the public about different types of contaminants, how contaminants move in the food chain and into human organ systems, and why arctic ecosystems may be particularly affected.

Regional Consultations

Community Workshops

Community workshops were held in Taloyoak (Spence Bay) in June, Fort Simpson in October, Rankin Inlet in February, Lac La Martre in March and Iqaluit in April. These workshops provided community and health representatives with an overview of environmental contaminants issues, and current environmental monitoring activities, including maternal and cord blood monitoring. As well, the workshops provided opportunities for information exchange between communities and organizations. The workshops were very successful and resulted in the formation of two Consultation Working Groups on Environmental Contaminants.

The Mackenzie and Kitikmeot Consultation Working Groups have held regular meetings/conference calls regarding regional contaminants issues including the review and expansion of the maternal and cord blood protocol.

Community Meetings

At the annual conference for nurses in Kitikmeot Region the maternal and cord blood monitoring program was presented and input was received for further protocol development.

A community health fair, held in Cambridge Bay in September 1993 provided an opportunity for presentations and discussions of contaminant issues. Contaminants in the food chain were a central focus.

Local radio stations in a number of communities (e.g. Pelly Bay, Iqaluit) have aired summaries of workshop discussions as well as interviews with wildlife and health experts regarding environmental contaminants.

UTILIZATION OF RESULTS

Discussions regarding environmental contaminants will continue to be fostered in all regions of the NWT. This will provide a basis from which human health monitoring initiatives can be supported in a culturally and regionally appropriate manner.

Expected project completion date: March 31, 1997

CONTAMINANTS CURRICULUM - A PROGRAM OF INTEGRATED CURRICULUM DEVELOPMENT FOR NORTHERN EDUCATION/COMMUNICATION

PROJECT LEADER: W. Carpenter, Environmental Director, Métis Nation

PROJECT TEAM: J. Pin, Program Developer, Métis Nation; A. Najduch, Science Coordinator, Curriculum Development, Government of Northwest Territories Education; J. Farrow, Education Consultant, Métis Nation

OBJECTIVES

Short-term:

To give Northerners a better understanding of all issues relating to the Northern Contaminants Program under the Arctic Environmental Strategy (AES).

Long-term:

To give Northerners some of the necessary information and tools to make their own informed decisions regarding health risks associated with anthropogenic contaminants present in the Northern food chain.

DESCRIPTION

In order for there to be environmentally responsible decision making at all levels of society and in future generations, the subject of contaminants needs to be more formally understood and integrated into environmental education in the school curriculum, as well as in adult education programs in Northern Canada. This program of educational materials is being developed to integrate with the existing NWT school curriculum for grades 6 to 9, and with adult basic education and technology courses offered through Arctic College.

ACTIVITIES IN 1993/94

Initially, the literature was reviewed and a data base was created of all existing material collected in Phase I, related to the NWT school curriculum and existing environmental science programs. A network of expert contacts was established and an outline of the program to identify components was completed.

The outline covered the specific areas under the objectives of the Northern Contaminants Program: Names, Sources and Pathways (Sources, Pathways and Sinks); Effect on the Environment (Ecosystem Uptake and Human Health) and Man's Attempt to Improve the Environment (Education and Communications). The first drafts of the teaching units to be developed were based on contaminant sources such as agriculture, pulp and paper, mining, petrochemical industry and nuclear industry. A unit on Air Quality which addressed long-range transportation of contaminants was also developed in the initial stages.

A process for developing the units was identified which included a basic information package, references and resources from industry, links to the curriculum, and classroom activities for each unit. The lessons in the unit should provide an integrated learning experience which incorporates science, language arts, social studies and thinking skills. Many of the lessons were modeled in a cooperative learning style designed to seek the advice and consultation of people in the community, thus providing a model for enhancing environmentally responsible decision making at all levels of society and in future generations.

A Teachers' workshop was held in Yellowknife in early November with teachers from regional school boards of the NWT. A collection of suggested program activities was developed at this workshop.

A draft document of teaching units was completed in early March. The units were keyed to the existing school curriculum for grades 6 to 9 by a curriculum links table. The majority of the activities are linked to the science and social studies curricula. The draft document was reviewed by an independent consultant. The reviewer made recommendations with regard to organization and presentation of the teaching units, content and support materials. These recommendations were discussed with the project Steering Committee for inclusion in an enhanced draft to be undertaken in the next phase of the program.

A second database of Arctic Environmental Strategy's Northern Contaminants Program (NCP) research was established. All NCP research has been listed, according to contaminants, location in the NWT, species affected and an abstract of the paper. The database was designed as a research tool for the program developer, teachers and other interested individuals.

In January, work was begun on an Adult Education component. The objective was to identify and produce a draft outline of activities and support materials appropriate to the Arctic College Adult Basic Education (ABE) Science Literacy 110-130. Key aspects of the Northern Contaminants Program have been cross referenced to the existing course outline. The program embraces the view that local knowledge should be a vital component. Whenever possible experiences at the local level are used as a focus upon which to build to a regional and global perspectives. Lesson plans conform to the model requested by Arctic College. Suggested delivery methods cover a wide range of activities appropriate to the adult learning situation and mindful of the fact that many students are using English as a second language. Information files based on NCP research have been set up to provide background information to students and instructors. It is anticipated that these files will continue to be updated as current research becomes available.

RESULTS

To date the project has produced a database of school reference materials that are contaminant related; a first draft document of teaching materials for grades 6 to 9 in NWT schools; a development outline for Arctic College ABE Science 110 - 130; and a database of AES NCP research papers and other related research.

DISCUSSION/CONCLUSIONS

The review of the schools program document has helped to identify some omissions and deficiencies that should be addressed before field testing the program. As the project moves forward into the next Phase, a more integrated approach to program development will be adopted, the school program and adult education components are seen as part of a whole rather than separate entities. With Steering Committee direction and guidance from the Department of Education, an enhanced draft of the school program will be prepared.

The next phase will produce a document for pilot testing in schools and a document for pilot testing in adult education, prepare and deliver a first round of inservice training with teachers and adult education instructors and plan future components for Arctic College technology programs. The database will be fine tuned to meet the needs of the program developers, instructors and community groups.

Expected project completion date: This project seeks to communicate the results of NCP research to northerners and it is anticipated that this project will continue to update our program as results are available. Expected completion date is June 1995.

MEETING THE INFORMATION NEEDS OF INUIT ON CONTAMINANTS ISSUES: TOWARDS THE DEVELOPMENT OF AN EFFECTIVE COMMUNICATIONS STRATEGY

PROJECT LEADER: P.J. Usher, Director, Research Department, Inuit Tapirisat of Canada

PROJECT TEAM: P.J. Usher, M. Demmer, M. Baikie, M. Stiles, M. Stevenson, D. Nakashima

OBJECTIVES

To enhance communication in an appropriate social and cultural context among producers and consumers of country food; public health agencies; and scientific researchers about:

1. the presence and nature of contaminants in country foods;
2. the risks associated with their consumption (and with the disruption of their production and consumption); and
3. alternative options and strategies where continued consumption is a significant health risk.

The results of this project will contribute to more informed decision-making by producers and consumers about their activities, and to a more comprehensive and widely accepted set of criteria by which scientific and public health information are provided and received.

DESCRIPTION

The Arctic homelands of Canada's Inuit have long been perceived as a pristine wilderness, untouched by the environmental pollution associated with the industrialized regions of the world. Unfortunately, research has shown that this is not the case. Trace contaminants including heavy metals and organochlorines have been detected in the lands, waters and animals of the Arctic. The presence of these contaminants poses a potential threat to the physical and cultural health of Inuit who retain close links to the land and water and rely heavily on the "country foods" that the wildlife on those lands and waters provide.

Consequently, information about the levels and possible implications of trace contaminants is of direct importance to Inuit for nutritional, cultural and socio-economic reasons. But crossing cultural, perceptual and linguistic barriers to achieve meaningful communication between Inuit and non-Inuit has proven difficult.

Information on contaminants must therefore be accessible and understandable to, and usable by, Inuit in the communities where they live. While the development of educational programs may provide long-term assistance in this regard, this project is intended to address the short to medium-term needs of contaminants communication.

There are two components to this project. Part I is an inventory and assessment of programs for and experiences with contaminants communications in aboriginal communities. These include, for example, the Health Canada mercury program in Ontario and Manitoba, the Cree mercury program in Quebec and the PCB episode in Broughton Island. Part II undertakes to develop a current perspective and appreciation of how Inuit now view the problem of contaminants, and how they identify their information needs.

The two components (Parts I and II) are closely linked. First, the way in which Inuit understand and interpret contaminants is a function of the nature and source of the incoming information, the social context in which this information is received, and the cognitive models by which this information is interpreted and understood. Secondly, the development and implementation of new approaches to contaminants communication should be based on both an assessment of previous programs and actual current circumstances.

ACTIVITIES IN 1993/94

This is a one-year project scheduled to be completed by September, 1994. At the time of submission of this report, the conclusions and recommendations arising from the results of the field work and research are in draft form only. The following briefly describes the project activities for 1993/94:

Part I

There are two major sections to Part I of this project. The first provides an overview of the principles and methods of risk determination and communication with respect to health and contaminants. It also considers the particular situation of Inuit (and other aboriginal) communities, as it affects the application of these principles and methods there. This section is based primarily on a review of current literature.

The second section consists of brief case studies of selected incidents of country food contamination in Aboriginal communities, and a review of certain programs to respond to such incidents. These are based primarily on unpublished documentation and key informant interviews. There is no overall or coherent contaminants communication program or procedure in Canada, nor is there a comprehensive review of actual experience in this regard, as it relates to Aboriginal communities. This report is intended to promote knowledge and understanding of both.

In undertaking to conduct the case studies, a preliminary list of incidents of country food contamination in Aboriginal communities was developed on the basis of our own knowledge, the literature review, and key informants. The objective was not to develop a complete inventory, but to represent the variety and diversity of incidents across the country. An incident was included if it involved a community whose residents were primarily of Indian, Inuit, or Metis ancestry, and engaged in harvesting (hunting, fishing, or gathering) country food for household or community consumption.

We selected certain incidents for more detailed examination, based on two main criteria. The first was that the known or hypothesized existence of a contaminant situation had generated a public health concern on the part of the community and/or the responsible public authorities. The second was that the response of the latter included both risk determination and communication. Additional criteria were the availability of information, and the potential relevance and utility of the example to contemporary Inuit communities.

More detailed examination of the selected contaminant episodes was based primarily on the acquisition of unpublished documentation, and key informant interviews. In keeping with the resources available for this study, key informant interviews were limited to knowledgeable individuals involved in each episode, either on behalf of public authorities or the communities. Key informants were thus largely those responsible for program delivery -- public servants and medical personnel, most of whom are non-aboriginal and located in southern Canada. A comprehensive case study approach would require inclusion of the views of those most directly affected by contaminants, i.e. the residents of affected Aboriginal communities, who are also program recipients. The "mini" case studies in this report provide a starting point for such a study. Both documentary and key informant data were collected on the basis of a framework developed from various models of the steps taken in risk assessment, management and communication.

Part II

This part of the project undertakes to provide insight into the perceptions and information needs of Inuit from three communities in the Northwest Territories: Qamani'tuaq (Baker Lake), Tuktoyaktuk, and Sanikiluaq. The selection of communities was by mutual agreement of the Inuit Tapirisat of Canada (ITC) and the communities, and the detailed research design was negotiated according to the guidelines for ethical research outlined by the AES Aboriginal partner organizations.

During the development stage of this project, ITC had received the support of the respective Hamlet Councils (HC) and Hunters' and Trappers' Associations (HTA). The field researchers contacted the HC and HTA two months prior to the beginning of the field-work to introduce themselves and schedule meetings. At these meetings, the project was discussed in detail and arrangements were negotiated with the community organizations for them to achieve the level of involvement that they desired. It was established that the HC and HTA wanted involvement in the review and critique of the respective Part II community reports. Therefore, the draft reports have been submitted to the three communities for their review and commentary. They accept that the draft report will be in English (due to financial limitations) and they will undertake to discuss their critique with the communities at large.

The fieldwork took place in the early winter of 1993 with each researcher spending approximately one month in the respective communities. The research was conducted through key informant, semi-directed interviews based on an interview guide prepared by ITC. The guide consisted of two parts: specific questions relating to information sources and needs; and less structured questions relating to perceptions of contaminants, country foods and fitness or health. In order to understand how important country food is to people and the risks they might accept in eating it, we asked people for their own perceptions about: 1) personal judgement about health and safety of country food; 2) the concepts of invisible contaminants and/or chronic health effects as they relate to food; and 3) their willingness to consume meat containing contaminants. The questions about how people would react to meat containing contaminants were probed based on personal judgement. If it appeared that the questions made people nervous about safety, the issue was not pursued.

The criteria used to select key informants were: (1) interest in environmental issues; (2) gender; (3) age; and (4) representation of various social groups within the community (e.g. hunters, professionals, etc.). The interviews were conducted through house to house visits and lasted on average for about one and a half hours.

Analysis of the interview results was based on a qualitative interpretation of interviews, conversations and general observations (i.e. not a formal content analysis). Each researcher was asked to include in their reports some recommendations based on the information they had received on further research and/or projects to improve the communications situation on contaminants issues.

In the final project report, the three community reports will be prefaced by a summary which will draw out the common themes and present an overview of the findings.

Expected project completion date: The final report of this project will be available in Fall 1994.

INFORMATION AND EDUCATION ON CONTAMINANTS IN THE YUKON

PROJECT LEADERS: Yukon Technical Committee on Contaminants in Northern Ecosystems and Native Diets (Contact: M. Palmer, Chair)

PROJECT TEAM: Yukon College; Environment Canada; Council for Yukon Indians; Health Canada; Indian and Northern Affairs Canada; Yukon Territorial Government Renewable Resources Department

OBJECTIVES

Short-term:

To make technical information on contaminants available to Yukoners through a library contaminants collection and through fact sheets.

Long-term:

1. To "demystify" contaminants issues by providing information relevant to the Yukon in an accessible form.

2. To improve communications and local decision making on contaminants issues in the Yukon.

DESCRIPTION

Local decision-making and local control of communications on contaminants issues have been identified as important goals of the Yukon components of the Contaminants Program of the Arctic Environmental Strategy. It is critical that decision-makers, those involved in communications, and the general public, become better informed about contaminants and issues surrounding contaminants.

It is currently very difficult for Yukoners to obtain scientific information on contaminants as it relates to the north. In an attempt to increase public awareness and provide Yukoners with the information required to make an informed choice, two initiatives were started. The first was to introduce information (books, journals) on contaminants into the Yukon College library. This information will offer different levels of complexity as well as different perspectives on contaminants. The second initiative is to produce a series of fact sheets providing simple explanations of selected contaminants as they relate to the north.

ACTIVITIES IN 1993/94

The Contaminants library, which was established at Yukon College in 1992, was expanded in 1993/94 to include new information on contaminants. The new additions were for heavy metals, including cadmium. Approximately 30 new books and journals were added to the collection at Yukon College.

Two local contractors were hired to complete facts sheets on cadmium and on heavy metals. The cadmium fact sheet was chosen as a result of the elevated cadmium levels found in caribou liver and kidney. The heavy metals fact sheet was selected as a result of the numerous abandoned mines located throughout the Yukon.

CONCLUSIONS AND UTILIZATION OF RESULTS

All of the new publications can be viewed at Yukon College in Whitehorse. The two fact sheets have been completed in draft form and are under review. They will be distributed as part of the proceedings from the Contaminants Workshop held in Whitehorse this past winter.

Expected Completion Date: March 31, 1997

TECHNICAL SUPPORT FOR THE YUKON CONTAMINANTS PROGRAM TOWARDS EFFECTIVE COMMUNICATION OF THE ARCTIC ENVIRONMENTAL STRATEGY PROGRAM AND RESULTS

PROJECT LEADERS: Yukon Technical Committee on Contaminants in Northern Ecosystems and Native Diets (Contact: M. Palmer, Chair)

PROJECT TEAM: Yukon College; Environment Canada; Council for Yukon Indians; Health Canada; Indian and Northern Affairs Canada; Yukon Territorial Government Renewable Resources Department; Yukon Territorial Government Health Department

OBJECTIVES

1. To improve communication of the contaminants program, including Arctic Environmental Strategy (AES) objectives, study results and health risks, among AES program managers and the affected public, including First Nations.

2. To prepare summaries of AES research results in plain language for distribution to First Nations people and the general public.

3. To provide translation of research reports into relevant First Nations languages and translation during public meetings.

4. To retain technical experts on an as-required basis to assist Yukon Contaminants Committee in presenting the contaminants program to the public.

DESCRIPTION

One of the objectives of the Arctic Environmental Strategy includes better decision making through the integration of local, regional and national interests as part of new cooperative arrangements. The Strategy recognizes the need to reflect changing political and constitutional arrangements in the Arctic as land claims and devolution proceed. Clearly, there is a need to adjust program priorities and delivery mechanisms to reflect these objectives.

The workplan for the Contaminants component of the Strategy also undertakes to provide timely health advice to northern people, with the intention of renewing local confidence in country foods as a safe dietary source. The Strategy states its support for active participation by northern communities in program development and delivery as well as communication of program results to community members.

While the first years of the Strategy program have focused on study, it is necessary to now address the issue of effective mechanisms to ensure that northern communities are active participants in communication of study results and determining action plans. This need for greater attention to effective communication was raised both during the program audit and the priorities workshop.

The Yukon Contaminants Committee (YCC) was established to facilitate regional and local involvement in the contaminants program and to ensure more effective communication of information among federal and territorial government departments, First Nations and the Yukon community. The YCC is now struggling to meet the communication and consultation demands made by concerned Yukon First Nations and Yukon communities for detailed explanations of the program and study results. The YCC requires improved access to technical experts to provide information on environmental and human health risks to affected communities. Resources are required to translate technical reports into user friendly language. First Nations are requesting establishment of special working groups to address their needs and concerns regarding contaminants. Consistent with the Strategy, it is critical that we be able to respond to the desire by local communities to participate in communications with their members.

ACTIVITIES IN 1993/94

The key activities undertaken under this project are outlined below:

- A contaminants workshop was held in January 1994. This was a three day workshop covering education, communication of results and pubic feed back. Over 175 people attended the workshop, at which presentations were given by over 30 researchers.
- The YCC supported an Environmental Summit organized by the Council for Yukon Indians. The Summit was intended to provide Yukon First Nations with an understanding of risk assessment.
- Travel by YCC committee members to communities and to participate in workshops, etc.

RESULTS AND DISCUSSION

The efforts under this program have provided for better communication of results and participation of Yukoners in the AES Contaminants Program. The information gathered during the workshop has allowed the YCC to map out a more effective communications strategy for the remaining years of the program. The workshop proceedings will be available in late 1994.

Expected project completion date: March 31, 1997

INDIGENOUS SCIENCE COOPERATIVE STUDIES

PROJECT LEADERS: E.C. Carmack and R.W. Macdonald, Institute of Ocean Sciences, Fisheries and Oceans Canada

OBJECTIVE

To incorporate traditional knowledge into the planning and interpretation phases of our science program.

DESCRIPTION

For the past several years we have spent time with Jimmy Jacobson (an elder from Tuktoyaktuk, Northwest Territories) discussing our work, seeking advice on travel, and contracting native field guides. During this process our conversations have evolved into many issues of concern to Jimmy and we have found many of his insights to be helpful in focusing our work on relevant oceanographic phenomena.

ACTIVITIES AND RESULTS

We have completed a manuscript which is presently in review (Water and Ice Related Phenomena in the Coastal Region of the Beaufort Sea: Some Parallels Between Native Experience and Western Science, Carmack, Macdonald and Jacobson).

DISCUSSION/CONCLUSIONS

In this work we have discussed four specific aspects of native insight and how they have led our scientific inquiry:

1. Ice Characteristics and fish abundance in terms of tidal dispersion and mixing patterns in winter.
2. Maintenance of a small, ice-free area, used by animals as a salt lick, by vertical heat flux associated with channel flow.
3. Overflooding of nearshore ice in winter due to storms.
4. The importance of wind direction on ice features and circulation in Liverpool Bay.

Expected project completion date: We plan to continue this work with Northern Natives and with Local Natives beyond the life of this program.

NORTHERN AQUATIC FOOD CHAIN CONTAMINATION DATABASE

PROJECT LEADER: H. Careau, Public Health Center (Québec Region), Centre Hospitalier de l'Université Laval (CHUL)

PROJECT TEAM: H. Careau, É. Dewailly, P. Ayotte

OBJECTIVES

1. To provide an update of a computerized database on contamination levels in northern aquatic food chains (including humans).

2. To make this research tool available to those who would like to use it to advance their own research.

DESCRIPTION

Since the beginning of the last decade, research activities on levels and trends of contamination of northern ecosystems of Canada and Québec have increased considerably. This is largely due to the Arctic Environmental Strategy (AES) initiated by the Canadian government, but also because of interest in supporting the way of life of northern native communities and the sense that the North can function as an environmental pulse of other regions of North America and other parts of the world. All this interest has generated (and is still generating) a considerable amount of data from a variety of sources describing levels of contamination found in the various organisms living in this vast northern region.

The Northern Aquatic Food Chain Contamination Database project was initiated to provide a tool to manage a large amount of contamination data for which each mean concentration level is attached to a variety of indissociable attributes. In fact, it is meant to allow fast access to contamination data covering the Canadian Arctic, Northern Québec and Greenland, through searching by restrictive parameters when needed. Since it covers published and unpublished data, it is expected to be as complete as possible.

ACTIVITIES IN 1993/94

With one of the main objectives being the accessibility of the database to other researchers and organizations, some modifications were made to the structure of the database in order to render it as user friendly as possible without sacrificing its desirable flexibility. In order to ensure data input consistency, a review of the data was carried out for each variable.

Concurrently, a user manual was produced in both English and French. The manual was written so that the reader with a minimal knowledge of Macintosh (or Windows system) can proceed with ease. The content of the database, the possible difficulties, as well as hints as to how to best proceed are discussed at length.

The distribution of the Northern Aquatic Food Chain Contamination Database (Macintosh platform) was initiated at the beginning of 1994 when the data review and both versions of the user manual were completed. The collection of new data, its review and the input of new data is an on-going process. Approximately 3000 new concentration levels have been added since 1992/93.

DISCUSSION/CONCLUSION

Important steps were taken during this period and will be taken in the near future to ensure the greatest accessibility of this collection of data as possible. The major problem encountered so far is the incompatibility between Macintosh and PCs. However, this gap is closing with the arrival of new types of computers (Power PC) which can run on both platforms, and with the imminent conversion (into PC environment) of the software 4th DIMENSION. It is only a question of a short period of time before anyone wishing to access the research potential of the Northern Aquatic Food Chain Contamination Database will be able to.

Expected project completion date: On-going update

PARTNERS

Hydro-Québec; Health Department of Government of Northwest Territories; Health Canada

REFERENCES

Ayotte, P., É. Dewailly, H. Careau and A. Vézina. 1994. Arctic air pollution and human health - What effects should be expected. In press in Science of the Total Environment (Fall 1994).

Careau, H. 1993. Banque de données: Contamination de la Chaîne Alimentaire Aquatique Nordique. Guide de l'usager, version 1.0 F. Centre de Santé Publique, région de Québec. 67 pp.

Careau, H. 1993. The Northern Aquatic Food Chain Contamination Database. User manual, version 1.0 E. Centre de Santé Publique, région de Québec. 65 pp.

Careau, H., É. Dewailly and P. Ayotte. 1993. Northern aquatic food chain contamination database: continued development. Pp. 245-248 *in*: Synopsis of Research Conducted Under the 1992/93 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 70. Indian and Northern Affairs Canada. 285 pp.

Careau, H. and É. Dewailly. 1994. The northern aquatic food chain contamination database: A research tool. In press in Science of the Total Environment (Fall 1994).

Dewailly, É., Ayotte, P., Careau, H., Vézina, A. 1992. Use of the Arctic Contaminant Database to estimate human exposure. Pp. 188-192 *in*: Synopsis of Research Conducted Under the 1991/92 Northern Contaminants Program, J.L. Murray and R.G. Shearer (eds.). Environmental Studies No. 68. Indian and Northern Affairs Canada. 213 pp.

ARCTIC SPECIMEN BANKING

PROJECT LEADER: B. Wakeford, National Wildlife Research Centre (NWRC), Canadian Wildlife Service (CWS), Environment Canada

PROJECT TEAM: M. Kasserra, B. Braune, R. Norstrom (NWRC, CWS)

OBJECTIVES

1993/94:

1. To print and distribute the Arctic Specimen Bank Catalogue as a CWS Technical Report.
2. To upgrade the CWS Specimen Banking facility. To ensure the expanded facility at NWRC is adequately organized to accommodate existing specimens and those being collected for CWS projects funded by the Northern Contaminants Program.

Long-term:

1. To preserve, catalogue and support the housing of Arctic biota specimens to be used for research in the Northern Contaminants Program.
2. To develop an Arctic Specimen Bank consisting of a network of facilities which house important collections of Arctic biota.
3. To develop policies and procedures which will allow access to Arctic tissues within the network of facilities.

RATIONALE

In April 1991, there was agreement among members of the Science Managers Committee, that Arctic specimen banking was important and that an Arctic Specimen Bank should be established in the form of a network of existing and new facilities. The exercise was intended to develop a cost effective approach for allowing increased research to be performed on Arctic specimens which are costly to collect. This agreement was further strengthened at a meeting of representatives of Canadian Wildlife Service, Fisheries and Oceans Canada, Health Canada, Parks Canada and Government of Northwest Territories in October 1991. As a first step toward the objective, a survey of existing facilities was to be conducted and the results published in a catalogue. At the request of DIAND, CWS agreed to manage a contract to deliver the survey and to publish it and assure that it was distributed to the widest possible interested audience.

CWS has been recognized as a world leader in specimen banking. It hosted the International Workshop on Specimen Banking in 1989; it participated actively in the steering committee of the Great Lakes Regional Specimen Bank feasibility study (funded by the Great Lakes Protection Fund) in 1992/93. Its collection of wildlife specimens, especially of avian species, has been built up since the 1960s and is considered the most comprehensive one of its kind.

The facilities were expanded in 1982 with the building of walk-in freezers, enabling specimens to be stored indefinitely at -25 and -40 °C. The locations and pertinent information of these specimens are indexed in a computer database. However, the facility is at capacity and expansion is required in order to fulfil its mandate to ensure tissues can continue to be housed properly.

ACTIVITIES IN 1993/94

1. Publication of the following document was completed in October 1993:

   The Arctic Specimen Bank Catalogue - Holdings of fauna and flora in Canada and the United States
   B. Wakeford and B.M.Braune (Eds.)
   Technical Report Series No. 184
   Headquarters 1993, Canadian Wildlife Service

This 200 page catalogue provides listings of 79 different Arctic collections from government, university and museum collections in both countries. Approximately 400 copies were distributed throughout North America and Europe to survey participants and to a number of institutions and individuals provided from a mailing list supplied by the Northern Contaminants Program in DIAND.

The document was shown to interested researchers at the Arctic Monitoring Assessment Program meeting held in Tromsø, Norway in February 1994. Interest was particularly strong among the Swedish delegation who are promoting a similar Specimen Bank in northern Europe.

2. Expansion of facilities at CWS

A construction project which will increase the long-term storage capacities at the NWRC was initiated in late 1993/94. The project, which was completed in July 1994, comprises the construction of 2 new walk-in freezer rooms to be kept at -40 °C and relocation of chest freezers to a renovated adjacent room. The entire project costs $192 K of which $25K has been funded from the Northern Contaminants Program. It is anticipated that these expanded facilities will accommodate CWS needs for at least 5 years.

DISCUSSION

Work in 1994/95 will be focused on three tasks:

1. To set up new freezer storage rooms at CWS in a coherent manner for the storage of Arctic and other Specimen Bank tissues. The planned expansion of the CWS Specimen Bank will increase the long-term storage facilities by 40-50%. Existing temporary storage facilities will have to be completely reorganized to make efficient use of the new facilities.

2. To develop procedures/protocols/access guidelines for the CWS node of the Network which will be a model for other nodes in the Arctic Specimen Bank network.

3. To act as principal contact of the Network and develop mechanisms to steer overall policies.

Expected project completion date: March 31, 1997

ARCTIC MARINE MAMMAL AND FRESHWATER FISH SPECIMEN BANK

PROGRAM LEADERS: D. Muir and W.L. Lockhart, Freshwater Institute (FWI), Fisheries and Oceans Canada, Winnipeg, Manitoba

PROJECT TEAM: C.A. Ford, B. Thompsen, R. Stewart (Fisheries and Oceans, Winnipeg)

OBJECTIVES

To obtain tissues of representative Arctic marine and freshwater biota and place them in long-term storage in order to make possible retrospective analyses for contaminants or pathologies associated with contaminants or other potential causes. To provide appropriate sample archive for tissues to be analysed for contaminants, biomarkers or destined for pathological examination. The long-term objective is to provide data from which the health of the marine ecosystem can be assessed and from which retrospective analyses of contaminants can be made.

INTRODUCTION

The Northern Contaminants Program has stimulated the collection of large numbers fishes and marine mammal tissues as well as sediment cores which are currently at the Freshwater Institute (FWI) in Winnipeg or in commercial storage. Combined with existing collection of fish and marine mammal tissues of Fisheries and Oceans biologists also at FWI we may have one of the largest collections of tissues in Canada according to the recent Canadian Wildlife Service (CWS) survey (Wakeford and Braune 1993). Many of these tissues are not homogenates but are large bulk samples or whole fish. CWS has taken the lead on specimen banking for the Arctic contaminants program, however, their program is intended to store only a small number of valuable samples. The purpose of this project is to increase storage space for homogenates and small nonhomogenized samples at FWI in order to provide a long-term archive for contaminants measurements and other future studies.

PROGRESS TO DATE

The funds received in 1993/94 went toward renovation of a suite of Controlled Environment (CE) Rooms into freezers (-38°C to - 45°C). Because funding was only about 50% of that requested we were unable to build new freezers, however, the CE rooms were available and only required addition of new condensers, and refrigeration units. The cost is still substantial and funding to be received in 1994/95 will be needed to complete the work. The new freezer capacity (2 small rooms, approx. 12 m^2 total floor area) will increase our storage capacity significantly. Work has begun on creating a database to track all of the samples received, including storage conditions and location.

PARTNERS

The work will be coordinated with CWS and, if necessary, with Health Canada.

REFERENCES

Wakeford, B. and B.M. Braune. 1993. Arctic specimen bank catalogue. CWS Tech. Rpt. 184. Environment Canada, Canadian Wildlife Service, Hull, PQ.

INTERLABORATORY QUALITY ASSURANCE PROGRAM FOR ANALYTICAL DATA PRODUCED BY NORTHERN CONTAMINANTS RESEARCH PROJECTS OF THE ARCTIC ENVIRONMENTAL STRATEGY (AES)

(Final Report of 1992/93 and 1993/94 Quality Assurance Program)

PROJECT LEADER: J. Zhu, The Centre for Analytical and Environmental Chemistry, Carleton University

PROJECT TEAM: S.L. Han, D. Muir, R. Norstrom, M. Alaee, R. Macdonald, H. Schwartz

SUMMARY

This program was initiated during 1992/93 and started with a survey of the existing internal QA/QC program, followed by a series of interlaboratory comparison exercises, including PCBs and organochlorines (OCs) in polar bear extracts, metals in caribou kidney, and PCB standards in isooctane solution. Other activities of the program include site visits to laboratories and review of results from a Canadian-Russian interlaboratory comparison.

The interlaboratory comparison on PCBs and organochlorine pesticides in an extract of polar bear fat shows the relative standard deviation (%RSD) of inter-laboratory variation was around 20 to 30 percent for major PCB congeners and pesticides. The minor components have much larger %RSD mainly due to difficulties in identification of the peaks and interferences because most of the laboratories are not familiar with the polar bear sample. The %RSD of two major pesticides, dieldrin (40%) and oxychlordane (57%), were relatively large.

To offset the bias caused by complexity of polar bear sample, a PCB standard solution (in isooctane) was distributed for intercomparison. The %RSD was found at a level of 15 to 25 percent, which is very close to the results from polar bear extract. It is also demonstrated that inter-laboratory variance is the major contributor to the total analytical variance among the participating laboratories. Meanwhile laboratories demonstrated high intra-laboratory precision. The inter-laboratory variance is caused primarily by the quantitation standards. Similar results were observed in other intercalibrations. For example, %RSD of 20 percent or greater was found among the participating laboratories in an intercomparison on PCB congeners in solution conducted by Environment Canada for The Integrated Atmospheric Deposition Network (IADN).

Compared to organic results, interlaboratory comparison on three heavy metals, cadmium, lead and total mercury in caribou kidney reveals a satisfactory result. The %RSD were about 5, 10 and 30 percent for cadmium (mean concentration 697 ppm), mercury (7.6 ppm) and lead (0.6 ppm), respectively.

In addition to a number of recommendations and guidelines already made to the management of the Northern Contaminants Program in our previous reports (see Appendix) some further recommendations are given in this final report. They are 1) intercomparison on metals may not

be of high priority, 2) the reliability and accuracy of quantitation standards should be improved, 3) further intercomparison on organochlorine pesticides in solution shall be conducted, 4) analytical problems identified through intercomparison shall be solved, 5) matrix-free solutions shall be available for other analytes, and 6) future site visits will be restricted to new-coming laboratories to the Northern Contaminants Program.

INTRODUCTION

The Northern Contaminants Program (NCP) is a major component of the Arctic Environmental Strategy (AES). Among the objectives of the Program are identification of contaminant sources and pathways to the Arctic, assessment of contaminant levels in the Arctic ecosystem, and assessment of ecosystem health (including human health) effects. High quality and consistent measurement data are essential to meet these objectives.

Quality Assurance is defined as "planned activities designed to ensure that the quality control activities are being properly implemented", whereas the quality control is "planned activities designed to provide a quality product" (Garfield 1991).

The nature of the NCP is such that it involves analysis of different contaminants at trace and ultra trace levels (parts-per-billion and parts-per-trillion) in various matrices including air, snow, water, sediments, plants, fish, mammals and humans. It is such a big program that many laboratories are involved and the question of comparability of data must be answered. It is therefore very important to have a specifically designed Quality Assurance (QA) program to ensure that comparability of analytical results exists among these matrices and among laboratories participating in the NCP.

Although interlaboratory comparison exercises are the main activities of this QA program, others such as site visits and survey of existing QA/QC programs are also important to achieve the goals of this program. Combining all these efforts, we will be able to evaluate the quality of data of the NCP which will provide information on uncertainties of the data to the management of the NCP.

ACTIVITIES AND RESULTS OF THE QA PROGRAM

The QA program was initiated during 1992/93 when increased concerns about ensuring high standards for overall data quality and comparability of data produced by the participating laboratories were raised.

The program started with a survey of existing internal QA/QC programs. Information was gathered through a questionnaire containing questions about project leaders, contact persons, laboratories performing analyses, analytes/matrices, methodologies, relevant QA programs and participation in any other interlaboratory comparisons, etc. The questionnaire was sent to about twenty project leaders who were receiving AES funding. It was found that although all participating laboratories under the survey had a QA/QC program, commercial laboratories had, in general, more adequate written documents of QA/QC programs. Based on findings of the survey, a brief QA/QC program guideline, which outlines basic requirements of the program was issued to the management of NCP (see part 1 of the QA program report entitled "Summary of QA/QC Program Inventory From Laboratories/Institutes Involved in the Northern Contaminants Program").

Three interlaboratory comparison exercises were conducted under the QA program. The first was for polychlorobiphenyls (PCBs) and organochlorines (OCs) in an extract of polar bear fat tissue, provided by National Wildlife Research Centre (NWRC) in Hull. The second intercomparison was for toxic heavy metals (cadmium, lead and total mercury) in caribou kidney supplied by the Tissue Bank in NWRC. The third intercomparison was for PCB congeners in an isooctane solution.

Review of the results of the interlaboratory comparison on PCBs and OCs in polar bear extracts was included in part 2 of the QA program report entitled "Comparability of Analytical Data for PCBs and Chlorinated Pesticides: Review of Polar Bear Fat Extract Results". The relative standard deviation (%RSD) of major PCB congeners for the seven participating laboratories was about 20 to 30 percent. Congeners with large %RSD were either of low concentration (PCB 149, 195 and 209) or had been associated with other problems such as misidentification (PCB 47/48, 74 and 56/60). The large %RSD of PCB 105 and 206 (both about 50%) might be related to the quantitation standards. Polar bear extract is a very unique check sample. It was unfamiliar to many participating laboratories and that may have resulted in large %RSD for many minor components. The main components of other organochlorines such as *p,p'*-DDE, t-nonachlor, heptachlor epoxide (HE), HCHs and polychlorobenzenes had good interlaboratory precision (%RSD was about 20%). The large %RSD for dieldrin was caused by an extremely low value from one laboratory, while oxychlordane was caused by an extremely high value from one laboratory and a low value from another laboratory. The possible switch of DDT and DDD number by one laboratory was the reason for the large %RSD of these two compounds. The large %RSD for octachlorostyrene was probably due to its low concentration in the sample. The reference laboratory demonstrated that a %RSD of about 10 percent or less can be achieved within a laboratory. This indicates that the interlaboratory deviation is about two to three times larger than intralaboratory deviation.

Interlaboratory comparison of metals concentrated on three most important elements, cadmium, lead and total mercury. The results indicated that the deviation of metal analyses among the participating laboratories was much better than for organic analyses. The %RSD were about 5, 10 and 30 percent for cadmium (mean concentration 697 ppm), mercury (7.6 ppm) and lead (0.6 ppm), respectively. Another aspect of the satisfactory results was that the mean concentrations of these three elements are in good agreement with the data generated a year ago by a contract laboratory. The results from the seventh laboratory were delayed and therefore were not included in our earlier report. The concentrations of mercury and lead from this laboratory were eliminated from this data set as they were the obvious outlier. It was stated by the laboratory that in fact these two concentrations were very close to their method detection limit and could be inaccurate. The results of the comparison can be found in part 3 of the QA program report entitled "Progress of 1993/94 QA/QC Program During April and September 1993".

The other interlaboratory comparison exercise was based on a matrix-free check sample containing PCB congeners only. The results of this exercise show good internal precision for most participating laboratories. %RSD was calculated based on the mean value of six replicate direct injections reported by participating laboratories.The majority of PCB congeners achieved a %RSD of 10 to 20 percent. %RSD of PCB 99, 138 and 180 was about 25 percent. Larger %RSD was found with PCB 74 (37%) and 187 (33%). Although the six injections were made over three weeks, all laboratories demonstrated good precision of the replicate analysis over time. Similar precision was found in triplicate analyses, including the sample clean-up procedure in the exercise . Review of this exercise was included in part 5 of the QA program report entitled "Interlaboratory Comparison on PCB Congeners in Isooctane Solution".

Results of a Canada-Russia interlaboratory comparison conducted in 1992 by R. Norstrom of the Canadian Wildlife Service were reviewed. Three Canadian and two Russian laboratories participated. There were significant differences between the two countries, whereas the data among three Canadian laboratories were more comparable (see report entitled "Canada-Russia Interlaboratory Comparison Results of Polar Bear Test Sample").

As part of the QA program activities, the following laboratories have been visited: 1) Centre du Toxicologie du Quebec, Laval University, 2) Great Lakes Institute, University of Windsor, 3) National Water Research Institute, Environment Canada, 4) AXYS Analytical Services Ltd., 5) Freshwater Institute, Fisheries and Oceans Canada, 6) Institute of Ocean Sciences, Fisheries and Oceans Canada, and 6) Canadian Wildlife Service, Environment Canada.

OVERALL DATA QUALITY AND RECOMMENDATIONS

1) The results for metals show that good interlaboratory precision exists among the participating laboratories. We may expect that within the normal concentration range the %RSD will be about 10% or less, whereas for low concentrations the %RSD will be larger, at about 30 percent. The data from participating laboratories are considered to be comparable. Further interlaboratory comparison on these metals (cadmium, lead and total mercury) may not be of high priority and resources should be devoted to organic contaminants. Site visits to any new-coming laboratories to the NCP may be conducted on an individual case basis to ensure the existence of adequate capability of performing analytical work.

2) Good estimation of the quality of the PCB data set can be made based on the above mentioned two interlaboratory comparisons. The %RSD at normal concentration range would be 10 to 20 percent for the same matrix and up to 30 percent when considering all the matrices. Results of Interlaboratory comparison of PCB in matrix-free solution demonstrated that interlaboratory (or between-laboratory) variation, also referred to as bias, is a major factor contributing to total variation of the PCB data. The bias might result largely from the different sources and concentrations of quantitation standards used by participating laboratories. This can be confirmed by the fact that %RSD using polar bear extract is only slightly larger. Table 1 shows the comparable %RSD of seven congeners, which are the major congeners in polar bear, from both interlaboratory comparisons.

Table 1. Comparison of %RSD on main PCB congener in polar bear sample and PCB solution.

Congener	Polar Bear (n=7)	PCB Solution (n=10)	
		Dir. Inject (n=6)	Extraction (n=3)
PCB 118	19	13	11
PCB 153	25	14	12
PCB 138	21	12	8
PCB 156	29	23	24
PCB 180	20	16	12
PCB 170	18	12	10
PCB 194	27	20	27

3) The intercomparisons on PCBs in both polar bear extract and the solution provide valuable information about the variability of PCB data of the Northern Contaminants Program. Generally speaking, the %RSD at a range of 20 to 30 percent in standard solutions is comparable to the other PCB intercomparisons. For example, %RSD of 20 percent or greater was found among the participating laboratories in the intercomparison on PCB congeners in solution conducted by Environment Canada for The Integrated Atmospheric Deposition Network (IADN) (Environment Canada 1993). Using a common reference standard was recommended as the result of that study. Although use of a common reference standard can reduce the variability among the participating laboratories we will not recommend it because it will introduce the bias for the whole AES project and therefore will cause difficulties for comparing the data of AES with the data of other programs.

4) Interlaboratory comparison of organochlorines (OCs) such as polychlorobenzene, HCHs, DDTs, and chlordane related compounds in polar bear demonstrated that the typical %RSD of major components is a 15 to 25 percent such as for HCB (15%), α-HCH (12%), β-HCH (17%), Heptachlor epoxide (16%), t-nonachlor (14%) and *p,p'*-DDE (17%). The large %RSD for oxychlordane (57%) and dieldrin (40%) are two exceptions. Further interlaboratory comparison on OCs using a matrix-free check sample shall be conducted.

5) Some problems identified in the previous section should be addressed. Laboratories should be aware of and solve the common problems such as co-elution on GC chromatogram, poor column resolution, misidentification of minor components and, probably the most important aspect, improper calibration of quantitation standards. Some problems associated with the work up procedures such as loss of volatile components, split of single compound in two fractions and incomplete elution of polar components on the separation column will also affect the quality of analytical data.

6) Interlaboratory comparison of PCB congeners in a matrix-free solution is demonstrated as a suitable exercise for the AES Contaminants Program. Similar practice should be also available for other analytes such as chlorinated pesticides, PCDD/PCDFs, PAHs and so on.

7) Future site visits will be restricted to new-coming laboratories to the NCP since the site visits conducted so far indicate that all the existing laboratories are well managed and capable of performing analytical work.

REFERENCES

Environment Canada. 1993. Interlaboratory Study 92-1: Polychlorinated Biphenyl (PCB) isomers Standard Solutions. Environment Canada ARD Report: 93-11.

Garfield, F.M. (Ed.) 1991. Quality Assurance Principles for Analytical Laboratories. AOAC International.

Appendix: List of Reports of QA/QC Program in 1992/93 and 1993/94

1. Summary of QA/QC program inventory from laboratories/institutes involved in the Northern Contaminants Program. (Part 1 of QA program report, January 29, 1993).

2. Comparability of analytical data for PCBs and chlorinated pesticides: review of polar bear fat extract results. (Part 2 of QA program report, April 26, 1993).

3. Canada-Russia interlaboratory comparison results of polar bear test sample. (June 3, 1993).

4. Progress of 1993/94 QA/QC program during April and September 1993. (Part 3 of QA program report, September 27, 1993).

5. Progress of 1993/94 QA/QC program during October and December 1993 (Part 4 of QA program report, December 31, 1993).

6. Interlaboratory comparison on PCB congeners in isooctane solution. (Part 5 of QA program report, March 23, 1994).

ARCTIC MONITORING AND ASSESSMENT PROGRAMME

At Rovaniemi, Finland in June 1991, Ministers from all eight Arctic countries signed a declaration adopting the Arctic Environmental Protection Strategy (AEPS). The AEPS sets out the shared environmental objectives of the eight countries, and identifies the principles which should guide their implementation. It reviews the nature of Arctic environmental problems, assesses the existing institutional and legislative arrangements for dealing with them, and finally, identifies specific actions which should be implemented. One of these actions commits the eight governments to establish a comprehensive Arctic Monitoring and Assessment Programme (AMAP).

The mandate of AMAP is to monitor the levels of, and assess the effects of, anthropogenic pollutants in all components of the Arctic environment. It was envisaged that AMAP should as far as possible be built upon existing national and international programs, which are to be developed into a circumpolar framework. Initial priority is to be given on a circumpolar basis to persistent organic pollutants, selected heavy metals and radionuclides, and on a regional basis (Fennoscandinavia) to acidification.

To implement AMAP, a Working Group has been established comprised of delegates from each of the participating nations (Canada, Denmark, Finland, Iceland, Norway, Russia, Sweden, United States), observing countries (Germany, Netherlands, and the United Kingdom), and organizations of indigenous people (Inuit Circumpolar Conference, Nordic Saami Council and the Russian Association of Peoples of the North). Canada has been elected to Chair the Working Group, and Sweden to Vice-chair. Norway has provided a Secretariat, based in Oslo.

The Monitoring Programme for AMAP was completed in 1993, providing direction for monitoring activities for the Atmosphere, the Marine, Freshwater and Terrestrial environments, and Human Health. The requirements of the Monitoring Programme are fulfilled by the sum of the member countries' Implementation Plans. Canada's Implementation Plan is comprised largely of the projects being conducted under the Arctic Environmental Strategy's Northern Contaminants Program. Implementation is greatly facilitated by the fact that the goals and objectives of AMAP are directly compatible with those of the Arctic Environmental Strategy.

Output from AMAP will take the form of comprehensive "State of the Arctic Environment" assessment reports for the eight circumpolar Ministers, the first of which will be produced in 1997. In March 1994, an Expert Meeting was held in Tromsø, Norway of scientists specializing in various aspects of environmental pollution. These experts drafted detailed annotated contents for the core chapters of the first assessment report. The chapter titles are listed in Table 1.

The assessment will have two products:

1) State of the Arctic Environment Report (SOAER)

   This report will be intended for an educated general public and will be prefaced by an executive summary with recommendations specifically addressed to Ministers.

2) AMAP Assessment Report (AAR)

> This will be a comprehensive technical and scientifically presented assessment of all validated data available (from both published and unpublished sources) of the status of the Arctic Environment relative to the AMAP mandate. This fully referenced document will provide the scientific basis and validation to the statements made in the SOAER.

Lead for the core chapters of the AAR has been divided among the AMAP member countries as follows: Physical Characteristics - Canada/Norway, Persistent Organic Pollutants - Canada/Sweden, Heavy Metals - USA/Russia, Radioactivity - Norway/Russia, Acidification - Finland, and Human Health - Denmark. The drafting process is coordinated by an Assessment Steering Group (ASG) which is comprised of the AMAP Board, the lead for each chapter and one Indigenous Peoples' representative.

The first draft of the AMAP Assessment Report is expected in March 1995, at which time the AMAP Secretariat will begin drafting the State of the Arctic Environment Report.

Table 1. Structure of the AMAP Assessment Report.

Foreword	
Conclusions and Recommendations	
Chapter 1	Introduction
Chapter 2	Physical-Geographical Characteristics of the Arctic Region
Chapter 3	Characteristics of Ecosystems and Human Populations Relevant to Pollution Issues
Chapter 4	Physical Processes Influencing Pollutant Transport in and into the Arctic
Chapter 5	Persistent Organic Pollutants
Chapter 6	Heavy Metals
Chapter 7	Radionuclides
Chapter 8	Acidification and Arctic Haze
Chapter 9	Sub-Regional Stress Factors
Chapter 10	Influence of Global Environmental Processes on the State of the Arctic Environment
Chapter 11	Integrated Pollution Effect on Arctic Ecosystems
Chapter 12	Human Health

UNITED NATIONS ECONOMIC COMMISSION FOR EUROPE (UN ECE) TASK FORCE ON PERSISTENT ORGANIC POLLUTANTS (POPs)

Persistent organic compounds with a high potential chronic toxicity (such as PCBs, dioxins and toxaphene) have been found to occur in surprisingly elevated concentrations in biota at the top of the arctic food chain, particularly in many of the favoured dietary items of northern indigenous people. Some of these substances (such as PCBs) have been found in blood and breast milk from Inuit residents of Broughton Island, NWT and northern Québec at concentrations which exceed levels recommended by Health Canada. Similarly, in the Yukon, it has been necessary for Territorial health officials to issue dietary health advisories concerning the consumption of some species of fish due to tissue concentrations of the pesticide toxaphene. The situation has led to general concern relating to human health and ecosystem implications.

Many of these chemicals are prohibited (or have never been widely used) in Canada (e.g. toxaphene). They are carried to the Arctic primarily in the atmosphere, after being released to the environment at mid and low latitudes. Therefore, a key component of Canada's strategy to deal with this issue has been to pursue the development of international controls on emissions and discharges to the environment.

To achieve our goal, we have focused on the Convention on Long-Range Transboundary Air Pollution (LRTAP), administered under the United Nations Economic Commission for Europe (UN-ECE). This instrument is attractive on two counts. First, the UN-ECE membership includes all east and west European nations, together with the United States, Russia and Canada. It therefore captures a significant proportion of the northern hemisphere's users and manufacturers of persistent organics. Second, the Convention has developed a proven track record in achieving consensus and action in the challenging arena of acid rain generating pollutants within the fifty-member countries.

Following proposals from Canada, the UN-ECE established a special Task Force in November 1990 to report on the magnitude of the persistent organic pollutant problem. The Task Force (co-chaired by Canada (DIAND) and Sweden), subsequently prepared a report stating that the situation is of sufficient concern that development of the elements of a protocol for the control of these substances should be immediately initiated under the LRTAP Convention. In November 1991, the Executive Body to the LRTAP Convention responded by modifying the mandate of the Task Force to provide by 1994, the basis for elements of a possible protocol. At a meeting hosted by Canada in May 1992, the Task Force agreed upon a Work Plan to achieve this goal. The key components of the Work Plan were as follows:

1) preparation of a schedule of priority substances to be covered by the protocol (led by the United Kingdom);

2) establishment of emission and discharge inventories upon which compliance with a protocol would be based (led by Canada and the United States);

3) development of monitoring and modelling capability to evaluate the effectiveness of proposed control strategies (led by Sweden);

4) evaluation and recommendations relating to optimal control technologies and strategies for principle pollutant sources;

   a) stationary industry (led by Germany and the Netherlands)
   b) transportation (led by the United States)
   c) pesticides (led by Canada and Germany); and

5) preparation of a report for the Executive Body to the LRTAP Convention in November 1994, to provide the basis for a protocol (led by Canada and Sweden).

Germany hosted the third meeting of the Task Force (May 16-20, 1993) at which time progress on the five Work Plan components was evaluated. A small group of experts, led by Canada and Sweden, met in London in December 1993 to prepare the supporting documentation for the Task Force Substantiation Report on POPs (*State of Knowledge Report of the UN ECE Task Force on Persistent Organic Pollutants)*. Canada prepared a technical background paper (*An Overview of Persistent Organic Pollutants in the Environment*) which formed the basis for a chapter of the State of Knowledge Report. The final Substantiation Report, including the basic elements for a protocol, was drafted and approved at the fourth Task Force meeting, conducted February 21-25, 1994 in the Netherlands (The Hague).

The POPs Task Force Reports and recommendations were presented to the UN ECE LRTAP Convention's subsidiary bodies (Working Groups on Technology and on Effects) on June 28, 29, 1994 in Geneva, Switzerland. The Working Groups endorsed the Task Force reports and recommendations, and these will be forwarded to the Executive Body for their consideration in November 1994. At that time, it will be decided whether or not to begin the preparation of a legal, internationally binding protocol to control persistent organic pollutants under the LRTAP Convention.

Much of the momentum for this initiative can be attributed to the Arctic Environmental Protection Strategy (AEPS) which was adopted by Ministers from the eight Arctic countries in Rovaniemi, Finland in June 1991, and which included a strong commitment to support the work of the UN ECE Task Force. At their second meeting in Nuuk, Greenland on September 16, 1993, the AEPS Ministers agreed to support the development of a protocol under the UN ECE LRTAP Convention.

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