Indian and Northern Affairs Canada
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Environmental Studies No. 73

Synopsis of Research Conducted Under the 1994/95 Northern Contaminants Program

Canada

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Northern Affairs Program

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FOREWORD

This report summarizes the results of research and monitoring studies on contaminants in northern Canada. These studies were conducted under the auspices of the Northern Contaminants Program, which is a component of Canada's Arctic Environmental Strategy.

The projects cover all aspects of the northern contaminants issues, 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 I.

PRÉFACE

Ce rapport résume les résultats de recherches portant 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, un volet de la Stratégie pour l'environnement arctique.

Ces projets représentent tous les aspects du problème des contaminants, incluant les sources et le transport, la contamination des écosystemes 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 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 traditionally harvested 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." with the intended result being "renewed confidence in traditional foods as a safe diet." 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 are chaired by Indian and Northern Affairs Canada, and which include representatives from the five northern Aboriginal organizations (Council for Yukon First Nations, Dene Nation, Métis 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). The strategic action plan outlining the priorities for the NCP is based on an ecosystem approach, focusing on three main categories: i) Sources, pathways and fate, ii) Ecosystem uptake and effects iii) human health. The priority work areas that 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 funded $19.9 M of research, representing over 100 projects, in addition to supporting the McGill Centre for Nutrition and the Environment of Indigenous Peoples (CINE), and participation of Aboriginal 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 traditionally harvested 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. Results from NCP sampling programs have been used in human health risk assessments for contaminants in traditionally harvested species. The use of NCP data in the health risk assessment process follows the protocol agreed upon by all NCP participants (federal, territorial and Aboriginal). Evaluation, validation and communication of health risk assessment results, including integration of benefits considerations, is done by the Territorial Contaminants Committtees, with support and cooperation from the AES NCP.

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. However, results from a pilot study in Northern Québec, completed in 1995, indicate that it is feasible to design a research project to investigate health effects on human newborns due to maternal body burdens of contaminants, accounting for small population sizes, confounding lifestyle factors, and cultural considerations, which may influence testing methods.

Exposure, effects and nutritition 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.

Therefore, in tandem with the Program's shift toward human health research, efforts to develop effective "com-

munity 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 was instituted in 1994/95 through the Guidelines for Responsible Research. Initiatives such as the Métis Nation's contaminants curriculum, ITC's research on communicating about contaminants in country food, and materials such as a layperson's overview booklet on Contaminants in Northern Canada, a variety of fact sheets and newsletters, and videos such as 'Environmental Contaminants in the North' developed by GNWT Health, form the beginning of an inventory of resources which support NCP communications. The strategic plan for coordination of Contaminants Program communication continues to evolve and form an important guide 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 substantiatation 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 circumpolar 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 all compartments of the arctic environment. Using information from current monitoring projects and from the published literature, AMAP is drafting an assessment 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.

In 1995, a substantive step toward control of international sources of POPs and Heavy Metals was made when the Executive Body of the UN ECE LRTAP Convention agreed to begin negotiation on legally binding international agreements for control of these contaminants. Canada leads the Preparatory Working Group on POPs, which is preparing the draft protocol for negotiation. In June of the same year, Canada played a leadership role in bringing POPs to the global agenda; cohosting with the Republic of the Philippines the *International Experts Meeting on POPs: Towards Global Action*, in Vancouver, B.C. The meeting identified concerns and management activities related to POPs, from both developed and developing world perspectives. It also outlined a series of recommendations for international action on POPs.

This report provides a summary of the research and activities which were undertaken in the 1994/95 fiscal year and funded by the Arctic Environmental Strategy's Northern Contaminants Program. A workshop was held in Calgary in late January 1996 at which researchers presented their results from 1994/95 as well as any available preliminary results from projects funded in the 1995/96 fiscal year. 1996/97, will be the last year of the NCP under the six-year Arctic Environmental Strategy, which is sunsetting at the end of the coming fiscal year.

I SOURCES, PATHWAYS AND FATE OF CONTAMINANTS

SOURCES, PATHWAYS AND FATE OF CONTAMINANTS
NEW FINDINGS

1) A modelling exercise has suggested "that arctic lakes act as conduits for chemicals, with minimal chemical being retained in bottom sediments. This result implies that the water column of lakes can respond relatively quickly to loading changes, depending on water residence time. The results also have implications for the use of sediment profiles to reconstruct historical loading patterns or comparing loadings lake-to-lake."

2) ^{129}I and ^{137}Cs in seawater in the Western Arctic Ocean from 1993 "clearly delineate the plume of Sellafield and Cap La Hague contaminants being transported across the Arctic Ocean. Reduced levels of ^{129}I and ^{137}Cs in surface water in the Chukchi Sea represent background fallout levels associated with water of Pacific origin while radionuclide levels an order of magnitude greater in surface water from the Makarov Basin, reflect inputs of Atlantic water contaminated by releases from the European reprocessing plants. Although levels of radioactivity in the Canada Basin are significantly in excess of background levels from nuclear weapons tests, they are still lower than those that would constitute a radiological threat to organisms or humans in the Arctic."

3) "Fugacity gradients indicate that the Bering-Chukchi Seas are outgassing α–HCH in late summer and that γ–HCH in surface water has shifted from undersaturation in 1988 to near- equilibrium with atmospheric concentrations in 1993. These changes appear to be a consequence of declining atmospheric levels over the last 14 years and particularly between 1990-1993."

"Results for other OCs show a decrease in the fugacity ratio from south to north. Dieldrin and *trans*-chlordane are oversaturated in the Bering Sea, but close to equilibrium or slightly undersaturated in the Chukchi. Chlorobornanes (CHBs) are undersaturated in all regions, implying air-to-sea transfer."

"HCH concentrations in the Canadian Basin water-column are about double those observed in the Chukchi and East Siberian Seas." This may be explained by preliminary sediment data which suggest that removal of contaminants to sediments occurs in highly productive regions of the Chukchi Sea.

4) Preliminary results for air measured during the Arctic Ocean Transect Cruise (from Nome, Alaska to Halifax, Nova Scotia across the North Pole) "show low values for α–HCH (66 pg/m^3), in line with the downward trend seen for post-1990 measurements at other arctic locations.

5) "HCHs, in particular α–(0.3-0.48 ng/L) and γ–(0.07-0.23 ng/L) isomers, are the most predominant OCs in the Yukon River System. Toxaphene concentrations in water range from 0.02-0.27 ng/L. Initial results indicate that atmospheric deposition is the major source of contaminants into the Yukon River basin. Aqueous concentrations of toxaphene in summer are higher than those in the winter. This can be attributed to higher air concentrations in the summer. Small differences in the concentrations of HCHs and toxaphene in the lakes and rivers indicate that there is no major point source in the Yukon River system."

6) HCH and ΣPCB were the most abundant OC compounds reported in 1992 and 1993 in the Amituk Lake watershed, Cornwallis Island, NWT. HCH levels in all media dropped between 1992 and 1993. For example, concentrations in valley snow decreased from 6392 to 4106 (pg/L) and in lake water at 20 m depth declined from 2417 to 1324 pg/L. ΣPCB concentrations were in the range of 763-1615 pg/L in valley snow and 427-469 pg/L in 20 m depth lake water. "Volatilization of OC compounds, particularly from the shallow (<1.0 m) snowcover, is apparent as the snow pack heats up in May-June."

Investigations in the Yukon have revealed the DDT levels are higher in Lake Laberge and Watson Lake than in other lakes investigated. These two lakes are in areas where extensive spraying of DDT for mosquito control was carried from the 1940s and 1960s. PCBs also appear to be higher in Lake Laberge, likely attributed to past use and disposal practices in this area.

7) Concentration of PAHs in the Beaufort Sea region are high for a pristine area. "The main sources of PAHs to this region are the natural inputs from the Mackenzie River. Although concentrations are below thresholds thought to induce toxic effects, the high natural background may make this region sensitive to added PAHs from human activities."

8) Fish in numerous lakes in the NWT contain levels of mercury in excess of 0.5 ppm, the recommended maximum for human consumption. Core profiles in these lakes "suggest that most mercury loadings to lakes in the western NWT and Yukon are of natural, geologic origin."

9) Air measurements at Alert on Ellesmere Island in the NWT show that PCBs peak in air from April to August. The di-, tri- and tetra-chlorinated PCBs peak in the winter while the penta-, hexa- and hepta-PCBs peak in the summer. Although use of PCBs has largely been discontinued, dumping activities and their persistence result in their continued presence in the environment.

10) Studies of ΣPCB deposition in the Yukon have shown that the amount of snowfall determines the deposition. Mean deposition of ΣPCB at Tagish and Whitehorse are 4.9 and 3.6 $ng \bullet m^{-2} \bullet day^{-1}$. In contrast, in the White Pass region, where snowfall is an order of magnitude greater than at Tagish and Whitehorse, "These deposition rates indicate that the atmosphere is a potential source of at least PCBs to the surface waters of the Yukon."

Significant levels of α–HCH and lindane were measured at White Pass, while these contaminants were not found at the other two sites. This is likely due to the deeper snow pack at White Pass retaining a larger amount of these volatile compounds.

11) Measurement of snow in the NWT show that concentrations of α-HCH, lindane, ΣDDT and ΣPCB in snowpack from Mould Bay and Alert, are higher than those to the west and south of these sites; values for Cape Dorset are intermediate between these two sites. Chlordanes show no variations and HCB levels in Cape Dorset are closer to those in the south and west than in the north.

12) In general, concentrations of organic contaminants in Canadian Arctic rivers are very low.

STUDY OF THE GLOBAL SCALE TRANSPORT OF SULPHUR AND PERSISTENT ORGANIC POLLUTANTS WITH SPECIAL EMPHASIS ON ARCTIC REGIONS

Project Leaders: J. Pudykiewicz, A.P. Dastoor, Atmospheric Environment Service, Environment Canada

OBJECTIVE

1. To trace the atmospheric transport of toxic materials to the Arctic.

DESCRIPTION

The main objective of the modelling of atmospheric processes in the context of environmental assessment of the northern ecosystems is to trace the atmospheric transport of toxic materials to the Arctic. Considering that this transport involves virtually all scales of atmospheric motions we need to consider the problem using the global coordinate system in a manner similar to the one used in numerical weather prediction and climate simulation. Technology of this type is essential to understand the origin of various toxic materials observed in the Arctic environment.

Atmospheric transport is an extremely complex process. In general terms, this process could be described using the conceptual model derived from the theory of mixing in continuous systems. Atmospheric transport is traditionally simulated using the mass conservation equation known in the literature as an "advection diffusion" or a "convection diffusion" equation. The calculation of atmospheric transport using the numerical solution of this equation requires the information about the state of the atmosphere, soil and hydrosphere, along with appropriate information about the emission field. The atmospheric part of the system is relatively, the best known part.

MODEL STRUCTURE

Atmospheric tracer technology was already employed for simulating the transport of various toxic materials to the Arctic ecosystem. The tracers included in these simulations were radionuclides released from nuclear reactors (Pudykiewicz 1988 and 1990), sulphur species (Dastoor and Pudykiewicz 1995) and finally, toxic materials including HCH. The first two tracers are relatively well understood with respect to transformation and deposition processes, hence simulations were performed using relatively sophisticated 3-D models.

In the case of toxic materials, most simulations reported in the literature were performed with relatively simple 2-D models, or even simpler box models neglecting the continuum-based description of the atmosphere. The major justification for work performed with box models was the desire to establish a mass balance for selected toxic materials. Considering the complex and nonlinear character of the transport processes in the atmosphere, this approach should be considered as extremely limited in its ability to explain the observed distribution of toxic material in the environment.

The current modelling of atmospheric transport of HCH at the Atmospheric Environment Service (AES) relies, therefore, on the existing 3-Dimensional meteorological models. The model employed in our studies is the Canadian global spectral model (Ritchie 1991). This model is based on primitive equations and uses the hydrostatic approximation. It has been modified to include cloud water and tracer transport conservation equations. The time integration is performed using a semi-Lagrangian semi-implicit approach. The model includes a relatively detailed treatment of condensation and cloudiness.

The chemistry included in the model represents the global sulphur cycle. The models are currently being extended to simulate the transport of persistent organochlorines (to be reported in final form in March, 1996). In this field, however, some additional work is still required to account for the interaction between atmospheric transport and the ocean. Although relatively simple in the context of box models, these interactions are more complex to address within the framework of 3-D models. The most severe limitation is related to the availability of data.

Emission data

The most uncertain element of the system is the information about the amount of toxic materials emitted into the atmosphere. Both the amount as well as the spatial distribution of emissions are usually not known and only recently has the issue of the assembly of the global emission inventory been approached in a systematic manner.

Essentially, there are two ways of acquiring this information. The first is based on the compilation of emission inventories (not always realistic, considering that information about emissions of some species is sometimes not known or kept confidential). The second way of acquiring emission data is formulated as an optimum control theory problem. It shows how to estimate emission information from observed concentrations. This method is based on the synergy between the model and data.

CONCLUSIONS

The numerical simulation of the sulphur transport to the Arctic was performed with the anthropogenic emission field of SO_2 (Dastoor and Pudykiewicz 1995). The sequence of the simulation performed with the 3-Dimensional atmospheric tracer model clearly indicated several interesting properties of atmospheric transport to the Arctic regions. The atmospheric mixing on a large scale is a complex and often chaotic process. One of the most characteristic features of this process is mass exchange between well-defined and often isolated macromixing regions.

Pollutant transport to and from the Arctic is essentially caused by mass exchange between two regions with different spectrums of eddy kinetic energy. In the mid-latitudes this spectrum exhibits a maximum at medium to low frequencies. This fact is a direct manifestation of the cyclones and anticyclones embedded in jet streams developing along the polar front. In the Arctic, the kinetic energy spectrum shows much less low frequency kinetic energy. This heterogeneous distribution of eddies in the mid-latitudes and the Arctic prevents the systematic mass exchange in the meridional direction over considerable distances.

These two regimes of flow in the mid-latitudes and Arctic regions could occasionally be coupled as a result of the so-called "blocking events." The relation of blocking to increased levels of air pollution in the Arctic regions was first noted by Raatz (1984). The problem was also studied by Iversen (1989) who described the meridional index as helpful in the classification of meteorological situations affecting air quality in the Arctic. The flow patterns associated with blocking are characterized in synoptic meteorology by a split in the jet stream with one branch turning toward the equator and the other in the direction of the North Pole. Efficient transport to the Arctic takes place mostly during these episodic situations. Considering the vertical wind profile during blocking events, it is evident that the most effective transport levels are located in the free atmosphere just above the top of the planetary boundary layer.

The most frequent areas of occurrence of blocking are in the northeast Atlantic and northeast Pacific. The frequency of Atlantic blocking events is statistically about 2.5 times more frequent than Pacific events (Rex 1950). The most important pathway of pollutant transport to the Arctic is therefore associated with blocking events over the Atlantic. The circulation pattern developing during this synoptic situation transports pollutants from source regions located mainly in Europe and North America.

The other important pathway of transport to the Arctic regions is related to the occurrence of blocking events over the Pacific. Although not as common as blocking over the Atlantic, they contribute significantly to the total mass of sulphur transferred to the Arctic. The injections resulting from Pacific blocking transfer sulphur, usually originating in sources located in Asia, and in sulphur from European sources carried by westerly circulation.

The kinematics of sulphur transport to the Arctic is reflected relatively well by the data from Resolute (Figure 1). Verification of the model results for Resolute quantitatively present the role of different processes affecting transport to the Arctic. The small discrepancy between the model results and observations is related to the fact that the comparison is performed between the actual realization of one year's transport and 10 years' observational average. The value of the concentrations, as well as values of the maximum and minimum concentrations are simulated with a high degree of accuracy.

The most pronounced feature of the model results is the presence of a strong yearly cycle exhibiting a maximum level during winter and spring months and a minimum during summer (Figure 2). This cycle could be explained by the statistical distribution of the blocking events over the Northern Hemisphere. The observed and simulated yearly cycles of pollutant concentration in Alert suggest that contaminant transfer to the Arctic exhibits a very strong episodic character.

The conclusions from the study analysing global sulphur transport are important for a better understanding of environmental pathways of toxics. To obtain a quantitative description of these pathways, the model simulating sulphur transport on a global scale is being extended to include HCH. The major modifications performed to the model are related to the meteorological part. Instead of relying on the predicted meteorology, we will use the sequences of objectively analysed meteorological fields. This solution will increase the certainty of the evaluation of HCH concentration.

The simulation of pollutants transport is being performed in two stages. In the first, our global model is applied in order to establish the concentration of the HCH emitted to the atmosphere from the world's oceans. This is particularly important because most of the HCH accumulated in the environment is stored in the oceans. The global tracer model is run for a period of one year using the forcing by the surface fluxes of HCH from the ocean into the atmosphere. These fluxes are evaluated from the concentration of HCH in the water. A map depicting the structure of the forcing employed in our calculations is depicted in Figure 3. This figure displays the global distribution of HCH concentrations in water of the World Ocean [ng/L]. The area shown was derived from a dataset of HCH concentrations measured in water, that was compiled by Terry Bidleman in February 1994. A composite set of measurements was created and mapped onto a latitude-longitude grid. Finally, an interpolation algorithm using a polynomial weight function was used to generate the distribution of HCH shown in the Figure 3.

Expected project completion date: In the second stage of the project, which will be completed before end of March of 1996, we will consider the fresh HCH emissions using the new emission inventories being currently compiled by Environment Canada. The results of the study will be verified using measurements of HCH concentration in Arctic regions. The model will provide an interesting assessment tool with important applications for monitoring the state of Northern Ecosystems.

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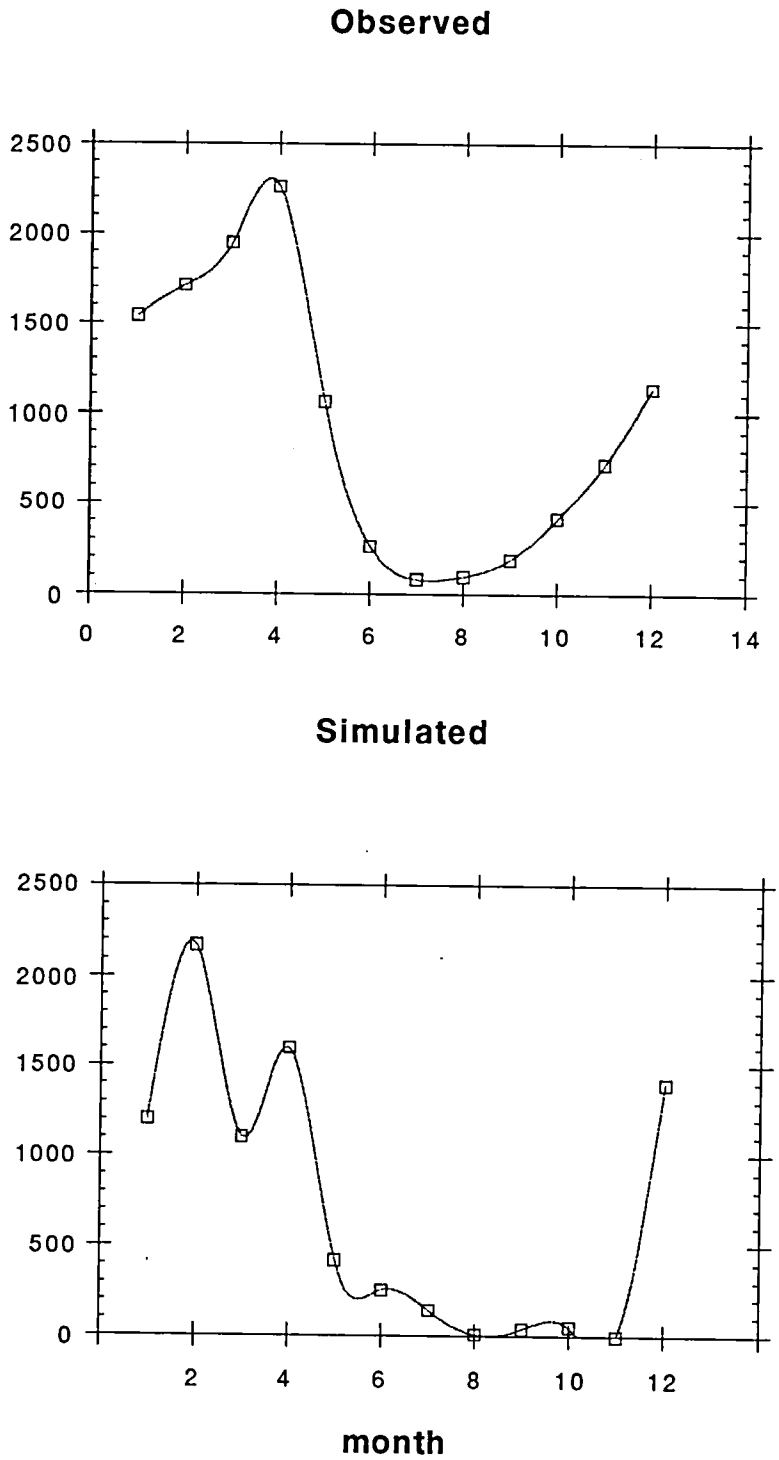
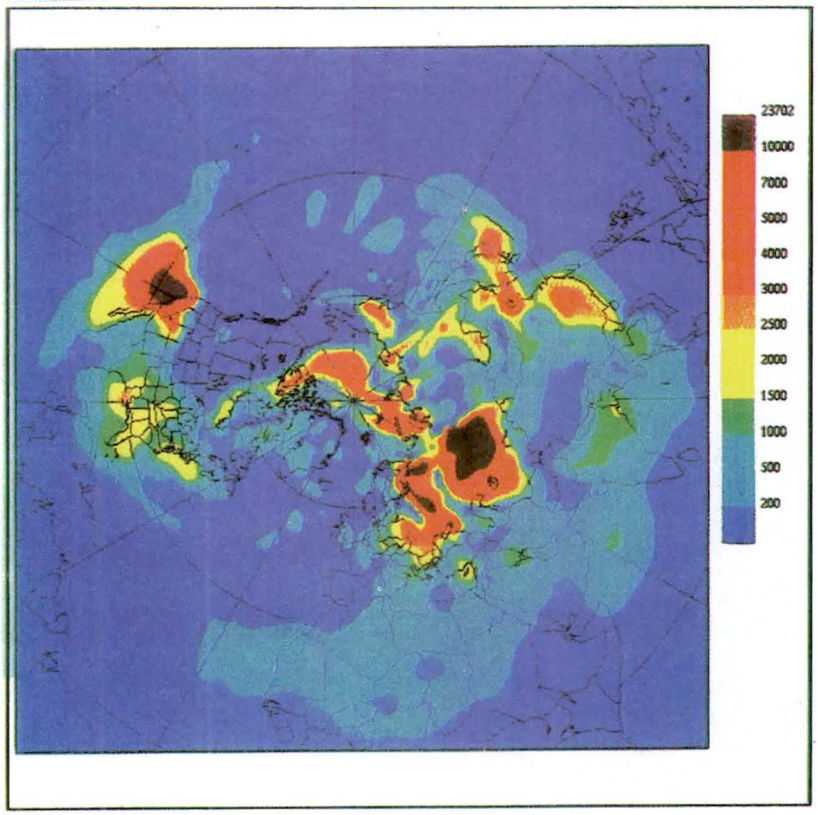


Figure 1. Annual cycle of sulfate aerosol in the surface air at a Canadian monitoring site "Alert" (82.3° N 62.2° W) in ng/m^3 (a) as observed and averaged for 1980-1990 and (b) as simulated for the year 1993



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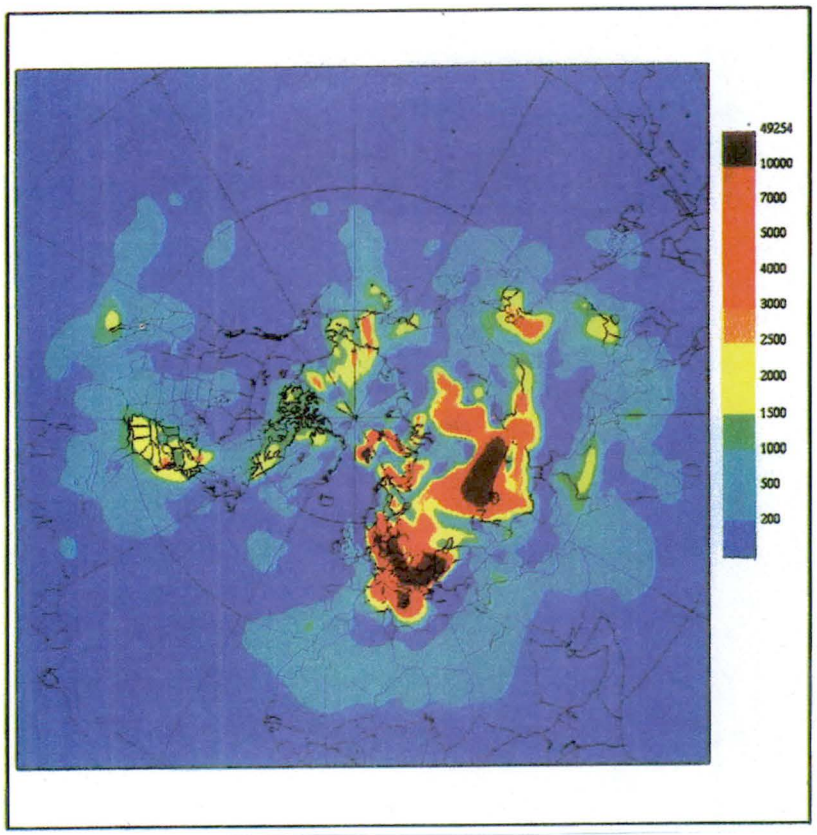


2b

Figure 2. Sulfate aerosol distribution in the surface air (ng/m^3) valid for (a) January 1, 1993, and (b) February 1, 1993

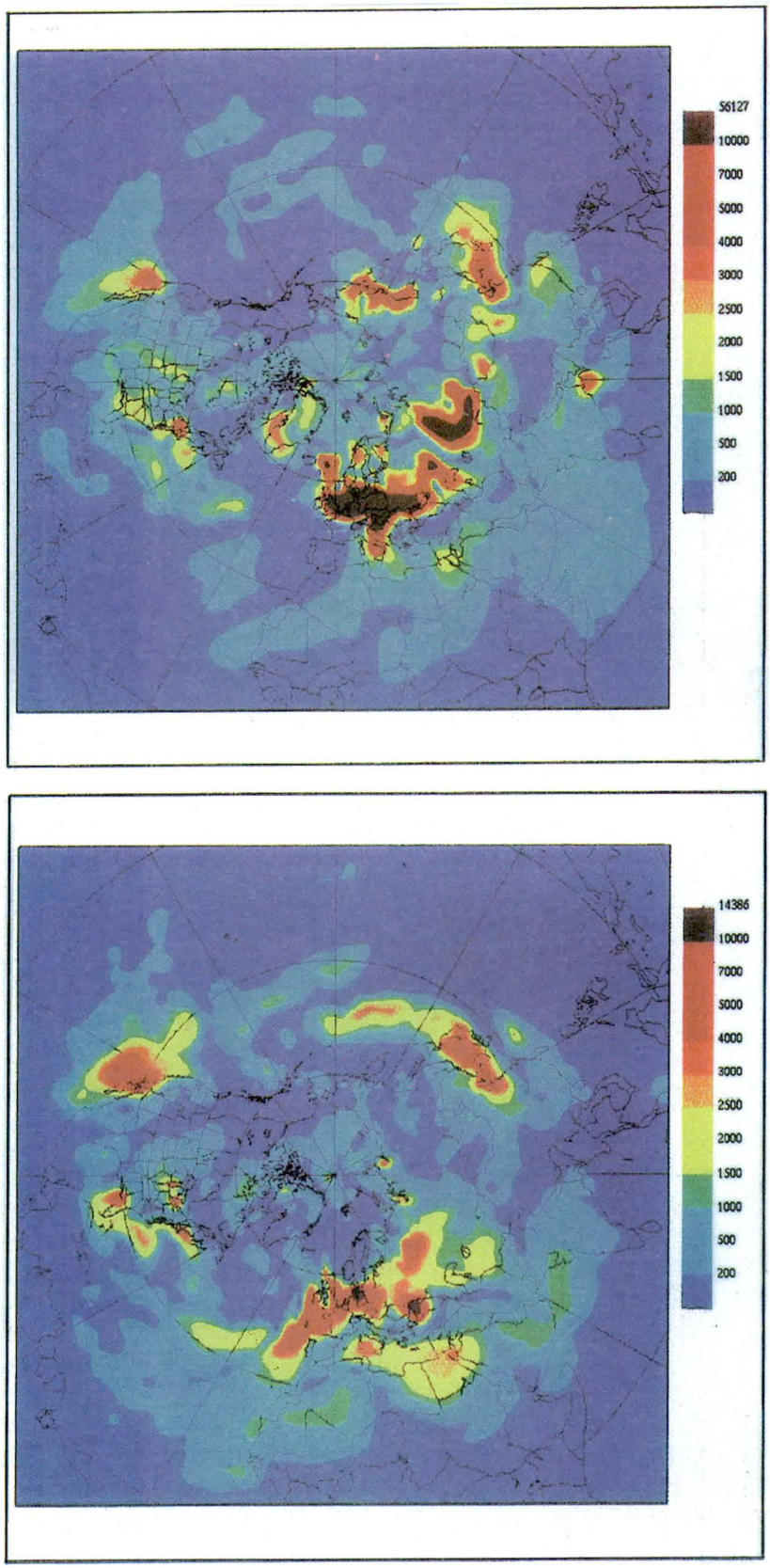
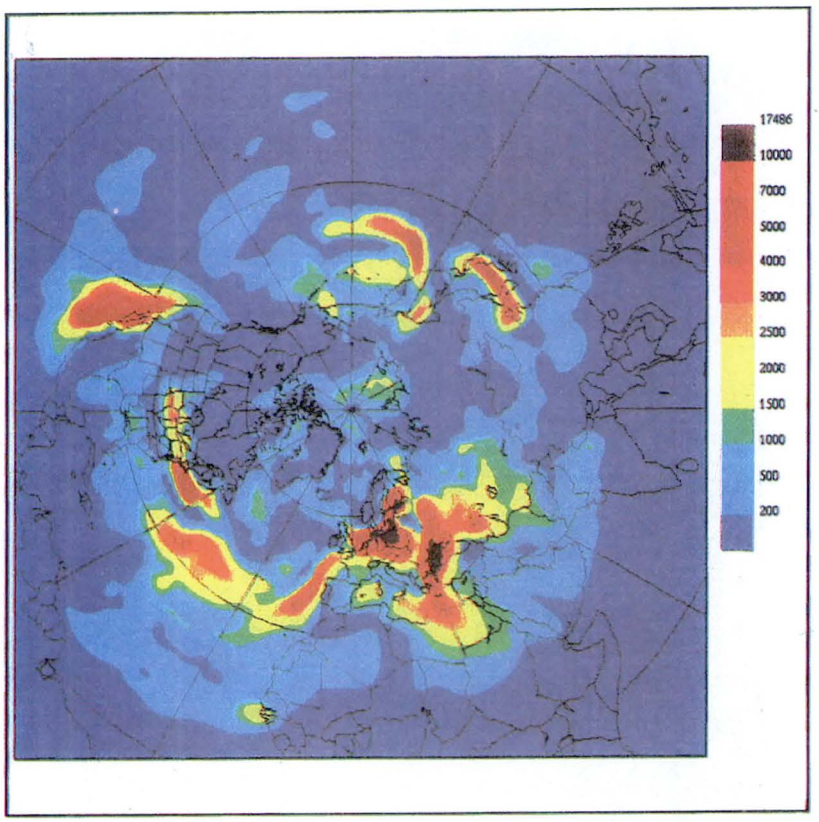


Figure 2. Sulfate aerosol distribution in the surface air (ng/m^3) valid for: (c) March 31, 1993, and (d) June 1, 1993



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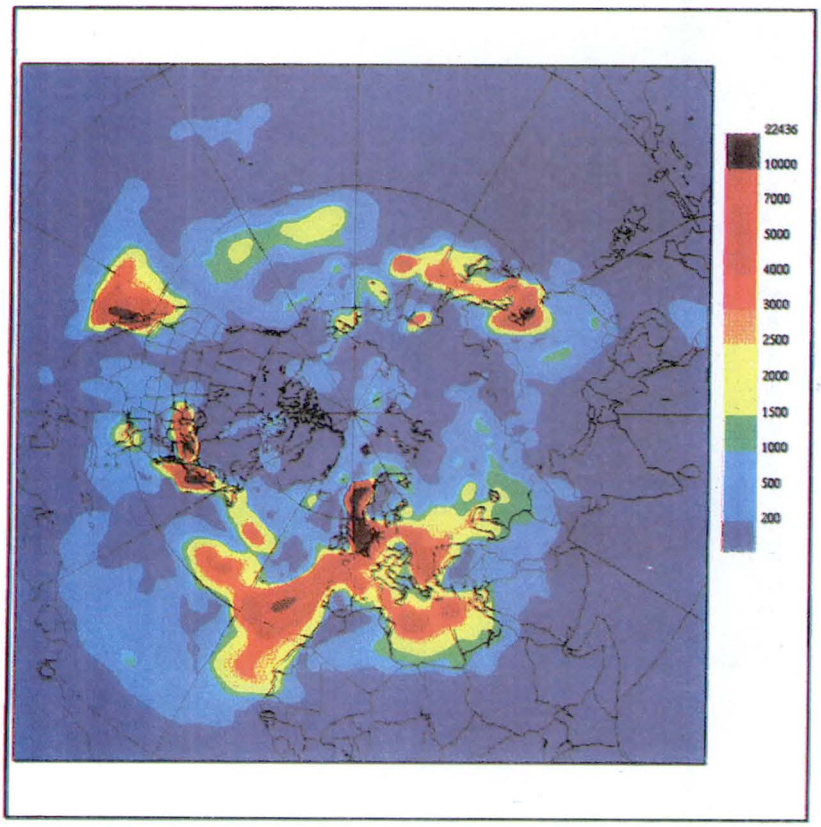

2f

Figure 2. Sulfate aerosol distribution in the surface air (ng/m^3) valid for: (e) July 1, 1993, and (f) August 1, 1993

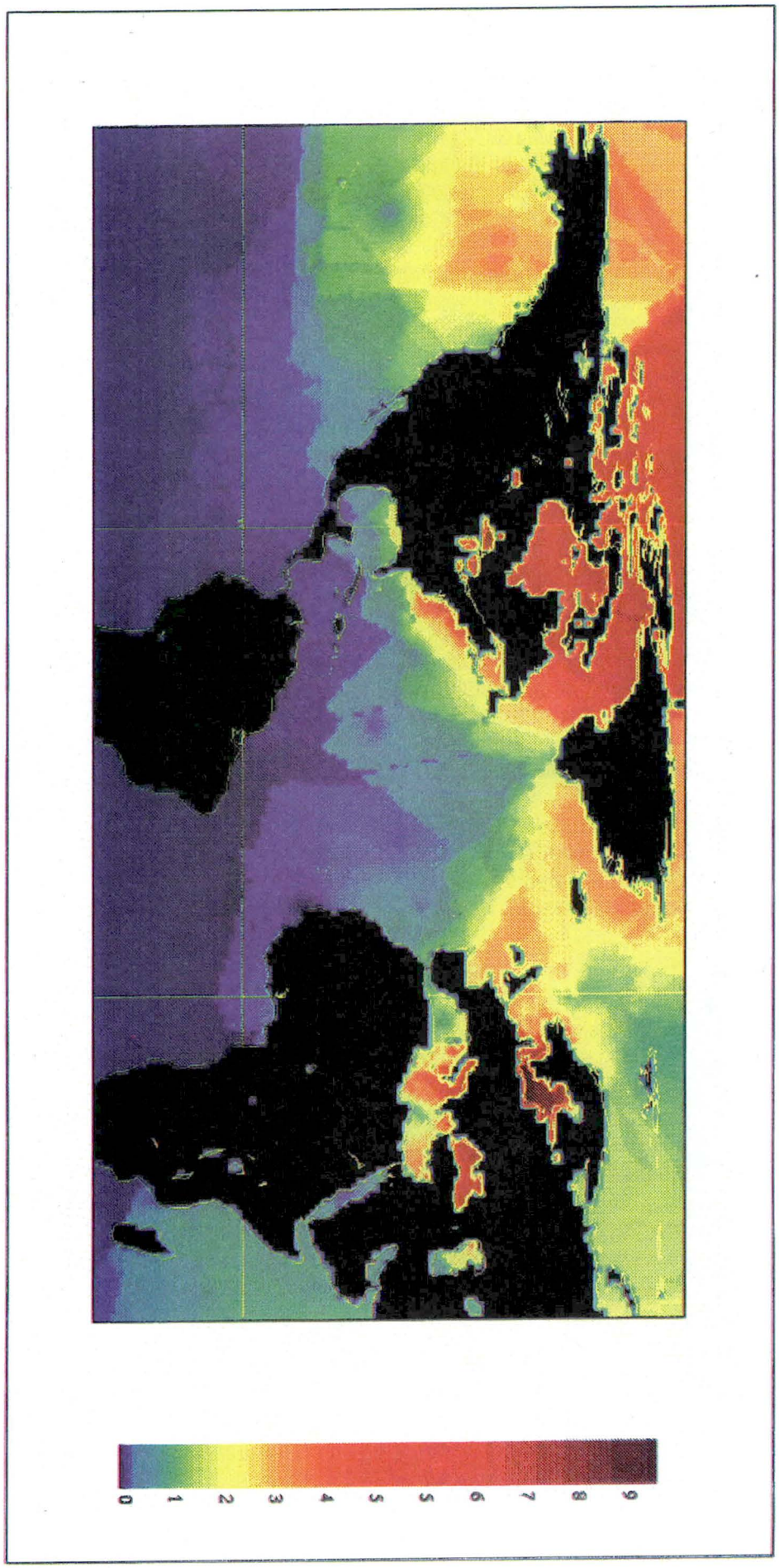

Figure 3. Global distribution of HCH concentrations in water of the World Ocean [n/L]

NORTHERN CONTAMINANTS AIR MONITORING: SEASONAL VARIATIONS OF SELECTED ORGANOCHLORINES AT ALERT NW.T. AND TAGISH YUKON

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

1. 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.

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 (Table 1). This research was supported by the Arctic Environmental Strategy Northern Contaminants Green Plan Program and the Department of External Affairs.

A hi-volume air sampler placed at: Alert, NWT (82.5° N, 62.3° W); Tagish, Yukon (60.3° N, 134.2° W); Cape Dorset, Baffin Island; and at the mouth of the Lena River on Dunay Island in Russia, was used to collect particulate and gaseous fractions of these airborne pollutants on filters and foam plugs. They were subsequently extracted in organic solvents and analysed at the Freshwater Institute for more than 80 organochlorines and for 20 PAHs by gas chromatographic techniques. The sampling schedule is shown in Table 1.

RESULTS

18 PAHs and 29 OCs plus many PCB congeners were measured in samples taken at Alert and Tagish. To date analyses are available to mid-1994 for these stations. Let us examine some of the seasonal variations of organochlorines from the point of view of solubility. This is represented by the Henry's law constant (H) of a constituent. Figure 1 shows several prominent organochlorines and PAHs ranked according to H.

Note that in order of greater to lesser solubility in water are the following compounds γ–HCH, endosulfan, α–HCH, dieldrin and chlordane. In the following series of observed seasonal variations of these compounds at Alert, there is a summer minimum in concentration corresponding to a summer maximum in precipitation (Figure 2). The depth of the summer minimum is roughly proportional to the substance's solubility in precipitation as indicated in Figure 1.

Seasonal variations observed at Tagish Yukon as indicated by results for HCH and endosulphan (Figure 3) do not show the summer dip in concentration. This is likely due to the strong influence of flow off the North Pacific Ocean over the Rocky Mountains into this site. In contrast, Alert sees air that has spent much time over the ice covered Arctic Ocean in an environment that has a strong summer maximum in precipitation.

The seasonal variation of PCBs at Alert is shown in Figure 4. PCBs are an industrial class of compounds previously used as hydraulic and transformer fluids. Their use has been largely discontinued, but dumping in the environment and their persistence make them an ever-present chemical group with about 209 congeners. The seasonal variation of total PCBs at Alert shows a peak from April to August. Most of the mass is in the gas phase but the particulate fraction is still important because it is more readily scavenged from the atmosphere than the gaseous fraction. The homologue sub-fractions of total PCBs vary differently seasonally. The di-, tri- and tetra-chlorinated PCBs peak in the winter while the penta-, hexa- and hepta- PCBs peak later in the summer.

The air data measured in this program is proving useful in explaining trends of HCHs in the Arctic (Bidleman *et al.* 1995), in the interpretation of snowpack and snowfall data, in linking atmospheric inputs to freshwater lake sediments (Muir *et al.*, this volume) and in verifying global chemical transport models(Pudykiewicz *et al.*, this volume).

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Table 1. The sampling schedule for the Canadian Northern Contaminants Monitoring Network.

Site	1992	1993	1994	1995	1996	1997
Alert	<test>I<———	———	———	———	———>I<———	———>I
Tagish	I<———	———	———	———>I		
Dunay I.		I<———	———	———>I		
C. Dorset			I<———	———	———>I<—>I	
W. Russia					I<———	———...

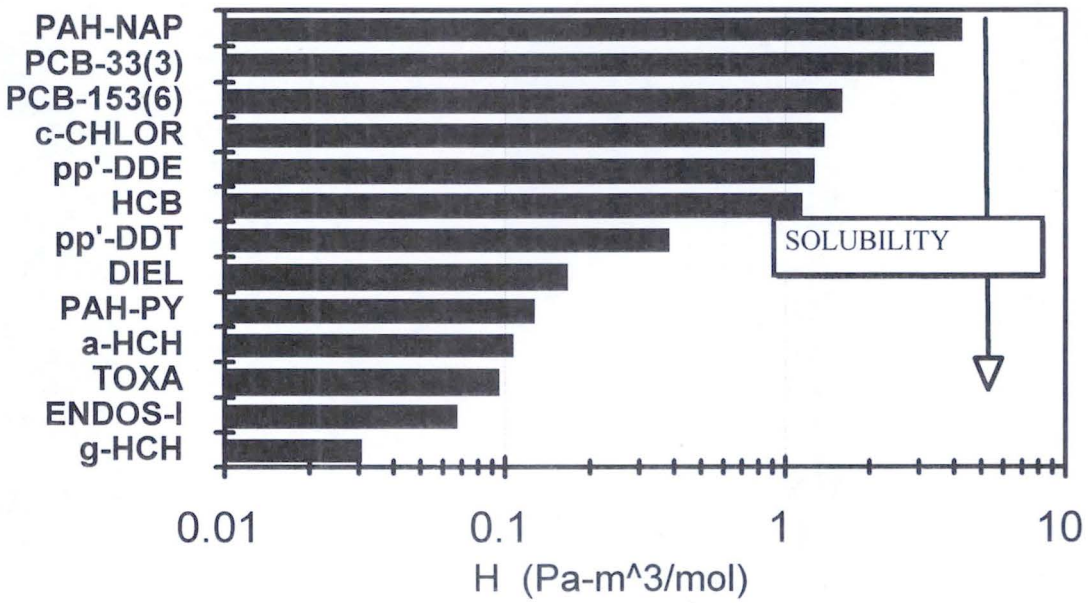

Figure 1. Henry's law constant (H) of various organochlorines and PAHs measured in Arctic air

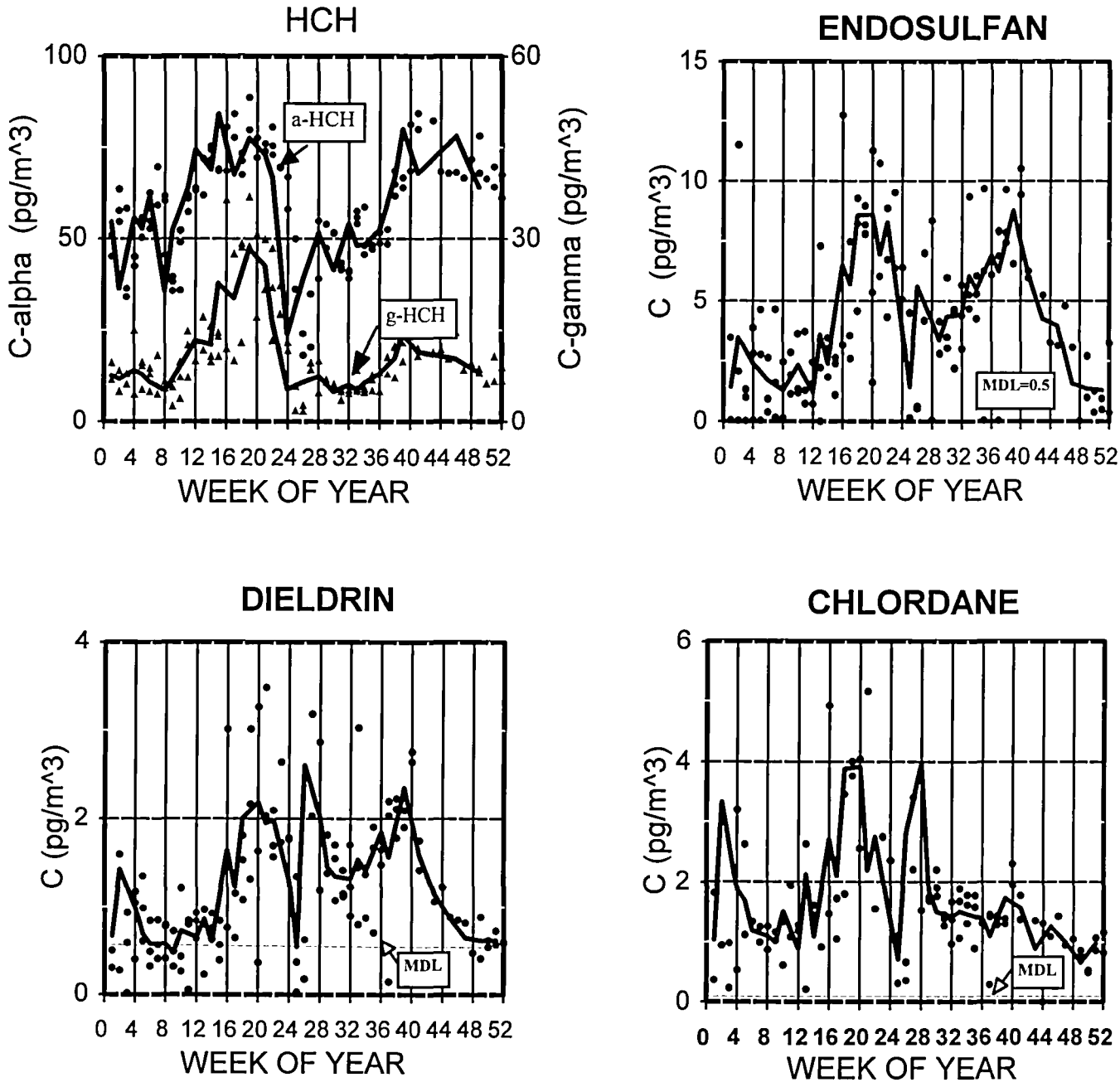

Figure 2. Seasonal variation of the weekly mean atmospheric concentration (C) of selected organochlorines at Alert based on data from Jan. 1992 to Aug. 1994. Note the dip in concentration during the summer months whose maximum corresponds roughly to the relative solubility of these compounds. The blue lines represent running means. Due to plotting quirks in the spreadsheet program, they lag the actual data by about 4 points

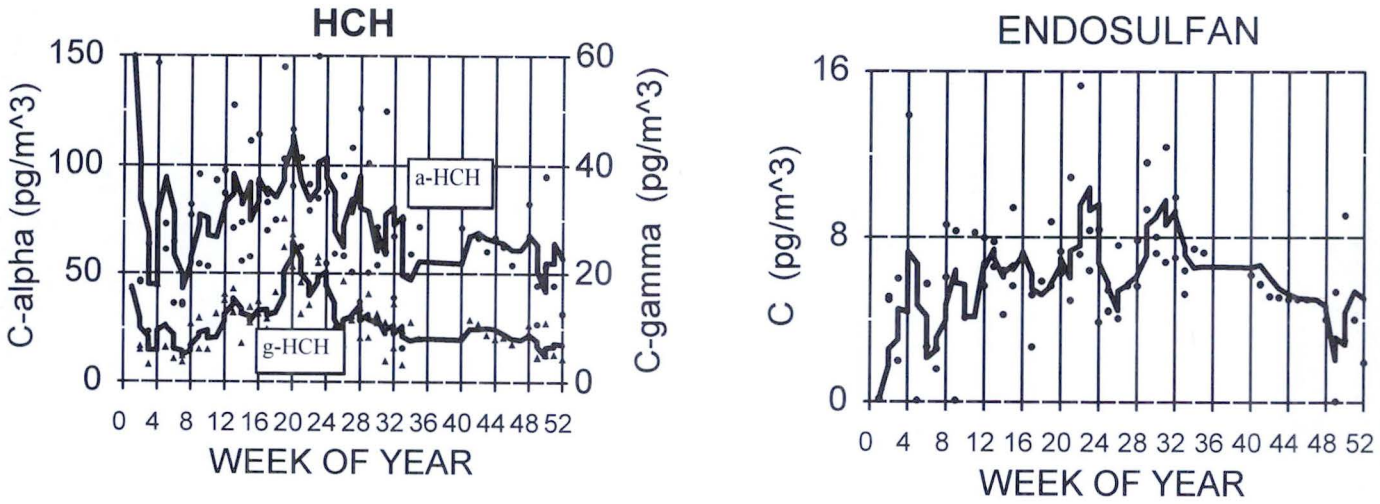

Figure 3. The seasonal variation of the weekly mean atmospheric concentration (C) of HCH and endosulfan at Tagish Yukon

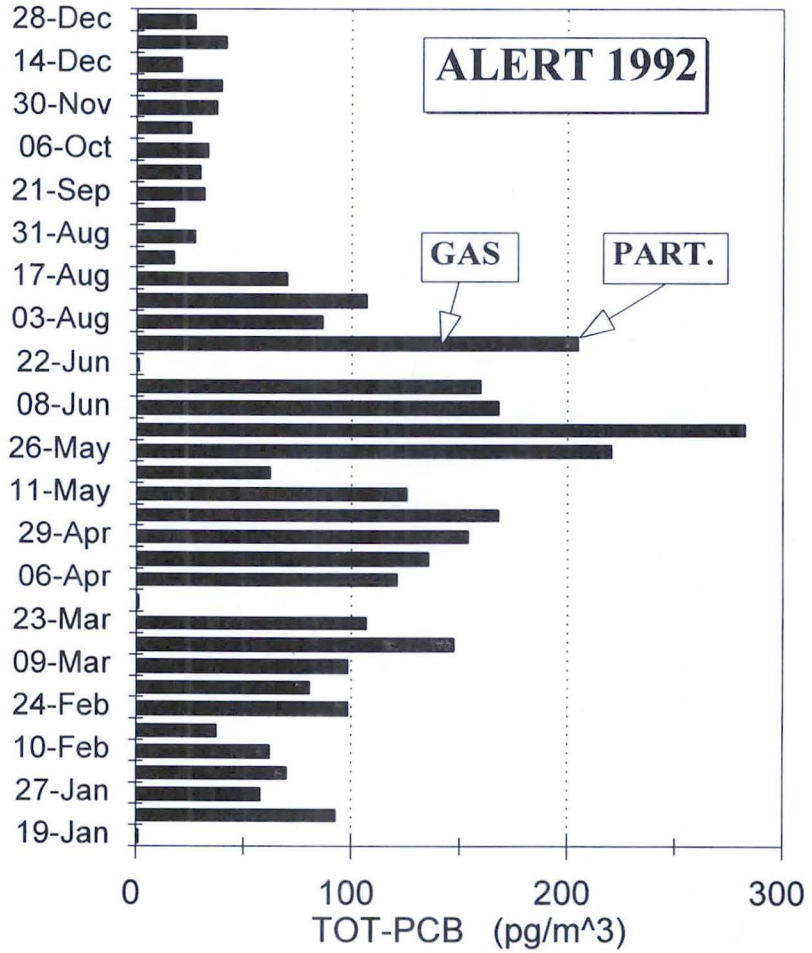

Figure 4. The seasonal variation of total PCBs at Alert in 1992 (Stern *et al.* 1995)

ATMOSPHERIC MERCURY MEASUREMENTS IN THE CANADIAN ARCTIC

Project Leader: W.H. Schroeder, Atmospheric Environment Service, Environment Canada

Project Team: A. Tham, T. Sandilands (Co-op student), D. Schneeberger , Tekran Inc.

OJBECTIVE

1. To assess the suitability of a new Canadian instrument—Tekran Mercury Vapour Analyzer—for use in the Arctic environment.

DESCRIPTION

The instrument assessment was performed in three distinct phases:

Phase I: Laboratory-based testing and evaluation (under controlled conditions of operation);
Phase II: Field trial at a rural/remote location (inter-comparison in North-Central Wisconsin with the traditional manual sampling and analytical methods for atmospheric mercury measurements);

Phase III: Testing and evaluation under field conditions, in the Canadian Arctic (at Alert, NWT)

RESULTS

Phase I

The Tekran Inc. (Model 2537A) instrument, an automated analyzer capable of high temporal resolution atmospheric mercury measurements (updating total gaseous mercury, TGM, concentration data as often as every five minutes), was subjected to extensive testing and evaluation with respect to its suitability, ruggedness and reliability for making such measurements in the Canadian Arctic in the future. This assessment included a variety of diagnostic procedures, exploratory tests, and carefully designed QA/QC experiments under controlled (laboratory) conditions, with both indoor and ambient (outdoor) air, at our Downsview laboratory.

Figures 1a and 1b display total gaseous mercury (TGM) concentrations for outdoor air in Downsview as measured on two weekdays (Tuesday and Thursday) during January 1994. The peaks, which are absent on the weekend (Figures 1c and 1d), coincide with rush-hour traffic. The results of a side-by-side laboratory-based inter-comparison of two such analyzers sampling outdoor air in Toronto is shown in Figure 2. It is evident that the two instruments track each other quite well and that concentration differences are small.

The accuracy of instrument readings was checked against known concentrations of mercury vapour in air (standards), which were introduced into the injection port of the instrument with a gas-tight syringe (Table 1). Potential losses of mercury vapour in the Teflon® sample line bringing ambient air to the instrument were found to be negligibly small (Table 2).

Phase II

Over a period of six days during September 1994, at a remote continental site in North-Central Wisconsin, US, the automated Tekran mercury vapour analyzer was compared with the traditional manual (sampling and analysis) methods for determining TGM in ambient air, which have previously been employed by other researchers (W.F. Fitzgerald *et al.*) at this site. Eighteen consecutive, side-by-side runs of the two methods were completed. The data from this study are given in Figure 3. After removal of a sampling artifact (sample line adsorption/description of mercury vapour), which clearly biased the first seven runs, the agreement between the manual and the instrumental methods was "good to excellent" (using the criterion of overlapping error bars). A paper on this inter-laboratory methods intercomparison was accepted for presentation at the 10th International Conference on Heavy Metals in the Environment (Hamburg, Germany, September 1995).

Phase III

This (final) phase of testing and evaluating the Tekran instrument was completed at Alert, NWT, during January of 1995. Figure 4 shows the experimental set-up used for "spike recovery checks," one of several QA/QC tests that were carried out at Alert before starting ambient air measurements with the Tekran analyzers. The median TGM concentrations determined at this site over a period of 10 days were independent of wind direction (Figure 5), as might be expected for a long-lived pollutant at a background site under certain meteorological conditions. The meteorological conditions prevailing during that time

period (January 9–19) are found in Figure 6. The observed concentrations of total gaseous mercury appear to be correlated with ambient air temperature (Figure 7). A statistical summary of the TGM air concentrations measured at Alert during the instrument evaluation period in January 1995 appears in Table 3.

CONCLUSIONS

The results of the aforementioned battery of tests (conducted in three phases) provide the basis for an objective evaluation concerning the usefulness and reliability of this new atmospheric mercury monitor for possible deployment in the Canadian North (and elsewhere in the Polar regions).

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Schroeder, W.H., M. Shoeib, L.A. Barrie, R. Ebinghaus, and K. Timoschenko. 1995. Atmospheric mercury measurements in the northern hemisphere from 56° to 82.5° N latitude. *Water, Air, Soil Pollut.* (in press).

Table 1. Comparison of Tekran #007 readings with AES calibration unit.

	Instrument Readings		
Date	**Time**	**ng/m³**	**Comments**
94-08-30	14:00h	12.51	injected at the injection port
94-08-30	14:05h	12.65	" "
94-08-30	14:10h	12.46	" "
94-08-30	14:15h	12.66	" "
94-08-30	14:20h	12.45	" "
94-08-30	14:25h	12.62	injected at the injection port

Average: 12.56 ng/m³
Actual: 12.61 ng/m³
% Diff: –0.4 lower than actual concentration

Conclusion: The instrument readings are in excellent agreement with the calibration spikes manually injected through the injection port.

Table 2. Evaluation of sample line losses with a new (3 m long) Teflon® line.

	Instrument Readings		
Date	**Time**	**ng/m³**	**Comments**
94-08-30	15:20h	12.54	injected at front of the sample line
94-08-30	15:25h	12.71	" "
94-08-30	15:30h	12.53	" "
94-08-30	15:35h	12.61	" "
94-08-30	15:40h	12.50	" "
94-08-30	15:45h	12.63	injected at front of the sample line

Average: 12.59 ng/m³
Actual: 12.61 ng/m³
% Diff: –0.2 lower than actual concentration

Conclusion: There is no significant loss of vapour-phase mercury in the Teflon® sample line (3 m long) at normal room termperatures.

Table 3. Statistics summary for TGM concentration measurements at Alert (from January 9–19, 1995).

Mean Value	1.54 ng/m³
Standard Deviation	0.13 ng/m³
Median Value	1.54 ng/m³
Minimum Value	1.14 ng/m³
Maximum Value	1.95 ng/m³
Number of Observations	2385

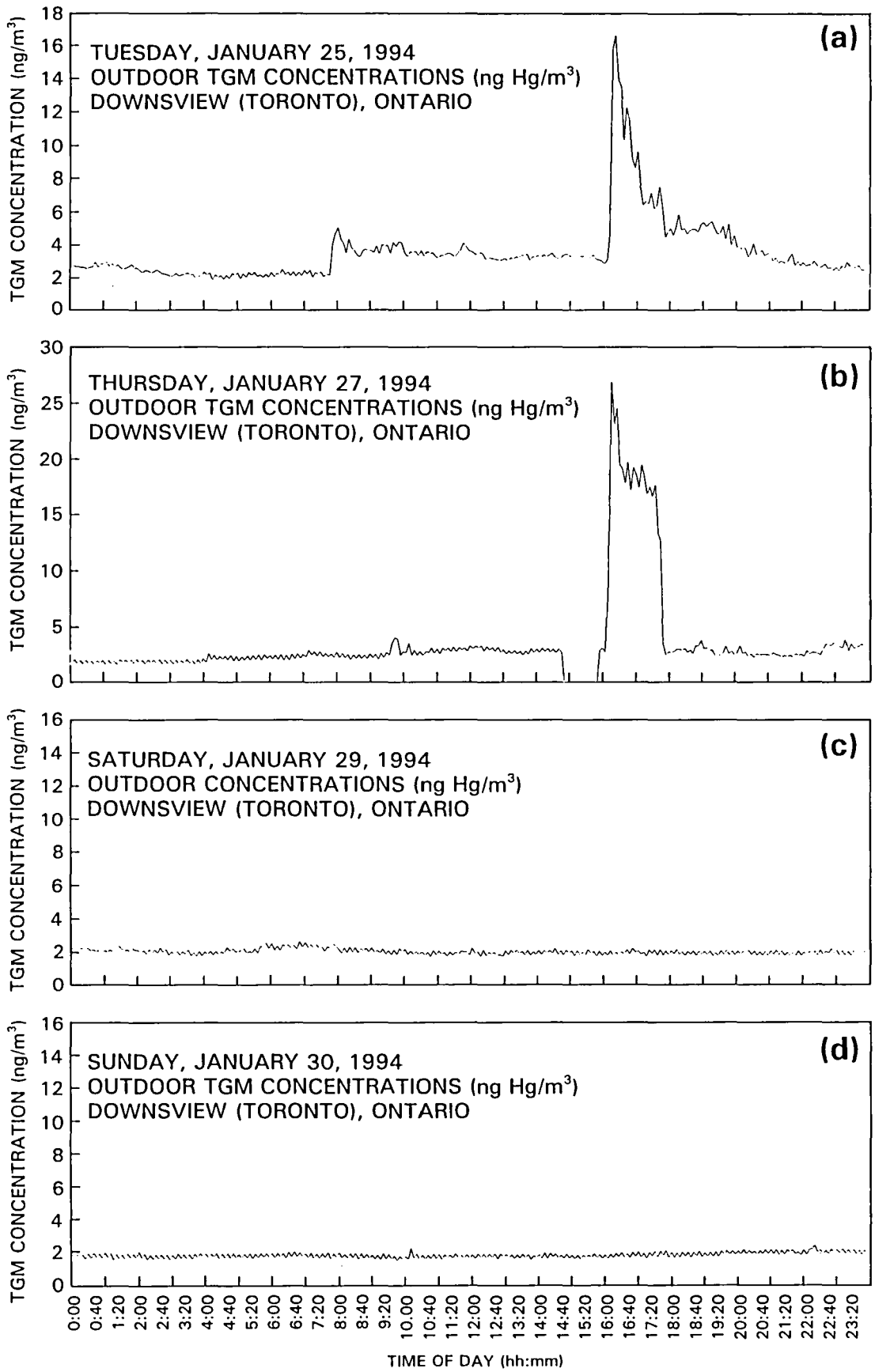

Figure 1. Outdoor total gaseous mercury (TGM) concentrations in Downsview, Ontario, determined with a Tekran (Model 2537A) Ambient Air Mercury Vapour Analyzer: a) Tuesday, January 25, 1994; b) Thursday, January 27, 1994; c) Saturday, January 29, 1994; d) Sunday, January 30, 1994

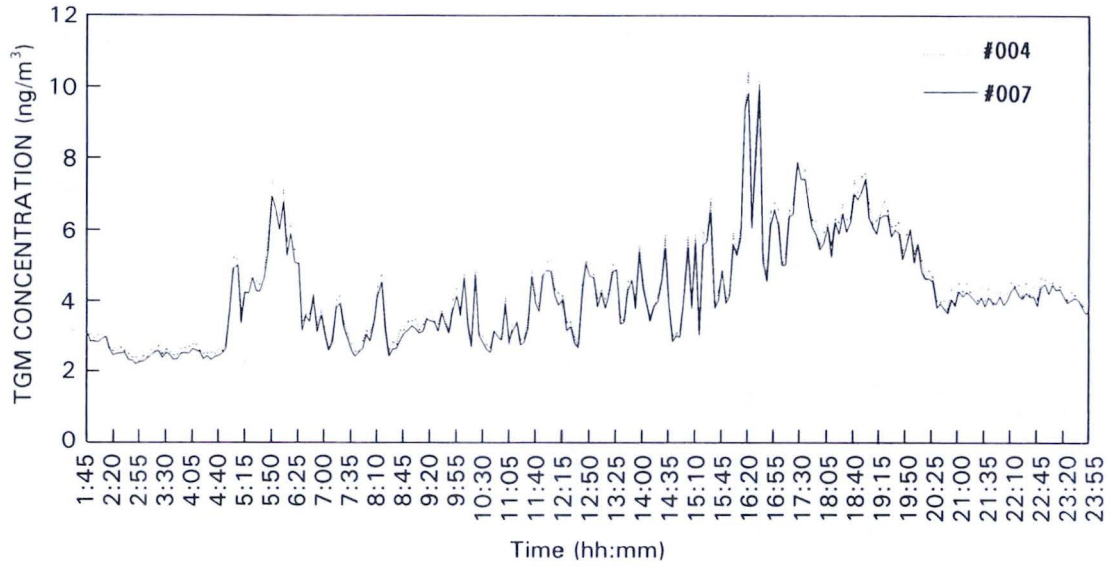

Figure 2. Side-by-side laboratory intercomparison of two Tekran (Model 2537A) Ambient Air Mercury Vapour Analyzers (Toronto: August 6, 1994)

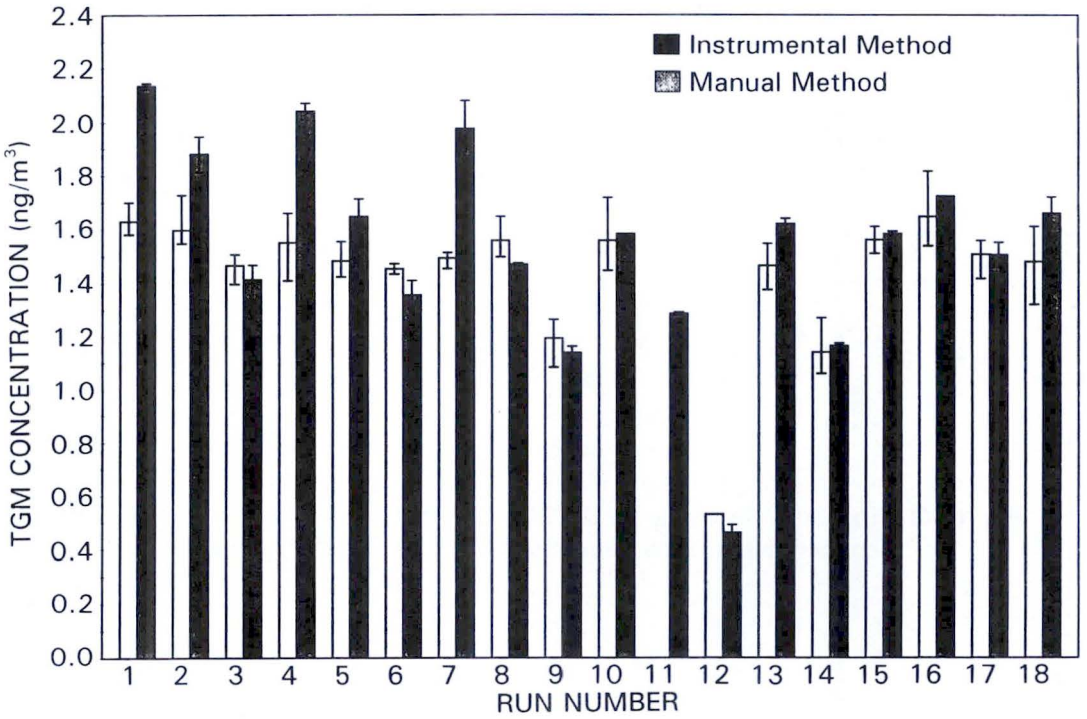

Figure 3. Results from Wisconsin Field Intercomparison: Average values of total gaseous mercury (TGM) concentrations in ambient air from two Tekran Instruments and a manual sampling and analysis method operated at a remote continental site in North-Central Wisconsin

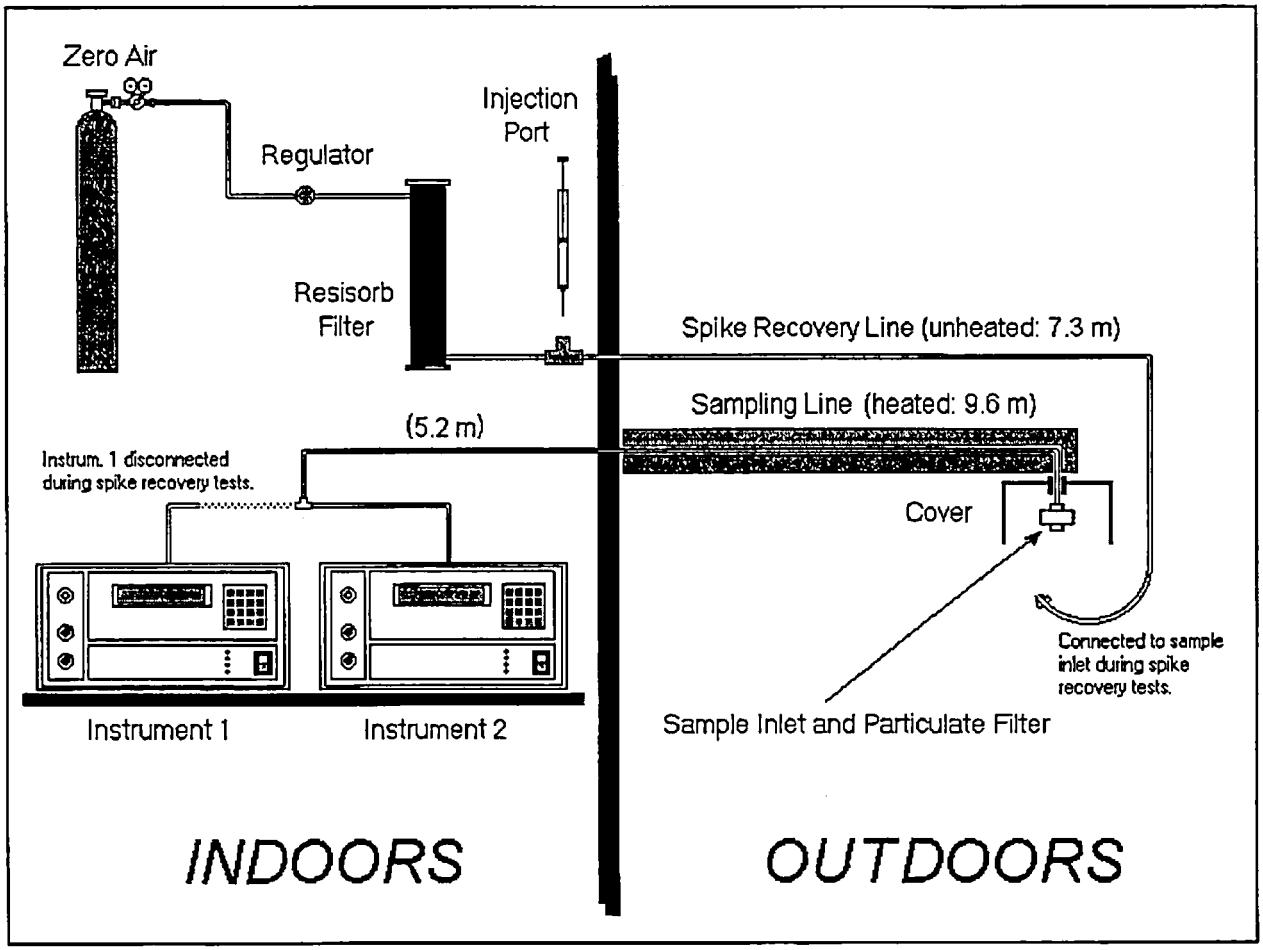

Figure 4. Experimental set-up for QA/QC tests and total gaseous mercury (TGM) concentration measurements at Alert, NWT during January 1995

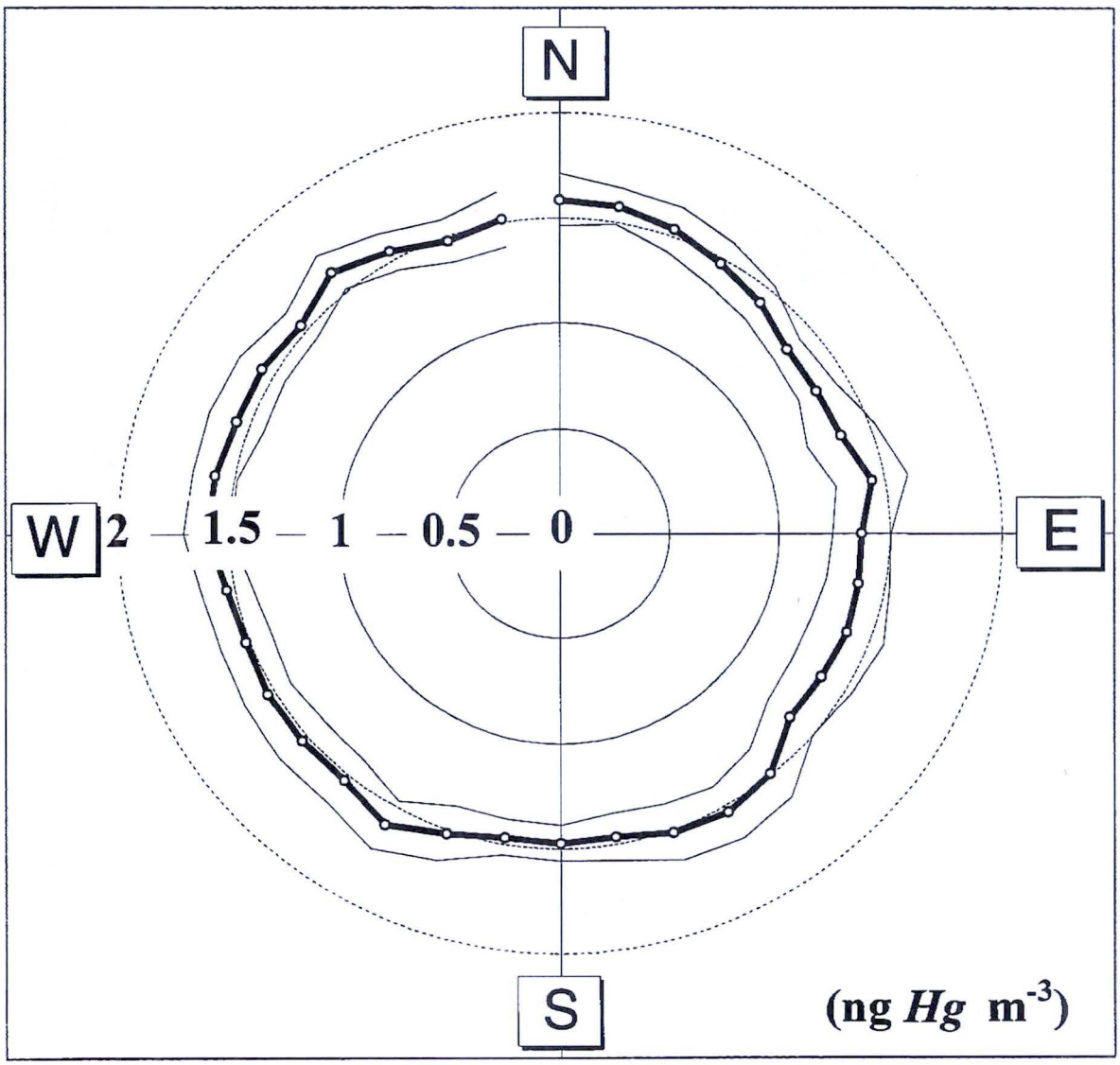

Figure 5. Values of median total gaseous mercury (TGM) concentrations found in 10° wind direction bins (heavy line) between January 9–19, 1995 (The two solid lines represent one standard deviation on each side of the median values)

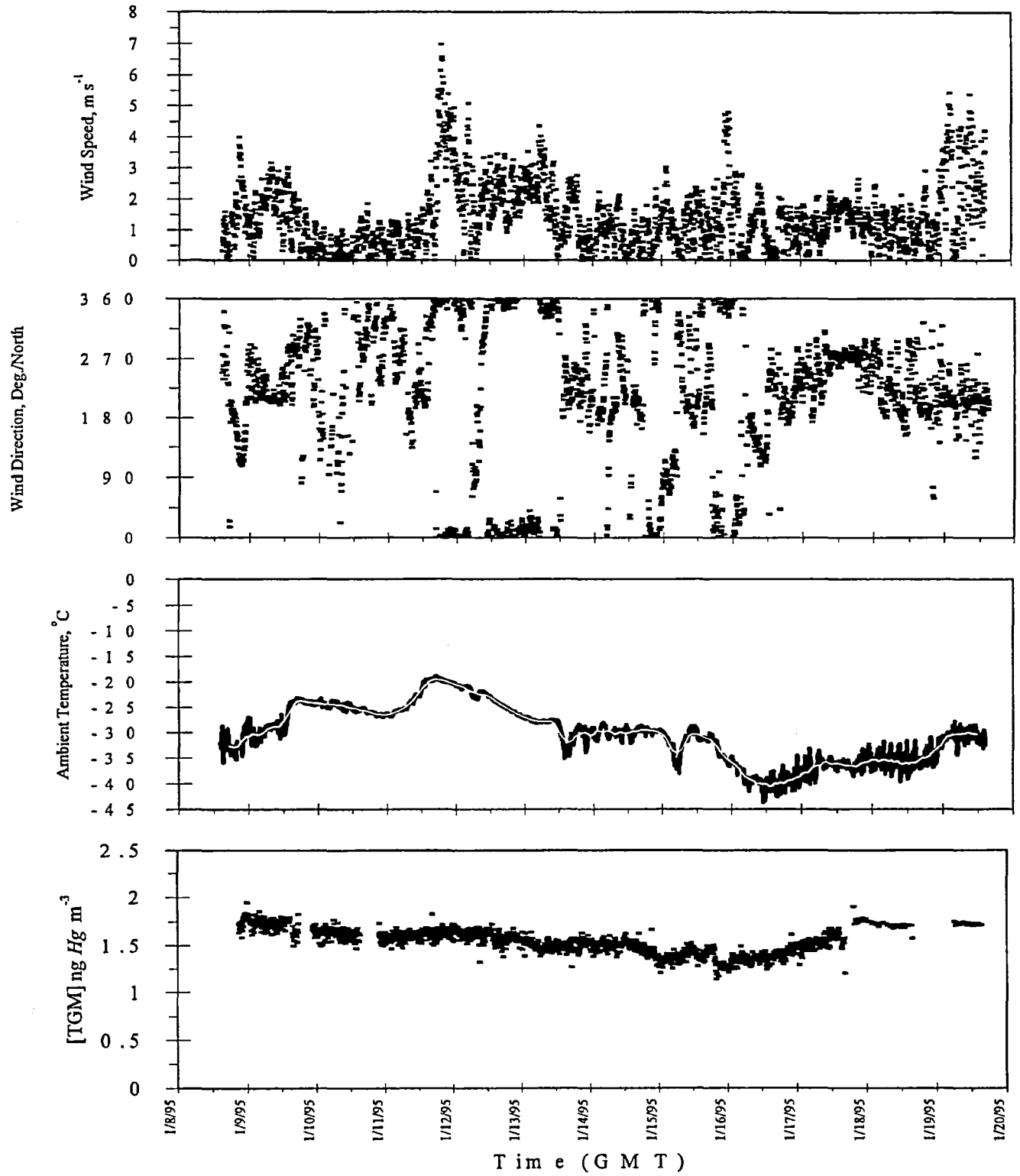

Figure 6. Time series of: wind speed, wind direction, ambient temperature and ambient air TGM concentrations measured at Alert, NWT between January 9–19, 1995

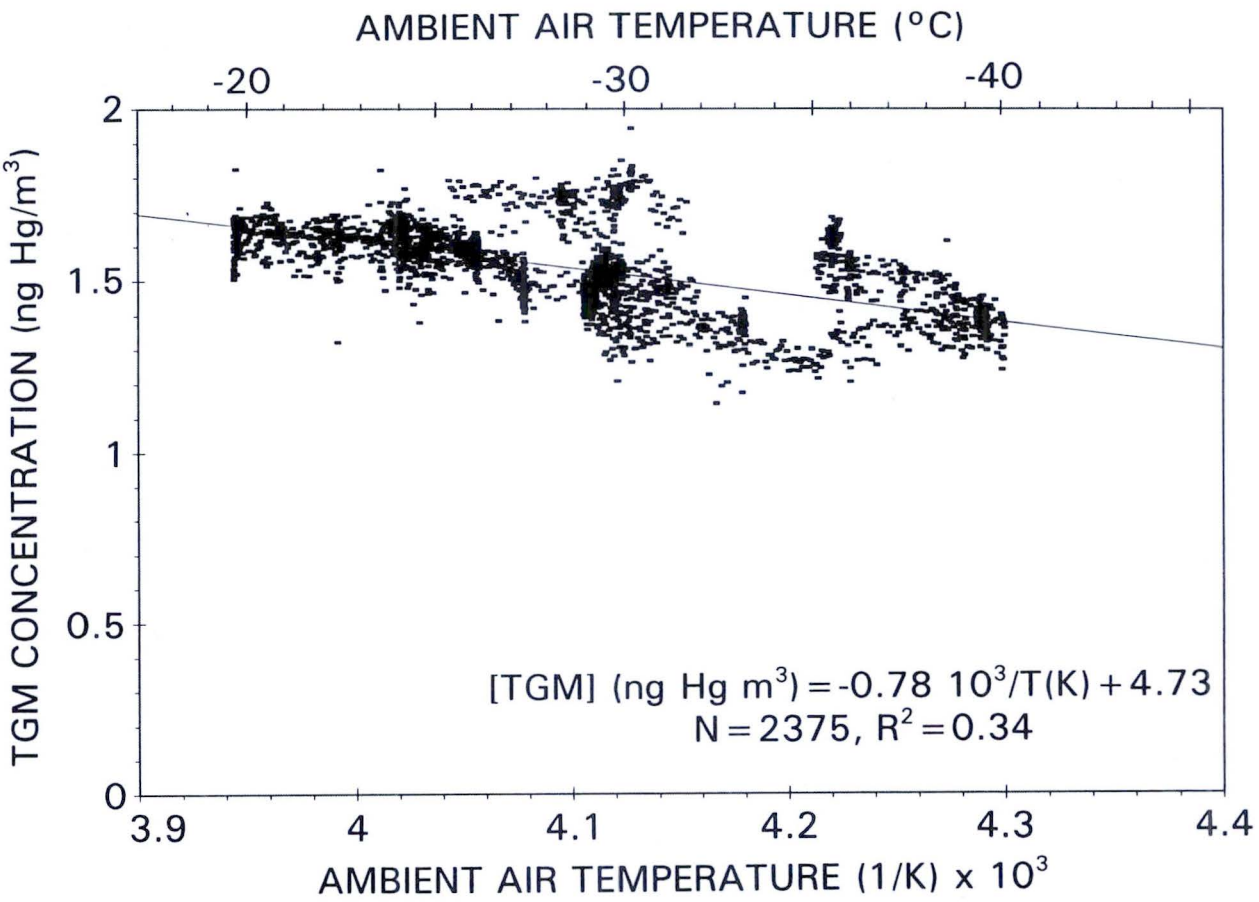

Figure 7. Linear correlation plot of TGM concentrations and ambient air temperatures measured at Alert, NWT between January 9–19, 1995

ATMOSPHERIC TRANSPORT AND CYCLING OF TOXAPHENE AND OTHER ORGANOCHLORINES IN THE ARCTIC

Project Leader: T.F. Bidleman, Atmospheric Environment Service, Environment Canada

Project Team: L.M. Jantunen, R.L. Falconer, L.A. Barrie, J. Pudykiewicz, D.J. Gregor, R. Semkin, C. Teixeira, W.M.J. Strachan, D. Burniston, B.T Hargrave, R. Macdonald, M.D. Walla

OBJECTIVES

1. To determine concentrations and compare gas exchange rates of chlorobornanes (CHBs, e.g. toxaphene) and hexachlorocyclohexanes (HCHs) in arctic waters;

2. To determine the physicochemical properties of CHBs that affect their atmospheric transport and deposition;

3. To characterize the changes in the CHB profile that accompany transfer from air to water to the lower food chain;

4. To compile and review literature data on HCHs in environmental media for use in a global transport model.

DESCRIPTION

CHBs are major organochlorine (OC) pesticide residues in fish and marine mammals in the Canadian Arctic (Kidd *et al.* 1995, Norstrom and Muir 1994) and have been found in milk from women in arctic Québec (Stern *et al.* 1992). Yet CHBs remain the most poorly characterized OCs with respect to levels in polar air and water, physicochemical properties and transformations in the environment. HCHs are the most abundant OCs in arctic air and water (Bidleman *et al.* 1995a). More information is available on environmental concentrations and properties of HCHs than for any other OC, making them the best candidates for investigating transport and exchange processes and for global-scale modelling.

Based on measurements made in the 1980s, air-sea gas exchange during summer months was estimated to account for over 90% atmospheric loadings of OCs to the Arctic Ocean (Bidleman and McConnell 1995, Cotham and Bidleman 1991). Once in the ocean, OCs are subject to a number of removal processes: revolatilization, sedimentation, hydrolysis and microbial attack. Substantial changes in the congener distribution of CHBs take place during transfer through the food chain. Chromatographic patterns of highly metabolized CHBs in burbot liver, narwhal blubber and human milk are dominated by only two compounds: 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) (Bidleman *et al.* 1993, Stern *et al.* 1992). Less drastic profile changes are evident in CHB residues from ringed seal blubber and marine amphipods (Hargrave *et al.* 1993).

This investigation is being carried out to determine the current situation of air-sea gas exchange for CHBs, HCHs and other OCs and to characterize the CHB profiles in air, water and biota representing the lower food chain (plankton, amphipods). Studies at Resolute Bay in 1992 and the Bering-Chukchi seas in 1993 have been discussed in three papers (Bidleman *et al.* 1995a, Falconer *et al.* 1995ab, Jantunen and Bidleman 1995) and in last year's report to Indian and Northern Affairs Canada (INAC) (Bidleman 1995). Our sampling and analytical methods and quality control information are also described in these publications.

ACTIVITIES IN 1994/95

We have continued to add published information on HCH concentrations in air and water to a Lotus spreadsheet database. These data are being used by J. Pudykiewicz in a global-scale model of HCH transport. Long-term trends of HCHs in arctic air and water have been reviewed and used to interpret observed changes in the air-sea gas exchange direction (Bidleman *et al.* 1995b).

In July-September, 1993 we collected air and water samples in the Bering-Chukchi (B-C) seas from the Russian ship OKEAH ("Ocean"). The gas exchange

results for α–HCH which show reversal in the air-sea flux from deposition in the 1980s to volatilization in 1993 have been published by Jantunen and Bidleman (1995). On this cruise W.M.J. Strachan (National Water Research Institute) also collected 1000-L surface water samples and separated particulate matter from the dissolved phase with a continuous flow centrifuge. Approximately 80 L of the particle-free water was extracted on board ship with dichloromethane in a Goulden apparatus. In 1994/95 the dissolved fraction of combined water samples was analysed for CHBs, dieldrin, endosulfan, chlordanes and nonachlors by GC-NIMS in our laboratory. Combined air samples were also analysed for these OCs to obtain atmospheric concentrations for gas exchange calculations.

Air and water samples were collected for CHBs, HCHs, and other OCs on the 1994 Arctic Ocean Sections (AOS) cruise from Nome to Halifax, across the North Pole. The same collection and analytical methods were used as for the Resolute Bay and BERPAC-93 studies (Bidleman *et al.* 1995a, Falconer *et al.* 1995a, Jantunen and Bidleman 1995). Approximately two-thirds of the air samples have been processed for HCHs. Analysis of the remaining samples for HCHs and other OCs will be done 1994/95.

Preliminary estimates of liquid-phase vapor pressures were made for nine CHB and chlorocamphene congeners, supplied by D. Hainzl and H. Parlar, University of Kassel. These measurements were made by a capillary GC technique, using *p,p'*-DDT as a vapor pressure standard (Hinckley *et al.* 1990).

We participated in two INAC intercalibration exercises, one for co-planar PCBs and OC pesticides in standard solutions and the other for OC pesticides in seal blubber.

RESULTS AND DISCUSSION

Trends of HCHs in Polar Air

Concentrations of α–HCH in arctic air have declined over the last 14 years with a time for 50% decrease of 4 y in summer-fall and 6 y in winter-spring. The trend in γ–HCH is less pronounced, but a decrease is also suggested from measurements in the Canadian Arctic and the B-C seas. A preliminary assessment of these trends appeared in the 1994/95 INAC report (Bidleman 1995) and the full story was recently published (Bidleman *et al.* 1995b). Reasons for the drop in α–HCH levels are unclear, but we have information that India embarked on a program in 1990 to phase out technical HCH. India was one of the largest users of technical HCH, accounting for ~25,000 tonnes annually. Reduction in α–HCH concentrations in arctic air has led to volatilization from surface water during the summertime (Bidleman *et al.* 1995b, Jantunen and Bidleman, 1995).

Bering-Chukchi Seas

Summaries of OCs in B-C air and surface water are given in Tables 1 and 2. Except for HCHs very few measurements of OCs have been made in northern waters. A comparison with available data (Table 2) indicates that concentrations of CHBs, chlordanes + nonachlors, and dieldrin are lower in the B-C seas than at Resolute Bay or the Ice Island. Endosulfan I (α–endosulfan) was found in all air and water samples at average concentrations of 2.7 pg/m^3 and 2.0 pg/L. Endosulfan is one of the few OC pesticides still permitted for use in Canada and the US (Bidleman *et al.* 1995a, Muir and Grift 1995). It is considered to be a degradable pesticide, with reported half-lives of <14 d in fresh water (Muir and Grift 1995) and 4.9 d in seawater at 20°C (Cotham and Bidleman 1989). The presence of endosulfan in the B-C seas is compelling evidence that chemicals classified as "low persistence" in temperate climates are more recalcitrant in the Arctic.

Chromatographic profiles of CHBs in air and water of the B-C seas (Figure 1) are similar to each other and also to profiles found at Resolute Bay in 1992 (Bidleman *et al.* 1995a). Pure standards of CHB congeners T2 and T12 were used to establish their retention times in chromatograms of air and water samples. However other octa- and nonachlorobornanes coelute with T2 and T12 on the DB-5 column used for analysis, hence it is uncertain that the corresponding peaks in B-C samples are single compounds.

Water-air fugacity ratios for OCs were calculated from:

$$\text{Fugacity Ratio} = C_W H / C_a RT \quad (1)$$

where C_W and C_a are the dissolved and gaseous concentrations in water and air, H is the Henry's law constant (Pa m^3/mol) at the water temperature, T is the air temperature (K) and R = 8.31 Pa m^3/deg mol. Henry's law constants for HCHs as a function of temperature were from Kucklick *et al.* (1991). For the other OCs, selected constants at 20-25° were extrapolated to temperatures of the surface water (Cotham and Bidleman 1991). Results for HCHs were reported by Jantunen and Bidleman (1995). Fugacity gradients indicate that the B-C seas are outgassing α–HCH in late summer and that γ–HCH in surface water has shifted from undersaturation in 1988 to near-equilibrium with atmospheric concentrations in 1993. As discussed

above, these changes appear to be a consequence of declining atmospheric levels over the last 14 years and particularly between 1990-93 (Bidleman *et al.* 1995b).

Results for other OCs (Figure 2) show a decrease in the fugacity ratio from south to north. Dieldrin and *trans*-chlordane are oversaturated in the Bering Sea, but close to equilibrium or slightly undersaturated in the Chukchi. The difference in behavior of the two chlordane isomers (Figure 1) was also seen at Resolute Bay (Bidleman *et al.* 1995a) and may result from depletion of *trans*-chlordane relative to *cis*-chlordane in the arctic atmosphere during summer. CHBs are undersaturated in all regions, implying air-to-sea transfer. It is important to recognize that (except for HCHs) these conclusions are preliminary because of inadequate knowledge of the Henry's law constants.

The enantiomeric composition of α–HCH in water from the B-C seas was determined using chiral-phase GC with detection by negative ion mass spectrometry. Surface water is depleted about 10% in (-)α–HCH. This is opposite of the trend in Resolute Bay and Amituk Lake, which show a 7-30% loss in (+)α–HCH (Falconer *et al.* 1995ab). Reasons for this are not known, but other systems show preference for either the (-) or (+) enantiomer, depending on the enzymatic pathway (Möller *et al.* 1994).

Arctic Ocean Sections Cruise

Preliminary results for about two-thirds of the air samples (Table 1) show low values for α–HCH (66 pg/m^3), in line with the downward trend seen for post-1990 measurements at other arctic locations (Bidleman *et al.* 1995b). The cruise mean for γ–HCH (16 pg/m^3) is also typical of recent values from the Canadian Arctic and B-C seas (Table 1). Analysis of the remaining AOS-94 samples will be completed by the end of 1995/96.

Vapor Pressure Measurements

Vapor pressures were expressed by the relationship:

$$\text{Log } p°_L \text{ (Pa)} = m/T + b \qquad (2)$$

Initial estimates of vapor pressure for nine compounds at 25°C ranged from 9.0 x 10^{-3} Pa for a hexachlorocamphene to 2.7 x 10^{-4} Pa for a decachlorobornane. Additional measurements are required to verify the slopes and intercepts of eq 2 for the different CHBs. Based on the preliminary eq 2 parameters, estimates of the fraction sorbed to haze aerosols at -30°C were made from the Junge-Pankow adsorption model (Bidleman 1988):

$$\phi = c\theta/(p°_L + c\theta) \qquad (3)$$

where θ is the surface area concentration of haze aerosols (4 x 10^{-7} cm^2/cm^3 air) (Patton *et al.* 1991) and c = 17.2 Pa-cm. The particulate fractions ranged from 50% for hexachlorocamphene to 100% for decachlorobornane. Congeners T2 and T12 were predicted to be 78% and 95% associated with aerosols. These estimates will be used to improve the assessment of dry particle deposition for CHBs.

Intercalibration Exercises

Our results for co-planar PCBs and OC pesticides in standard solutions (Table 3) and OC pesticides in seal blubber (Table 4) compared favorably with the accepted value (standards) or the mean of other laboratories (seal blubber) with two exceptions. We were about a factor of two high for *p,p'*-DDD in the OC standard, possibly because we failed to notice co-eluting *cis*-nonachlor. Our result for α–HCH in seal blubber extract (32.8 ng/μL) was lower than the mean (61.1 ng/μL), however, the range of reported values from the eight laboratories was very wide (30 - 101 ng/μL).

Project completion date: March 31, 1996.

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Table 1. Concentrations of OCs in Air, July - September, pg/m^3.

	AOS Cruise 1994	B-C Seas 1993	Resolute Bay 1992	B-C Seas 1988 [a]	Ice Island 1986 [b,c]
α–HCH	66	91	114	272	546
γ–HCH	16	23	10	68	31
CHBs		3.9	6.9	38	44
Trans-chlordane		0.75	0.51	2.3	1.1
Cis-chlordane		1.2	1.4	2.8	2.8
Trans-nonachlor		0.59	0.77	1.5	1.5
Dieldrin		1.1			1.9
Endosulfan I		2.7	3.9		7.1

[a] Hinckley *et al.* 1991
[b] Patton *et al.* 1989.
[c] Hargrave *et al.* 1988

Table 2. Concentrations of OCs in Surface Seawater, pg/L.

	B-C Seas 1993	Resolute Bay 1992	B-C Seas 1988[a]	Ice Island 1986[b]
α–HCH	2000	4700	2350	5590
γ–HCH	450	440	590	510
CHBs	20	48		160
Trans-chlordane	0.95	7.3		3.7*
Cis-chlordane	0.76	4.5		
Trans-nonachlor	0.47	1.5		0.5
Dieldrin	3.6			15
Endosulfan I	2.0			

[a] Hinckley *et al.* 1991
[b] Hargrave *et al.* 1988
* *Trans*- + *cis*-chlordane.

Table 3. Intercalibration Results for Coplanar PCBs in a Standard Solution, ng/μL.

Congener	Our Value	True Value
37	1.29	1.37
77	0.56	0.62
126	0.94	1.00
169	0.71	0.73

Table 4. Intercalibration Results for OC Pesticides in a Standard Solution and Seal Blubber Extract, ng/μL

	Standard Solution		Seal Blubber	
Pesticide	**Our Value**	**True Value**	**Our Value**	**Mean of Labs**
HCB	5.0	5.2	13.6	15.8
α–HCH	2.6	3.2	32.8	61.1
β–HCH	2.6	3.1		
γ–HCH	2.0	2.2		
p,p'-DDD	3.9	2.0		
p,p'-DDE	4.1	5.2	212	286
p,p'-DDT	1.3	1.7		
Heptachlor	1.5	1.8		
Hept. epox.	4.2	5.7		
Cis-chlordane	2.4	2.8		
Trans-chlordane	2.9	3.6		
Trans-nonachlor	6.2	7.5	15.6	16.6
Dieldrin	2.4	2.8	9.0	10.2

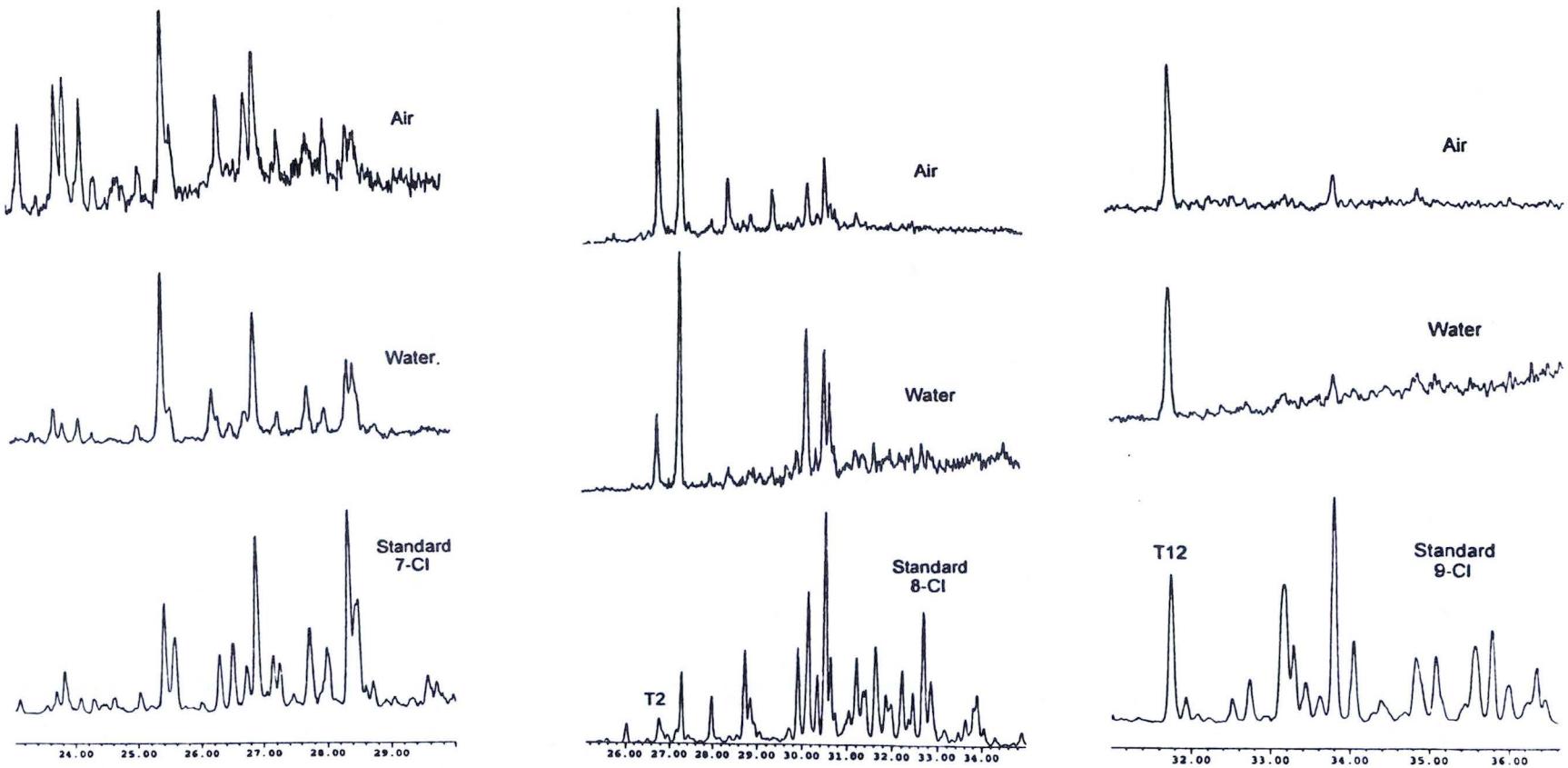

Figure 1. Chromatographic profiles of CHB homologues containing 7-9 chlorines in air and water from the Bering-Chukchi seas, August 1993

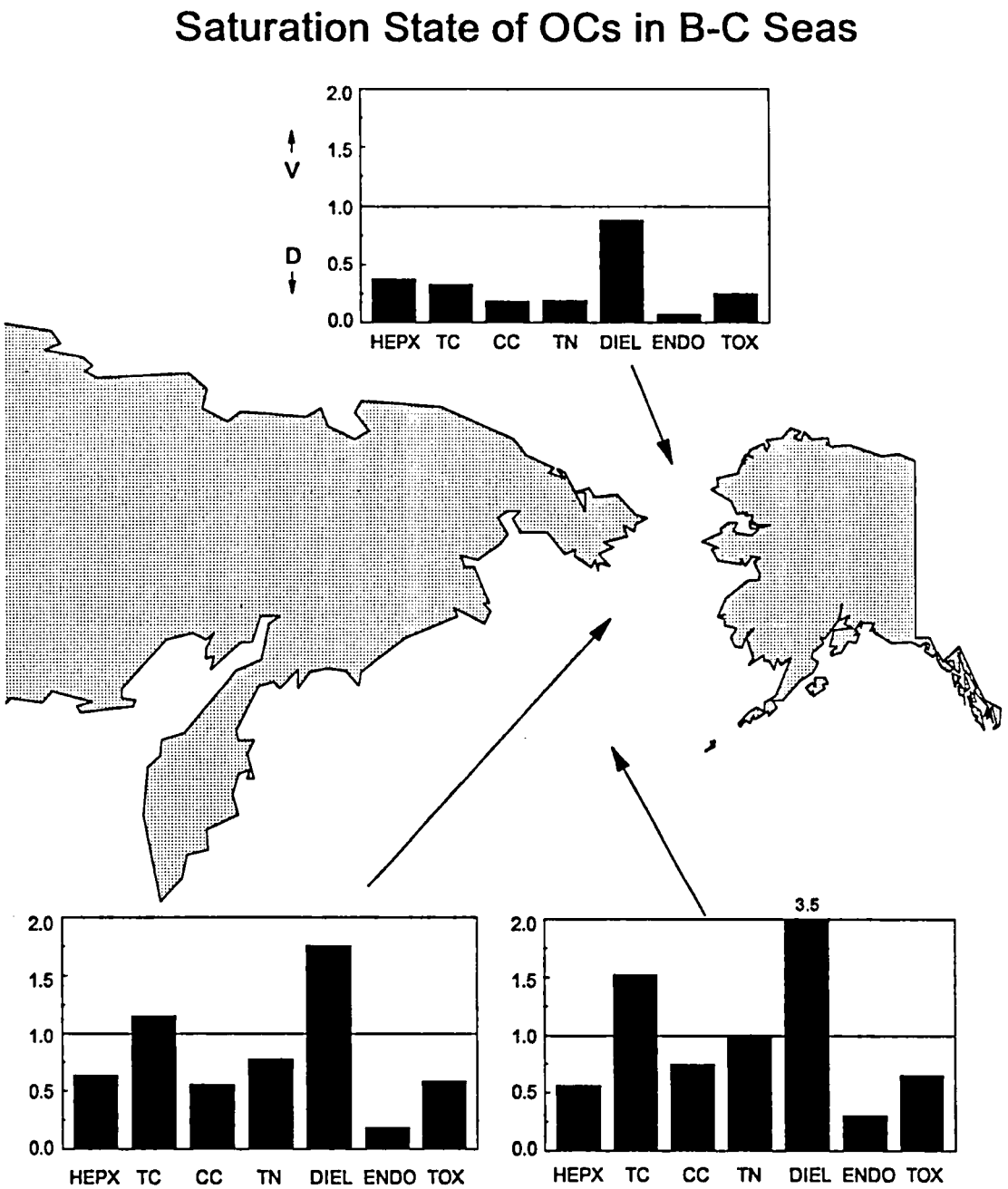

Figure 2. Water/air fugacity ratios (f_w/f_{a1} Y-axis) from equation 1 for OCs (HEPX = heptachlor epoxide, TC = *trans*-chlordane, CC = *cis*-chlordane, TN = *trans*-nonachlor, DIEL = dieldrin, ENDO = endosulfan I, TOX = CHBs (toxaphene)). Fugacity ratios > 1.0 (oversaturation) and < 1.0 (undersaturation) imply net gas-phase volatilization and deposition

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

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Project Team: F. Wania, C. Jia, K. Qiang, J. Hoff

OBJECTIVES

1. To develop, modify and publish in the international refereed scientific literature, conceptual multimedia mass balance models describing the global transport and distribution of organic contaminants, with particular emphasis on their transfer into 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. To provide a scientific basis for assertions that some contaminants require international control because of their propensity to migrate to cold regions;

3. To provide tools to identify, understand and quantify the sources, pathways and sinks of organic contaminants in the Arctic ecosystem and foods;

4. To assist in the design of future research and monitoring programs by identifying major gaps in the available data;

5. To identify the environmental and chemical-related factors that control the long-term distribution of organic contaminants on a global scale.

DESCRIPTION

In recent years our group had developed a series of computer programs describing the effect of temperature on contaminant distribution in the environment. A preliminary version of a global model was developed for calculating the latitudinal distribution of organic contaminants over the time period 1945 to 1995. We have used it tentatively to calculate the global environmental fate of hexachlorobenzene, toxaphene and DDT. This work confirms that such multimedia environmental fate models can be a useful tool for obtaining a comprehensive picture of contaminant behaviour in the entire global environment and in the Arctic ecosystem, and thus satisfying the above objectives. By establishing mass balances for chemicals in various interconnected media, models help to identify compartments of contaminant accumulation, the major transport pathways through the ecosystem, and the principles governing contaminant transport to, and behaviour in, cold regions. Model calculations also yield characteristic residence times of chemicals in environmental compartments, and are the only method of predicting future trends in contaminant concentration.

We hope that the international dissemination of the results of this work will enhance the process of gaining international cooperation to control discharges of these chemicals and find more benign substitutes.

ACTIVITIES IN 1994/95

The model has been subjected to continuing improvement by refining expressions used to calculate equilibrium, transport and transformation rates. Data have been gathered and assessed on emission rates and on environmental concentrations. Attempts have been made to gather data on global emission rates and on prevailing concentrations with a view to applying and "validating" the model. Most effort has been devoted to DDT, lindane (γ–HCH), α-HCH and toxaphene. These calculations have generally been done over the period 1945 to 1995, but can be run prospectively into the future.

RESULTS

Figures 1 and 2 give illustrative results for γ-HCH. These calculations clearly show the tendency for a "semi-volatile" chemical such as γ-HCH to achieve higher-than-expected concentrations in Northern ecosystems as a result of "global fractionation". Figure 3 shows a comparison of model results with observed concentrations by latitude. It is apparent that despite their remote location and distance from sources, concentrations in the Arctic are comparable to those in temperate regions and in some cases the levels are higher, especially in the "condensed" media of soils and water. Essentially the entire planet is bathed in an atmosphere containing these chemicals.

The simulations of the global fate for a few selected chemicals revealed that while the model performed quite satisfactorily for the HCHs, it is less successful in fitting the observed environmental behaviour of DDT. While measured air concentrations in the tropics are often higher than the calculated values, those in the higher latitudes are much lower than the model predicts. The model thus forecasts a considerably higher meridional mobility of DDT than is actually observed. The major difference between the atmospheric behaviour of DDT and the HCHs is that the latter are relatively volatile and present in the atmosphere mostly in the vapour phase, while the former is present in appreciable fractions absorbed to aerosol particles. Presumably, the assumption of complete vertical and zonal mixing is too simplistic to describe accurately the global atmospheric fate of aerosol-associated contaminants and leads to erroneously high meridional transfer rates.

In order to address this shortcoming, we modified the treatment of atmospheric transport in the existing model (Wania and Mackay 1995) by introducing a vertical dimension. The atmospheric segment of each climate zone is now subdivided into four vertical layers representing the atmospheric boundary layer, the lower troposphere, the upper troposphere and the stratosphere. This resolution of the description of the atmosphere is adapted from Strand and Hov (1995). The derivation of the parameters describing the diffusive and advective transport between these compartments is based on the approach outlined by these authors. This modified version now allows the inclusion of both advective and diffusive atmospheric transport, while this was necessarily lumped in the previous version. Special consideration was given to the treatment of wet deposition processes. Precipitation forms in various altitudes and falls through the atmospheric layers below its layer of origin. A model that has several vertical atmospheric layers thus requires a more complex treatment of wet deposition processes than is usual.

Another modification involved the addition of a sub-polar zone in the Southern hemisphere by splitting the former S-Polar zone. The primary incentive for this subdivision was the large temperature difference between the Southern Ocean and the Antarctic continent, which was not reflected in the previous model version. There are now 90 compartments (ten zones with each nine compartments) in the model, including 40 atmospheric compartments.

Some preliminary simulations indicate that the calculated meridional mobility of low volatility organic contaminants such as DDT is considerably less with this model and calculated concentration profiles with latitude are thus closer to observed profiles. We now also believe that snow is a very much more efficient scavenger of substances such as DDT. A deposition model specific for snow is being developed.

A second problem which we have addressed is the extensive volume of the computation which involves numerical solution of 54 differential equations (in the simpler model) with a short time step of days over a 50 year period. Efforts have been made to speed up this process and we were recently successful in devising a matrix technique that greatly simplifies the computation and enables the user to retain better mental contact with the model results. Early results are encouraging.

Output data obtained from the numerical solution of the existing model are used to define values in two nine by nine unit matrices which summarize the global system response. These matrices are then used with defined input of discharge data to deduce the quantities of the chemical, and concentrations, existing in all model compartments at all times. The large amount of data generated by the existing model makes the interpretation and evaluation of the model results difficult and time consuming. The matrix model helps to focus the attention on the particular aspect of the model that is of most interest, i.e. the net meridional transport to higher latitudes. It also helps to address the problem of uncertain emission information because it allows the user to calculate the fate of numerous emission scenarios very rapidly.

A computer program for this model approach was written and some calculations were performed using matrices derived from the previous global simulations for γ-HCH.

An interesting conclusion from these calculations is that although only a relatively small fraction of the global inventory of persistent organic contaminants is actually transported to the Arctic, this small amount is enough to cause elevated concentrations in Arctic environmental media. The processes of global distillation and cold

condensation do not imply that the bulk of the chemical burden present in the global environment will eventually reach high latitudes. Fortunately, most of these chemicals are retained in the soils of emission areas and slowly dissipate in the atmosphere. Most eventually enter the oceans. One reason for this is that the polar areas are relatively small in area compared with the tropical belt, thus a large source area adjoins a rather small sink area. Furthermore, due to their shallow to non-existent soils and the sparse vegetation, Arctic terrestrial systems tend to have a low capacity to retain organic contaminants, and these contaminants are more readily transferred to the marine environment.

DISCUSSION

We believe that the model is proving valuable not only for elucidating the global geochemistry of these chemicals, but also for helping to create an international awareness of the issue of northern contamination. To this end we are working to publish these findings in internationally reputable peer-reviewed journals.

During the year Dr. Wania completed his Ph.D. thesis on this topic and has moved to Tromsø, Norway to take up a position with NILU, the Norwegian Institute for Atmospheric Research. We will continue to collaborate with him and others in Europe and, especially, in Scandinavia.

A vital component of this effort is the availability of reliable emission data. We have sought to collaborate in this regard with Dr. Arthur Li of the Atmospheric Environment Service and we are assured of being provided with data in mid- to late-1995. This should prove to be a most mutually beneficial collaboration.

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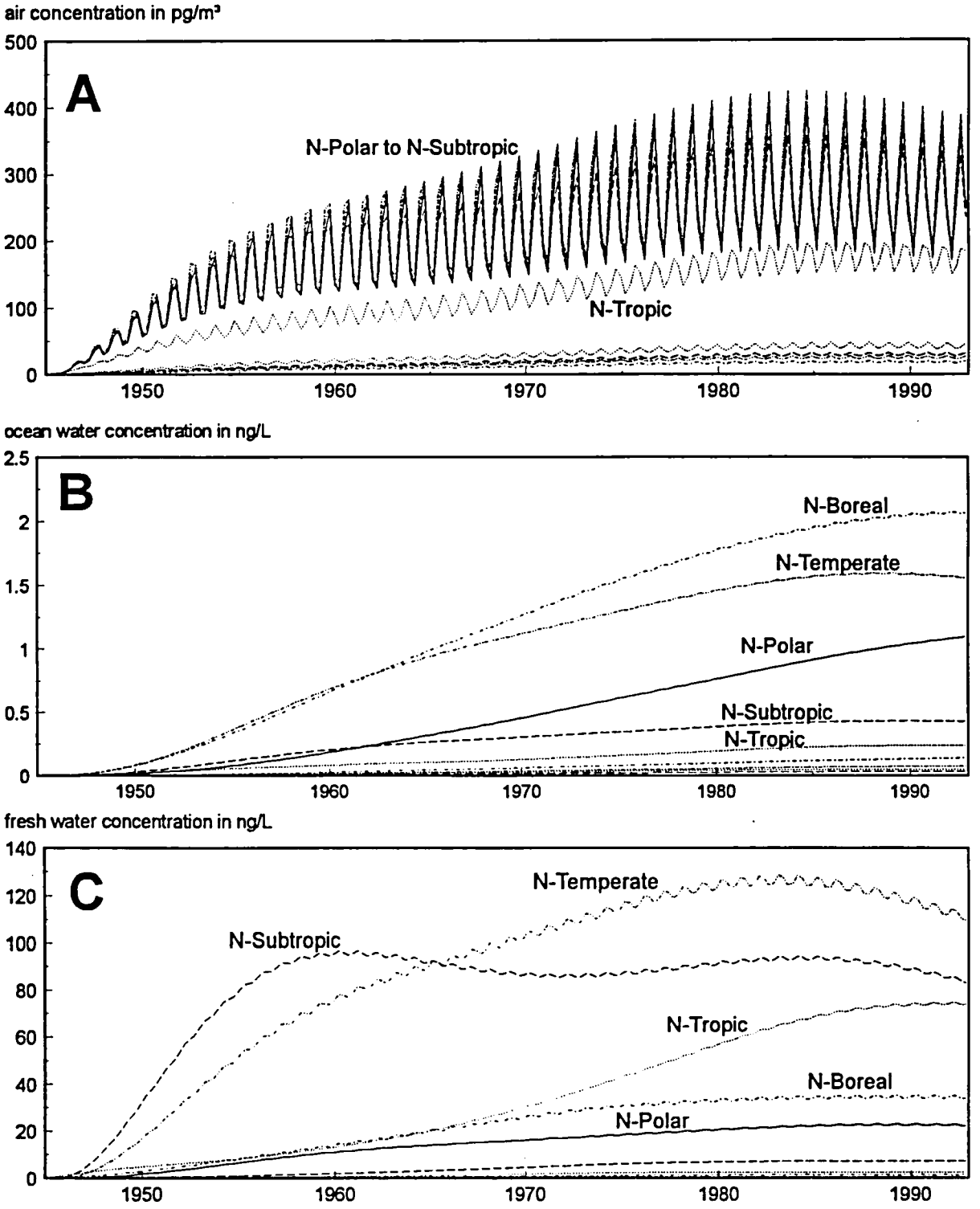

Figure 1. Time course of the zonal mean concentration of γ–HCH in air (A), ocean water (B), fresh water (C) as calculated by the global distribution model

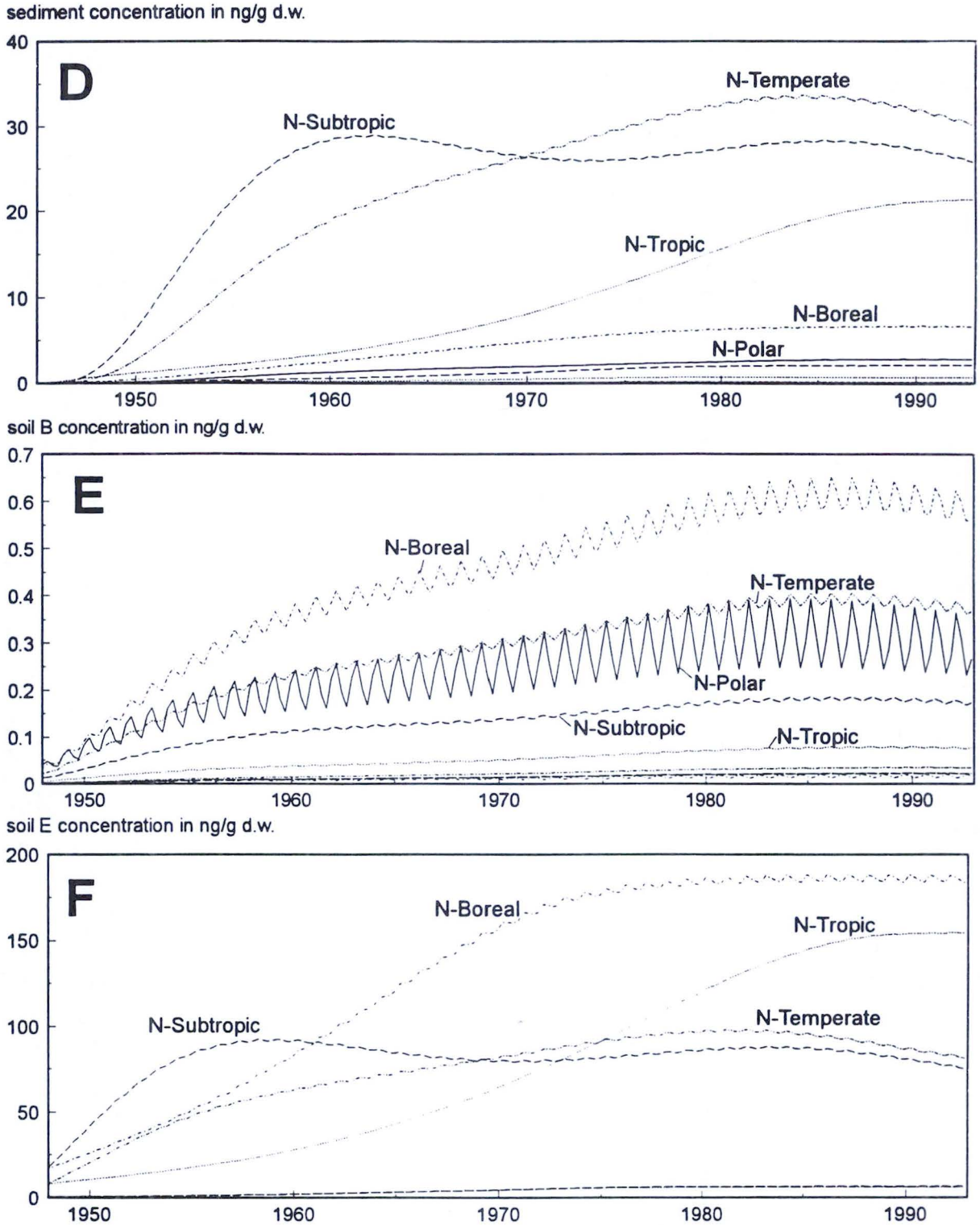

Figure 2. Time course of the zonal mean concentration of γ–HCH in fresh water sediment (d), uncultivated (E) and cultivated soil (F) as calculated by the global distribution model

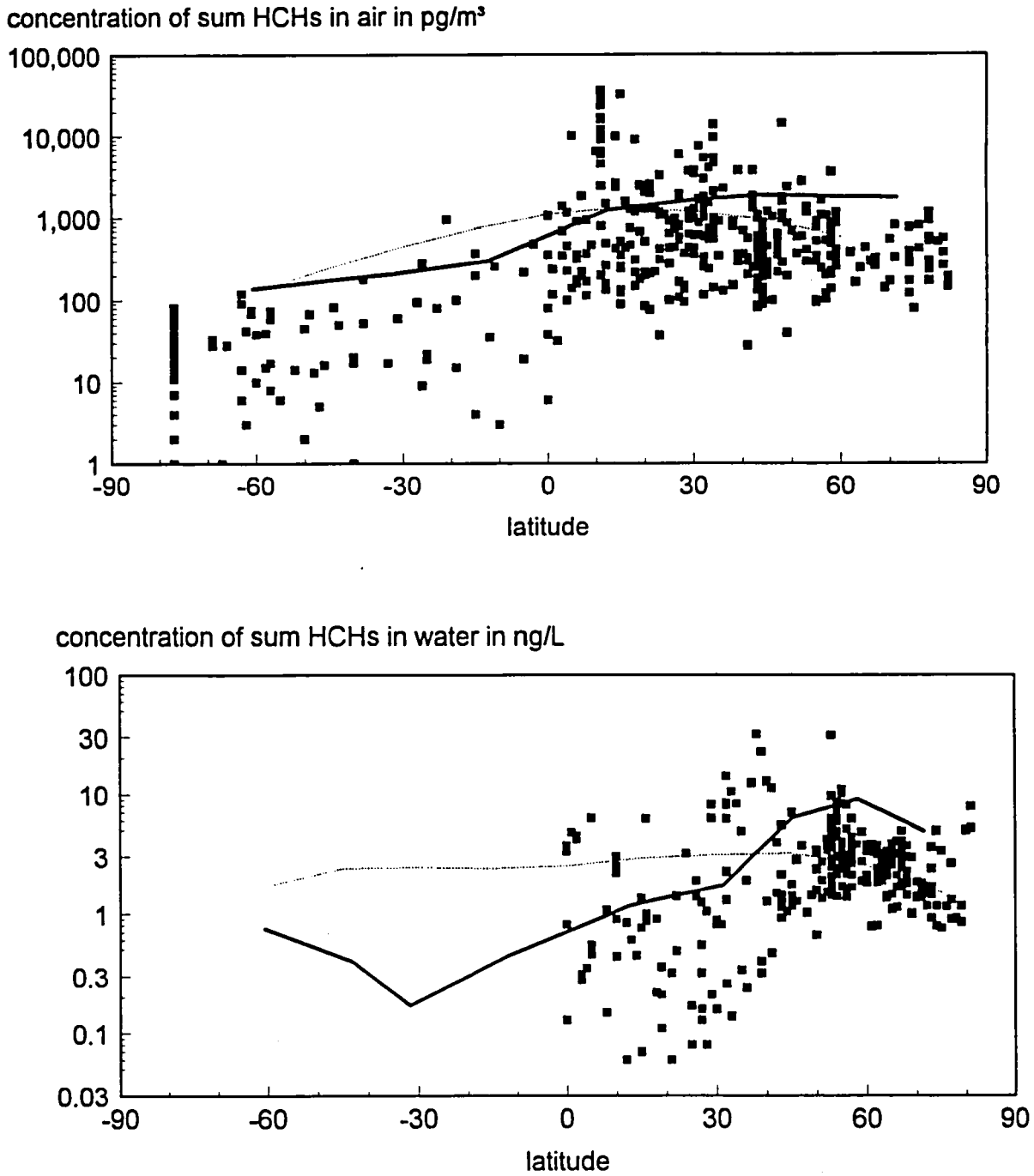

Figure 3. Calculated and measured HCH concentrations in air and ocean water as a function of latitude. Squares reflect measured data from different time periods compiled from various publications (Bidleman, pers. comm.). Profiles calculated by the global distribution model reflect the annual average for 1985. The thin lines are the concentrations calculated by a model by Strand and Hov

LONG-RANGE TRANSPORT OF CONTAMINANTS TO THE CANADIAN BASIN

Project Leaders: R.W. Macdonald, F.A. McLauglin, E.C. Carmack, Fisheries and Oceans Canada, Institute of Ocean Sciences, Sidney, B.C.

Project Team: D.W. Paton, M.C. O'Brien, R. Pearson, D. Sieberg, L. Adamson, D. Tuele

OBJECTIVES

1. To determine the composition, quantity and distribution of persistent organic contaminants within the Western Arctic and Arctic Interior Ocean (Canada Basin) by measuring relative amounts of these compounds contained within biogeochemical compartments (e.g., particulate, dissolved, biological).

2. To model the rate of transfer of these compounds within the Arctic Ocean.

DESCRIPTION

The various sources of contaminants to the Arctic Ocean are rivers entering the ocean via the broad, shallow shelves, Pacific (Bering Strait) and Atlantic (Fram Strait) waters entering the Arctic Ocean, and atmospheric transport and deposition.

The various sinks of contaminants are outflow through Fram Strait and the Canadian Archipelago and, within the Arctic Ocean, scavenging to sediments on the shelves, slopes and basins, and kinetic loss through degradation or metabolization.

Accurate determination of the above sources and sinks as well as the rates of transport within the Arctic Ocean are required in order to predict the consequences of actions taken to reduce sources.

Our work in the western Arctic focuses on the oceanographic processes that control the distribution of persistent organic contaminants (in particular HCHs), and on determining the temporal and spatial patterns of contaminants. To these ends we have established a time-series station in the Canada Basin making measurements of water-mass distribution, vertical particle flux and contaminant burdens in the water, biota and sediments. To set in context the temporal trends, we have examined the spatial distribution of contaminants by two transects of the interior ocean of the Canadian Basin (Larsen-93 and AOS-94) as well as a station in the Lincoln Sea. Our field work has been carried out in collaboration with the Canadian Coast Guard, who have provided icebreakers as oceanographic platforms, and with other Northern Contaminants Program workers: Smith and Ellis (radionuclides) and Bidleman and Jantunen (organic contaminants).

ACTIVITIES AND RESULTS IN 1993/94

Time-series station

HCH profiles at the time-series station (A01, Canada Basin, Figure 1) were collected in 1992 (XAD column and bottle) and in 1993 (bottle only) (Figure 2). There is reasonable agreement between data obtained using *in situ* pumps with XAD columns and data obtained using bottle samples with liquid-liquid extraction. Our data for the Canada Basin also agree well with those collected in 1986 at the Ice Island (Hargrave 1988). Noteworthy differences between the Ice Island data and the A01 station data are also evident. The 1993 data show an ingrowth of HCH throughout the water column down to about 300m (approximately 20% increase in total burden). HCH is also observed deeper in the water column, evidence of diffusive and/or advective processes that transport HCH to depth. We are presently interpreting these data in the context of water masses and conservative tracers.

Completion of analyses of samples collected during Larsen-93

In 1993, we carried out sectional work across the Chukchi and East Siberian Seas (Figure 1) collecting water samples, biological samples and sediment box cores. The geochemical tracer data suggest that large-scale, rapid water-mass changes are occurring within this region; we believe this will have important consequences for contaminant transport (McLaughlin *et al.* 1995, Carmack *et al.* 1995). Our transect allows us to compare our time series data with the data collected in the Bering and Chukchi Seas (Jantunen and Bidleman 1995, Hinckley *et al.* 1991) and at the Ice Island. For HCH, there is clearly significant spatial

variation in the water-column burden (Figure 3). The HCH concentrations in the Canadian Basin, at Station A01 and at the Ice Island, are about double those observed in the Chukchi and East Siberian Seas. We are presently interpreting these data in the context of biological and physical processes that differ between the Chukchi/East Siberian seas and the interior basin. Preliminary sediment data suggest that removal of contaminants to sediments occurs in highly productive regions of the Chukchi Sea and this may be, in part, why HCH concentrations are lower in the surface waters. The HCH data collected in the Lincoln Sea provides us with a characterization of waters leaving the Arctic Ocean (Figure 4). These data, together with the AOS-94 data will considerably enhance our understanding of HCH distributions in both of the major basins of the Arctic Ocean. In addition, large volume filtration, *in situ* column extractions, sediments and zooplankton samples will provide a data base encompassing a broad range of organochlorine compounds.

The Arctic Ocean Section, 1994

A transect was completed across the Arctic Ocean (Figure 1) during which contaminant samples were collected at many of the sites from ice, water, suspended sediments, fish, zooplankton and sediments. These samples are presently undergoing analyses for a suite of contaminants. Geochemical tracer data confirm and extend the Larsen-93 findings of large-scale, rapid water-mass replacements in the Canadian Basin.

Examination of sources and significance of PAHs on the Canadian Beaufort Shelf

Recent efforts under the Arctic Monitoring and Assessment Programme (AMAP) and the Canadian Northern Contaminants Program have emphasized organochlorine compounds and metals, because they are susceptible to biomagnification, and radionuclides, because of the concern over their release to the Russian Shelves (Yablokov 1993). As a result, PAHs have not received much attention, in spite of being included as an important AMAP contaminant. As a comprehensive data set was collected under the Northern Oil and Gas Action Plan (NOGAP) program, we decided to examine the PAH data from the Beaufort Sea in the context of contamination (Yunker and Macdonald 1995). We found the main source of PAHs for this region to be natural inputs from the Mackenzie River and noted that concentrations are high for a pristine area. Although concentrations are below thresholds thought to induce toxic effects, the high natural background may make this region sensitive to added PAHs from human activities.

DISCUSSION/CONCLUSIONS

The interior Arctic Ocean, which comprises about two-thirds of the ocean area, is important both for physics and biology. However, there exist practically no data from this region with which to make an assessment of contamination. With the completion of the AOS-94 sample analyses, we will have a data base that will allow us to make assessments of the distribution of priority contaminants within the water and within the food web. These data will encompass a wide area with diverse oceanographic and biological features, from the shelves to the basin interiors. Preliminary analysis of the data to 1993 suggest that the Canada Basin interior is unique in having HCH levels that are a factor of two higher than found in other marginal seas of the Arctic. The question arises whether this is unique to the Canada Basin and whether this enhancement is transferred up the food chain. The higher concentrations of HCH may be due partly to ice cover limiting air-sea exchange and, partly to low biological activity.

Expected project completion date: 1997

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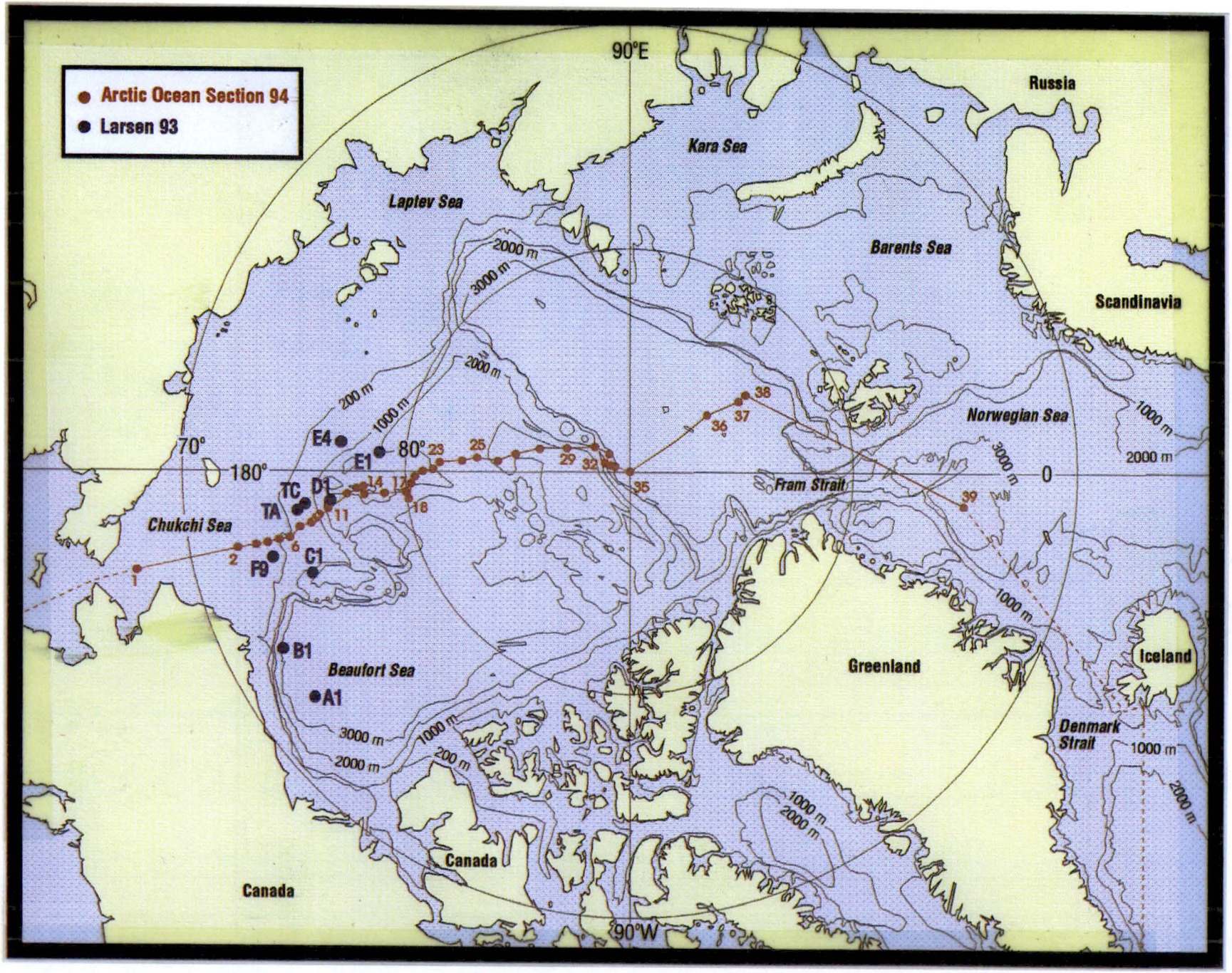

Figure 1. Sampling sites for the Larsen-93 expedition and the Arctic Ocean Section - 94 expedition

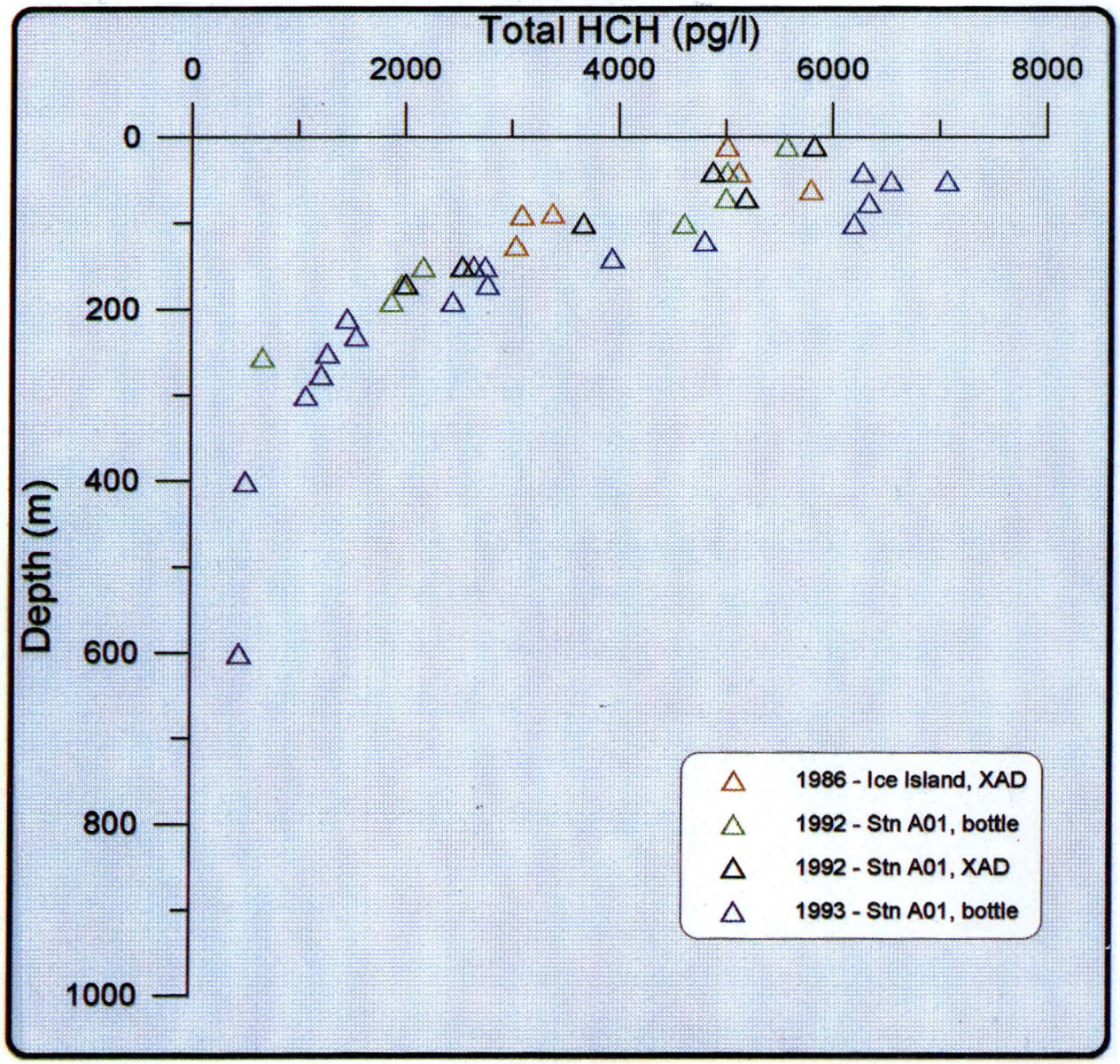

Figure 2. Total HCH time-series data for the Canada Basin (the Ice Island data are from Hargrave *et al.* 1988)

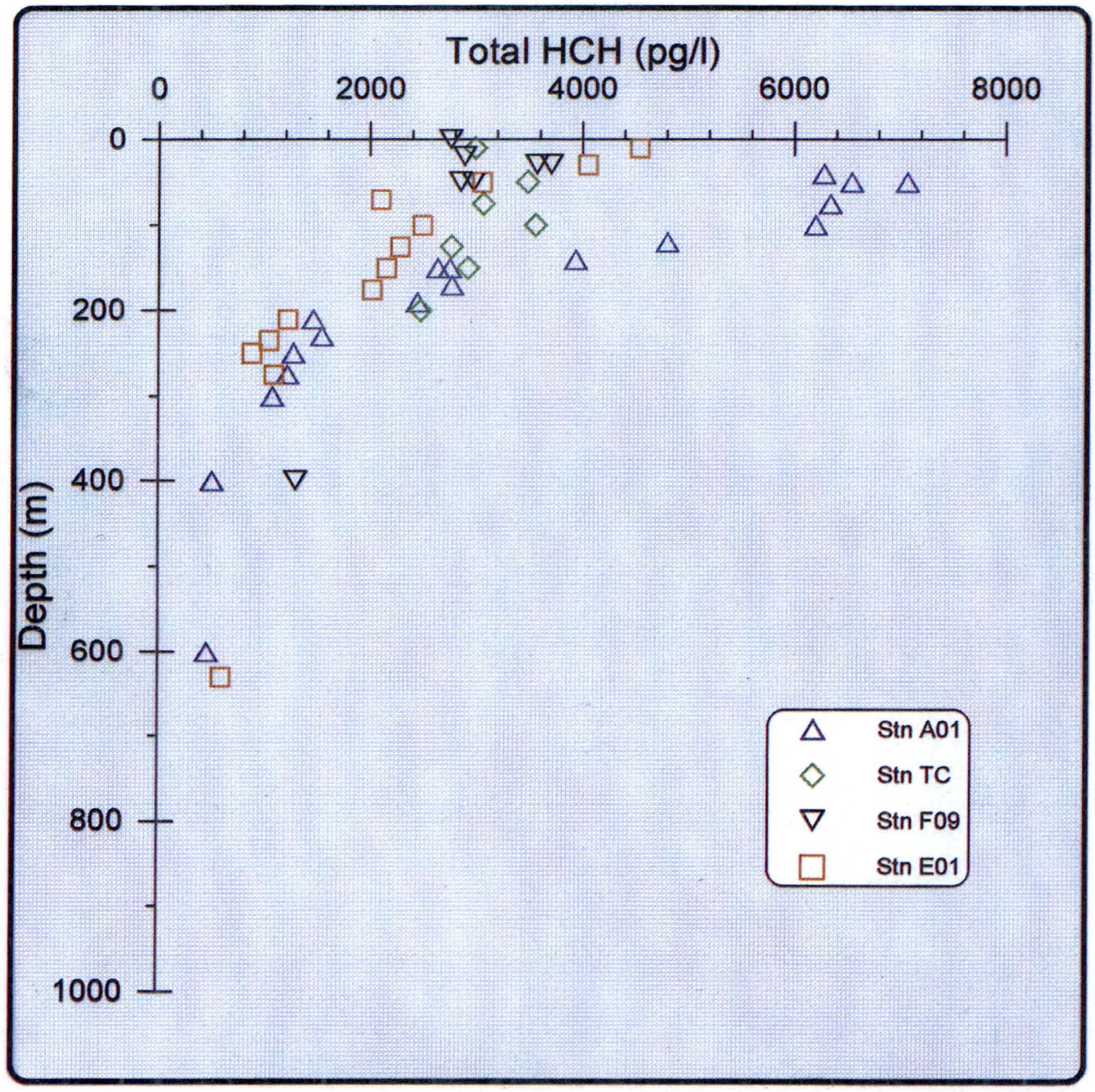

Figure 3. Vertical profiles for total HCH at the stations sampled during Larsen-93 (Figure 1 shows station locations)

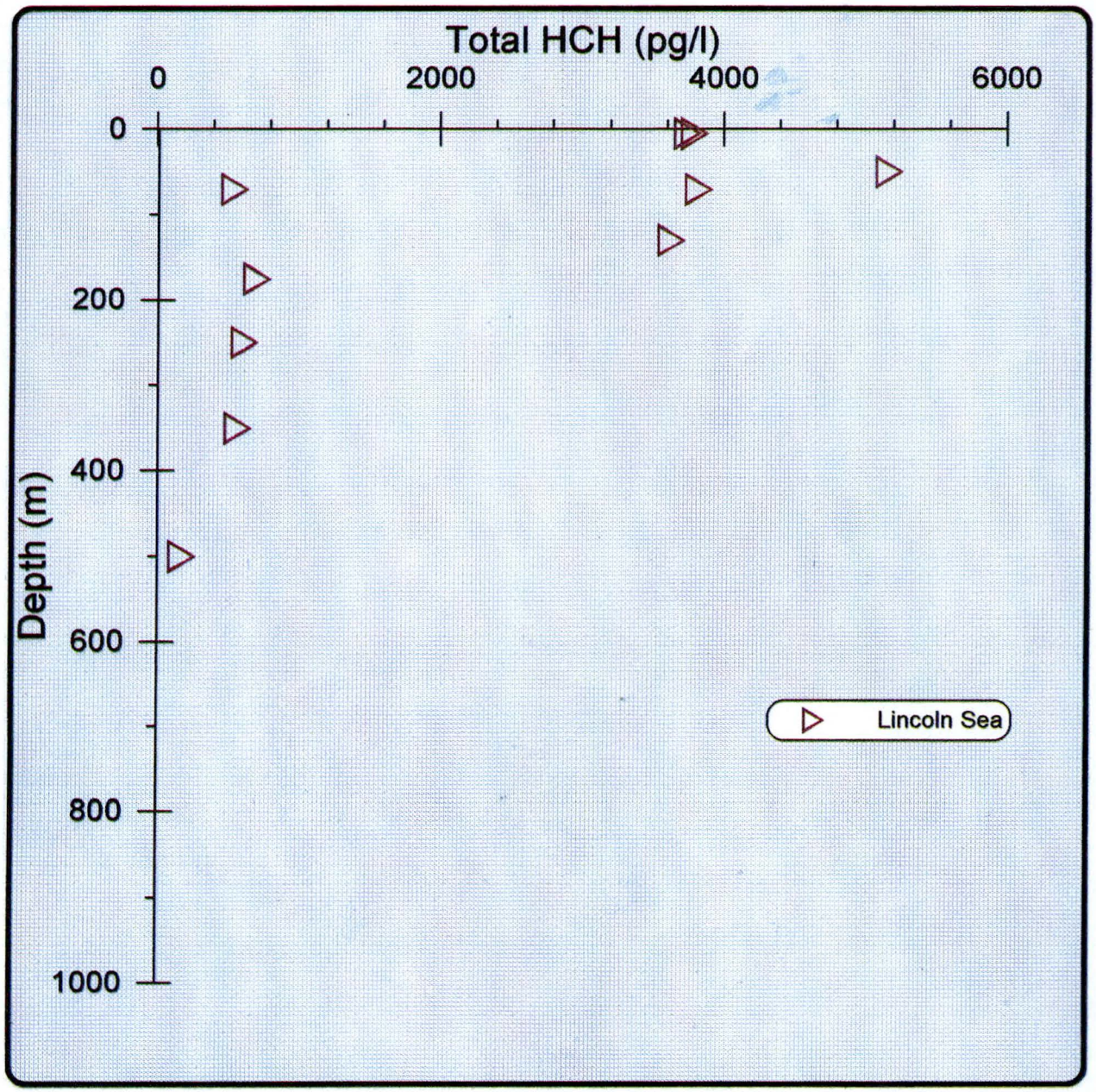

Figure 4. Vertical profile of total HCH in the Lincoln Sea (Spring, 1994)

MEASUREMENTS OF RADIOACTIVE CONTAMINANTS IN THE ARCTIC OCEAN

Project Leader: J.N. Smith, Fisheries and Oceans Canada (DFO), Bedford Institute of Oceanography (BIO)

Project Team: K. Ellis (BIO), R. McDonald (Institute of Ocean Sciences, DFO), 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, Tromsø, 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 1994/95

The field and analytical activities in 1994/95 included: (a) radionuclide analyses of sediment, seawater and biota samples collected in 1993 near a submerged, radioactive waste storage site in the Kara Sea; (b) radionuclide analyses of sediment samples collected in 1993 in the Ob and Yenisey River estuaries; (c) radionuclide analyses of sediment and seawater samples collected in 1993 in the East Siberian Sea aboard the CSS Henry Larsen; (d) the collection of sediment and seawater samples aboard the CSS Louis S. St. Laurent during the Transarctic-94 cruise across the Arctic Ocean, (e) the collection of samples from the White Sea and Kara Sea through collaborations with Russian and Norwegian investigators, and (f) the submission for publication of three papers of which one has been published and two are in press.

RESULTS

Cruise Activities

The principal cruise activity in 1994 involved the collection of samples for radionuclide analyses during the Arctic Ocean Section (AOS) cruise to the North Pole. Two BIO scientists from the BIO Radioactivity Section accompanied the CSS Louis S. St. Laurent and collected sediment and seawater samples to determine radionuclide (^{137}Cs, ^{90}Sr, ^{129}I, $^{239,240}Pu$) distributions and fluxes across the Arctic Ocean. Sediment samples were subsampled from eight box cores collected from a range of shelf, slope and basin sediment regimes. Analyses of these cores for ^{210}Pb will provide insight into sedimentation and biological mixing rates in Arctic Ocean sediments. Measurements of artificial radionuclides such as $^{239,240}Pu$ and ^{137}Cs will be used to identify the principal "depo-centres" for particle- reactive contaminants from European sources, possibly transported across the Arctic Ocean with particle laden ice. Large volume (50 L) seawater samples were collected from a range of water depths and passed through filters and resins to extract particulate and dissolved radionuclides (e.g. ^{137}Cs and $^{239,240}Pu$), while smaller 1 litre samples were collected for ^{129}I analyses. Four Challenger *in situ* pumps were deployed and used to process the large (> 300 L) volumes of seawater required to measure radionuclides such as ^{137}Cs and ^{234}Th at low levels in surface and deep waters. Measurements of ^{234}Th made

aboard the vessel using a portable Ge detector will permit estimates of organic and inorganic fluxes through the halocline. The primary focus of this work is to determine the extent to which radioactive contaminants from the Russian marginal seas and European Reprocessing Plants have been transported through the Arctic Ocean and into the Canada Basin and to evaluate any environmental impacts on the North American continental shelf.

Analytical Work

Canada Basin

Sediment and seawater samples collected during the CSS Henry Larsen cruise to the Western Arctic Ocean in 1993 were also analysed in 1994/95. Measurements of ^{210}Pb, ^{137}Cs and $^{239,240}Pu$ conducted on sediment samples from box cores collected on the continental margins of the Makarov and Canada Basins reveal elevated radionuclide levels in slope compared to shelf and deep basin sediment regimes. Radionuclide sediment-depth profiles have been introduced into bio-diffusion models to constrain sedimentation and bioturbation rates. ^{129}I and ^{137}Cs analyses of seawater samples clearly delineate the plume of Sellafield and Cap La Hague contaminants being transported across the Arctic Ocean. Reduced levels of ^{129}I and ^{137}Cs in surface water in the Chukchi Sea represent background fallout levels associated with water of Pacific origin while radionuclide levels an order of magnitude greater in surface water from the Makarov Basin reflect inputs of Atlantic water contaminated by releases from the European reprocessing plants (Figure 1). The concentrations of radionuclides are most highly elevated in the lower halocline indicating that comparatively rapid transport may occur from the Barents and Kara Sea regions into the Western Arctic Ocean along lower halocline pycnoclines. Elevated $^{137}Cs/90Sr$ and $^{129}I/^{90}Sr$ ratios are indicative of post-1975 releases from European reprocessing plants and these measurements are being used to establish the timing of radioactivity transport through the Arctic Ocean.

Barents and Kara Seas

Studies conducted on samples collected in 1992 indicated that there were high levels of radioactivity in the sediments of Chernaya Bay, a fjord located on the western coast of Novaya Zemlya. Chernaya Bay is the site of at least two underwater nuclear weapons tests conducted by the former Soviet Union in the 1950s and the high levels of $^{239,240}Pu$ represent fallout from these tests. In 1993, a BIO scientist accompanied the Russian ship, R/V Geolog Fersman, to Chernaya Bay and sediment cores were collected throughout the fjord in collaboration with Russian scientists from Okeangeologia in St. Petersburg. Several hundred radionuclide measurements were carried out in 1994 on this second set of sediment samples and these have revealed $^{239,240}Pu$ activities in excess of 10 000 Bq/kg, in addition to elevated levels of other isotopes such as ^{137}Cs and ^{60}Co. These are among the highest $^{239,240}Pu$ activities ever measured in the marine environment and are equivalent to levels measured at the US nuclear test site in the Marshall Islands in the Pacific Ocean. The sediment-depth distributions of radioactivity indicate that most of the plutonium inventory is contained in the upper 20 cm of the sediment column and there is some evidence of deleterious biological impacts on sediment fauna. Application of a biodiffusion model to these sediment profiles permits the determination of mixing depths and biodiffusion coefficients (Figure 2).

During the 1993 Fersman cruise, sediment and seawater samples were collected in the vicinity of a submerged vessel, identified using side-scan sonar in the Novaya Zemlya Trough in the Kara Sea, which is reported to have contained over 200 curies of radioactive wastes when it was scuttled in 1980. An environmental monitoring operation was conducted through the collection of sediment and seawater samples at well-defined locations proximal to the vessel. Radionuclide analyses were conducted on these samples in 1994 and the results have revealed little evidence for the release of radioactive contaminants from the dumpsite (Figure 3). The radioactivity in surrounding seawater and sediments can be entirely explained by inputs from nuclear weapons fallout and transport into the region of water labelled with European reprocessing wastes. Sediment samples collected in 1993 in the Ob and Yenisey River estuaries were also analysed in 1994. The results have revealed elevated levels of ^{137}Cs and ^{60}Co in a fine-grained depositional regime at the mouth of the Yenisey River which are apparently derived from nuclear facilities located several thousand kilometers upstream. Although radioactivity levels are elevated, they are not in excess of concentrations considered hazardous to human health or the environment.

DISCUSSION/CONCLUSIONS

Kara and Barents Sea

The elevated levels of plutonium in Chernaya Bay indicate that this fjord represents a potential source of radioactivity contamination to the Barents Sea and Arctic Ocean. However, measurements of the distribution of $^{239,240}Pu$ and ^{241}Am with distance from Chernaya Bay

into the Barents Sea reveal that only a small amount of plutonium has been transported out of Chernaya Bay and the fjord remains an effective trap for particle-associated radioactivity from the nuclear tests. Nevertheless, this fjord is the most highly contaminated sediment regime yet identified in the Russian Arctic and there is considerable potential for future environmental impacts in this region. It is particularly important to determine whether there have been any significant long term biological or toxicological effects associated with the dissemination of radioactivity through the fjord. Chernaya Bay has great potential as an arctic laboratory for studying biological effects of environmental radioactivity and the assimilation of plutonium into Arctic food chains.

Studies of radionuclide distributions in sediments and seawater in the vicinity of the scuttled ship loaded with radioactive wastes which was identified in the Novaya Zemlya Trough have revealed negligible releases of radioactivity. Since the ship is relatively intact, it can be assumed that measures taken to isolate the radioactive wastes from dissolution in seawater have been relatively effective. However, it is difficult to predict the time-table for any future releases and continued monitoring of this dumpsite will be required in the future.

Radioactivity results from the CSS Larsen cruise of 1993 have revealed the presence of Sellafield tracers in the Canada Basin. In particular, the Sellafield tracer results provide evidence for the rapid transport of Atlantic water through the lower halocline into the Canada Basin. Comparisons of the $^{129}I/^{137}Cs$ ratios measured in water samples with source function data permit estimates of time scales (10-14 years) for the transport of water from Sellafield into the Canada Basin. Although levels of radioactivity in the Canada Basin are significantly in excess of background levels from nuclear weapons tests, they are still lower than those that would constitute a radiological threat to organisms or humans in the Arctic.

Future activities in Russia will focus on the collection of sediment and seawater samples in Kola Bay, near Murmansk, which is the home of the Russian nuclear fleet and on sample collection on the island of Novaya Zemlya. Activities in the Western Arctic Ocean will involve the collection of water samples under the arctic ice cover from a US navy submarine and the collection of large volume water samples during the cruise of the CSS Louis St. Laurent to the Canada Basin in 1995.

Expected project completion date: March 31, 1997

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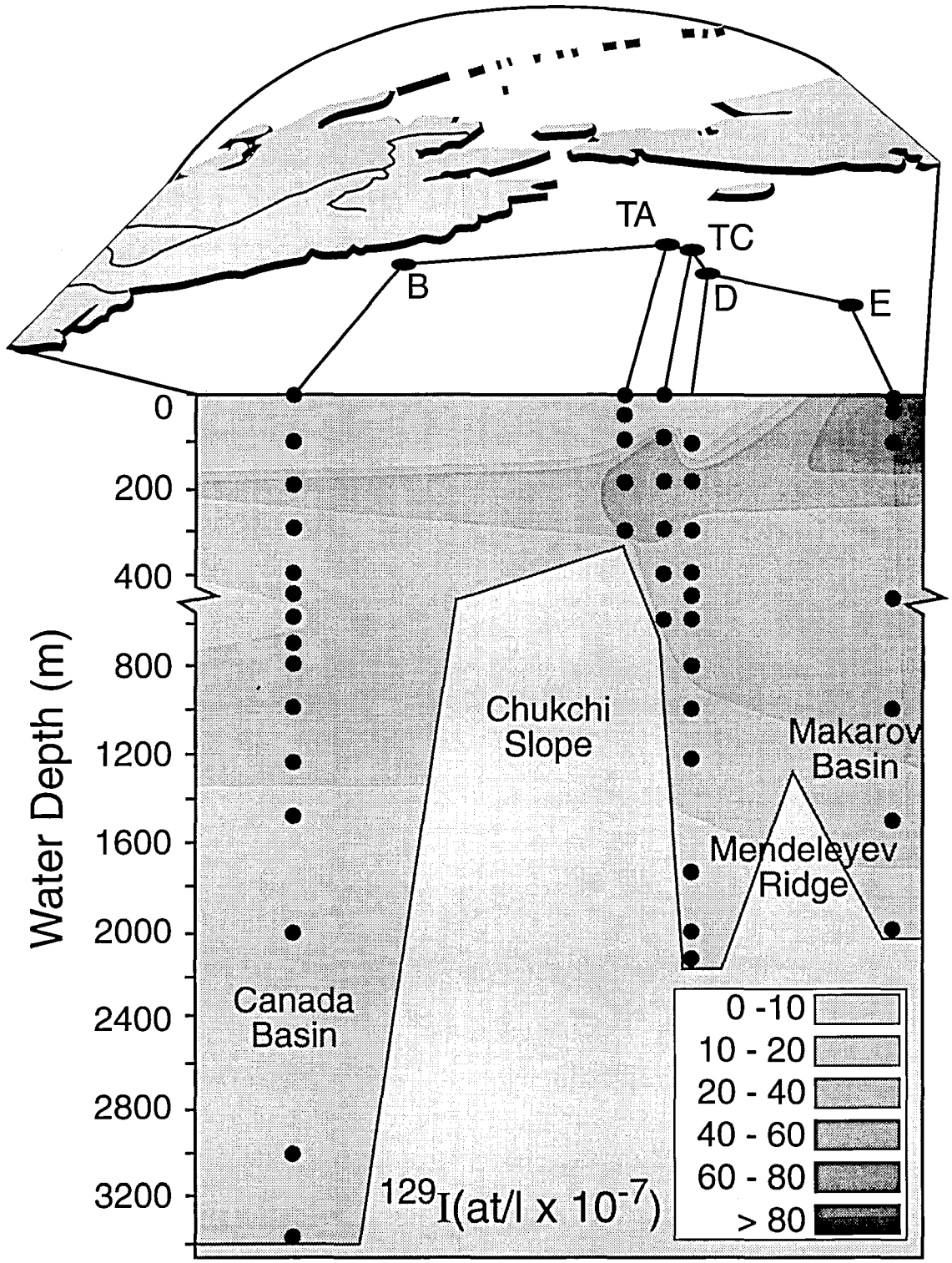

Figure 1. Section from CSS Larsen cruise (1993) shows transport of ^{129}I labelled Atlantic water at depths of 100-200 m from Makarov Basin (Sta. E) into Canada Basin (Sta. B). ^{129}I levels<10 x 10^{7} at/l are typical of fallout levels in North Pacific Ocean while elevated levels> 20 x 10^{7} represent inputs from European reprocessing plants

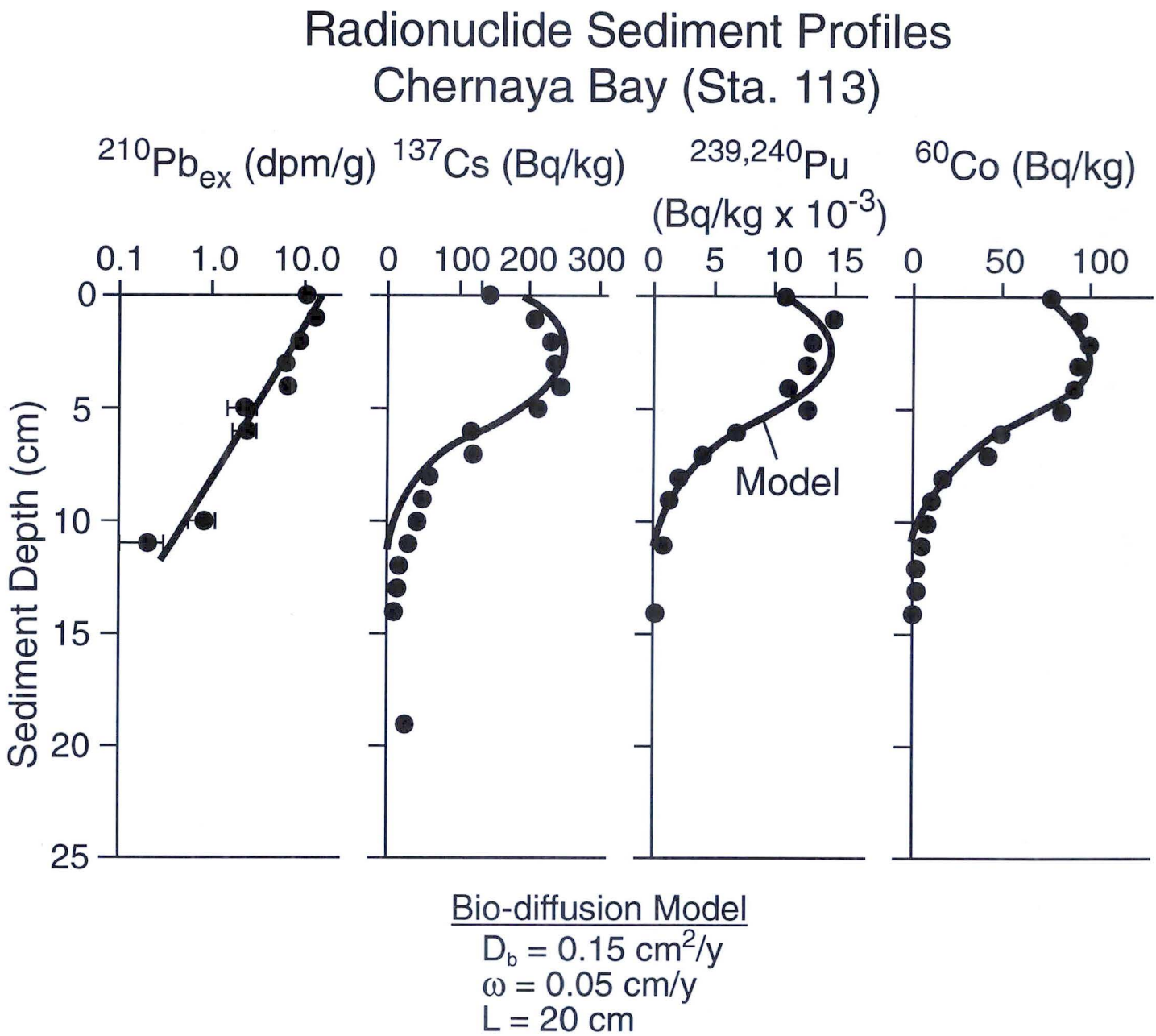

Figure 2. Radionuclide sediment-depth profiles (Sta. 113) in Chernaya Bay are simulated by biodiffusion model using steady-state flux of ^{210}Pb, and 1957 pulsed input of artificial radionuclides. Plutonium concentrations are among the highest ever recorded in the marine environment

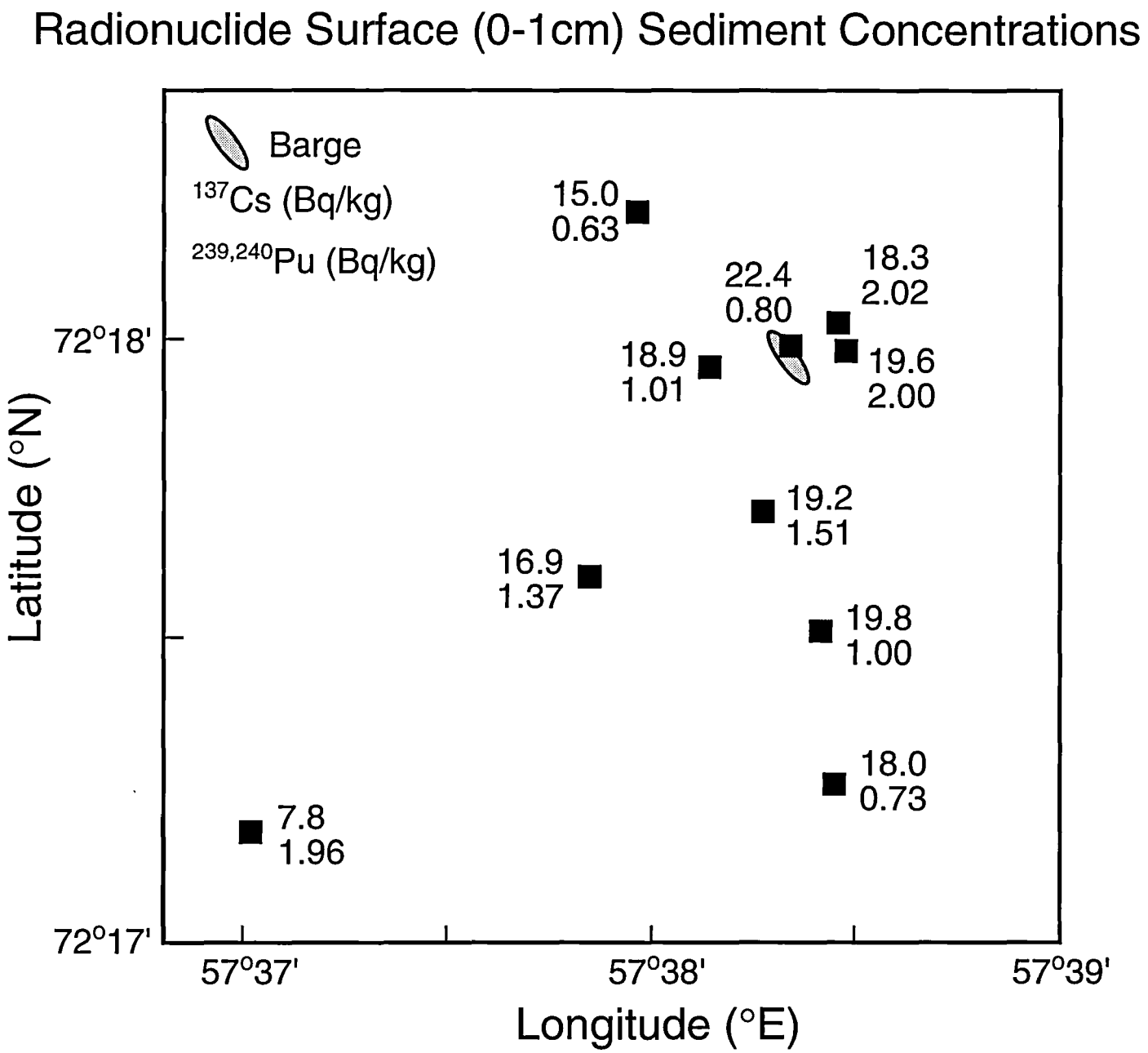

Figure 3. Surface sediment ^{137}Cs and $^{239,240}Pu$ activities are consistent with fallout levels and show no evidence for releases from the dumpsite. ^{137}Cs and $^{239,240}Pu$ inventories in the upper 10 cm of most cores near dumpsite are <1000 Bq/m^2 and < 100 Bq/m^2, respectively

SNOW, ICE AND TEMPERATURE AS DETERMINANTS OF ORGANIC CHEMICAL FATE IN NORTHERN ECOSYSTEMS

Project Leader: D. Gregor, Waterloo Centre for Groundwater Research, University of Waterloo

Project Team: J. Hoff and E. Sudicky, Department of Earth Sciences, University of Waterloo; J. Sloan and J. Pawliscyn, Department of Chemistry, University of Waterloo; D. Mackay and C. Jia, Department of Chemical Engineering; University of Toronto

OBJECTIVES

1. To contribute to an improved understanding of the role of ice and snow in depositing semi-volatile organic contaminants from the atmosphere and in determining their subsequent migration and fate in the Arctic environment;

2. To utilize this information to better interpret existing data on contaminant levels in snow obtained under the Northern Contaminants Program and to collaborate with others to ensure that the information developed in this study is integrated with information developed in other studies within the framework of the Arctic Environmental Strategy;

3. To communicate the results of this study in the refereed scientific literature.

DESCRIPTION

Persistent organic contaminants are transported to the Arctic by the atmosphere. It is postulated that low temperatures are responsible for concentrating the contaminants in polar regions and that snow scavenges semi-volatile organic contaminants from the atmosphere by adsorption of gaseous chemical to the ice surfaces and by scavenging aerosol particles with their associated chemical. Snow and ice are temporary storage media that influence exchange with soil, vegetation, surface water and groundwater. The physico-chemical nature of the association of contaminants with snow governs the efficiency of scavenging and the subsequent behaviour of contaminants in the snow pack. For example, spring snowmelt may cause a pulse of contaminant loading to surface waters during periods of intense biological activity and to groundwaters. This information is also needed for interpreting the glacial record of global organic chemical concentration.

ACTIVITIES IN 1994/95

Initial efforts have focused on developing methods for investigating the partitioning of semi-volatile contaminants between air and snow and for measuring the specific surface area of snow. This information will be used to model scavenging and post- depositional processes.

An experimental method, which combines the best features of two techniques previously used to study volatile compounds, has been developed for investigating partitioning of semi-volatile organic contaminants between air and snow (Hoff *et al.* 1995). The method, which is calibrated using a series of normal alkanes, was used to determine the adsorption constant, K_{ia} ,values for several chlorinated benzenes. K_{ia}, is defined as the concentration of chemical at the interface (mol • m^{-2}) divided by the concentration in the air (mol • m^{-3}).

A method for measuring the specific surface area (SSA) of snow has been developed and applied to determining the SSA of fresh precipitation collected at the University of Waterloo during December to March. The method is based on the BET nitrogen adsorption technique and utilizes the Micromeritics™ Gemini 2375 surface area analyser. The precision and lower limit of determination are being investigated by a Monte Carlo study of error propagation in which errors in adsorbed volumes are used to calculate the resulting errors in SSA.

Complementary modelling studies have been carried out by C. Jia and D. Mackay at the University of Toronto. These studies address the implications of adsorption of organic contaminants on snowflake surfaces for depositional and post-depositional processes.

RESULTS

The adsorbed volumes of hexane, octane, nonane and decane were measured at -12°C for a clean granular snow that had been stored in a freezer for one year at -20°C. The SSA was calculated by regressing the adsorbed volumes on the K_{ia} values for the alkanes at the air-water interface extrapolated to -12°C. The result is 730 $cm^2 \cdot g^{-1}$, which corresponds to a spherical particle diameter of 0.09 mm. The 95% confidence interval for the SSA is 240 $cm^2 \cdot g^{-1}$. Using this value for the SSA of the snow, the K_{ia} values for a series of chlorobenzenes were determined very recently. The value for monochlorobenzene is smaller than the lower limit of determination, and the values for 1,3–dichlorobenzene and 1,2,4–trichlorobenzene at -0.5°C are 0.002 (0.00056) cm and 0.02 (0.0032) cm, respectively, where the numbers in parentheses are the estimated standard deviations taking into account errors in adsorbed volume and in SSA. The K_{ia} value for 1,3–dichlorobenzene compares favorably with the value obtained earlier for 1,4–dichlorobenzene, 0.003 cm (Hoff *et al.* 1995), and the value for 1,2,4–trichlorobenzene is not vastly different from that for 1,2,3–dichlorobenzene, 0.06 cm, estimated by extrapolating data for volatile nonpolar compounds (Hoff *et al.* 1995). The experimental values obtained for the chlorobenzenes support the earlier conclusions by Hoff *et al.* (1995) that K_{ia} values should increase by a factor of four to five for every tenfold decrease in vapour pressure.

The apparatus is well suited to determining adsorption constants for the intermediate members of the series of chlorinated benzenes, but modifications are required to obtain the constants for the higher chlorinated compounds. The sorption vessel will be redesigned to further reduce extraneous sorption, and solid phase micro-extraction will replace direct electron capture detector monitoring of vapour phase concentrations to increase sensitivity and eliminate interference from volatile impurities in the compounds. These modifications will be implemented in the next few months, and the adsorption constants for semi-volatile organochlorine compounds of interest, such as PCBs and chlorinated pesticides, will be determined.

The values obtained for the specific surface area of fresh snow samples collected during six snowfall events between December and March at the University of Waterloo ranged from 0.1 to 0.3 $m^2 \cdot g^{-1}$. These values agree with the scant literature data available (range 0.2 to 7.7 $m^2 \cdot g^{-1}$) and the size and geometry of snow crystals. A specific surface area of 0.1 $m^2 \cdot g^{-1}$ corresponds to a snowflake of thickness 0.02 mm. The data thus support the earlier conclusion (Hoff *et al.* 1995) that the SSA of fresh snow is likely to be between 0.1 and 1.0 $m^2 \cdot g^{-1}$. The preliminary results of the Monte Carlo study indicate that the coefficient of variation for SSA is rather high—about 50%. The procedure will be modified and a larger sample container will be used to improve precision; the method will be applied to further investigate the natural variability of freshly fallen snow and the decrease of its surface area with time as the snow ages. A paper is being written on the method and the preliminary results.

DISCUSSION/CONCLUSIONS

In a previous study of sorption of organic compounds by synthetic snow using two complementary techniques (Hoff *et al.* 1995), adsorption constants and their temperature dependencies were measured for twelve volatile nonpolar compounds. It was shown that the K_{ia} values for volatile nonpolar compounds on ice can be estimated by extrapolating those for water to lower temperatures and that partitioning in the thin quasi-liquid layer is not important. The K_{ia} values for hexachlorobenzene (HCB) and γ-HCH (lindane) were predicted on this basis using the empirical relationship for the air-water interface derived by Hoff *et al.* (1993). The environmental implications of partitioning at the air-ice interface were also discussed. The calculations indicated that there can be as much contaminant in a 10 cm layer of snow as in 10 km of atmosphere for low vapour pressure compounds like HCB and HCH. We do not yet have sufficient experimental K_{ia} data for semi-volatile compounds to test this model, but we can say that the few values that we have obtained so far do not contradict it.

One way of assessing the importance of snow scavenging of semi-volatile organic contaminants from the Arctic atmosphere is to include a term for wet gaseous scavenging by snow in the atmospheric deposition calculations of Cotham and Bidleman (1991). The wet gaseous scavenging coefficient for snow can be calculated as $K_{ia} \cdot SSA$, with K_{ia} estimated according to Hoff *et al.* (1995) and SSA taken as 1.0 $m^2 \cdot g^{-1}$. When this term is included, the total winter fluxes of HCH and HCB are increased by factors of 167 and 32 times, respectively. The wet gaseous winter fluxes of HCH and HCB are 1012 and 339 $ng \cdot m^{-2} \cdot mo^{-1}$ respectively, which are 99% and 97% of the total winter fluxes for these compounds. Gaseous scavenging by snow during winter is two to three orders of magnitude more important than gaseous scavenging by rain during summer for these compounds. It can be concluded that i) wet deposition by adsorption on snow exceeds all other contributions to deposition for these compounds,

including wet deposition by rain and air-sea gas exchange, and ii) winter deposition is the major contributor to total deposition in the Arctic environment.

Although these calculations are simplistic, they certainly suggest the importance of adsorption on snow surfaces. However, the parameter values have large uncertainties. The accuracy of the estimated adsorption constant values and the specific surface area of Arctic snow is not known with much certainty. The dry deposition velocity and the particle scavenging coefficients are also uncertain, and the precipitation value for winter (4 $mm \cdot mo^{-1}$) may be underestimated by as much as a factor of three. The Arctic atmosphere is relatively isolated from the mid-latitude sources of contaminants during summer, and this fact may not be properly taken into account in the calculations.

The expected post-depositional change in the fugacity capacity of snow has also not been taken into account in these calculations. It is expected that contaminants will tend to diffuse out of the snow layer (revolatilize) after being deposited due to the decrease in the specific surface area of snow during metamorphosis. Preliminary modelling calculations (C. Jia, pers. commun.) indicate that a temporary buildup in contaminant concentration in interstitial air may occur very soon after deposition, which might explain why ground-level air concentrations sometimes increase soon after a snowfall.

Expected project completion date: March 31, 1996

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DEPOSITIONAL TRENDS - LAKE AND MARINE SEDIMENTS

Project Leader: W.L. Lockhart, Freshwater Institute (FWI) Department of Fisheries and Oceans Canada (DFO), Central and Arctic Region

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, K. Ramlal (metals), H. Kling (biogenic remains)

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 of down-core profiles of polycyclic aromatic hydrocarbons, organochlorines, and metals. In addition, sediments from marine locations will 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 US border to northern Ellesmere Island, and work is now underway in the western Northwest Territories (NWT) and the Yukon;

2. To derive the long-range transboundary air pollution (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 (generally 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 analysed for a series of contaminants (metals, hydrocarbons, organochlorines). Time intervals for the deposition of each slice are estimated using several models (supplied by Dr. J. Robbins, National Oceanographic and Atmospheric Administration (NOAA), Ann Arbor, US) that account for mixing of the upper layers. 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.

Recently the interpretation of cores has been challenged by the Geological Survey of Canada (1995) who argue that down-core profiles of certain metals are artifacts of sedimentary processes and not records of deposition. (For an opposing view of pollution by heavy metals, see Nriagu 1995). There is no doubt that certain metals do become concentrated in surficial sediments due to natural processes within sediments (e.g. iron, manganese) and that these could be misinterpreted as indications of pollution; however, there is no evidence that metals important as pollutants (mercury, cadmium, lead) do this. Cores generally yield good records of purely synthetic substances (e.g. cesium-137, DDT, PCBs etc.) and these confirm the values of cores as archives recording histories of inputs. Furthermore, inputs of even natural substances like mercury at sites of known historical contamination have been recorded by sediment cores. This is not to say that cores (or any other technique) always produce the records sought; they can be misleading due to mixing and other processes, but analytical techniques allow this to be determined.

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 the US Environmental Protection Agency (EPA). We have obtained the appropriate GPS/SONAR equipment and software to produce these ourselves, and it was "ground-truthed" during 1994 and applied successfully to YaYa Lake in the Mackenzie Delta.

In 1992 and 1993, marine cores were obtained by participating with DFO ship cruises to Hudson Bay. In 1994 we were able to obtain cores from Lake Winnipeg, Manitoba, using the Coast Guard ship Namao. These cores were taken using conventional box corers, with 10-cm diameter push cores being taken from the box cores. It is hoped that we can extend the geographic coverage throughout the Canadian Arctic and compare results with other locations worldwide. External cooperation is encouraged, and a number of Russian marine sediment samples were obtained from the Murmansk Marine Biological Institute late in 1993. Three cores were also obtained from the Dnieper River, Ukraine, as part of a study there supported by the International Development Research Centre (IDRC).

ACTIVITIES IN 1994/95

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

The GPS/SONAR system was tested at West Hawk Lake, Manitoba, where excellent correspondence was obtained between previously known bathymetry and that generated by the system. With the assistance of our office in Inuvik, we were then able to apply the mapping technology at YaYa Lake in the Mackenzie Delta. We obtained the first bathymetric map of that lake during the summer of 1994 and at the same time, due to unusually calm conditions, we were able to collect cores. Late in the fiscal year, additional cores were obtained from three lakes in the NWT: Kellar Lake, Great Bear Lake, and Giauque Lake. Several cores were also taken in Great Slave Lake for Dr. Marlene Evans (Environment Canada, Saskatoon). Several cores were taken from Yukon lakes (Watson, Hanson) but those are described under the Yukon project. Independent but relevant work was also conducted on cores from reservoirs in the Dnieper River (Ukraine) and from Lake Winnipeg.

Handling of cores in the laboratory consists of freeze drying, analysis for unsupported lead-210 and cesium-137, and then, if the radionuclide profiles suggest datable sequences, slices are partitioned to several laboratories for bulk sediment chemistry, organochlorines, polycyclic aromatic hydrocarbons, and several metals. Down-core profiles of lead-210 have been analysed using mathematical mixing models provided by Dr. John Robbins (NOAA, Ann Arbor). The amount of analytical work required for each core is surprisingly large in view of the number of analytes; consequently the analyses lag behind the sampling by long periods.

For the analyses of metals, the sediment samples were freeze-dried and then subsamples of the freeze-dried material were digested with nitric, perchloric, hydrofluoric and sulfuric acids in teflon beakers; final volumes were adjusted to 25 mL. All the metals reported, with the exception of mercury and cadmium, were analysed by flame atomic absorption spectroscopy. Cadmium was analysed by graphite furnace atomic absorption, and mercury by cold vapour atomic absorption. Samples for mercury required a separate digestion with aqua regia. National Research Council of Canada standard reference sediments were analysed concurrently with sediment samples as a measure of analytical quality.

For organic compounds, sub-samples of freeze-dried sediments were Soxhlet-extracted with dichloromethane (DCM) for 16 hours. Internal standards of aldrin and octachloronaphthalene (OCN) were added at the extraction step. Internal standards of deuterated PAHs were added at the extraction step. The DCM extract was split 1:1 for determination of PAHs and OCs. Sulfur was removed using activated Cu filings. 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.* 1990,1995).

Results were communicated as they became available through several scientific and public channels. Notable among these were public presentations to northern people in Yellowknife, Whitehorse and Inuvik.

RESULTS

The new sites where cores were obtained during 1994/95 are listed in Table 1. In addition to these cores, as parts of other programs, ten cores were obtained from Lake Winnipeg and three from Dnieper River reservoirs (Ukraine). Several of the Russian Arctic Ocean surface sediment samples obtained in 1993 were also analysed.

If further cores cannot be collected under the Northern Contaminants Program, several large geographic gaps will occur in our coverage, notably northern Québec, the eastern, central, and western archipelago, the southern Keewatin, and central and northern Yukon. Numerous lakes in the NWT yield fish (lake trout, walleye, northern pike) that contain levels of mercury in excess of 0.5 ppm, the recommended maximum for human consumption. These high levels frequently give rise to the question as to whether the mercury levels reflect natural sources within the watershed or pollution. A similar situation has been described in northeastern Minnesota (Swain and Helwig 1989). The core profiles to date sug-

gest that most mercury loadings to lakes in the western NWT and Yukon are of natural, geologic origin. The basis for this suggestion is that mercury concentrations in the uppermost slices of sediment deposited recently differ little from those in the deepest slices. In the eastern NWT, however, mercury is typically higher by two to four-fold in the upper slices than in the deep ones, leading to the conclusion that most current inputs arise from outside the drainage basin. The mercury levels at the base of a core are taken as an estimate of natural processes within the basin. Increases above the levels in the basal slices are taken as evidence of some kind of "enrichment" supplying mercury in excess to the normal processes. Generally this enrichment is taken to be related to human activity, notably the burning of coal and municipal garbage and hence it has been described as 'cultural enrichment' (Robbins and Edgington 1976). Cultural enrichment is interpreted as increased inputs during the time intervals when the upper slices were deposited. Taking this interpretation, the core profiles offer perhaps the best insight we can obtain on whether the mercury inputs to a given lake originate mainly from within the basin by natural means or whether additional, more recent sources outside the watershed are also important.

The first bathymetric map of YaYa lake is shown in Figure 1 with core sites indicated. Core 1, from one of the deepest parts of the lake, has been analysed radiochemically for isotopes used in dating, namely lead-210 and cesium-137. Profiles for these are shown in Figure 2. The curve for lead-210 suggests two different sedimentation rates, one for the top few slices (476 g m^{-2} yr^{-1}) and a more rapid one for the deeper slices (550 g m^{-2} yr^{-1}). The lead-210 dates shown on Figure 2 indicate that the interval for maximum fallout of cesium-137 was from about 1963 to 1968, the period expected. The following metals have been analysed in slices of core 1 from YaYa lake: mercury, lead, cadmium, copper, iron, manganese, nickel, titanium, vanadium, and zinc.

The down-core profiles of several of these are shown in Figure 3. Taking slice ages from Figure 2, it is evident that the metals commonly associated with contamination (lead, cadmium, mercury) have increased very little or not at all in the upper, more recent slices as compared with deeper, older slices. The only metal with a striking increase in surficial sediments was manganese. The increased concentration of this metal near the surface of sediments has often been observed, and is believed to result from a natural redistribution process following redox gradients within sediments; it is not interpreted as increased recent inputs of manganese.

The most likely interpretation of these profiles is that the metals in YaYa Lake are of geological origin with any pollution component too small to be distinguished from background values. The flux of mercury (or other components) can be estimated as the product of the sedimentation rate and the concentration of mercury in a given slice. By this calculation, the flux of mercury to the uppermost slice of core 1 was 51.4 μg m^{-2} yr^{-1} and that to the deepest slice was the same at 51.5 μg m^{-1} yr^{-1}. These fluxes, although seemingly constant over time, are higher than those reported for the upper layer of Hawk Lake, NWT (5 μg m^{-2} yr^{-1}) and even Lake 375 much farther south (21 μg m^{-2} yr^{-1}) (Lockhart *et al.* 1993). Even if these fluxes of mercury to YaYa Lake originate from natural processes, they are high enough to prompt analysis of the fish.

Some cores collected in previous years have been examined for organochlorine compounds and PAHs. Figure 4 shows profiles of ΣDDT and PCB-related components in Lakes Belot and Ste Therese in the western NWT. Concentrations and historical profiles of DDT and PCB-related components in each core were similar. Maximum concentrations of ΣDDT were found in slices from the mid-1960s in Lac Ste Therese similar to observations in the Great Lakes (Eisenreich *et al.* 1989) and in other mid-continental cores (Muir *et al.* 1995). Low sedimentation rates in Lake Belot result in poor resolution and evidence of diffusion of some organochlorines into pre-1900 slices. Lac Ste Therese shows evidence for downcore dechlorination of *p,p'*–DDT to form *p,p'*–DDD. We previously found that the relationship of ln DDD/(DDD+DDT) vs median age of slice, which is a measure of DDT transformation, was linear in Hawk and Amituk Lakes (r^2=0.88, 0.41, respectively; Muir *et al.* 1995), similar to observations in Lake Ontario (Oliver *et al.* 1989).

Core 1 from Lac Ste Therese has been analysed for PAHs in the top 12 slices; concentrations of total PAH (excluding perylene and retene) ranged from 199 to 278 ng g^{-1} dry sediment with no tendency toward higher values in the top slices. As reported last year, there was no consistent pattern in PAH deposition throughout the histories represented by cores from Lakes Amituk, Belot, and Kusawa. Lac Ste Therese fits the same pattern in its failure to show increasing inputs of PAHs over background levels. PAH deposition appears to vary regionally just as mercury appears to do (Johansson 1985). Five of the six sediment samples analysed from the Russian Arctic fell under 200 ng g^{-1} dry sediment but the sixth one (sample 03-14) was higher at 742 ng g^{-1}. For comparison, two samples from the Canadian Ice Island (supplied by the Geological Survey of Canada,

Calgary) had values of 146 and 175 ng g^{-1} dry sediment. Perylene was virtually absent from the Russian samples (maximum 1 ng g^{-1} dry sediment) but it was present at 8 and 13 ng g^{-1} dry sediment, respectively in the two Ice Island samples.

DISCUSSION/CONCLUSIONS

Our coverage of northern lakes continues to improve as we expand the original north/south transect to a grid covering the Canadian North, but several very large areas are still not represented. The ability of the cores to offer insight into the geological vs. pollution components of mercury (and probably cadmium, lead and other metals) is proving to be quite helpful. Many populations of fish in the NWT have levels of mercury above consumption guidelines and the question is whether these result from basin geology or from pollution. As shown above, the major effort during 1994/95 was on YaYa Lake in the Mackenzie Delta and in that lake the first core shows no indication of a source other than background geology. Fluxes of mercury are high in that lake, but there is no indication that they have increased over at least the last century and a half. In other northern lakes reported in previous years we have seen consistent increases over time and we have attributed them to fallout of mercury to the watersheds as a result of atmospheric transport of mercury from outside the watersheds. One of the lakes cored successfully late in the fiscal year was Giauque Lake, which has received tailings inputs from the Discovery mine with a known historical sequence. This lake offers a valuable opportunity to calibrate the down-core profiles against known historical events.

More generally, perhaps the most important products of the sediment work are calculations of actual rates of delivery of contaminants to the systems under study, insights into how these inputs have been changing over time, partitioning sources into natural and contamination, and information on regional geographic variations.

Expected project completion date: Scientifically, the project will not be complete until a detailed grid covering both lakes and marine habitat has been completed. Several more lake locations are required and we have so little information about Arctic marine sites that it is difficult to predict the coverage needed. The two most northerly locations sampled to date should be revisited during an open-water season to try to obtain bathymetry information since essentially none was available at the time those cores were taken. The observation of increasing mercury levels in several cores from Hudson Bay points to the need for more marine samples. With the end of the Northern Contaminants Program in 1996/97, it seems unlikely that additional collections will be possible beyond 1995. If future sites are to be done (and several existing cores analysed), then it may be necessary to support them from other sources.

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. Similarly, fish from Lac à Jacques near Fort Good Hope have high mercury levels and cores will probably have to be taken from there.

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Table 1. Cores collected in the Northwest Territories under the Northern Contaminants Program for 1994/95

Lab ID #	Sample date	Lake Name	Sample site Latitude	Sample site Longitude
YaYa 1	1-Sept-94	YaYa L. (NWT)	69 10 27 N	134 39 45 W
YaYa 2	1-Sept-94	YaYa L. (NWT)	69 12 13 N	134 38 05 W
YaYa 3	1-Sept-94	YaYa L. (NWT)	69 11 19 N	134 37 22 W
WAT-1	23-Feb-95	Watson L. (YT)	60 06 25 N	128 46 00 W
WAT -2	23-Feb-95	Watson L. (YT)	60 06 22 N	128 47 49 W
HAN-1	27-Feb-95	Hanson L. (YT)	64 00 32 N	135 20 47W
HAN-2	27-Feb-95	Hanson L. (YT)	64 01 43 N	135 21 22 W
KEL-1	10-Mar-95	Kellar L. (NWT)	63 55 19 N	121 26 43 W
GB-1	13-Mar-95	Great Bear L. (NWT)	65 05 49 N	120 47 00 W
JQ-1	14-Mar-95	Giauque L. (NWT)	63 11 20 N	113 53 13 W
JQ-2	14-Mar-95	Giauque L. (NWT)	63 10 39 N	113 49 56 W
GSL-7*	11-Mar-95	Great Slave L. (NWT)	62 31 47 N	110 26 24 W
GSL-8*	16-Mar-95	Great Slave L. (NWT)	61 37 05 N	113 53 17 W
GSL-9*	16-Mar-95	Great Slave L. (NWT)	61 44 57 N	113 52 28 W
GSL-10*	16-Mar-95	Great Slave L. (NWT)	61 40 27 N	114 03 13 W
GSL-11*	17-Mar-95	Great Slave L. (NWT)	61 26 58 N	113 48 55 W
GSL-12*	17-Mar-95	Great Slave L. (NWT)	61 53 06 N	113 39 55 W
Russia 11-29	27-Aug-93	Russian Arctic, 123 m	77 40 09 N	102 08 03 E
Russia 20-49	09-Sep-93	Russian Arctic, 200 m	77 06 02 N	126 21 38 E
Russia 03-14	14-Aug-93	Russian Arctic, 2785 m	81 40 07 N	30 18 08 E
Russia 22-53	11-Sep-93	Russian Arctic, 3237 m	79 14 00 N	122 52 03 E
Russia 27-69	21-Sep-93	Russian Arctic, 530 m	78 41 55 N	112 31 75 E
Russia 14-32	02-Sep-93	Russian Arcitc, 3000 m	78 42 37 N	132 22 02 E

*Cores collected for Dr. Marlene Evans, Environment Canada, Saskatoon

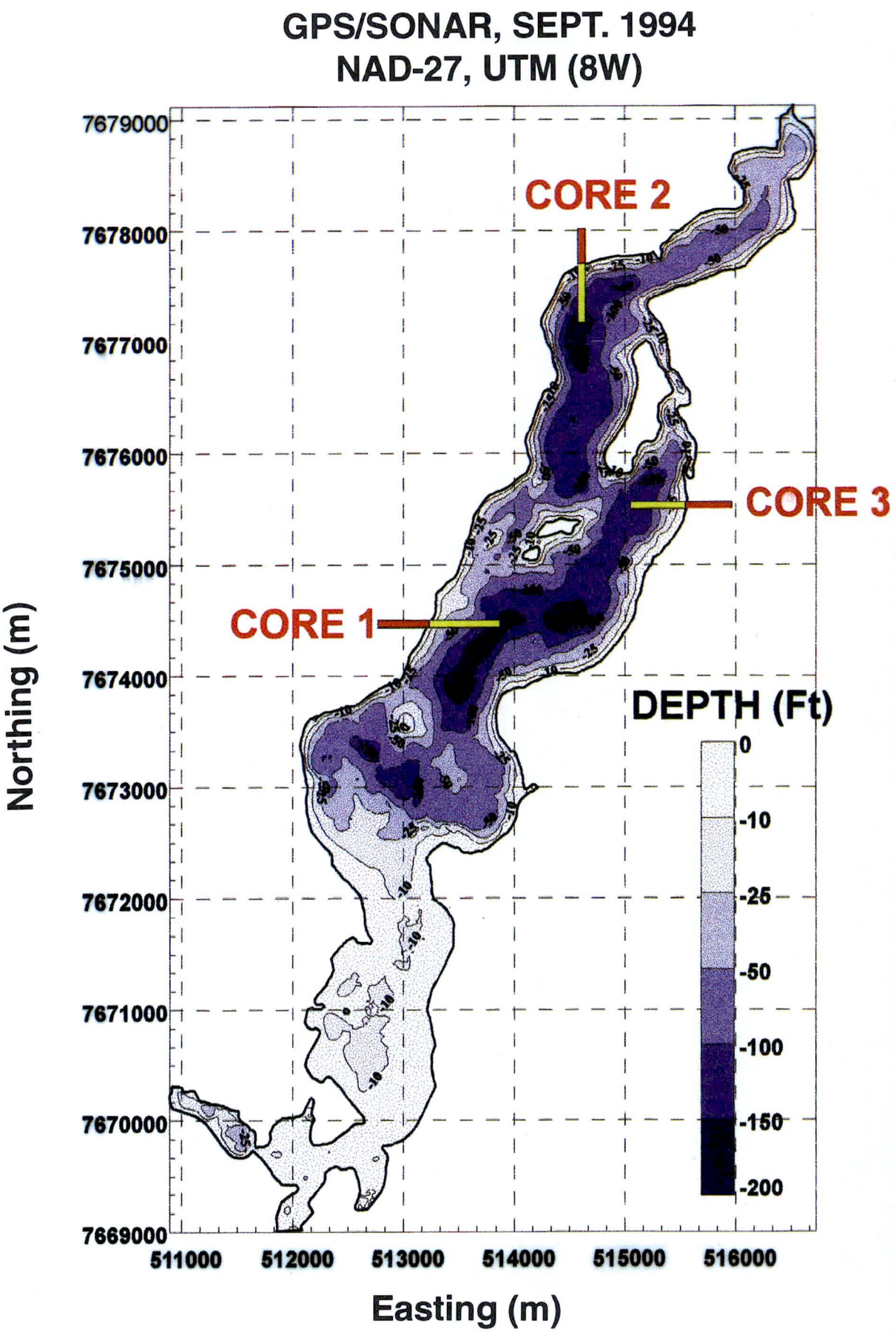

Figure 1. Bathymetric map of YaYa Lake, NWT

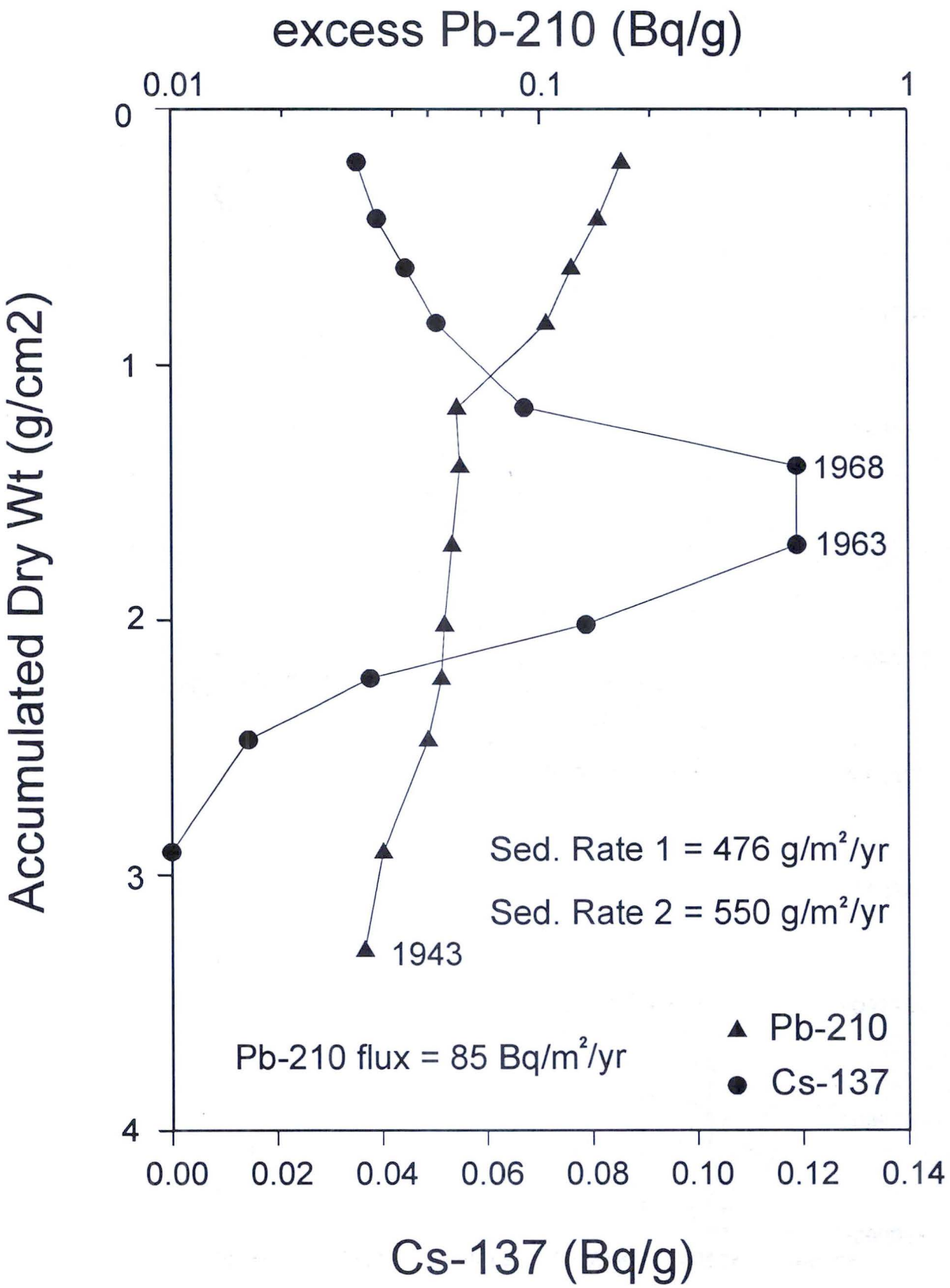

Figure 2. YaYa Lake 10 cm KB Core 1 Excess Pb-210 (Bq/g)

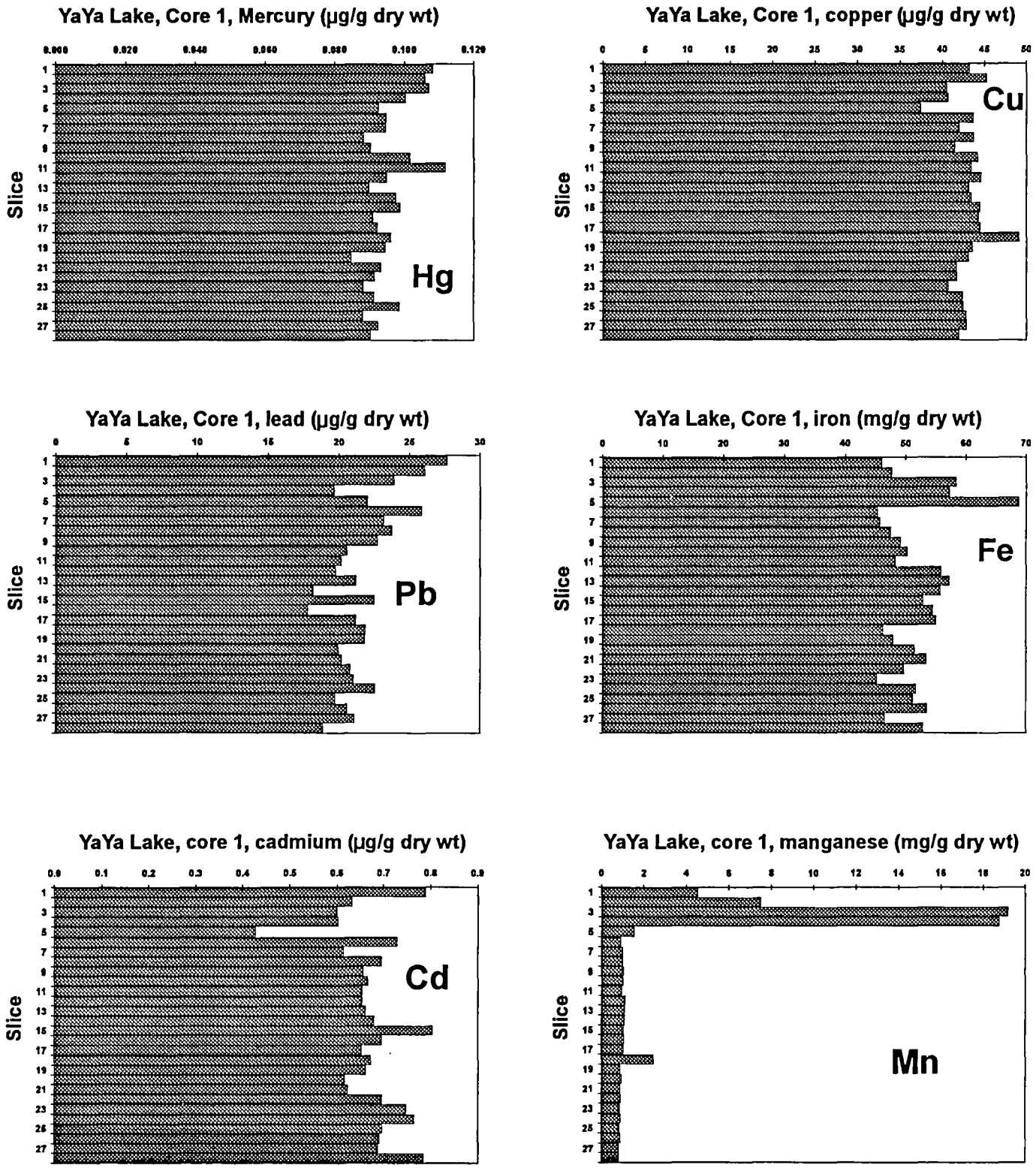

Figure 3. Some metals in YaYa Lake sediments, core 1, 1994

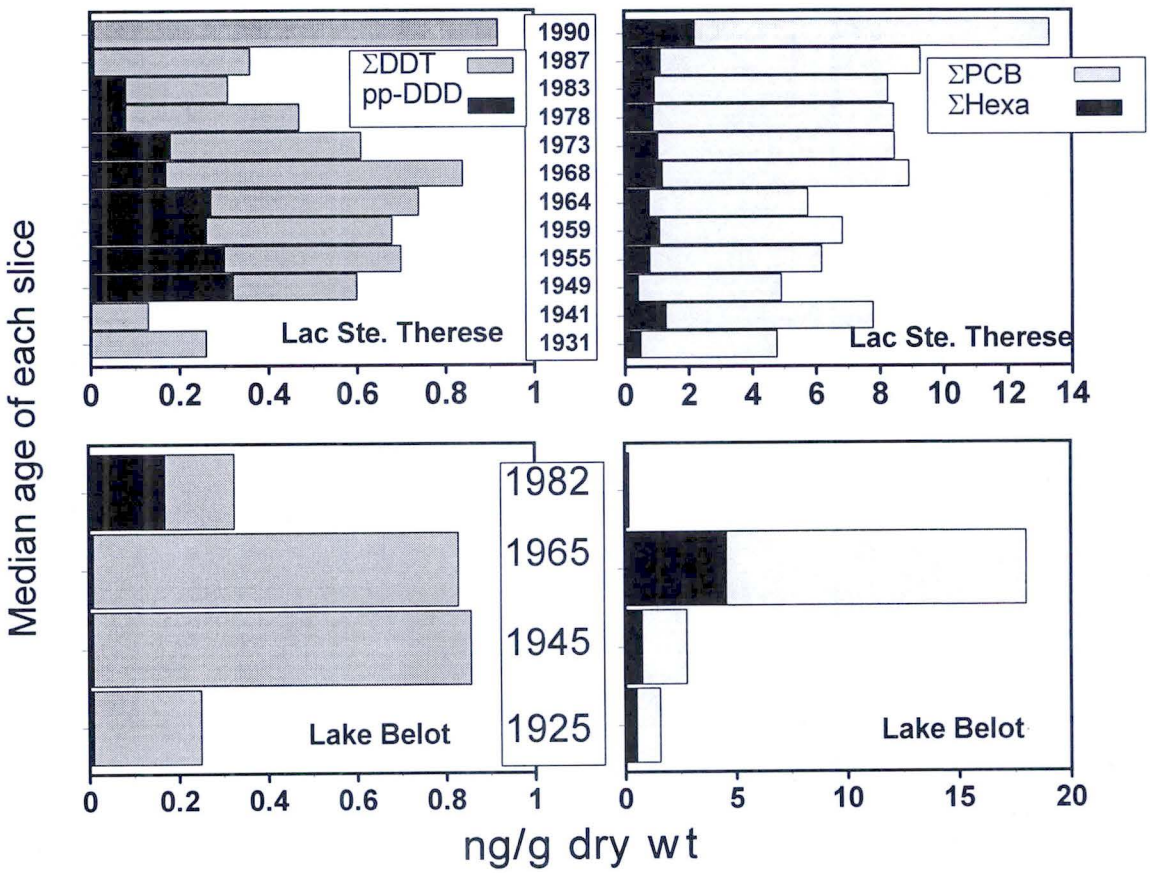

Figure 4. Profiles of DDT and PCBs in sediments of Lac Ste Therese, NWT, 1993

CURRENT CONTAMINANT DEPOSITION MEASUREMENTS IN ARCTIC PRECIPITATION (SNOW)

Project Leaders: M. Palmer, Contaminants Committee, Indian and Northern Affairs Canada; W.M.J. Strachan, National Water Research Institute, Environment Canada; M. Swyripa, Water Resources Division

Project Team: D.J. Gregor, University of Waterloo; M. Alaee; D. Burniston; C. Teixeira, EC/NWRI

OBJECTIVES

1. 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.

BACKGROUND/DESCRIPTION

Canada has major land and water areas located in the Arctic which can be defined here as the area north of latitude 60°N or some sub-set of the drainage area feeding the Arctic Ocean. The Arctic encompasses several million square kilometres representing a major sink for the deposition of persistent toxic chemicals that can be transported via the atmosphere. This in turn is a potential environmental and human health problem, since many of the compounds in question bioaccumulate in fatty tissue and the levels stored there increase with consumption and movement up the food chain. That the problem is real is attested to by the observation of significant residues of these chemicals in body burdens of higher trophic levels of biota—including humans—which are resident in the region.

Most of the compounds, currently designated as "LRTAP POPs" (long-range transboundary air pollution, persistent organic pollutants), are not, and in many cases never have been, in use in significant quantities in the Canadian Arctic. Other river studies in the Northern Contaminants Programme (NCP) have not been able to identify sufficient quantities in the rivers feeding the region to account for the levels of contaminants measured. Atmospheric transport is an obvious suspect, especially since it has been well established as a mode of introduction of the same compounds to other areas of Canada and the world—areas that also have little other contact with the chemicals.

There are three "modes" of introduction of atmospherically transported material to the terrestrial and aquatic environments. "Wet" precipitation via rain and snow is one; the others are dry deposition of particulate matter and gas exchange between air and various surfaces—water, soil, vegetation, ice/snow. All three modes are governed, to one degree or another, by temperature both on the surface following their arrival there and in the atmosphere during their partitioning among several phases there. In the instance of gas phase exchange, the direction of the movement of the chemicals will depend upon the relative concentrations in the air and in the different surface media. In the case of snow, evidence is mounting that there is a significant flux of the chemical out of the fallen snow and back to the atmosphere. Certainly much of the chemical is not retained in the snow.

These aspects of LRTAP POPs have been the subject of this study, which incorporates two parallel efforts ongoing in both the Yukon (YT) and the Northwest Territories (NWT). The ultimate goal of the project is to define the fluxes of the chemicals—not only as they fall but also their longer term introduction into the terrestrial and aquatic environments of the region. The medium selected for examination has been snow which accounts for the bulk of the precipitation in the region. Preliminary results from related studies may allow an estimate of the flux via rain which, while small in overall amount relative to snow, may be significant because it occurs at a time of higher temperatures and presumably higher atmospheric POP burdens.

Table 1. Snow Sampling Locations for 1994/95 Winter

Tagish, YT (3 samplers)	Mould Bay, NWT
Fraser, BC	Cape Dorset, NWT
	Baker Lake, NWT
Alert, NWT	Snare Rapids, NWT

ACTIVITIES IN 1994/95

Snow collections during 1994/95 were from locations indicated in Table 1. The Tagish site was chosen to determine some statistics for the collections, and three of the Yukon samplers were deployed there; the only other site in that region was at Fraser, BC. The sites for

the NWT region are the same as those employed during previous years. At some of the sites, polished aluminum trays were set out in order to collect quality accumulated snow samples. All samples have been extracted with dichloromethane using Goulden extractors at either Whitehorse (all YT samples), Yellowknife (Snare Rapids and Baker Lake) or Resolute Bay (Alert, Cape Dorset and Mould Bay). These have all been received at the NWRI laboratories where they are undergoing further processing and analysis.

Analyses reported here are those from the winter of 1993/94 at the sites indicated. During 1994/95, analyses of all samples from the winter of 1993/94 were completed. Quantification was done for a total of 19 organochlorine pesticides or residues, 11 chlorobenzenes including the hexa- congener, and 123 PCB congeners, separately quantified; total PCB burden was estimated from the sum of the congeners. Approximately 150 samples, mostly with analyte concentrations near the detection limit were examined together with a number of blanks and other quality control samples. The results presented in Table 2 are for a selection of these compounds. They are corrected for blanks, are uncorrected for internal surrogate spikes, which were added in the field (and generally were recovered at over 50%), and the individual results composited on a volume weighted basis to give the fluxes (ΣFj) and concentrations (C_{vwj}) shown. Fluxes refer to the period of collection and use the volume of snowmelt observed for each period. These fluxes will be recalculated with the "official" precipitation amounts for the collection periods as soon as they become available.

DISCUSSION

The trends of higher fluxes and concentrations of a number of the analytes from sites in the north and east, observed for accumulated snow in last year's report, are largely confirmed with the fluxes from weekly snow sampling this year. For all analytes, except the chlordanes and HCB (Table 2), Mould Bay and Alert samples have higher C_{vwj}s and ΣF_js than samples from south and west; values for Cape Dorset are intermediate between the two sets. The intermediate aspect of Cape Dorset is particularly true for fluxes and concentrations of PCBs, but is also true though less pronounced for fluxes of the HCHs and DDT residues. The chlordanes (concentrations and fluxes) and HCB (fluxes only), are exceptions; chlordanes show no significant variations in either concentrations or fluxes throughout the region, while fluxes for HCB show Cape Dorset to be more like the south and west than the north. The concentrations and fluxes for the current reporting year (winter 1993/94) are apparently reduced relative to those reported earlier. In part, this is the result of a different treatment of higher blanks experienced in the present analytical year; in part it is due to the use of observed precipitation from the snow collectors, which are less efficient than the official nipher gauges.

Data Treatment

This project, together with all others from NWRI funded under the NCP, is an active participant in the quality assurance project supported by the program. The performance of this laboratory has been satisfactory in all of the test samples and round-robins that have been offered—both those relevant to samples of this project and those for biota which are not the primary subject of our studies. This analytical facility will continue to support and participate in this work. We are also active in a similar QA/QC programme in the Great Lakes (the IADN QAPP) where our results are typically among the closest to the median and target goals.

Project completion: At the 1994 meeting of the NCP Technical Committee, it was decided that the weekly collectors at sites other than those co-located with air samplers of the Atmospheric Environment Service (Alert, Cape Dorset and Tagish) would be dismantled. Sampling for the winter of 1994/95 was already underway at the time and the decision was taken to refer to the winter of 1995/96. Following the analyses of the current samples (those collected in winter 1994/95), sampling in 1995/96 under the NCP will be continued only at the Alert, Cape Dorset and Tagish sites. Analytical activity during 1996/97 will be limited to the approved sites; analyses during 1995/96 will be the last for the broader sampling base.

Acknowledgment: 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. Concentrations and Fluxes at Winter 1993/94 Weekly Snow Collection Sites.

	α–HCH		Lindane		α–Chlordanes		α–DDT residues		HCB		Σ–PCBs	
Locations/ Territory	C_{vwj} ng/L	Σ_{Fj} ng/m^2	C_{vwj} ng/L	Σ_{Fj} ng/m^2	C_{vwj} ng/L	Σ_{Fj} ng/m^2	C_{vwj} ng/L	Σ_{Fj} ng/m^2	C_{vwj} ng/L	Σ_{Fj} ng/m^2	$_{vwj}$ ng/L	Σ_{Fj} ng/m^2
Yukon Territory												
Dawson	0.98	24.	0.37	9.1	0.14	3.5	0.32	8.0	0.06	1.6	3.0	75.
Whitehorse	0.53	17.	0.20	6.4	0.08	2.4	0.14	4.3	0.03	0.9	1.2	37.
Tagish	0.77	27.	0.35	12.	0.13	4.6	0.21	7.4	0.07	2.4	2.5	89.
Fraser	1.1	27.	0.23	5.7	0.09	2.2	0.17	4.1	0.02	0.5	1.4	35.
Northwest Territories												
Snare River	0.59	25.	0.29	13.	0.02	1.0	0.13	5.5	0.09	4.0	1.7	71.
Cape Dorset	0.60	40.	0.38	25.	0.04	2.4	0.27	18.	0.05	3.3	2.4	157
Mould Bay	2.9	110.	1.5	58	0.10	3.7	0.56	21.	0.55	21.	4.6	173
Alert	4.8	155.	1.9	63.	0.11	3.6	0.70	23.	1.5	47.	5.3	172

CURRENT CONTAMINANT DEPOSITION IN SNOW IN THE YUKON TERRITORY

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Project Team: D. Gregor, University of Waterloo; G. Whitley, Pollution Control, Water Resources Division, Indian and Northern Affairs Canada; R. Bailey, Atmospheric Environment Service; M. Alaee, Wm. Strachan, C. Teixeira and N. Jones, Lakes Research Branch, National Water Research Institute (NWRI) Environment Canada

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 the country, including the Yukon Territory. Precipitation is an effective means of removing trace organic contaminants from the atmosphere. These contaminants can 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 it thus follows that snow is an effective scavenger of semi-volatile organic contaminants from the atmosphere. 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 during 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).

In this context, 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, can the relative importance of other sources, including local landfills, be assessed relative to the total contaminant burden of the Yukon River system.

ACTIVITIES

Samples

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 at 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 staff at Environment Canada's National

Water Research Institute (NWRI). Thus results are comparable to similar work undertaken in the Northwest Territories (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 Yukon Territory. Bulk snow samples were collected at the same sites sampled in 1992/93 and at four additional sites: 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. The 1993/94 samples have been extracted and forwarded to NWRI for analyses, which had not been completed as this report was sent to print.

Only the collectors at Tagish and White Pass were operated during the winter of 1993/94 and the bulk snow pack samples were collected at the same locations as in 1994. These samples have been extracted and the extracts have been forwarded to NWRI for analysis.

RESULTS

This discussion is 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 seven samples were collected here in the period between November 1, 1992 and the end of March, 1993. Nevertheless, the PCB congener patterns 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 homologue composition for bulk snow samples and the snow collectors at the Tagish, White Pass and Whitehorse sites is made in Figure 2. Homologue concentrations are lowest at the Whitehorse site. A comparison of samples from Tagish and White Pass, however, indicates that concentrations are generally lower at Tagish, but demonstrate a general increase in concentration for the homologues 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 also compared in Figure 2. There is a clear similarity with respect to the homologue 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. Again, this 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 factoring in the amount of snow collected in the snow collector. The computed deposition for each sample in $ng \cdot m^{-2} \cdot day^{-1}$ is compared among the three collectors in Figure 3. 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 $ng \cdot m^{-2} \cdot day^{-1}$. These values are quite comparable with High Arctic sites from the NWT. In contrast, the mean deposition at White Pass for the winter of 1992/93 was estimated at 100 $ng \cdot m^{-2} \cdot day^{-1}$.

The mean ΣPCB deposition at Tagish and Whitehorse appears to agree 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 $ng \cdot m^{-2} \cdot day^{-1}$ (Figure 3). 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) (DIAND 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 (Table 1). Results for the key chlorinated benzenes are presented in Figure 4 for the Tagish, White Pass and Whitehorse sites respectively. 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, White Pass and Whitehorse (Figure 5). Once again there is a major difference between the deposition rates calculated for the different sites with daily deposition throughout the winter at White Pass an order of magnitude greater than that at Tagish or Whitehorse. 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 scrubbing 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, NWRI; Yukon Territorial Government Yukon College; University of Waterloo; Yukon Contaminants Committee

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Table 1. Mean concentrations of selected organochlorines collected at Tagish, White Pass and Whitehorse in the Yukon Territory for 1992/93. Concentrations are expressed as pg/L (sample size (n), number of non-detects).

	Tagish	White Pass	Whitehorse
Trans-Nonachlor	153 (16, 7)	23 (14, 10)	16 (7, 5)
Heptachlor Epoxide	40 (16, 14)	ND (14, 14)	ND (7, 7)
A Chlordane	716 (16, 3)	788 (14, 0)	369 (7, 0)
G Chlordane	190 (16, 10)	275 (14, 3)	108 (7,3)
Endosulfan I	640 (16, 3)	868 (14, 0)	374 (7, 0)
Dieldrin	251 (16, 3)	288 (14, 0)	132 (7, 0)
o,p-DDT	25 (16, 13)	70 (14, 9)	5 (7, 6)
p,p-DDE	139 (16, 3)	149 (14, 2)	51 (7, 2)

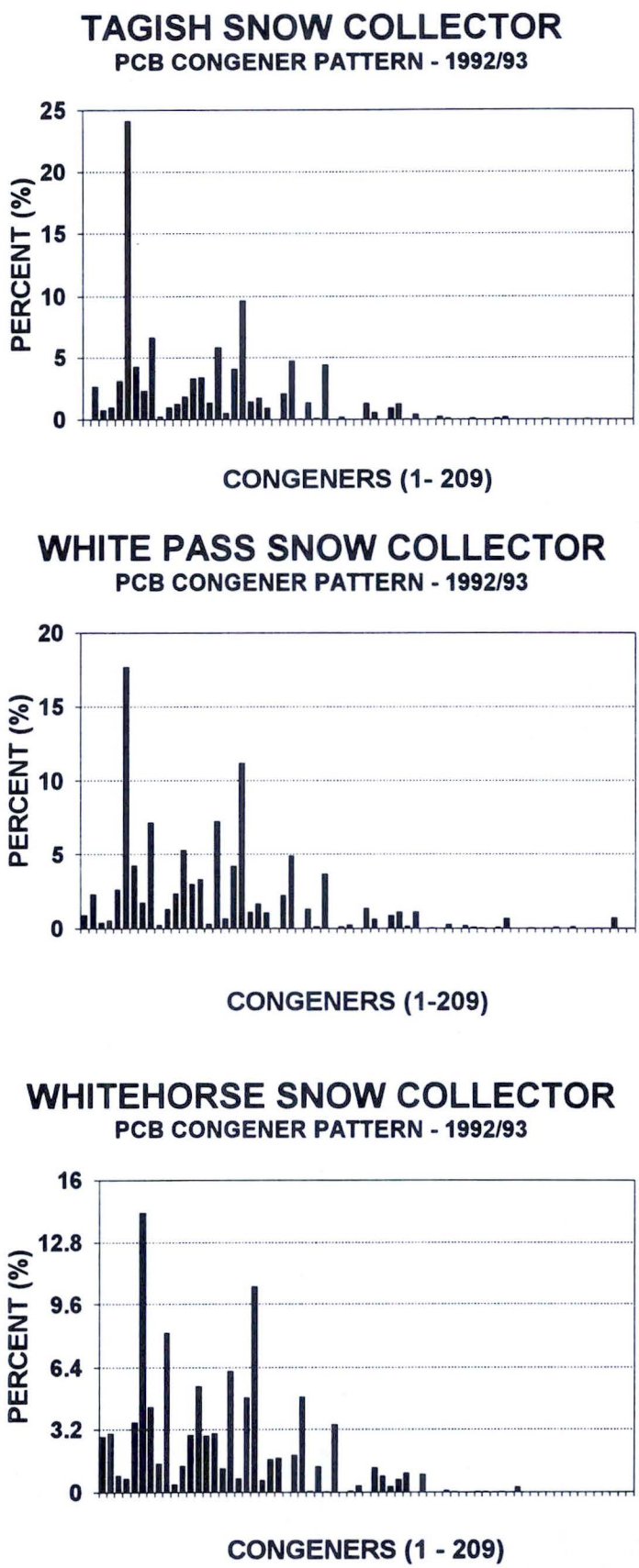
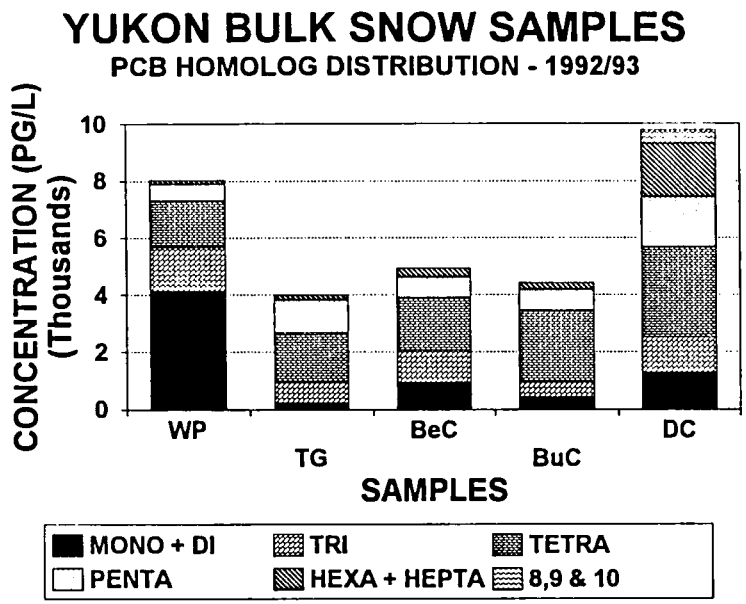
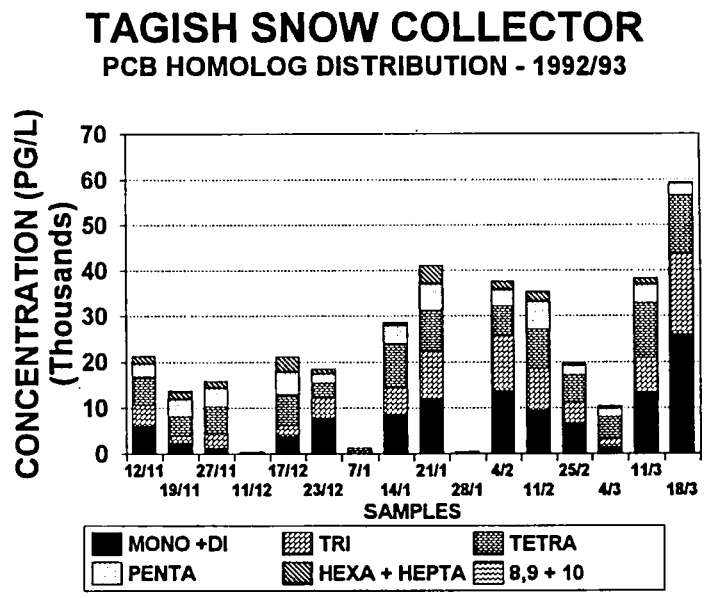
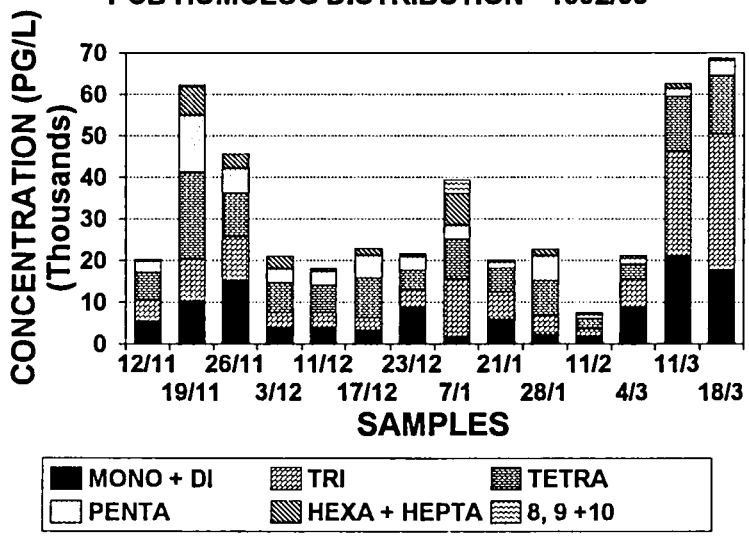


Figure 1. Comparison of the relative contribution of individual PCB congeners averaged for all samples from snow collectors for the winter of 1992/93 for Tagish, White Pass and Whitehorse







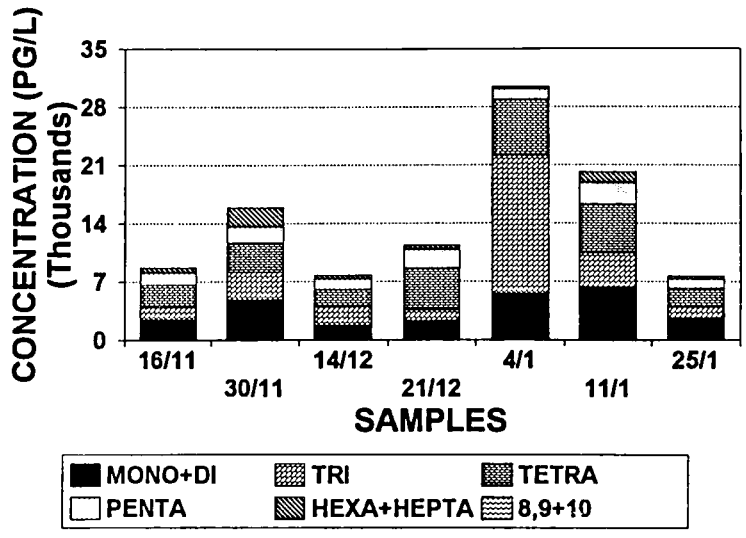


Figure 2. PCB homolog composition of bulk snow samples collected in early March 1993 from White Pass (WP), Tagish (TG), Beaver Creek (BeC), Burwash Creek (BuC) and at Dawson City (DC) and of individual samples collected using the large area snow collectors at Tagish, White Pass and Whitehorse during the winter of 1992/93. The sample dates shown on the Y-axis are the end dates of the snow sampling period

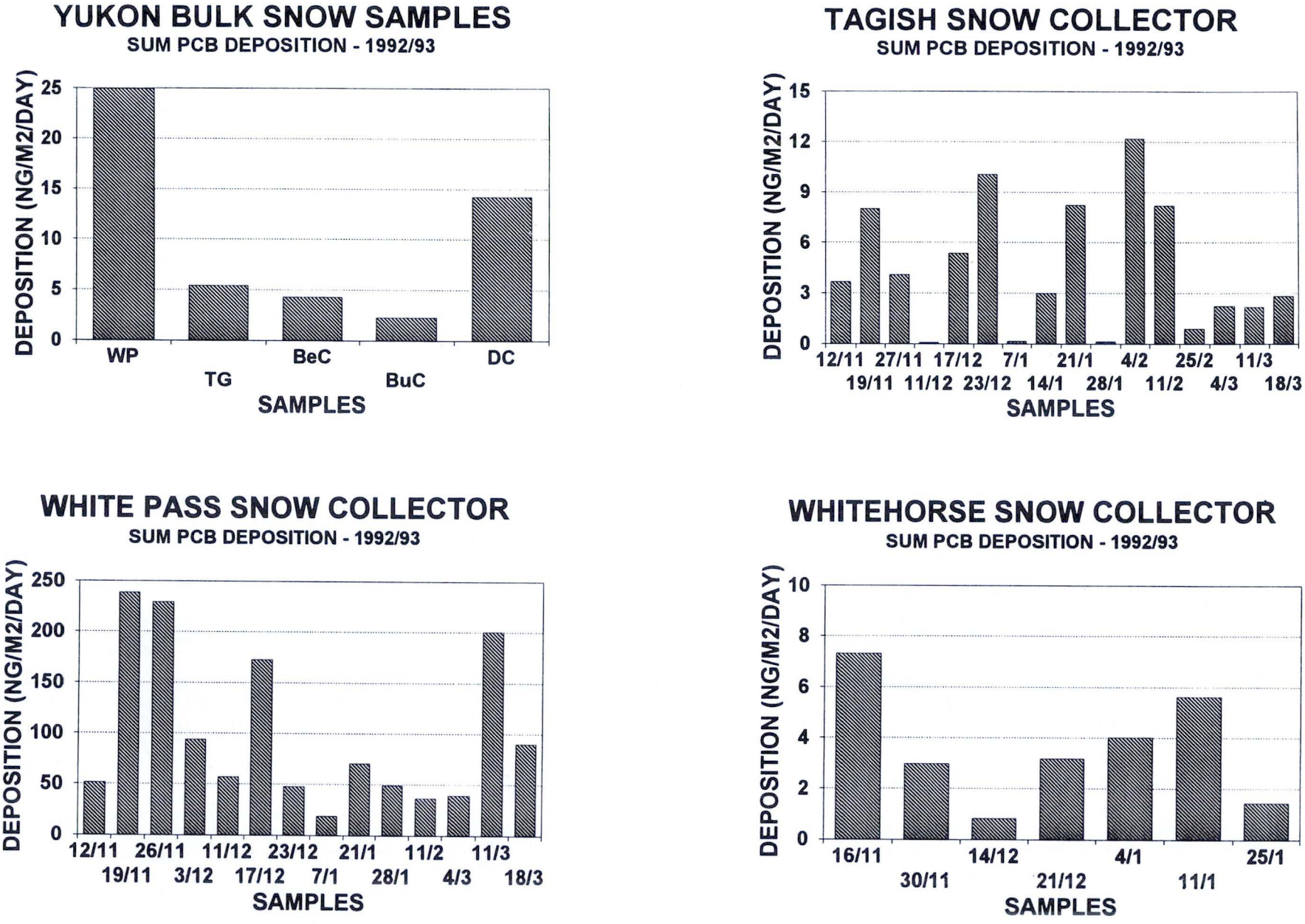


Figure 3. Comparison of the sum PCB deposition as determined for the bulk snowpack samples and for the samples collected from each of the snow collectors

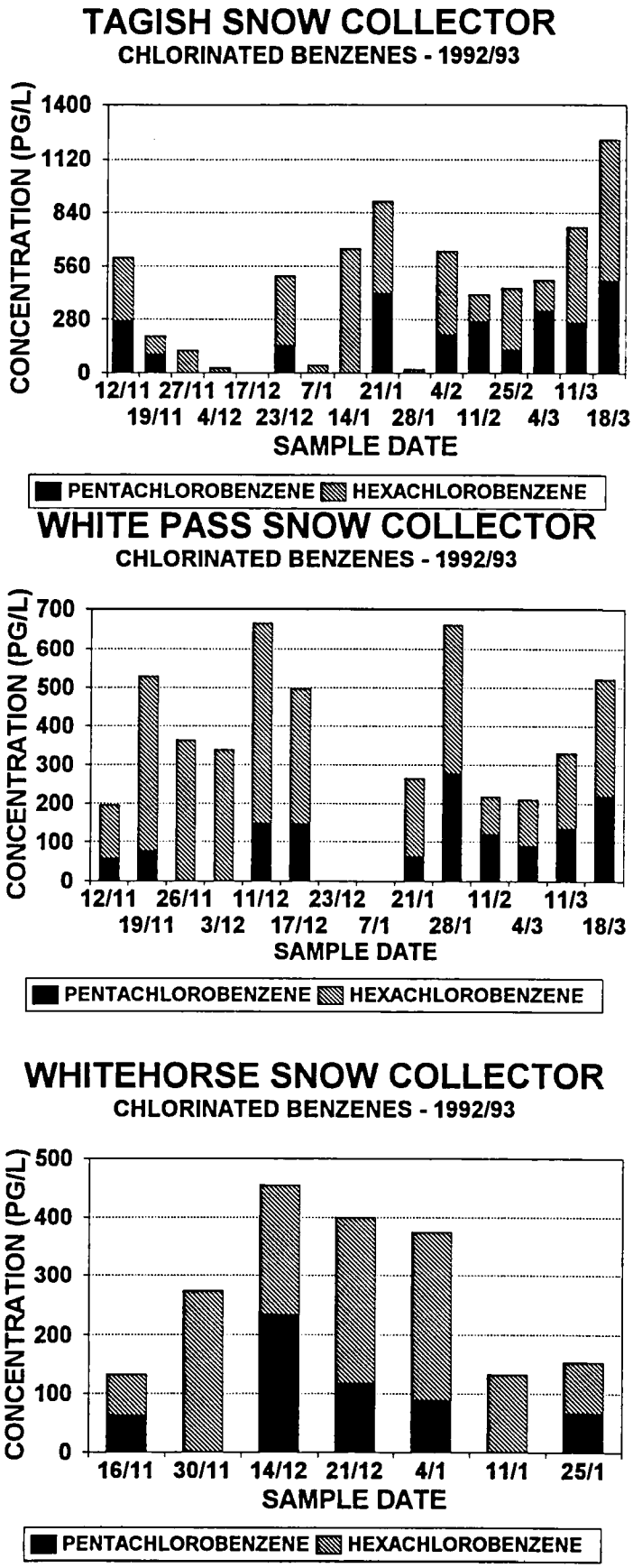


Figure 4. Concentrations of penta– and hexachlorobenzene for individual snow samples from Tagish, White Pass and Whitehorse

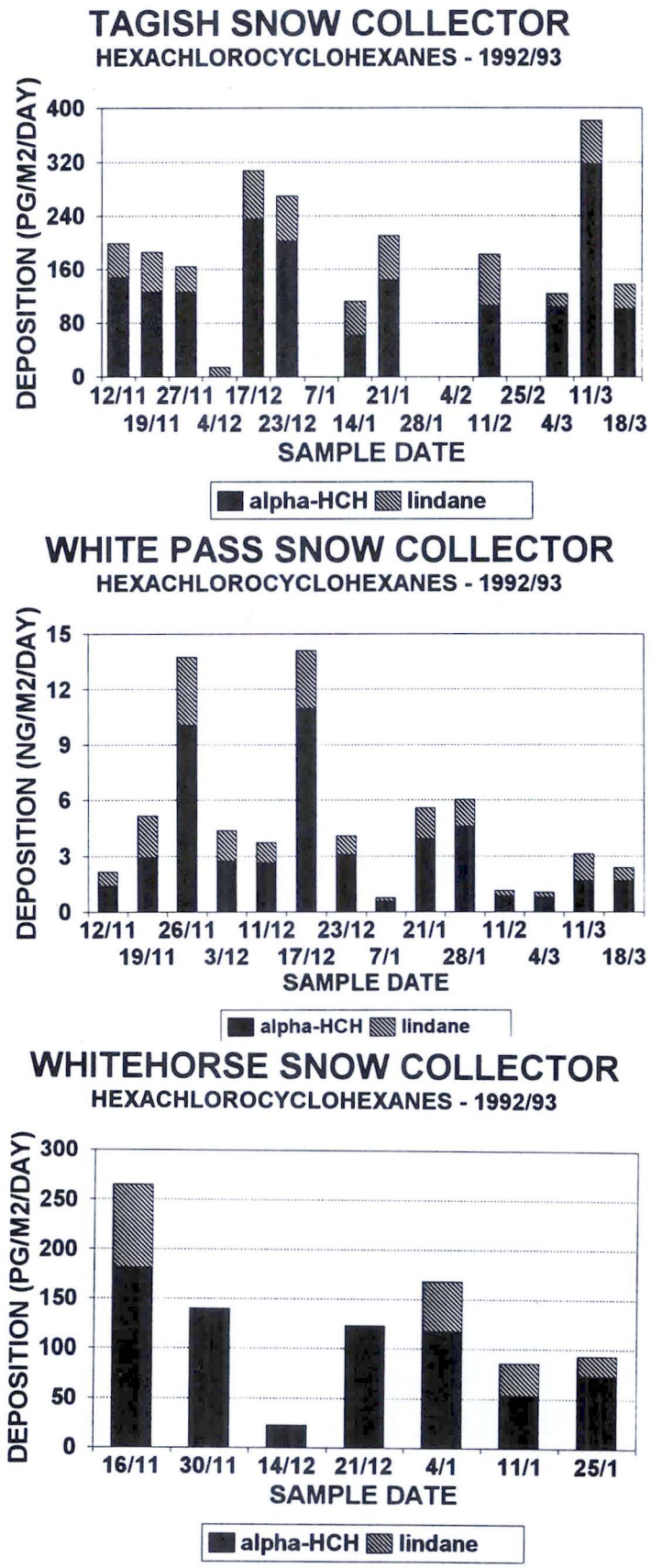


Figure 5. Calculated daily depositions of α–HCH and lindane for the Tagish, White Pass and Whitehorse snow collectors for the winter of 1992/93. Note that the units are different for samples collected at the White Pass site relative to the other two sites

RIVERINE INPUTS OF CONTAMINANTS TO THE ARCTIC MARINE ENVIRONMENT

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OBJECTIVES

Short-term

1. 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

1. 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. Information on contaminant loadings to the Arctic Ocean from any northward flowing river is limited. Prior to the commencement of this study, what information did exist for North America focussed on the Mackenzie River since it is the largest riverine system. However, in order to ensure that no major contaminant pathway has been missed, river systems that drain other ecozones (e.g. tundra) and flow into estuarine rather than deltaic environments must be considered as well.

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 the Arctic Environmental Strategy (AES) and for Arctic Monitoring 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 1994/95

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. Maps of sampling locations and basic water quality data were provided by Jeffries *et al.* (1994). Sample processing and laboratory analyses commenced in the fall and winter of 1992/93.

Follow-up sampling was conducted at all sites in 1993/94. A greater number of field blanks were collected to improve quality control. The three Mackenzie River sites were sampled on three 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.

ACTIVITIES IN 1994/95

Sample Collection

The three Mackenzie River sites were sampled on three occasions during the ice-free season and once under the ice (i.e. as in 1993/94) to permit evaluation of between-year and seasonal variability. Replicate samples were collected at the Arctic Red River site to assess between-sample variability. To evaluate the past variations in contaminant loading in the Mackenzie River, sediment cores were also collected in 94/95 at 8 stations in shallow lakes within the Mackenzie Delta (see Figures 1, 2, and 3).

Sample Analysis and QA/QC

Methods used for sample collection and processing, chemical analysis and laboratory QA/QC were described previously by Jeffries *et al.* (1994). Mackenzie River water and suspended sediment samples from 1994/95 were handled similarly. Briefly, large volume water samples were extracted using the Goulden apparatus (Neilson *et al.* 1988, Comba *et al.* 1993). Suspended sediment samples were extracted with hexane/acetone. The extracted alkanes, PAHs and organochlorine pesticides (OCs) were separated on a silica column and recovered using suitable eluants. Eight chlorobenzenes, 20 OCs, 120 PCB congeners, 17 PAHs, several alkylated PAHs and acyclic hydrocarbons were quantified using capillary gas chromatography or capillary GC-mass spectrometry. The laboratories participating in this project include several at Environment Canada's National Water Research Institute (NWRI) and the DIAND-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.).

The sediment cores collected in 1994/95 were sectioned, and the sub-samples freeze-dried and extracted with dichloromethane. The sediment cores were dated using ^{137}Cs and four of the cores (49 samples) were analysed for contaminants as above.

RESULTS

Lake sediments collected from shallow lakes within the delta were used to examine temporal trends in the deposition of particle reactive contaminants (OCs, PAHs, heavy metals). Results for Core 1 collected from Lake 3 in the outer delta (see Figure 2) are given in Tables 1–4 as an example of the concentrations and range of organic compounds that we have detected. Data for the remaining cores are similar. The core was dated and a sedimentation rate of 0.25 mm • yr^{-1} determined.

The concentration ranges of selected organic compounds detected in water samples are presented in Table 5. These compounds represent approximately one third of the analytes included in this study. However, we have chosen to focus on water concentrations for this brief report because suspended sediments are less likely to be the predominant locus for riverine contaminant transport in the NWT. Suspended particulate (SPM) concentrations in our samples are very low (1-10 $mg•L^{-1}$), and the ratio of dissolved organic carbon (DOC) to particulate organic carbon (POC) varies from 20 to 200 $mg•L^{-1}$. The Mackenzie River is the only exception; its SPM varies from 50 to 200 $mg•L^{-1}$. Extremely low major ion, nutrient and heavy metal concentrations observed in Keewatin river waters (see Jeffries *et al.* 1994) reflect the geochemical unreactivity expected in Arctic Shield terrain. For example, Ca^{2+} concentration in 9 of the 11 rivers is ≤2 $mg•L^{-1}$. The Andrews River (27 $mg•L^{-1}$) and the Coppermine River (6.4 $mg•L^{-1}$) are the exceptions.

DISCUSSION

As a general rule, the concentration of organic contaminants observed in Canadian Arctic rivers is very low. The 22 compounds (or groups of compounds) presented in Table 5 exhibited both the widest absolute concentration ranges and were detected in at least half (and usually most) of the samples. With the exception of total n-Alkanes and α–HCH, the low end of the ranges were always below analytical detection limits (BDL). Our remaining analytes (not shown in Table 5) had even lower concentrations and many more "BDL" occurrences. Whether or not these concentrations constitute a significant contaminant loading to the Arctic Ocean will be evident once the data are combined with river flow.

The predominance of α–HCH in our river samples and the occurrence of the other pesticides presented in Table 5 is similar to the distribution of OCs observed in

Arctic snow (Gregor and Gummer 1989) although the concentration ranges are consistently lower. We must still evaluate whether the terrestrial basin is acting as a sink, or if the concentration differences between snow and river reflect a re-emission process. The compounds in Table 5 are listed according to their GC retention time, a general indicator of volatility. The fact that the more volatile species within a given class often exhibit the highest maximum concentrations supports the distillation-condensation model of transport from warm source areas to the Arctic (Wania and Mackay 1993).

There are substantial spatial and temporal differences in particulate phase PAH levels found at the three Mackenzie sites and among the Keewatin rivers. Detailed evaluation of these data will yield important information on their source and the processes controlling transport from terrestrial to aquatic environments.

Expected project completion date: March 31, 1997

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Table 1. n-Alkane Results for Mackenzie Delta Core Samples (ng/g dry wt.).

Station	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**
Core Section (cm)	**0-1**	**1-3**	**3-5**	**5-7**	**7-9**	**9-11**	**11-13**	**13-15**	**15-17**	**17-19**	**19-21**
Dry Wt. Extracted (g)	**10**	**30**	**30**	**30**	**30**	**30**	**30**	**30**	**30**	**30**	**30**
% Organic Carbon	**2.27**	**1.99**	**2.09**	**2.37**	**1.41**	**2.14**	**1.53**	**1.42**	**1.49**	**1.60**	**1.48**
n-Undecane	4100	1000	1500	2400	3100	140	700	880	940	770	530
n-Dodecane	1900	620	790	970	1200	300	420	620	540	460	330
n-Tridecane	360	190	240	210	210	170	210	190	140	200	140
n-Tetradecane	400	220	260	220	220	270	250	220	160	240	170
n-Pentadecane	550	300	340	290	290	350	300	270	200	290	230
n-Hexadecane	570	310	370	310	300	380	320	290	200	300	240
n-Heptadecane	630	340	390	340	330	390	330	330	230	330	270
n-Octadecane	620	350	400	360	320	440	360	330	230	350	280
n-Nonadecane	590	330	380	360	320	420	340	310	220	330	260
n-Eicosane	710	370	440	400	350	480	400	370	250	400	310
n-Heneicosane	900	400	530	410	380	500	460	410	290	530	310
n-Docosane	1400	500	450	420	420	500	660	560	400	920	330
n-Tricosane	2100	690	1100	560	600	700	970	810	550	1000	440
n-Tetracosane	2600	800	1300	560	650	670	1200	1000	670	1800	480
n-Pentacosane	2700	900	1400	680	770	1000	1300	1100	700	670	560
n-Hexacosane	2500	800	1300	510	600	620	1200	950	610	1800	440
n-Heptacosane	2700	1000	1500	820	940	2000	1500	1200	770	2500	730
n-Octacosane	2000	670	1100	410	480	530	1100	860	540	1800	390
n-Nonacosane	2100	790	1300	640	720	1200	1300	1000	640	1600	610
n-Triacontane	1400	460	800	290	340	370	820	680	410	1300	290
n-Untriacontane	1600	580	1000	530	580	1000	1100	910	530	1600	540
n-Dotriacontane	1100	300	650	210	250	270	720	590	330	1100	230
n-Tritriacontane	1000	300	650	260	320	530	720	600	340	860	300
n-Tetratriacontane	670	150	410	120	160	160	500	410	220	750	150
n-Pentatriacontane	530	120	330	110	130	140	380	330	180	580	130
n-Hexatriacontane	390	73	230	66	83	86	300	240	120	460	85
Squalane	190	63	110	44	48	56	99	80	49	130	38
Pristane	370	200	240	210	200	300	250	220	160	240	190
Phytane	270	160	190	160	150	130	170	160	110	170	140
Total n-alkanes, nC11-C36	36000	13000	20000	12000	14000	14000	18000	15000	10000	23000	8800
Total nC11-C19	9600	3400	4400	5100	5800	2700	3600	3800	3100	3000	2400
Total nC20-C29	20000	6900	11000	5400	5900	8200	10000	8300	5400	13000	4600
Total nC30-C36	6800	2000	4100	1600	1800	2600	4500	3800	2100	6700	1700
Total nC15-C19	3000	1600	1900	1600	1600	2000	1700	1500	1100	1600	1300
Total nC23-C33	22000	7300	12000	5400	6200	9000	12000	9700	6100	16000	5000
OEP at C17	0.96	0.94	0.94	0.95	0.96	0.92	0.93	0.93	0.95	0.93	0.92
OEP at C25	0.95	0.99	0.97	1.27	1.17	1.42	0.94	0.96	1.00	0.59	1.15
OEP at C27	1.13	1.30	1.25	1.71	1.65	2.66	1.26	1.28	1.27	1.03	1.66
OEP at C29	1.73	2.14	1.94	2.86	2.71	4.45	1.91	1.92	1.97	1.70	2.75
Pristane/Phytane	1.35	1.27	1.26	1.27	1.36	1.31	1.46	1.41	1.50	1.42	1.44

Table 2. Polycyclic Aromatic Hydrocarbon (PAH) Results for Mackenzie Delta Core Samples (ng/g dry wt.).

Station	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**
Core Section (cm)	**0-1**	**1-3**	**3-5**	**5-7**	**7-9**	**9-11**	**11-13**	**13-15**	**15-17**	**17-19**	**19-21**
Dry wt. Extracted (g)	**10**	**30**	**30**	**30**	**30**	**30**	**30**	**30**	**30**	**30**	**30**
% Organic Carbon	**2.27**	**1.99**	**2.09**	**2.37**	**1.41**	**2.14**	**1.53**	**1.42**	**1.49**	**1.60**	**1.48**
Naphthalene	-	-	77	68	75	130	93	98	94	69	85
Acenaphthylene	-	-	0.18	BDL	0.10	0.092	0.079	0.065	0.067	0.050	0.070
Acenaphthene	-	-	-	-	-	-	-	-	-	-	-
Fluorene	-	-	22	21	20	33	22	25	27	21	22
Phenanthrene	-	-	120	120	110	180	120	130	140	110	120
Anthracene	-	-	2.1	1.1	1.3	2.0	1.7	1.6	2.2	2.7	1.4
Fluoranthene	-	-	20	19	18	28	18	19	17	13	17
Pyrene	-	-	33	32	30	50	33	35	37	33	32
Benz[a]anthracene	-	-	11	10	9	16	10	10	11	8.7	10
Chrysene	-	-	69	68	58	92	66	71	76	59	63
Benzo[b]fluoranthene	-	-	17	14	12	13	12	12	11	6.8	9.1
Benzo[k]fluoranthene	-	-	7.6	6.2	BDL	5.8	BDL	4.1	3.8	3.4	3.2
Benzo[a]pyrene	-	-	15	14	12	20	13	14	15	12	13
Perylene	-	-	130	120	130	210	130	130	140	100	130
Indeno[1,2,3-cd]pyrene	-	-	12	11	10	13	8.0	9.4	7.2	4.8	7.7
Dibenz[a,h]anthracene	-	-	7.5	7.1	6.4	7.5	5.2	6.2	5.2	3.8	4.3
Benzo[g,h,i]perylene	-	-	70	61	53	72	42	49	44	31	43
2-Methylnaphthalene	-	-	170	160	130	260	180	190	200	140	140
1-Methylnaphthalene	-	-	100	99	81	160	110	120	130	88	86
2,6 & 2,7-Dimethylnaphthalene	-	-	79	75	55	120	76	86	95	68	61
1,6-Dimethylnaphthalene	-	-	150	140	120	230	160	160	180	130	120
2,3- & 1,4-Dimethylnaphthalene	-	-	120	110	95	190	130	140	160	110	110
1,5-Dimethylnaphthalene	-	-	32	30	25	51	34	36	40	28	27
1,2-Dimethylnaphthalene	-	-	14	15	12	15	13	12	13	12	11
2,3,6-Trimethylnaphthalene	-	-	41	38	31	64	42	45	113	80	34
2,3,5-Trimethylnaphthalene	-	-	62	59	48	97	63	67	76	55	32
2-Methylphenanthrene	-	-	57	57	43	86	57	60	67	50	50
2-Methylanthracene	-	-	2.3	1.7	1.6	3.0	1.9	1.9	2.1	2.1	1.6
1-Methylanthracene	-	-	63	64	49	97	62	65	72	54	54
1-Methylphenanthrene	-	-	44	44	34	67	44	46	52	38	38
9-Methylanthracene	-	-	0.58	0.54	0.55	0.95	0.53	0.49	0.64	0.55	0.43
3,6-Dimethylphenanthrene	-	-	18	18	13	26	16	17	19	13	14
9,10-Dimethylanthracene	-	-	BDL	0.66	0.46	1.6	0.51	1.0	0.77	0.95	0.89
2-Methylfluoranthene	-	-	7.8	8.7	6.1	11	5.6	6.2	5.1	2.0	5.2
Percent Recoveries of Internal Standards.											
Naphthalene-d8	-	-	*58*	*69*	*61*	*69*	*67*	*66*	*71*	*65*	*55*
1-Methylnaphthalene-d10	-	-	*72*	*81*	*64*	*76*	*71*	*68*	*72*	*70*	*61*
Acenaphthylene-d8	-	-	*80*	*82*	*68*	*86*	*71*	*68*	*72*	*65*	*55*
Acenaphthene-d10	-	-	-	-	-	-	-	-	-	-	-
Fluorene-d10	-	-	*77*	*81*	*68*	*81*	*76*	*73*	*81*	*77*	*70*
Anthracene-d10	-	-	*82*	*85*	*72*	*85*	*81*	*79*	*83*	*83*	*74*
Pyrene-d10	-	-	*91*	*99*	*82*	*99*	*88*	*85*	*88*	*76*	*81*
Chrysene-d12	-	-	*93*	*106*	*84*	*94*	*94*	*89*	*88*	*88*	*79*
Benzo[a]pyrene-d12	-	-	*104*	*135*	*98*	*94*	*109*	*98*	*86*	*100*	*78*

BDL–Below Detection Limit

Table 3. Organochlorine Pesticide Results for Mackenzie Delta Core Samples (ng/g dry wgt.).

Station	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**
Core Section (cm)	**0-1**	**1-3**	**3-5**	**5-7**	**7-9**	**9-11**	**11-13**	**13-15**	**15-17**	**17-19**	**19-21**
Dry wt. Extracted (g)	**10**	**30**	**30**	**30**	**30**	**30**	**30**	**30**	**30**	**30**	**30**
% Organic Carbon	**2.27**	**1.99**	**2.09**	**2.37**	**1.41**	**2.14**	**1.53**	**1.42**	**1.49**	**1.60**	**1.48**
1,3-DCB	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
1,2-DCB	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
1,4-DCB	40	0.99	0.76	0.66	0.51	BDL	BDL	BDL	0.33	BDL	BDL
1,3,5-TCB	0.19	0.042	0.074	0.074	0.048	BDL	0.037	0.044	0.048	0.034	BDL
1,2,4-TCB	1.0	0.51	0.85	0.48	0.46	BDL	0.28	0.17	BDL	BDL	BDL
1,3,5-TCB	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
1,2,3-TCB	0.26	0.098	0.13	0.097	0.12	BDL	0.051	0.080	0.052	0.047	BDL
1,2,4,5-TTCB	BDL	BDL	BDL	0.047	0.110	BDL	BDL	BDL	BDL	BDL	BDL
1,2,3,5-TTCB	0.044	0.10	0.13	0.066	0.078	BDL	0.019	BDL	BDL	BDL	BDL
1,2,3,4-TTCB	0.14	0.090	0.093	0.066	0.058	0.018	0.065	0.037	BDL	0.020	BDL
PECB	0.11	0.057	0.061	0.23	0.35	0.032	0.042	0.049	BDL	0.026	0.023
HCB	0.25	0.14	0.15	0.19	0.20	BDL	0.083	0.061	0.019	0.034	0.017
HEPTACHLOR	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
HEPTACHLOR-EPOXIDE	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
ALDRIN	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
ENDRIN	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
DIELDRIN	BDL	BDL	0.076	0.12	BDL	BDL	BDL	BDL	BDL	BDL	BDL
o,p-DDE	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
p,p-DDE	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
o,p-DDT	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
p,p-DDT	1.0	0.46	0.20	0.48	0.33	BDL	BDL	BDL	0.95	BDL	BDL
o,p-DDD	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
p,p-DDD	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
MIREX	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
α-HCH	0.18	0.085	0.12	0.16	0.26	0.18	0.12	0.083	BDL	BDL	BDL
β-HCH	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
γ-HCH	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
α-CHLORDANE	0.32	0.047	0.23	BDL	0.12	BDL	BDL	BDL	BDL	BDL	BDL
γ-CHLORDANE	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
α-ENDOSULFAN	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
β-ENDOSULFAN	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
METHOXYCHLOR	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

BDL–Below Detection Limit

Table 4. Polychlorinated Biphenyl (PCB) Results for Mackenzie Delta Core Samples (ng/g dry wt.).

Station	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**	**3.1**
Core Section (cm)	**0-1**	**1-3**	**3-5**	**5-7**	**7-9**	**9-11**	**11-13**	**13-15**	**15-17**	**17-19**	**19-21**
Dry wt. Extracted (g)	**10**	**30**	**30**	**30**	**30**	**30**	**30**	**30**	**30**	**30**	**30**
% Organic Carbon	**2.27**	**1.99**	**2.09**	**2.37**	**1.41**	**2.14**	**1.53**	**1.42**	**1.49**	**1.60**	**1.48**
1	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
3	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
4-10	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
7-9	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
6	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
8-5	0.064	0.043	0.093	I	I	Tr	Tr	1	Tr	BDL	BDL
19	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
12-13	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
18-15	0.091	0.090	0.190	I	I	0.030	0.025	0.022	0.025	0.029	0.027
17	0.049	0.043	0.080	I	I	Tr	Tr	Tr	Tr	Tr	Tr
24-27	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
16-32	0.043	0.053	0.184	I	I	BDL	BDL	BDL	BDL	BDL	BDL
54	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
29	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
26	0.018	0.017	0.027	I	I	0.046	0.021	0.018	BDL	BDL	0.019
25	BDL	BDL	BDL	I	I	0.020	Tr	Tr	BDL	BDL	Tr
31	0.18	0.18	0.23	I	I	0.20	0.20	0.15	0.067	0.13	0.17
28	0.10	0.11	0.13	I	I	0.11	0.19	0.085	0.042	0.070	0.10
33-53-20	0.15	0.12	0.16	I	I	0.15	0.10	0.089	0.038	0.062	0.092
22-51	0.075	0.037	0.063	I	I	BDL	BDL	BDL	BDL	BDL	BDL
45	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
46	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
52	0.41	0.40	0.60	I	I	0.66	0.45	0.37	0.31	0.30	0.46
49	0.15	0.14	0.29	I	I	0.25	0.18	0.13	0.073	0.12	0.17
47	0.064	0.050	0.15	I	I	0.13	0.041	0.064	0.019	0.060	0.048
48	0.039	0.022	0.13	I	I	0.041	0.026	0.027	BDL	0.040	0.034
44	0.11	0.10	I	I	I	0.10	0.39	0.068	I	0.062	0.073
42-59	0.12	0.11	I	I	I	0.12	0.095	0.077	I	0.070	0.078
64-41-71	0.078	0.065	0.097	I	I	0.10	0.074	0.048	0.019	0.038	0.080
40	0.032	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
103-57	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
100-67	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
63	BDL	BDL	BDL	I	I	Tr	BDL	BDL	BDL	BDL	BDL
74	0.051	0.043	0.076	I	I	0.11	0.070	0.044	0.026	0.041	0.055
70-76-98	0.098	0.079	0.12	I	I	0.17	0.11	0.081	0.045	0.069	0.095
66	0.076	0.064	0.093	I	I	0.14	0.085	0.060	0.032	0.047	0.068
95	0.17	0.14	0.20	I	I	0.19	0.13	0.12	0.044	0.061	0.10
91-55	0.040	0.026	0.041	I	I	0.055	0.036	0.028	BDL	BDL	0.033
56-60	0.041	0.045	0.045	I	I	0.060	0.042	BDL	BDL	BDL	0.049
92	0.041	0.044	0.040	I	I	0.053	0.038	BDL	0.038	Tr	0.048
84	0.041	0.038	0.050	I	I	BDL	BDL	BDL	BDL	Tr	0.031
101	0.13	0.13	0.15	I	I	0.24	0.16	0.12	0.052	0.11	0.13
99	0.059	0.057	0.059	I	I	0.099	0.064	0.044	BDL	0.040	0.049
119	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
83	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
97	0.031	0.037	0.035	I	I	0.064	0.033	0.035	BDL	BDL	0.041
87-81	0.033	0.036	0.039	I	I	0.050	0.025	0.031	0.019	0.012	0.029
85	0.020	0.029	0.031	I	I	0.036	0.024	BDL	BDL	BDL	BDL
136-77	Tr	Tr	Tr	I	I	Tr	Tr	Tr	BDL	BDL	Tr
110	0.064	0.060	0.076	I	I	0.071	0.051	0.054	0.021	0.030	0.044
82	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
151	BDL	BDL	0.016	I	I	0.016	0.023	BDL	BDL	BDL	BDL
135-144-147	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
107	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
149-118-123	0.077	0.072	0.083	I	I	0.093	0.078	0.077	0.040	0.046	0.060
114	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
131-134	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
146	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL

Table 4. (continued)

Station	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1
Core Section (cm)	0-1	1-3	3-5	5-7	7-9	9-11	11-13	13-15	15-17	17-19	19-21
Dry wt. Extracted (g)	10	30	30	30	30	30	30	30	30	30	30
% Organic Carbon	2.27	1.99	2.09	2.37	1.41	2.14	1.53	1.42	1.49	1.60	1.48
105-132	0.015	0.014	0.016	I	I	0.014	BDL	0.014	BDL	BDL	BDL
153	0.035	0.035	0.038	I	I	0.036	0.033	0.037	Tr	0.021	0.024
141	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
179	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
176	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
138	0.022	0.020	0.027	I	I	0.067	0.024	0.025	BDL	0.015	0.021
158-160	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
129	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
178	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
175	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
187	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
128	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
183	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
167	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
185	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
174	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
177	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
171-156	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
157-202	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
173	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
200	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
172	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
180	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
193	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
191	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
199	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
170	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
190	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
198	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
201	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
203-196	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
189	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
195	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
208	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
207	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
194	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
205	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
206	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
209	BDL	BDL	BDL	I	I	BDL	BDL	BDL	BDL	BDL	BDL
Total	**2.8**	**2.5**	**3.7**	**I**	**I**	**3.5**	**2.8**	**2.9**	**0.9**	**1.5**	**2.2**

I: Interference
BDL–Below Detection Limit

Table 5. Concentration range of total PCBs, total n-Alkanes, and selected PAHs, methyl-PAHs, chlorobenzenes and pesticides detected in 22 water samples collected from rivers draining to the Arctic Ocean. "BDL" means "below detection limit."

Compound Class	Compound	Range ($ng \cdot L^{-1}$)
Total PCB		BDL - 0.050
Total n-Alkanes		50 - 500
PAHs	Naphthalene	BDL - 280
	Phenanthrene	BDL - 15
	Fluoranthene	BDL - 4.8
	Pyrene	BDL - 8.2
	Indeno[1,2,3-cd]pyrene	BDL - 3.7
Methyl-PAHs	2-Methylnaphthalene	BDL - 21
	1-Methylnaphthalene	BDL - 8.0
	2,6 & 2,7-Dimethylnaphthalene	BDL - 13
	1,6-Dimethylnaphthalene	BDL - 13
	2-Methylphenanthrene	BDL - 8.0
Dichlorobenzenes	1,4-DCB	BDL - 10
Trichlorobenzenes	1,2,4-TCB	BDL - 0.77
Tetrachlorobenzenes	1,2,3,4-TTCB	BDL - 0.033
	PECB	BDL - 0.10
Pesticides	*o,p*-DDD	BDL - 0.19
	Heptachlor epoxide	BDL - 1.0
	α–HCH	0.10 - 1.3
	γ–HCH	BDL - 0.32
	α-Chlordane	BDL - 0.16
	Dieldrin	BDL - 0.13

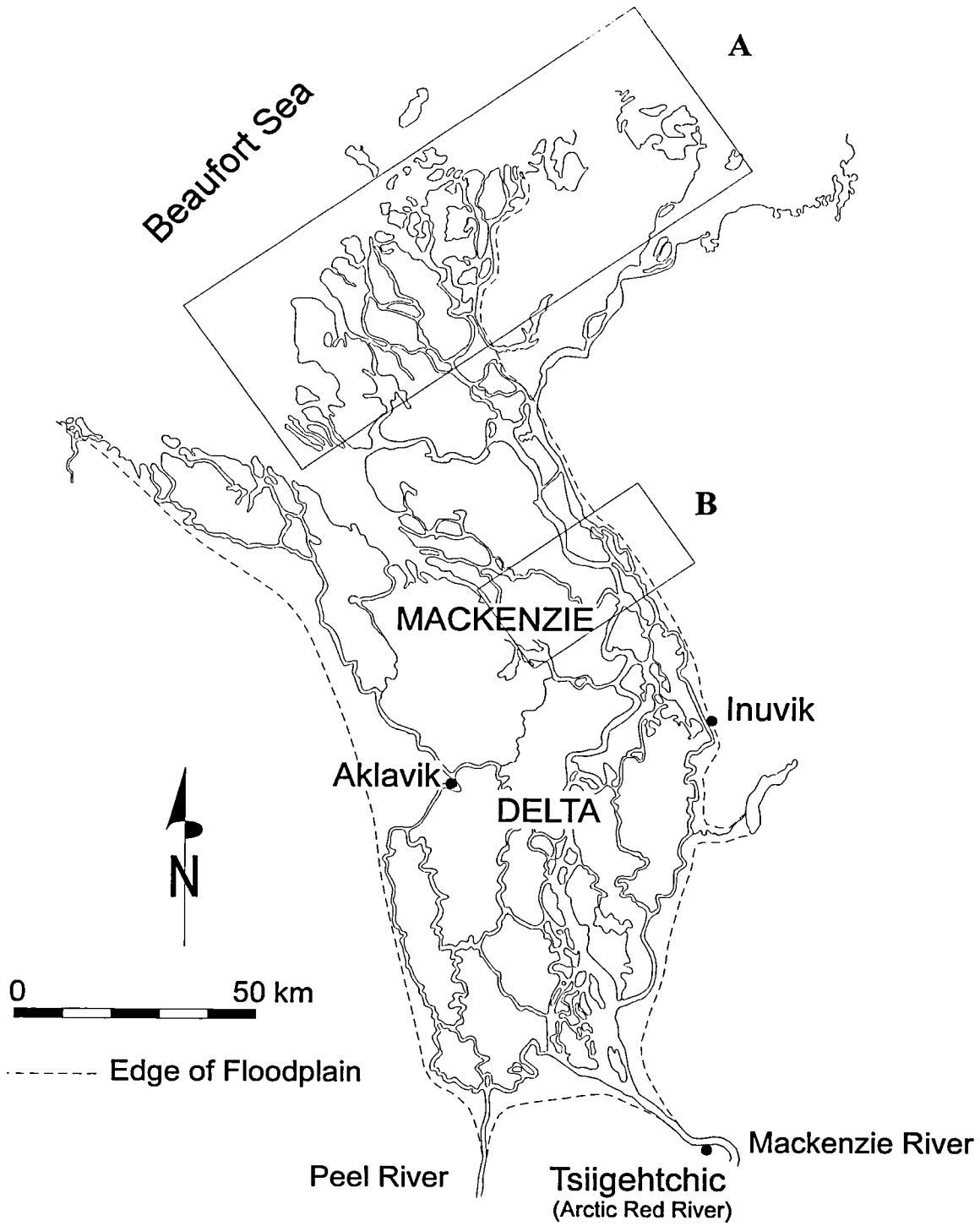

Figure 1. Sampling locations on the Mackenzie River

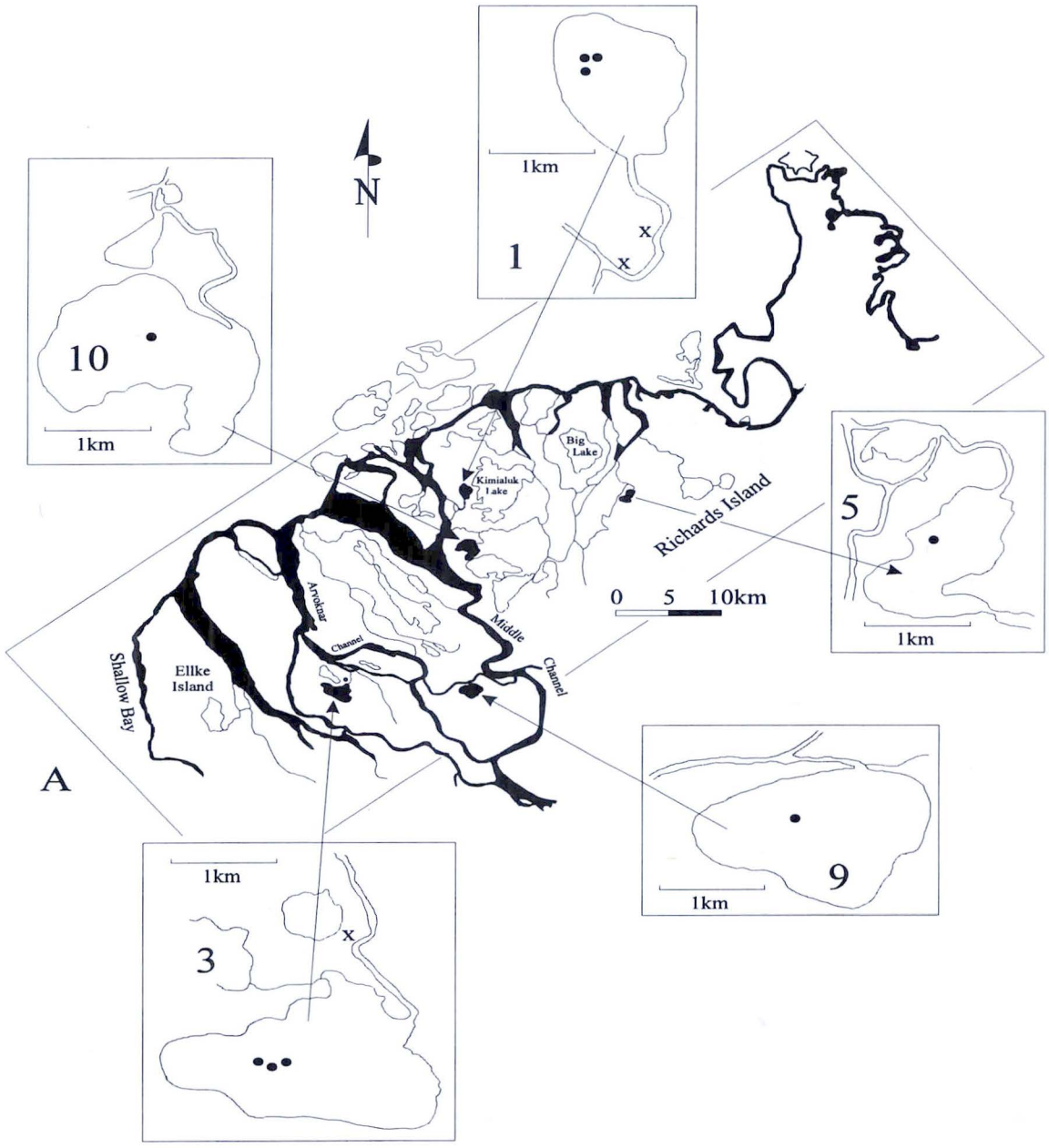

Figure 1a. Sediment core locations in the Mackenzie River Delta (area A)

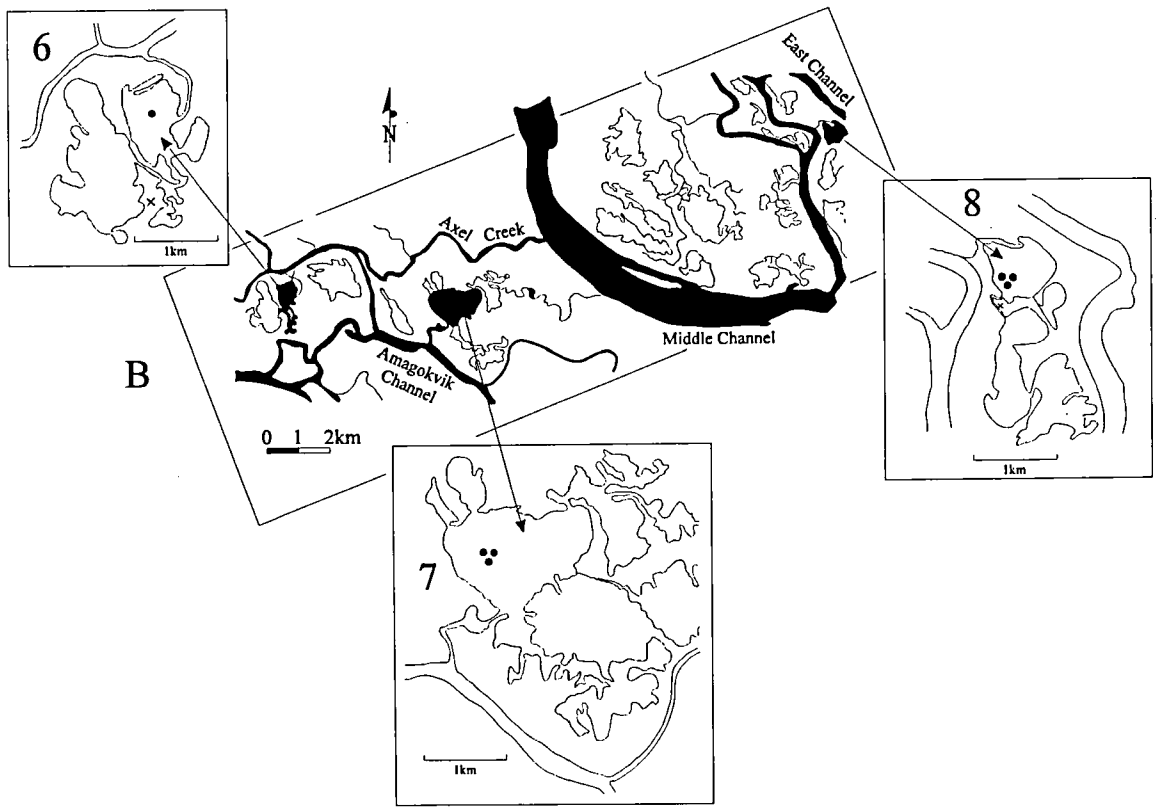

Figure 1b. Sediment core locations in the Mackenzie River Delta (area B)

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

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Project Team: C. Spencer, C. Hauta, NWRI; L. Sumi, University of Toronto; D. Hurlburt, T. Genier, Yukon College; M. Palmer, Indian and Northern Affairs Canada, Whitehorse; J. Eamer, Environment Canada, Whitehorse; D. Gregor, University of Waterloo

OBJECTIVES

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

2. To determine the fate of the contaminants in the Yukon River 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 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 spray between 1949 and 1969. Unknown quantities of household organochlorine pesticides and PCB containing electrical components were also abandoned in various sites along the Yukon River basin (Davidge 1994).

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 and/or by gas exchange. Snow deposition is currently measured under different Northern Contaminants Program projects; however, rain deposition is measured in this program. 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.

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 to be made about sources and transport into this ecosystem.

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

ACTIVITIES IN 1994/95

This year was the second of a two-year study. During this sampling season (mid-May to mid-August) a total of eight water samples (≈100 L), along with suspended sediments (5-20g), were collected from Takhini River using a continuous flow centrifuge. In addition, eight water samples (≈100 L) were collected from the Yukon River. The large volume water samples from Takhini and Yukon Rivers were extracted with dichloromethane using the Goulden Large Volume Extractor (GLVE). Due to technical problems with Infiltrex units, lake water samples were collected directly and extracted with GLVE at Yukon College. Thirty six (duplicate) lake water samples were collected from the six lakes. All samples collected in 1993/94 have been processed, and analysis of 1994/95 samples is ongoing. As part of L. Sumi's

project (4th year undergraduate), soil samples were collected from six locations in the Range Road dump site and various locations along the lakes in the Yukon River system. Also, to determine physical and chemical parameters such as temperature and conductivity in lakes during the course of study, a Hydrolab was launched on several occasions. Results from the 1993/94 sampling season along with some preliminary results from the 1994/95 season are presented.

SAMPLING AND ANALYTICAL PROCEDURES

Field Sampling: All sampling equipment was prewashed with Contrad, and rinsed with water, acetone, hexane and dichloromethane at Yukon College. Sampling devices were placed up-wind of the electrical generator to avoid fuel and exhaust fume contamination. Water was circulated through the pump and lines for at least 5 minutes before sampling was started. An Alfa-Laval continuous flow centrifuge was used to collect suspended solids from water samples. The centrifuge was operated at 4 L/min which corresponded to 90% recovery of particulate matter >0.45 µm (Ongley *et al.* 1981). Water from the outflow of the continuous flow centrifuge was collected in 5x20 L stainless steel containers and transferred to Yukon College for extraction. At Yukon college, water samples were spiked with a field spike (PCB 70, 1,3,5-tribromobenzene and 8 deuterated PAHs) and extracted into dichloromethane using GLVE (Goulden and Anthony 1985). The extracts were then shipped to NWRI for further cleanup and fractionation.

Lake water samples were collected using Infiltrex II. One hundred litres of water were pumped through precleaned and conditioned XAD-2 via a 0.5 µm Gilman glass fiber filter. Glass fiber filter was precleaned in a muffle furnace overnight at 350°C. XAD-2 was precleaned and conditioned as per NWRI-Lakes Research Branch Standard Operating Procedure Revision 1.1 (Burniston 1994). In short, XAD-2 was first washed with Milli-Q water, followed by soxhlet cleanup in methanol, acetonitrile, and dichloromethane each for 4 days. The resin was subsequently washed with 1N NaOH followed by methanol and dichloromethane. The dichloromethane fraction was analysed for non-interference with GC-ECD. The cleaning process was continued until no interference was observed. XAD-2 was then stored in glass jars under methanol. XAD-2 columns were packed at NWRI Laboratories and spiked with 25ng octachloro naphthalene and tribromobenzene prior to shipping to the field. Instrument failures were used as random blanks. Columns were returned to NWRI after sampling without any further processing.

Soil samples were collected as described by Sumi (1995). Briefly, several small pits about 0.30 x 0.30 x 0.30 m were dug. Fresh sample was then scraped and transferred into two pre-washed jars. The soil pits were filled in when the sampling was completed.

Analytical Methodology: Dichloromethane extracts were processed as described by Gregor *et al.* (1995) and Peters *et al.* (1995). Briefly, sample extracts were dried by passing the samples over anhydrous Na_2SO_4. in an Alihn funnel. The sample volume was reduced to 5 mL by rotary evaporator at 30°C. The sample was solvent exchanged with hexane and base washed with 0.1M K_2CO_3. The extract was then dried by passing though anhydrous Na_2SO_4.. The sample was spiked with PCB 65 and perthane followed by volume reduction to 2mL with a rotary evaporator. The concentrate was applied to 10g of 100% activated 60-mesh silica gel. Four fractions were collected: first with 80 mL of hexane, followed by 85 ml of 35% (v/v) dichloromethane in hexane; the third fraction was eluted with 85 mL of 60% dichloromethane in hexane; and the last fraction consisted of 50 mL of dichloromethane followed by 50 mL of methanol. Each fraction was spiked with 65 ng of octachloronaphthalene and the volumes were reduced to approximately 5 mL with a rotary evaporator. The concentrates were solvent exchanged with isoctane and reduced to a final volume of 1 mL. The extracts were then transferred to vials and stored at 4°C until analysis.

Solid phase columns (XAD-2) were extracted according to NWRI/LRB SOP (Burniston 1994); in short, XAD-2 was extracted with 200 mL methanol followed by 250 mL dichloromethane. The extract was then washed with 200 mL 3% NaCl . Organic phase was collected and processed in the same fashion as water extracts.

Suspended solid and sediment (soil) samples were processed according to Mudroch *et al.* (1994); samples were freeze-dried, and 10 g of each sample was soxhlet extracted with 50 mL of dichloromethane. Dichloromethane extracts were cleaned-up and fractionated as described above.

Organochlorine pesticides and PCBs were analysed using a Varian 3500 gas chromatograph equipped with dual ECD, 8200 auto-sampler, and Star data system. Two 30m, 0.25mm i.d. fused silica capillary columns SPB-1 (Supelco) and SPB-5 (Supelco) with 0.25 µm film thickness were used in these determinations. The gas chromatograph was operated under the following conditions; 2 µL of sample was injected into the injector operated in a splitless mode with a time delay of 0.50 min when the injector was purged. Column temperature was initially held at 80°C for 2 mins and ramped to 280°C at 4°C/min and held for 12 min. Injectors and detectors

were operated in an isothermal mode at 250°C and 330°C, respectively. Helium at 1mL/min was used as the carrier gas and the makeup gas was nitrogen at 30 mL/min. These samples were analysed for 101 PCB congeners and 40 organochlorine pesticides.

Polycyclic aromatic hydrocarbons (PAHs) were analysed by a capillary GC/ ITMS using a Varian 3400 GC, and a Varian Saturn III ion trap mass spectrometer as the detector. The ion trap was operated in scanning mode with a range of 120-280 amu. The operating conditions for the ion trap were: manifold was at 220°C and the transfer line temperature was maintained at 260°C. Separations were achieved using a 30m DB-5ms (J&W Scientific) 0.25mm i.d. and 0.10μm film thickness. The GC oven temperature was as follows: initial temperature 95°C held for 1 min ramped to 120 at 20°C/min held for 1 min ramped to 230°C at 7°C/min and held for 10 min. The GC was equipped with a Varian Septum-purged Programmable Injector (SPI) and was operated under the following conditions: initial temperature 90°C held for 0.5 min ramped to 300°C to 300°C/min and held for 30 mins. The injector was equipped with a large-bore salinized insert for on-column introduction of the sample. This, along with a 3 m, 0.53 mm i.d. deactivated and uncoated retention gap, enabled the injection of 5 μL sample volume.

Toxaphene analyses were accomplished using GC/ ECNIMS at the Freshwater Institute (FWI) (G. Stern) and at NWRI. The operating conditions at FWI were as follow: gas chromatographic separations were performed on a HP 5890-II using a 60m DB-5ms (J&W Scientific) column with 0.25 mm i.d. and 0.1 μm film thickness. The column was directly connected to the ion source. Electronic pressure control was used to maintain the flow of He (carrier gas) at a constant flow of 1 mL/min. A CTC autosampler controlled by a data system was used to inject the samples. Samples were introduced into a split- splitless injector maintained at 260°C and operated in a splitless mode for 2 min before the injector was purged. Mass spectrometry detections were performed on a Kratos Concept high resolution mass spectrometer (EBE geometry) equipped with a Mach 3X data system. The MS was operated in a M/ΔM ~ 12000 in selected ion electron capture negative ion mode. Mass calibration was accomplished using PFK as calibration gas. Source pressure was maintained at ~$2x10^{-4}$ with methane used as a moderating gas. Ion source temperature was 120°C, electron energy was adjusted to 180 eV and the accelerating voltage was 5.3 kV. The following ions were used to monitor hexa– to nanochlorobornane homologue groups; 308.9352, 310.9323 for Cl_6, 342.8952, 344.8933 for Cl_7, 376.8543, 378.8543 for Cl_8, and 410.8183, 412.8154 for Cl_9. Four separate windows consisting of various combinations of these ions were used to monitor different homologue groups. The operating conditions at NWRI were as follows: sample introductions were performed using a CTC A2000SE into a Varian 3400 CX gas chromatograph equipped with SPI injector. Injector conditions were as follows: initial temperature 120°C held for 2 min raised to 280 at 300°C /min held for 35 min. Analytical separations were performed using a 60m x 0.25mm i.d. SPD-5 (Supelco), column temperature was at 110°C held for 2 min raised to 180 at 15°C /min held for 1 min raised to 285 at 2°C /min and held for 10 min. The column was connected to the ion source of the MS via a Los Gatos transfer line held at 260°C by GC auxiliary electronics. ECNIMS was performed on a Finnigan 4500 quadropole mass spectrometer equipped with Teknevent data system. Methane was used as moderating gas and PFB (FC-43) was used as calibration gas. The MS was operated in selected Ion Monitoring (SIM) mode; monitoring m/e 309, 311 for Cl_6, 343, 345 for Cl_7, 377, 379, for Cl_8 , and 411,413 for Cl_9 corresponding to M- Cl ions produced by hexa– to nanochlorobornane in 3 separate windows with combination of Cl_6 and Cl_7 homologue series were monitored in the first window, Cl_6, Cl_7, and Cl_8 homologue series were monitored in the second window and the third window consisted of ions produced by Cl_8 and Cl_9 homologue series.

Quality Assurance/Control

All samples were processed and analysed for OCs using dual column GC/ECD, for PAH using GC/MS at NWRI. Toxaphene analysis using HRGC/ECNI/HRMS was done by G. Stern at FWI. To ensure 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 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) field blanks (at least three) are collected 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.

RESULTS AND DISCUSSION

Concentrations of Organochlorines in Water: Organochlorine results were presented at the 78th Canadian Society for Chemistry Conference and Exhibition in Guelph, Ontario (Alaee *et al.* 1995) . HCHs, in particular α-(0.3-0.48 ng/L) and γ–(0.07-0.23 ng/L) isomers, are the most predominant OCs in the Yukon River System. Values for 1993/94 sampling season are summarized in Table 1 and presented in Figure 1. These values are lower than those by Gregor and Eamer (1993) and by Alaee and Gregor (1994), which were collected from the same area during the winter, and also lower than values reported in Amituk Lake by Falconer *et al.* (1.3 ng/L for α– 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) as reported by Strachan (1994).

Toxaphene concentrations for water are presented in Table 2 and Figure 2, and suspended sediments are presented in Table 3. Water concentrations range from 0.02-0.27 ng/L. These values are higher than those reported last year (Alaee and Gregor 1994). However, these values are closer to those observed by Bidleman (1994) in Amituk Lake (0.15 ng/L), and by Muir *et al.* (1994) (0.07-0.2 ng/L) in northern Ontario lakes. Barrie (1994) showed a sharp increase in the concentration of toxaphene in air from 0.001 ng/m^3 in March to 0.008 ng/m^3 in May 1993. Unfortunately air concentration data for the summer months are not available at this time for comparison. However, higher air concentrations can cause the rise in the concentration of the water values. Overall, the concentrations and similarities in the toxaphene pattern suggest that the source is atmospheric. Concentrations of toxaphene in suspended sediment are presented in Table 3. Toxaphene concentration in suspended sediment from Lake Laberge is high (9 ng/g) relative to Takhini River (0.12 ng/g). However, the concentration of suspended sediment in Lake Laberge (0.61mg/L) is lower than in the Takhini River (460 mg/L in June and 62mg/ L in August), resulting in similar toxaphene concentration in the water.

PCB levels in soil samples from the Range Road dump site, Lake Laberge and Kusawa Lake are presented in Table 4. The Range Road site had a higher concentration of PCBs (77 ppb) compared with Lake Laberge (12 ppb) and Kusawa Lake (10 ppb). The relative intensity of the individual chlorine homologue groups is compared with chlorine homologue series of various Aroclors (Figure 3). Samples collected from the Range Road site had a similar pattern to Arochlors, particularly 1260 and 1254. RR5 had an almost perfect match to Archlor 1260, and RR3 matched a mixture of Archlors 1254 and 1260. This indicated that there was direct deposition of PCB-containing waste into this site, whereas samples collected from the lake sites were dominated by lower chlorinated PCB congeners indicating atmospheric deposition.

CONCLUSION

Initial results indicate that atmospheric deposition is the major source of contaminants into the Yukon River basin. Aqueous concentrations of toxaphene in summer are higher than those in the winter. This can be attributed to higher air concentrations in the summer. Small differences in the concentration of HCHs and toxaphene in the lakes and rivers indicate that there is no major point source in the Yukon River system.

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Table 1. Concentration of HCHs in the Yukon River Basin; mean concentrations of 0.41 and 0.17 and median concentrations of 0.40 and 0.17 ng/l for α– and γ– HCH respectively. The mean value for α/γ–HCH was 2.7 with median value of 2.4.

Location	No. Samples (ng/L)	α–HCH mean Dev.	α–HCH Std. (ng/L)	γ–HCH mean Dev.	γ–HCH Std.	α/γ–HCH
Llewellyn Glacier	3	0.32	0.09	0.15	0.07	2.1
Atlin Lake	2	0.39	0.04	0.20	0.01	1.9
Taghish Lake	3	0.39	0.05	0.15	0.02	2.6
Bennett Lake	4	0.34	0.10	0.11	0.04	3.1
Marsh Lake	5	0.48	0.13	0.20	0.09	2.4
Kusawa Lake	3	0.42	0.04	0.07	0.01	6.0
Takhini River	5	0.39	0.04	0.19	0.04	2.1
Lower Yukon River	4	0.44	0.03	0.23	0.04	1.9
Yukon R. before Whitehorse	5	0.48	0.07	0.21	0.08	2.3
Yukon R. after Whitehorse	7	0.45	0.08	0.16	0.07	2.6
Fox Lake	7	0.39	0.03	0.15	0.02	2.6
Lake Laberge	3	0.40	0.05	0.17	0.04	2.4

Table 2. Concentrations of toxaphene (polychlorinated bornanes) in water from Yukon River Basin.

Location	t–Toxaphene (ng/L)
Llewellyn Glacier	0.06
Atlin Lake	0.27
Taghish Lake	0.02
Bennett Lake	0.11
Marsh Lake	0.18
Kusawa Lake	0.20
Takhini River	0.10
Yukon River	0.16
Fox Lake	0.11
Lake Laberge	0.21

Table 3. Concentration of toxaphene (polychlorinated bornanes) in suspended solids in Yukon River Basin.

Location	Sampling Date solid (mg/L)	Suspended solid (mg/L)	Toxaphene in susp. solids (ng/g)	Toxaphene in susp. solids in water (ng/L)
Takhini River	Aug. 16/93	62	0.02	6.2
Takhini River	June 1/93	462	0.006	29.1
Lake Laberge	July 25/93	0.61	9.2	5.6

Table 4. Σ–PCB concentrations (ng/g) in soil at the Range Road dump site along with soil samples taken from the vicinity of Lake Laberge and Kusawa Lake.

Location	No. Samples	Minimum	Maximum	Mean	Median	Std. Dev.
Range Rd.	5	15	145	77	83	51
Laberge	8	5	29	12	11	8
Kusawa	8	3	24	10	9	6

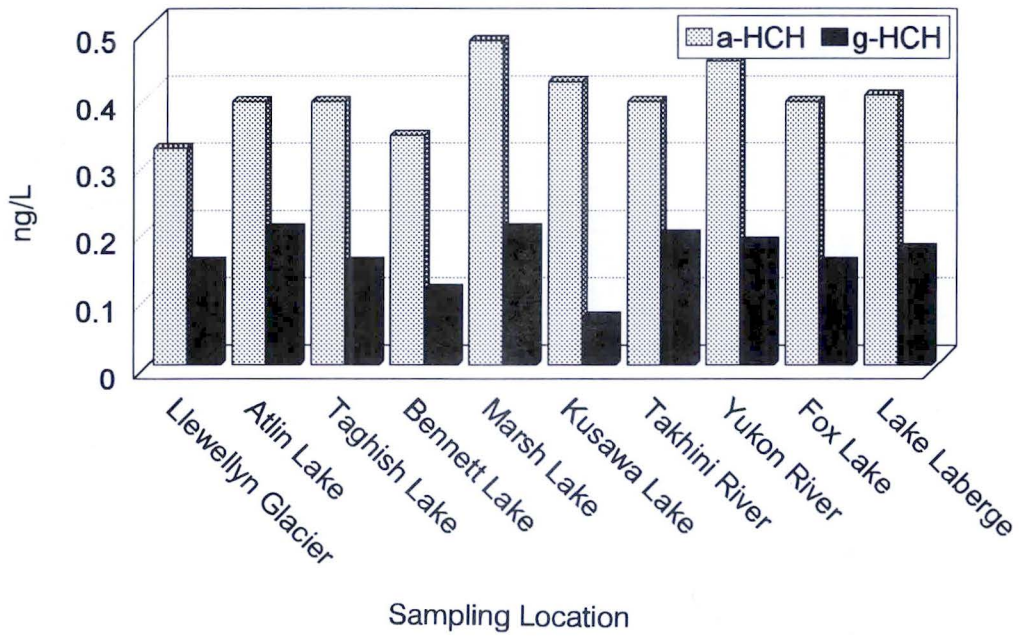

Figure 1. Concentrations of HCHs in Yukon River Basin water

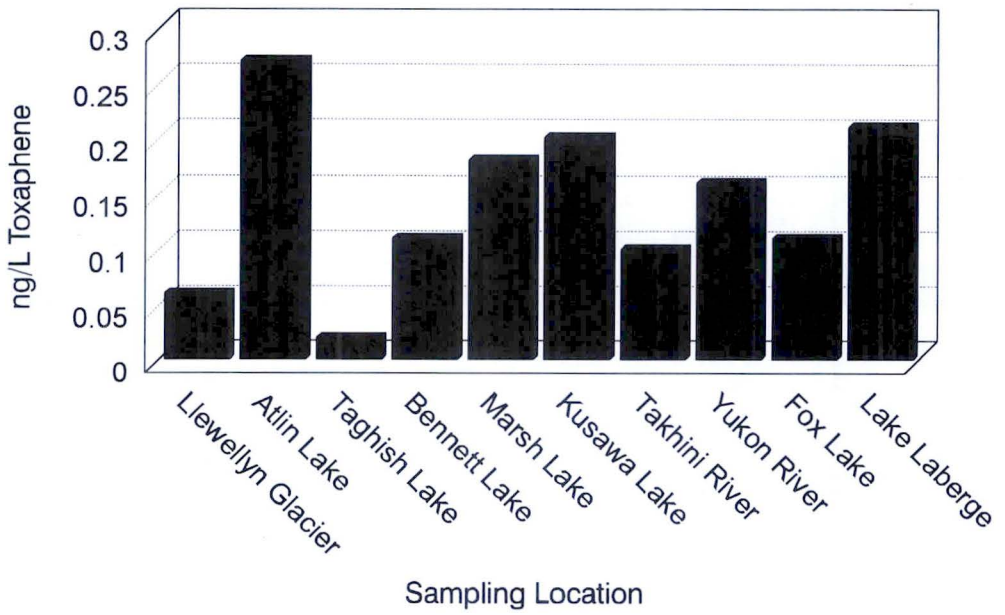

Figure 2. Concentrations of Toxaphene in Yukon River Basin water

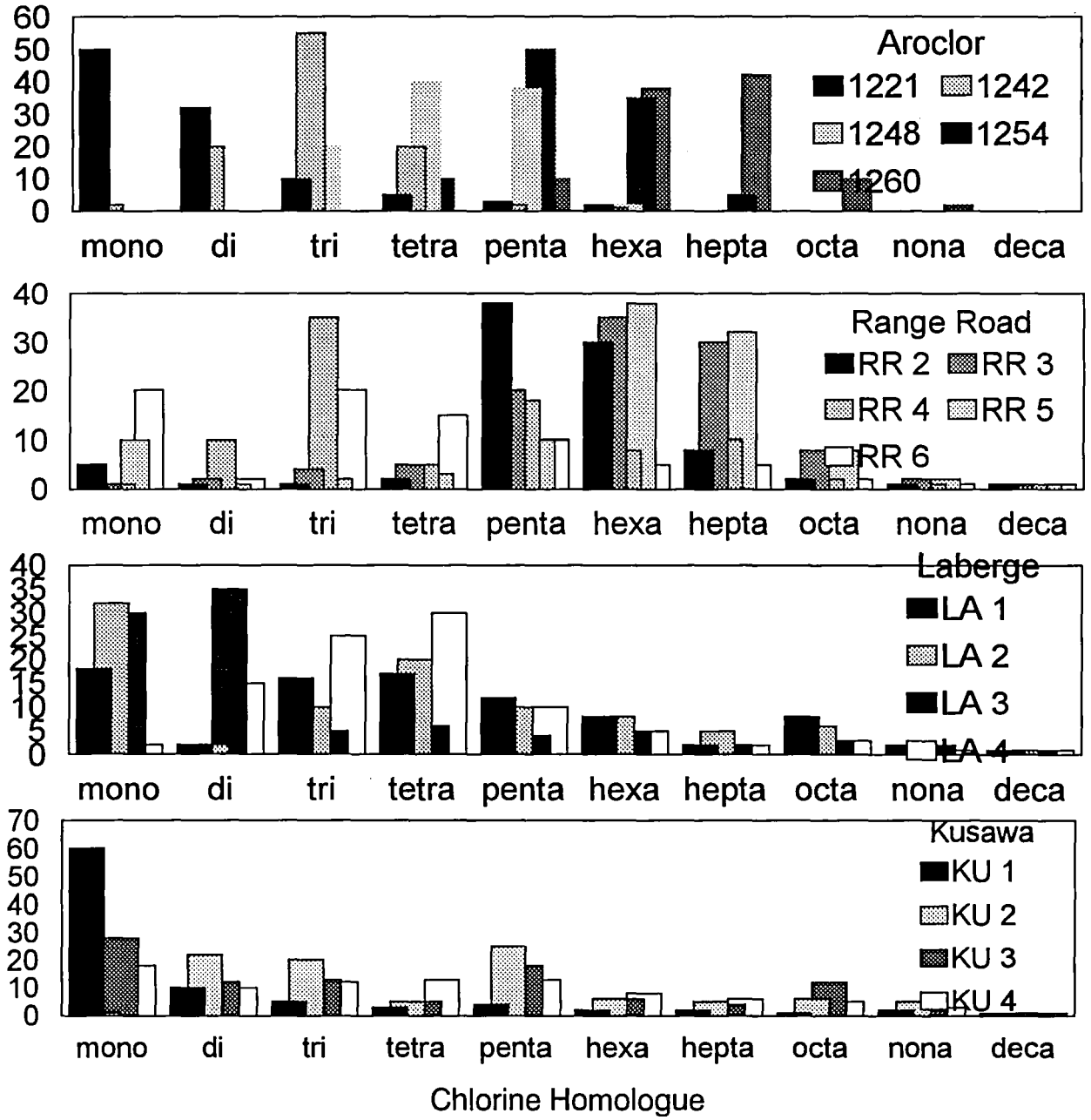

Figure 3. Percent PCB Homologues in Yukon Soil Samples

PROCESSES AND FLUXES OF CONTAMINANTS IN AQUATIC SYSTEMS – 1994/95

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OBJECTIVES

Short-term

1. To operate 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) of the Green Plan. The objective of the multi-disciplinary 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, is approximately 26 km^2 in area, and contains six 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 1994/95

The 1994 field season at Amituk Lake operated from June 1st to late-August. Prior to snowmelt, 52 shallow snow cores and six deep-valley composite cores were collected to assess the spatial variability in snowpack water content and chemical composition. Snow samples were analysed for major ions (H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, $SO^{2,4}$, Cl^-, Gran alkalinity), nutrients (NO^{-3}, NH^{+4}, TP, TN, DOC, POC, SiO_2) and suspended solids. An

additional 48 snow samples were taken across the watershed for organochlorine (OC) contaminant analysis, another 32 for total mercury content.

Continuous level recorders were installed in the six streams influent to Amituk Lake and at the lake outflow. Instantaneous discharge measurements were made throughout the field season at all sites. Streamwater samples were collected at the initiation of snowmelt and across the peak flow and low summer flow conditions. In total, 360 stream samples were gathered for major ion, nutrient and suspended solids analysis; 119 streamwater samples were collected for OC contaminant measurement and 149 samples for total mercury content.

Lake sampling was carried out weekly from June 15 to August 22 during which time eleven profiles for major ions and nutrients were made through the water column (n = 180 samples). Weekly samples (n = 33) for the analysis of TP, TN, POC, suspended solids and OC contaminants were also collected at three depths—3, 20 and 40m—during this period. Lakewater samples for total Hg content numbered 40. Chemical sampling was accompanied by weekly profiling of temperature, specific conductance, dissolved oxygen and light penetration. Sediment traps were installed at five sites in Amituk Lake; deployment depths were 3m below surface and 2m above bottom, with one additional trap at 20m in the deep lake hole. Suspended sediment was also collected via centrifugation at three depths in Amituk Lake and at the five main influent streams.

The role of groundwater in the hydrological budget of Amituk Lake was investigated by the emplacement of seepage meters and shallow piezometers in stream beds and along the lake shoreline. Groundwater and ground ice samples were collected for the analysis of the stable isotopes oxygen-18 and deuterium. These environmental tracers will help define the contribution of subsurface waters to both the stream and lake systems.

Biological surveys at Amituk Lake in 1994 investigated the seasonal variation in the phytoplankton and zooplankton populations. Plankton samples were collected via centrifugation at a 3m depth and by hauling a 150 µm-mesh net through the water column. In addition to species identification, OC contaminant determinations were carried out on selected organisms. Finally, an Ekman dredge was utilized to sample lake bottom sediments from which benthic organisms were extracted for species enumeration and OC contaminant content.

Continuous meteorological (air temperature, wind speed and direction, relative humidity, incoming and reflective solar radiation) and precipitation quantity measurements were made at the Amituk Lake base camp. Two high-volume samplers, employing polyurethane foam plugs to collect OC contaminants in air, were located at the base camp (AC-powered) and at a remote site (solar-powered).

RESULTS

The geological and morphological characteristics of the Amituk Lake basin have been described previously (Semkin and Gregor 1993). Snowpack surveys in 1994 involved the collection of 52 composite core samples across the watershed and at least one composite core in each of the six stream valleys. These were analysed for depth, density and snow water equivalence (SWE), and both inorganic and OC contaminant content. In addition, transects were run to define the snow depths across the stream valleys and on the upland plateaux. On the flats and on lake ice, the snow depth, density and SWE averaged 0.47m, 0.433 and 204mm respectively. In the stream valleys, the snow depth of samples averaged 2.76m, density 0.642 and SWE 1803mm. To determine basin snow storage, the watershed was divided into grid cells measuring 200m x 200m. From both field records and photographic imagery, the relative snow distribution was discretized into the grid map (see Woo and Rowsell 1993). Using grid counts, the mean SWE for the overall watershed was estimated at 116.48mm in 1994, compared to the 1993 value of 112.36mm.

The main hydrologic event at Amituk Lake was the influx of snowmelt in mid- to-late June. In 1994, the hydrograph at the lake outlet recorded peak flows under $5m^3/s$. The high discharge period lasted about three weeks, similar to 1993, but earlier and longer than what was observed in 1992 (Figure 2). As in past surveys, the stream and lake waters in 1994 were alkaline with pH ≥ 8.0 and with Ca^{2+} and alkalinity dominating the ionic pool (Figure 3). Temporal variation in major ion concentrations in Gorge Creek (the major contributor to Amituk Lake) demonstrated the importance of hydrology in determining surface water chemistry.

Table 1. Phytoplankton in Amituk Lake, June-August 1994.

	Cell Numbers/L	Biomass (mg/m^3)
Seasonal Minimum	235447	6.58
Seasonal Maximum	1451830	141.97

Profiles of temperature and specific conductance in Amituk Lake delineated the influx of cold, relatively dilute meltwater beneath the ice layer (Figure 4). During maximum streamflow, the depth of this incursion was about 4 to 5m, increasing to about 9m on the tail end of the stream hydrographs. Mixing with the lake water column appeared to be negligible. By the end of July, the warm influent streams and increased solar radiation to the lake water produced isothermal conditions and complete mixing in Amituk Lake.

One investigation (M. Hanna) focused on the OC contaminant levels in suspended matter (phytoplankton versus zooplankton). Samples were collected at a 3m depth from two sites having total depths of 41m and 23m from mid-June to mid-August. Amituk Lake is an ultra-oliigotrophic lake (Table 1). even though some of its nutrient levels (DOC and Silica) are much higher than those found in more productive Arctic lakes; its chlorophyll levels ranged from 0.18 to 1.20 µg/L throughout the season. Phytoplankton were composed largely of unicellular algae varying in numbers from 0.23 to 1.4 x 10^6 cells/L. Their diversity ranged from 18 to 48 species depending on site and date. Chrysophytes, dominated, by far, both in number of cells (>90%) and in biomass (>70%) at the two sites on all dates sampled. The second most important algal group was usually Cryptophyta, but it sometimes gave way to Chlorophyta. Cyanophytes were rare, possibly because of their sensitivity to photo-oxidation at low temperatures. The smaller algae, particularly µ-ultraplankton (2.1 to 5.0 µm), were dominant in numbers (>80%) in both sites and for all dates while the larger algae were far less numerous. Even though most of these characteristics have been observed in other arctic lakes, Amituk Lake is much less productive and has much lower species diversities.

Samples collected in 1994 for OC contaminant analysis are still in the laboratory; therefore, only results from the 1992-1993 field seasons will be presented. Table 2 summarizes OC contaminant levels measured in the snowcover (shallow and deep valley) and in surface waters in the Amituk Lake watershed. HCH and ΣPCB are the most abundant OC compounds reported in both years of study. The relative distribution of HCH and ΣPCB in the various sampling media at Amituk Lake is shown in Figures 5 and 6.

As observed with the major inorganic ions, hydrologic processes are very important in controlling the concentration of OC contaminants in streamwater at any given time. For example, α– and γ-HCH and endosulfan all showed elevated concentrations at the initiation of snowmelt in Gorge Creek, and exponentially decreasing levels with diminishing stream discharge (Figure 7). On the other hand, ΣPCB and ΣDDT increased in concentration with decreasing flows.

Using 1993 daily streamflow and mean discharge-weighted concentrations of selected OC contaminants, mass loadings were calculated for individual stream basins and for the Amituk Lake outflow (Table 3). These were compared to the OC contaminant burden in the June pre-melt snowpack which was assumed to contain 75% deep valley and 25% shallow snow.

DISCUSSION

The discussion will focus on the distribution and behaviour of OC contaminants in the Amituk Lake watershed. The physical limnology and hydrogeochemistry of the basin will only be mentioned in characterizing the key abiotic processes influencing contaminant fate and dynamics in this Arctic freshwater system.

The snowpack covering the Amituk Lake basin for eight to nine months of the year was rather complex. Not only did the water content vary significantly from flat plateau areas to the deep stream valleys but the chemical composition was quite heterogeneous. In terms of inorganic chemistry, the basin geology (limestone-dolomite) can greatly alter the alkaline nature of the snowmelt (Semkin and Gregor 1993). With respect to the OC compounds, a deeper snowcover can inhibit the volatilization of some contaminants that are more readily lost to the atmosphere in a shallow, warming snowpack. For example, three sets of triplicate snow samples collected on Amituk Lake in May 1993 by D. Gregor (personal communication) recorded mean concentrations of 3292 pg/L for 51 PCB congeners, 458 pg/L for ΣDDT, 175 pg/L for total chlordane and 95 pg/L for dieldrin. These same compounds registered 558, 29, 75 and 47 pg/L respectively in shallow snow sampled in June. The more volatile OC compounds also appeared to be lost from the valley snow as incident solar radiation increased in the early spring, although not to the extent observed in the shallow (<1.0m) snow. This was evidenced by the relatively higher levels of HCH, total chlordane and endosulfan in the 1992 and 1993 valley snow compared to the shallow snowcover (Table 2).

The process of snowmelt was quite rapid in the Amituk Lake basin as indicated by the sharp rise in the stream hydrographs (Figure 2). The maximum melt period lasted only several weeks in 1993. Gorge Creek first started to flow on June 19 1993; by July 14, 88% of the stream discharge had been measured. Because the ground was still frozen at the onset of snowmelt and the infiltration of meltwater into the subsurface appeared to be

negligible, the initial water flowing in the stream channels reflected the physico-chemical processes operative in the ablating snowpack. Fractionation of inorganic ions and the more water-soluble OC contaminants in the snowcover resulted in a chemically-enriched pulse of meltwater entering the streambed. This was observed in Gorge Creek for Ca^{2+} and alkalinity (Figure 3) and for the HCH isomers and endosulfan (Figure 7). The relatively high concentrations in the initial meltwaters and at high flow conditions dictated that the bulk of the transport of certain contaminants would be associated with the rising limb of the stream hydrograph. As an example, estimates of α--HCH loading in Gorge Creek showed that by day 181 (June 30), 51% of the total seasonal flow had been recorded at this site, but approximately 72% of the seasonal α–HCH loading had been accounted for. Less water-soluble OC compounds, such as PCB and DDT, did not display such an enrichment in the initial snowmelt relative to the parent snowpack (Figure 7).

As cold (O°C) and dilute snowmelt entered Amituk Lake, a layer of "new" water formed beneath the ice (Figure 4). The depth of the meltwater incursion increased with increasing streamflow, although there was a several-day lag period in the response of the lake to the rising stream levels. Because of the density difference between meltwater and lakewater, the stability of this layer was such that minimal mixing occurred with the water column in the lake. The meltwater and its chemical content essentially traversed the lake and exited via the outlet. Not until July 28 had the summer air temperatures and increased solar radiation warmed the meltwater/ streamwater and lakewater enough to develop isothermal conditions. It was at this point that Amituk Lake turned over and the chemical burden of the influent streams mixed thoroughly with the lake water column. It was also when new factors came to play in regulating the chemistry of the lakewaters. After the peak stream discharge period had passed, the composition of the influent streams was more reflective of chemical interaction with surficial rock materials in the lake basin. This was evidenced by increasing Ca^{2+} and alkalinity concentrations in Gorge Creek with reduced flows in August (Figure 3). Furthermore, isotopic studies at Amituk Lake using deuterium and oxygen - 18 suggested an increasing subsurface flow component to the stream system. Kinney (personal communication 1994) estimated that approximately 22% of the streamflow may have an active layer source. The longer residence time of the groundwater in the basin compared to snowmelt contributed significantly to an increase in the ionic strength of the lakewaters. Samples of groundwater for OC contaminant analysis have also been collected, but data is not yet available to quantify this contribution to the OC budget of the lake.

HCH was the most abundant OC compound reported at Amituk Lake in the two study years (Table 2). Concentrations in deep valley snow decreased from 6.4 ng/L in 1992 to 4.1 ng/L in 1993. The decrease also registered in shallow snow and surface waters. Shallow snow concentrations were less than 10% of the values in deep snow; moreover, a drop in the α/γ-HCH ratio from about 2.6 in the stream valleys to 1.4 in shallow snow (Table 2) suggested a preferential loss of the α-isomer in shallow snow compared with γ–HCH. This was also shown in the frequency distribution of the HCH isomers (Figure 5). In surface waters, the α/γ-HCH ratio increased from influent streams to the lake outflow, apparently at the expense of lindane. Microbial degradation of hexachlorocyclohexane was active in the Amituk Lake basin as evidenced by the enantioselective breakdown of α–HCH in stream and lake waters (Falconer *et al.* 1995).

The distribution of the PCB homologues in the snowcover at Amituk Lake (Figure 6) indicated a predominance of the lower-chlorinated congeners in the pre-melt snowpack. A further shift to the lower-chlorinated end members in surface waters relative to snow appeared to be at the expense of the penta- and hexa- PCBs (Figure 6) and may have reflected the preferential sorption of these compounds by suspended solids in the streams.

Loading estimates of HCH and ΣPCB (Table 3) were based on the data available. The snowpack OC contaminant composition can be qualified with reasonable success if sufficient samples are collected from both the deep stream valleys and the upland areas. What is complicated is the calculation of basin-wide snow water content. For our purposes, the stream valleys were estimated to contribute 75% of the snow available for streamflow. This was reasonable, and may even be on the low end, in view of the fact that the OC stream concentrations did reflect a deep valley snow source. Also, the shallow snow areas can be quite distant from the stream channels and the meltwaters may not make an immediate contribution to spring streamflow, but may only infiltrate to the active layer.

The stream loadings of HCH and ΣPCB were calculated by multiplying the mean discharge-weighted concentration times the seasonal flow. The hydrologic record appeared acceptable as shown by the good agreement between cumulative stream input and seasonal lake outflow. A main source of error was associated with the variability of OC contaminant concentration with stream discharge (e.g., Gorge Creek, Figure 7). Table 3 reports a α–HCH loading of 493 ng/m^2 for Gorge Creek, which, as mentioned, was based on mean flow-weighted concentrations. Using the stream arithmetic average for α–

HCH, the loading becomes 630±488 ng/m^2. If an exponential curve is fitted to the α-HCH data (Figure 7), daily estimates of α–HCH concentrations and loadings can also be made. Based on this method, the α–HCH output from Gorge Creek would be 615 ng/m^2. Although these differences are not great, the variability does emphasize the importance of sampling frequency in the calculation of mass loadings and basin calibration.

The OC contaminant loading values are from the pre-melt (June) snowcover. Because of apparent losses of OC compounds through volatilization as the snowpack heats up in May and June, these loading estimates must be considered less than values of winter atmospheric deposition. Nevertheless, the Amituk Lake OC contaminant loadings agreed reasonably well with data from other Arctic studies of winter snowpack (Table 3).

CONCLUSIONS

Research in the Amituk Lake basin has provided some insight into the distribution, behaviour and fate of many OC contaminants in an Arctic freshwater system. The following conclusions can be made:

1. HCH and ΣPCB are the most abundant OC contaminants in snow and surface waters at Amituk Lake.

2. Volatilization of OC compounds, particularly from the shallow (<1.0m) snowcover, is apparent as the snowpack heats up in May-June.

3. Spring melt is the major hydrologic event in Arctic freshwater systems. The influx of snowmelt and associated contaminants travels beneath the ice in Amituk Lake and essentially exits via the outflow with minimal mixing in the lake water column. The end sink is the Arctic Ocean.

4. Estimates of OC contaminant loadings in the pre-melt snowpack are complicated because of the variability in the snowpack water content.

5. Loading estimates of OC contaminants can be derived from stream concentrations and cumulative seasonal flow. Consideration must be given to the variability of contaminant concentration with stream discharge.

6. Groundwater contributions to Amituk Lake can be significant particularly in mid-to late-summer.

Expected project completion date: March 31 1997.

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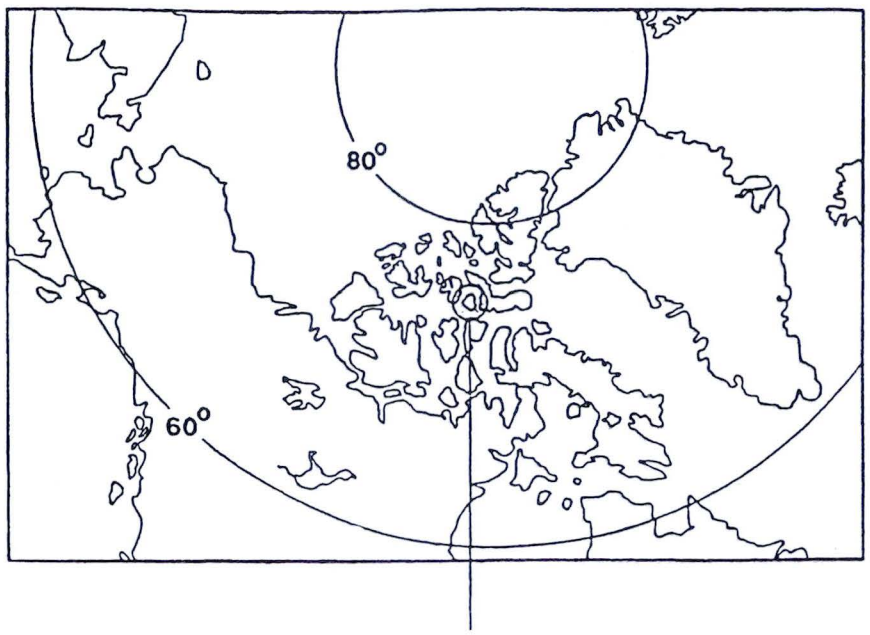
Table 2. Organochlorine Concentrations (pg/L) in Snow and Surface Water Amituk Lake 1992-1993.

	Valley Snow		Shallow Snow		Discharge-Weighted Influent Streams		20m Amituk Lake		Discharge-Weighted Lake Outflow	
	1992	1993	1992	1993	1992	1993	1992	1993	1992	1993
No. Samples	15	6	3	4	20	22	6	9	4	7
PentaCB	59	10	54	8	11	10	13	4	11	4
HexaCB	35	29	53	14	10	23	8	22	12	35
Dieldrin	181	111	106	47	62	64	51	56	71	56
Chlordane	309	290	114	75	93	136	42	124	93	140
Endosulfan	466	734	135	95	73	123	7	8	72	93
Mirex	8	0	0	62	201	420	211	12	184	509
HCH	6392	4106	525	250	2991	1378	2417	1324	3294	2051
α–HCH/γ–HCH	2.3	2.9	1.0	1.7	5.6	5.5	6.7	7.0	6.0	7.2
ΣDDT	113	56	71	29	15	36	4	40	7	62
ΣPCB	763	1615	1112	785	579	505	427	469	255	75

Chlordane = *cis*-and *trans*-chlordane + *trans*-nonachlor+heptachlor+heptachlor epoxide.
HCH = α–HCH+β–HCH+γ–HCH
ΣDDT = DDT and metabolites.
ΣPCB = 67 congeners

Table 3. Organochlorine Contaminant Loadings to Amituk Lake 1993.

Stream	Basin Area km^2	Cumulative Flow m^3/s	Contaminant Loading α–HCH ng/m^2	β–HCH ng/m^2	γ–HCH ng/m^2	SPCB ng/m^2
East	1.95	4.21	90.0	6.4	12.4	92.2
Rock	1.08	2.89	220.0	8.1	55.2	77.8
Cave	4.69	8.77	207.8	4.7	45.1	82.9
Gorge	10.29	33.46	493.2	9.0	113.8	208.4
Mud	5.22	8.27	144.3	5.9	25.5	59.9
Camp	0.44	0.26				
Cumulative Streams	23.67	57.85	234.0	7.3	49.6	106.6
Lake Outflow	26.57	62.02	349.8	8.2	55.5	95.9
Snowpack	26.57	SWE= 116.5mm	261.5	10.8	93.6	163.9
Arctic-Wide Snow Cores (Gregor)			95-285		73-104	73-95



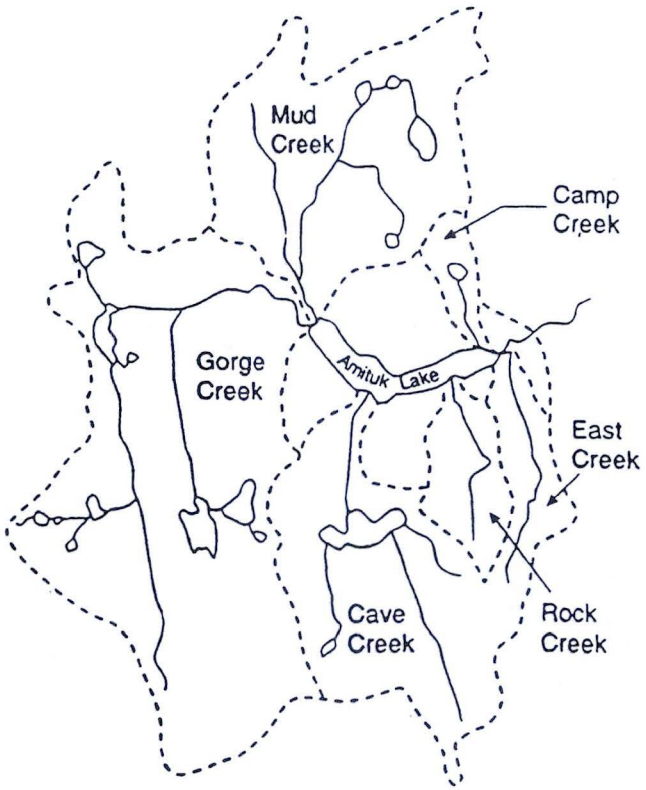


Figure 1. Amituk Lake and its watershed

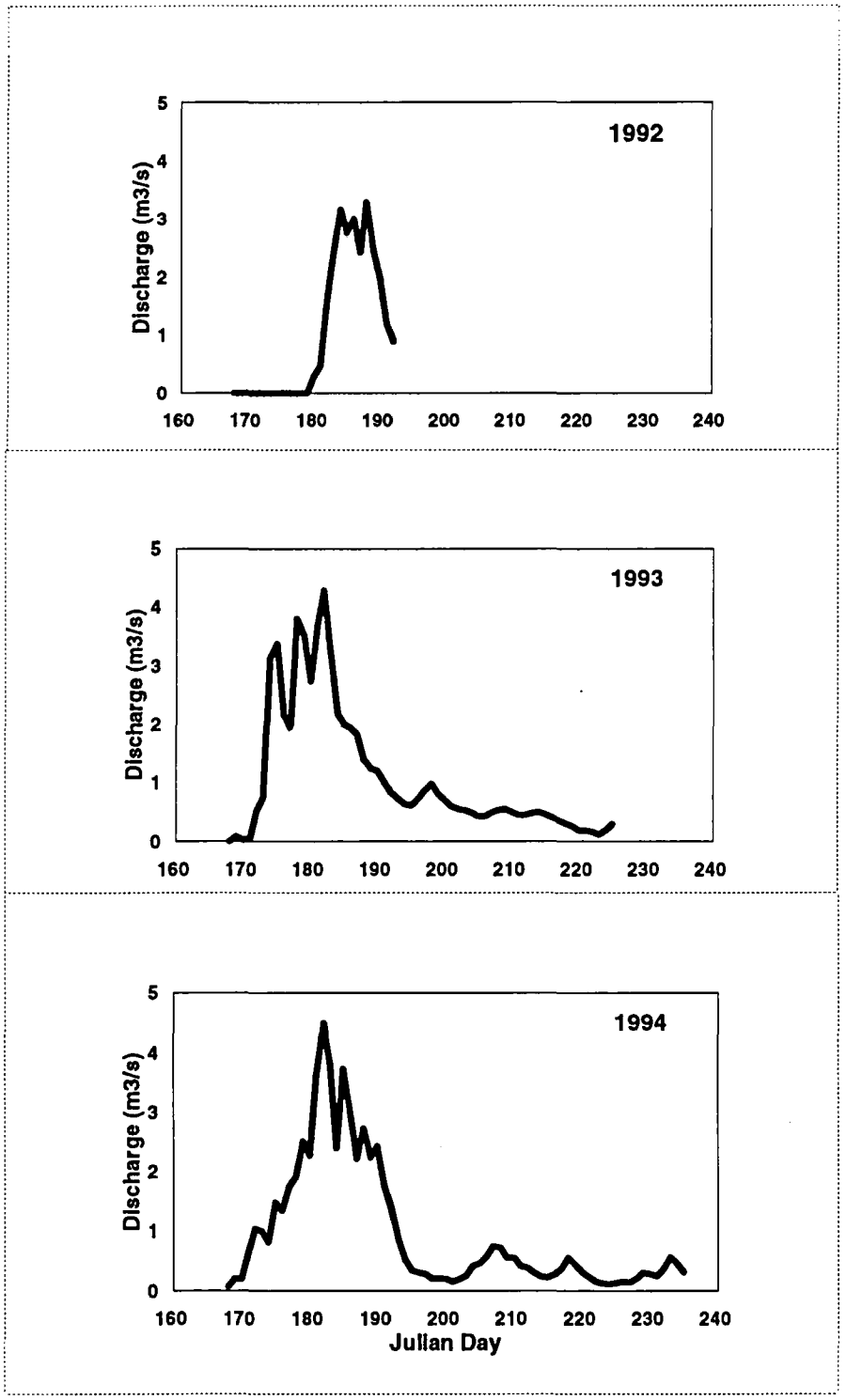


Figure 2. Stream hydrographs at the Amituk Lake outflow. The 1992 and 1994 records are from instantaneous flow measurements; the 1993 hydrograph is from a stage recorder

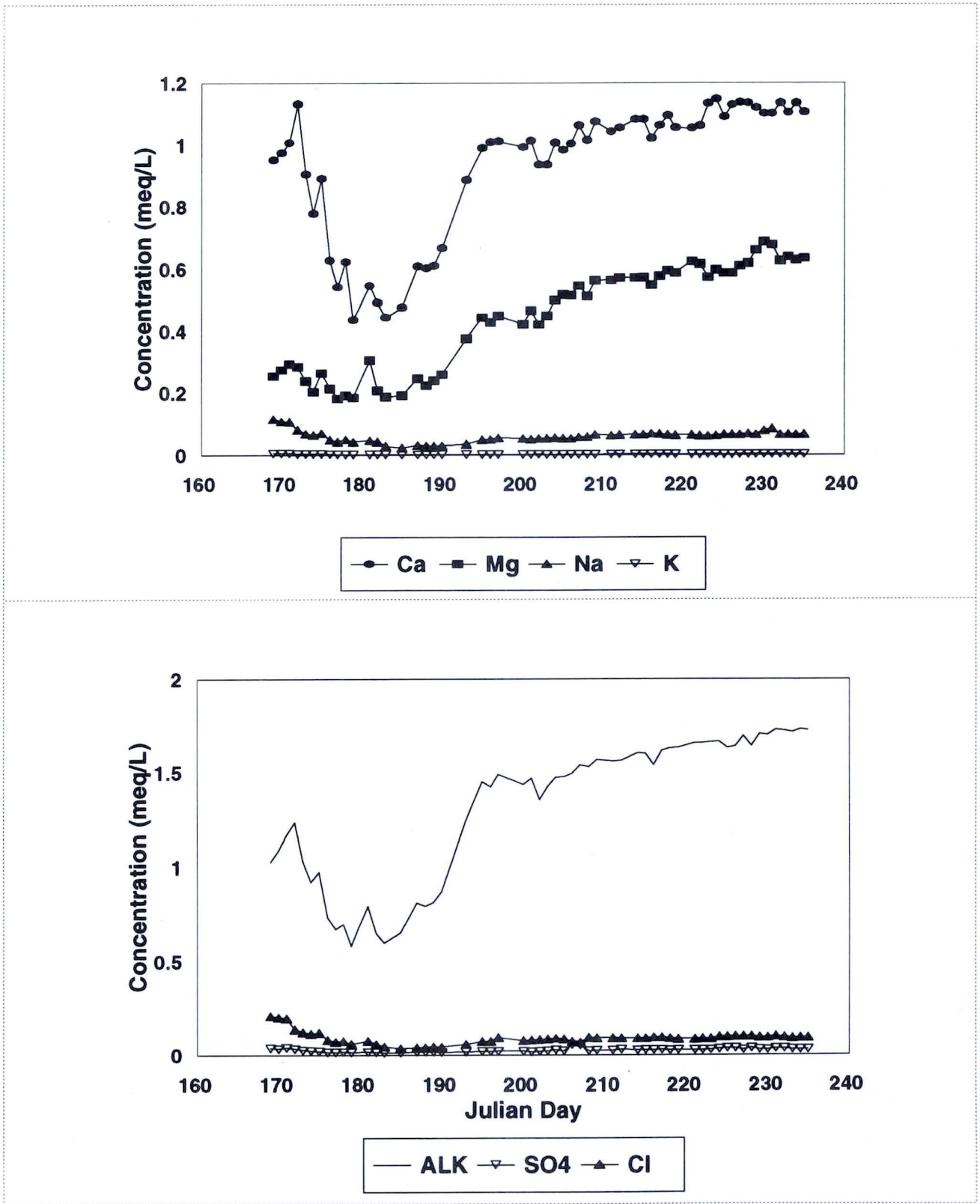


Figure 3. Temporal variation in major ion concentration Gorge Creek, 1994

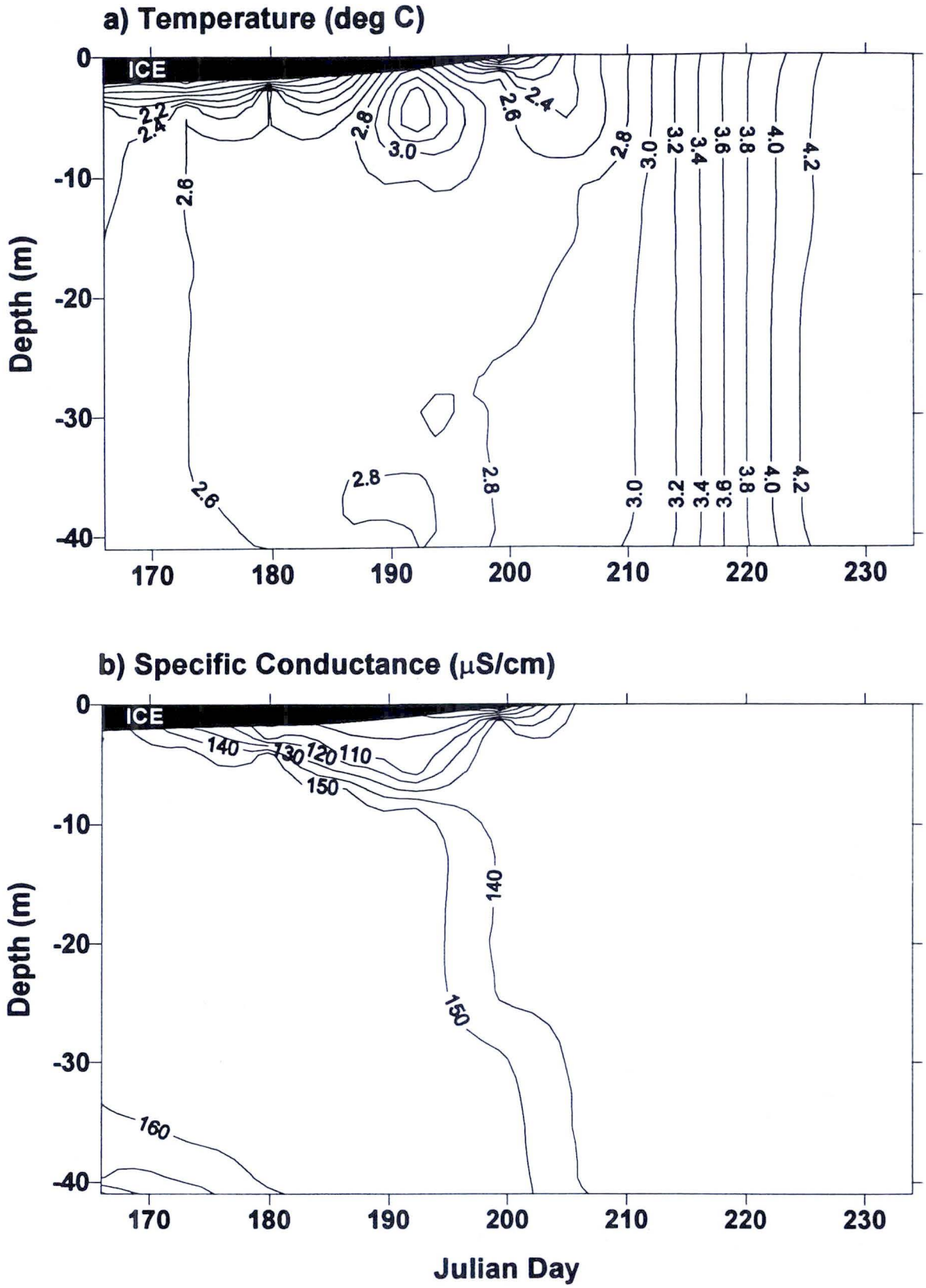


Figure 4. Temperature and conductivity isopleths in Amituk Lake 1994. Note the development of isothermal conditions by day 210, July 29, 1994, and mixing of water column

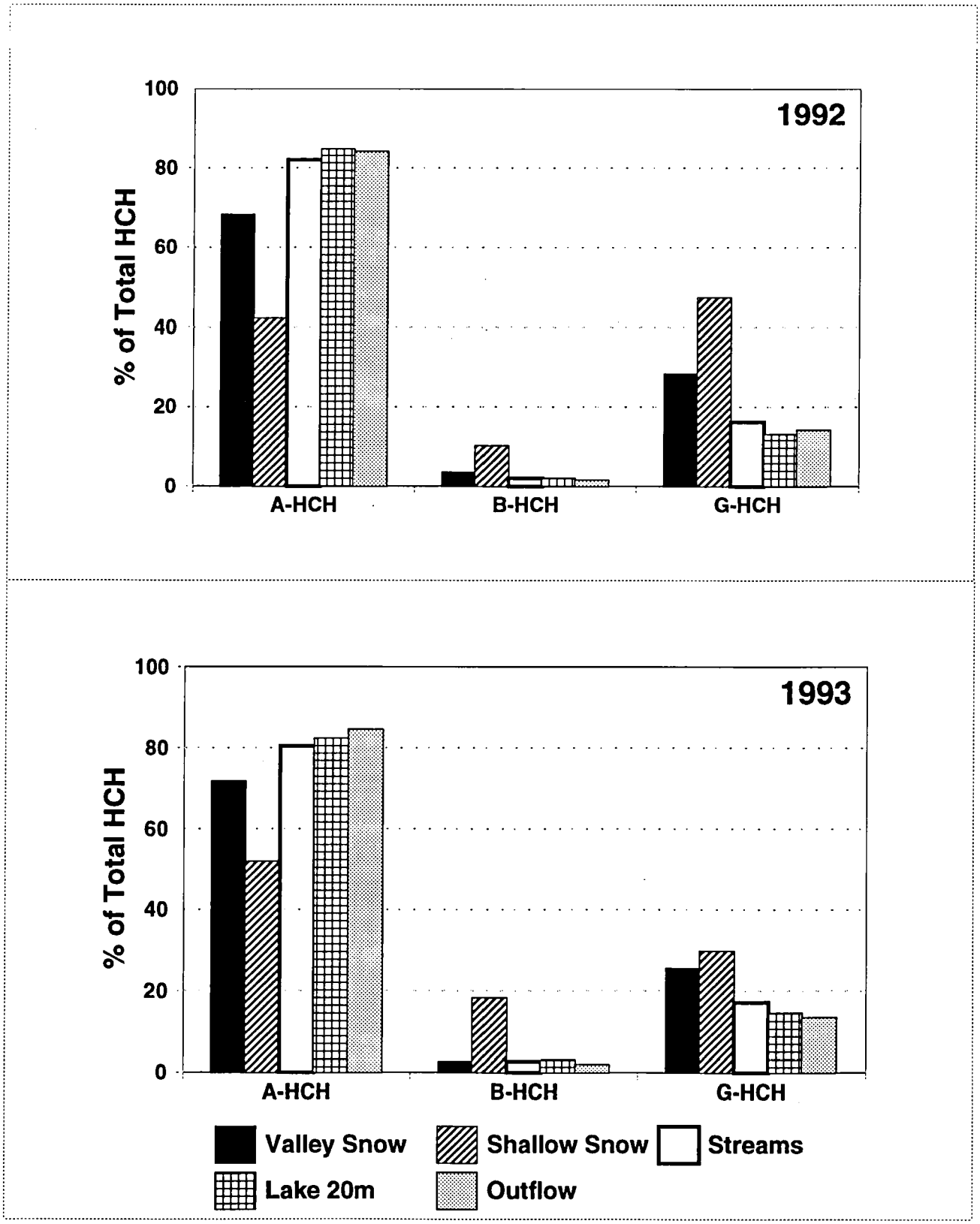


Figure 5. Distribution of HCH isomers in snowpack and surface waters, Amituk Lake 1992/93

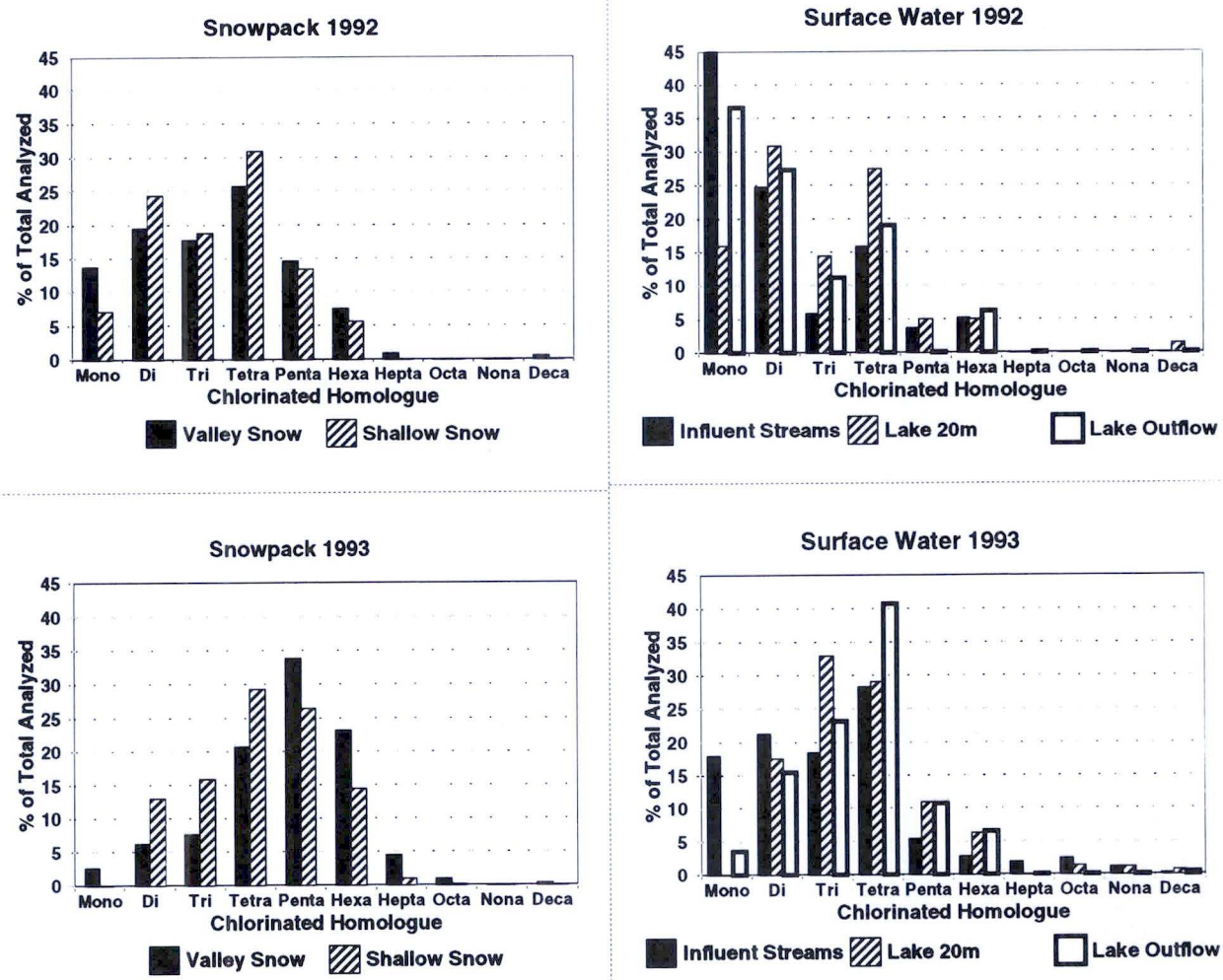


Figure 6. Distribution of PCB homologues in snowpack and surface waters, Amituk Lake 1992/93

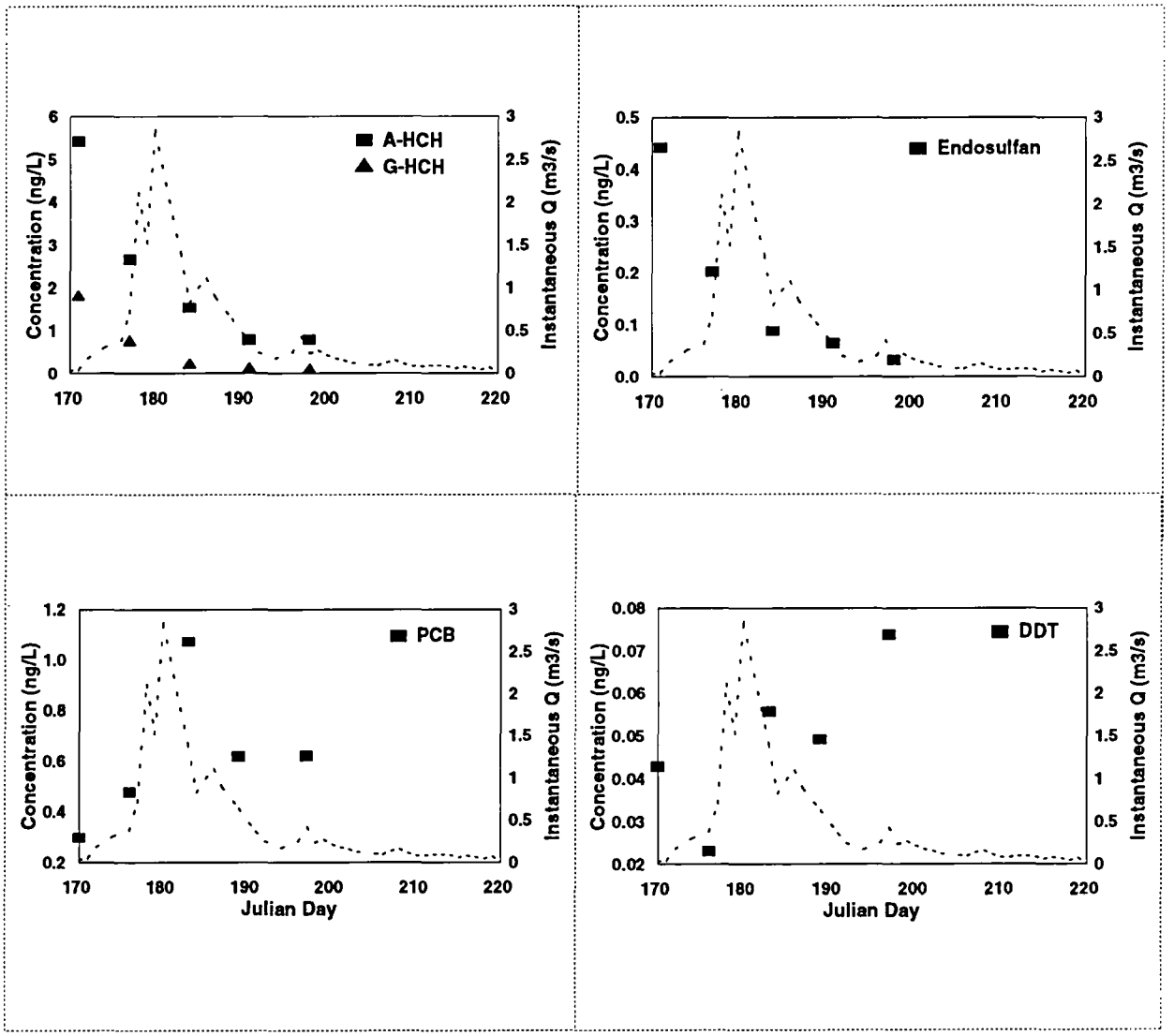


Figure 7. OC contamination variation with streamflow, Gorge Creek, 1993

MODELLING INORGANIC AND ORGANIC CONTAMINANTS IN ARCTIC FRESHWATER LAKES

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OBJECTIVES

Short-term

1. To compile mass balance models to estimate the fate and transport of inorganic and organic contaminants in arctic and subarctic freshwater lakes, including Char and Amituk Lakes on Cornwallis Island, and lakes of the Upper Yukon River Basin;
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 and subarctic lakes to changes in contaminant loadings.

Long-term

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

DESCRIPTION

The study aims to improve our understanding of contaminant dynamics in arctic and subarctic lakes for several reasons. First, we should determine whether arctic and subarctic lakes are sinks or repositories of contaminants, acting similarly to temperate lakes. If so, lakes can act as chemical sources when loadings are reduced. Second, the study can indicate abiotic factors leading to, and controlling, contaminant exposure to aquatic biota. Third, a quantitative understanding of whole lake chemical dynamics is necessary to interpret historical or inter-lake comparisons based on sediment core data. Fourth, the understanding gained on a small number of lakes can be applied to rationalize future monitoring efforts over broad geographic areas. Finally, deductions made on a whole lake basis can shed light on contaminant dynamics in the larger arctic and subarctic ecosystems.

To accomplish our goals, we have assembled a diversity of information pertaining to lakes, and used this information to generate models of whole lake chemical dynamics. Since 1992 we have participated in the Amituk Lake study of the Northern Contaminants Program, first suggesting sampling strategies that would optimize data collection and secondly, interpreting the resultant data through a whole lake model. Recently, we have examined chemical movement in lakes of the upper Yukon River basin, using historical limnological data and limited chemical data.

ACTIVITIES IN 1994/95

The arctic lake model developed by H. Freitas was refined and tested. The model can treat average conditions during summer or time dependent conditions throughout the year (including ice build-up and decay with cryoconcentration of solutes). It can by applied to single chemicals (e.g., HCB), chemicals that exist as

multiple interconverting species such as mercury, or groups of related chemicals such as PCB congeners or DDT and its decomposition products. The model was used to deduce the behaviour of HCHs, toxaphene (CHB or chlorobornanes), HCB, chlordane, DDT, PCBs and mercury in Char and Amituk Lakes based on 1992 Amituk Lake loading estimates.

M. Kawai developed a preliminary model of four lakes in the upper Yukon River basin. The lakes modelled included Atlin, Tagish, Bennett and Marsh. The model considers average annual conditions and can treat inorganic and organic chemicals. The model is preliminary since data for several important processes were lacking, or only available for neighbouring lakes. As well, insufficient data were available to test the model.

RESULTS

Arctic Lakes

Full details of the model, results and data interpretation are provided by Freitas (1994). Diamond (1994) summarized the model, calibration procedure and some of the salient results. Briefly, we obtained satisfactory agreement between measured and predicted water and sediment concentrations for phosphorus in Char Lake and organochlorines in Amituk Lake. Efforts during 1994 emphasized improving model estimates and interpreting results. For Amituk Lake we used contaminant data from the 1992 field season since data from 1993 and 1994 were not yet available. Because we relied only on the 1992 data, our results should be viewed as preliminary. While we were able to develop a credible model of Char Lake based on past studies (e.g., Rigler 1974, Schindler *et al.* 1974), unsuccessful attempts to core Char Lake sediments for contaminant analysis frustrated our attempts to improve the model.

Generally, model estimates for Amituk Lake are reliable to within a factor of 1.4 for PCBs and DDT, and 4 for HCH, HCB and toxaphene (CHB) (Figure 1). Results of contaminant dynamics in Char Lake are illustrative. The agreement for Amituk Lake was achieved by using empirical partition coefficients (particulate-to-dissolved phases) for HCH, HCB and toxaphene. We justified the use of empirical rather than organic carbon based partition coefficients based on the extremely low concentrations of organic carbon in the system which, we suggested, increases the importance of mineral matter for chemical sorption (e.g., Gerstl and Mingelgrin 1984, Grundl and Small 1993).

Chemical concentrations in the water of Amituk Lake varied from 58 to 5000 pg/L for HCB and HCH, respectively, and in the sediments, from 0.5 to 16.4 µg/g for HCB and PCB, respectively. Hydrology exerts the principal control over chemical dynamics in the lakes (Figure 2). First, the timing of snow melt and ice decay determine the amount of inflowing water, and hence chemical loading, that mixes with the water column rather than flowing directly through the lake (see Semkin, this volume). Secondly, most chemicals are lost from the lake via export through the outflow rather than being retained in the sediments. Export ranges from 95% for γ–HCH to 75% for ΣPCB. Burial or chemical retention rates are minimal because of extremely low rates of sediment deposition that deliver chemical to the sediments, as well as low rates of sediment burial. This implies that the sediments do not serve as a sink for chemicals and lake hydrology controls the response time to changes in chemical loadings.

The steady-state multispecies model was applied to mercury (the results are illustrative due to the unavailability of data), decomposition products of DDT and PCB homologues. Application of this model improved the agreement between measured and predicted water and sediment concentrations for DDT and PCBs, but the results were puzzling. We suggested three reasons to account for differences in the proportions of DDT decomposition products and PCB homologues among air, snow, water and sediment:

1. The model may be simply incorrect or inappropriate because the system is not at steady state, as assumed.
2. The differing proportions are analytical artifacts due to analysis of the various media in different laboratories.
3. Differences may illustrate year-to-year variability in snow and air, that are not reflected in water, and especially sediments, that integrate conditions over many years.

In reality, all three explanations probably pertain. The multi-species results do suggest that we should cautiously compare results obtained from different laboratories, particularly since reported concentrations are close to analytical detection limits.

Unsteady-state simulations were run to portray the seasonal behaviour of chemicals in the lake. Again, the results are illustrative, based on limnological and theoretical knowledge. The results indicate that chemical concentrations in water increase as ice cover builds due to cryoconcentration or the freeze-out of solutes from the growing ice mass (Figure 3). Water concentrations drop sharply in June as the ice melts and increases the volume of water. Water concentrations increase again in mid-September as ice forms on the lake.

The unsteady-state version of the model was also used to project declines in water and sediment concentrations in response to reduced chemical loadings. The results indicate that if all loadings ceased to Amituk Lake (a highly unrealistic situation), the lake would respond surprisingly fast (Figure 4). The response is due to the high proportion of chemical found in the water column rather than the sediments, and more dilute meltwater flushing the water column (i.e., the hydrologic control discussed above).

Yukon Lakes

Elevated concentrations of toxaphene have been found in several lakes in southern Yukon (Laberge and Atlin) (Kidd *et al.* 1993). Kidd *et al.* (1994) have presented convincing evidence that elevated organochlorine concentrations in predatory fish from Lake Laberge are due to the fish feeding at a higher trophic level than the same species in nearby lakes. The objective of our research was to understand the abiotic factors that could contribute to the high concentrations by modelling chemical dynamics in Atlin, Tagish, Bennett and Marsh Lakes (Figure 5). The model was adapted from a model of the Great Lakes (Astle 1987) that treated lakes in series. To develop the model we used data from studies conducted in the early 1980's by the National Water Research Institute, Pacific and Yukon Region (e.g., Kirkland and Marles 1983, Kirkland and Gray 1986, Carmack *et al.*, in prep). Kawai (1995) presents a full description of the model and model results. Hydrological details of the model are presented in Figure 6.

The model provided preliminary estimates of concentrations and rates of movement of toxaphene, α-HCH, HCB, and chlordane. The model and model results are considered preliminary due to a lack of limnological and chemical data for the lakes, i.e., the model could not be calibrated or tested. From the very limited available data, water concentrations agreed with measured values (e.g., Alaee *et al.* 1994) and did not differ significantly lake-to-lake. The model indicated that most of the chemicals entered the water column via lake inflows, and losses were via outflows (Figure 7). The results did not suggest any limnological or other abiotic factors that could account for higher chemical concentrations in pelagic fish from Atlin compared to the other lakes modelled.

From our literature survey we proposed three hypotheses factors that could contribute to the high chemical concentrations in bottom feeding fish (e.g., burbot, *Lota lota*) from Atlin Lake compared with the other lakes studied. Atlin differs from the other three lakes since it receives a high proportion of glacier-fed inflow from the Coast Mountains (Table 1).

1. Atlin Lake may receive elevated chemical loadings, particularly of the more soluble chemicals such as HCH, than the other inland lakes because: a) the higher volume and moisture content of snow that accumulates on the Llewellyn and Willison Glaciers that are fed by the Juneau Ice field in the Coast Mountains may more efficiently scavenge contaminants than snow east of the mountains (Palmer 1994); and b) higher chemical concentrations have been measured in snow from the Coast Mountains than inland at Whitehorse (Swyripa 1994).
2. Chemical loadings could be elevated due to the glaciers acting as a "cold trap" for chemicals by increasing chemical adsorption and decreasing volatilization (e.g., Wania 1994) relative to the snowpack in non-glacial areas.
3. Chemical loadings from the glaciers could be elevated as a result of minimal chemical retention during snowmelt as the meltwater becomes a supra glacial stream without contacting soil (Oerter and Reinwarth 1990). In comparison, some meltwater entering the other lakes contacts and infiltrates the soil where chemicals can be retained.
4. Bottom feeding fish in Atlin Lake may be particularly vulnerable to chemicals borne by glacial meltwaters as the water and chemical loadings may enter as "underflow" (Hambrey 1994) due to the increased density of turbid glacial meltwater in contrast to the lake water (Kirkland and Gray 1986).

CONCLUSIONS

Arctic Lakes

1. Models of chemical dynamics in Char and Amituk Lakes have been calibrated and applied to estimate the behaviour of ΣHCH and HCH congeners, ΣPCB and PCB homologues, ΣDDT and DDT and its decomposition products, toxaphene (chlorobornanes or CHB), HCB, chlordane, and mercury (three species). Versions of the model developed include single chemical steady-state, multiple chemical steady-state, and unsteady-state with seasonal time resolution. Results are still preliminary pending analysis of further chemical data from Amituk Lake.

2. Results of the models suggest that arctic lakes act as conduits for chemicals, with minimal chemical being retained in bottom sediments. This result implies that the water column of lakes can respond relatively quickly to loading changes, depending on water residence time. The results also have implications for the use of sediment profiles to reconstruct historical loading patterns or comparing loadings lake-to-lake.

3. Results of the multi-species model for DDT and its decomposition products and PCB homologues suggest that: Amituk Lake may not be at steady-state with respect to chemical loadings and among media; and differing proportions of chemicals in media may be an analytical artifact (particularly considering the extremely low concentrations measured).

4. Seasonal changes in hydrology and ice mass may lead to changes in chemical concentration due to cryoconcentration (the freeze-out of solutes from ice) and dilution during freshet.

Yukon Lakes

1. A preliminary model of Atlin, Tagish, Bennett and Marsh Lakes in the Upper Yukon River basin was developed based on past limnological data, but could not be calibrated or tested due to a lack of chemical data.

2. The results do not indicate any physical or limnological reasons for differing concentrations of organochlorines among the lakes.

3. Three hypotheses are suggested to account for higher chemical concentrations in fish from Atlin Lake than the other three lakes based on Atlin receiving most of its water (and chemical loadings) from two glaciers in the Juneau Ice Field.

Expected project completion date: December 1997

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Table 1. Annual measured (station #) and estimated flows in the lake modelled with catchment area (CA) and estimated net precipitation (mm).

Station #	Inflow name	(km³/y)	Flow Σ inflow	% of (km²)	CA ΣCA	% of mm	Ref.
Atlin							
09AA008	Pine Creek	0.16	5.4	697	10.2	233.86	1
09AA007	Lubbuck R.	0.13	4.4	1770	26.0	72.88	2
	sub-basin*	2.67	90.2	4343	63.8	614.32	3
09AA006	Atlin River	2.96		6810		436.12	1
Tagish							
09AA015	Wann River*	0.22	3.3	269	1.7	825.28	1
09AA014	Fantail River*	0.70	10.4	717	4.4	969.32	1
09AA013	Tutshi River*	0.51	7.6	992	6.1	517.14	1
	from Bennett	1.12	16.7	3775	23.3	301.99	4
	from Atlin	2.96	44.1	681.0	42.1	436.12	1
	sub-basin	1.20	17.9	3531	21.8	342.68	3
	Out flow	6.71		16171		414.94	4
Bennett							
09AA012	Wheaton R.	0.25	22.3	875	23.2	288.00	2
09AA010	Lindeman Cr.*	0.31	27.7	240	6.4	1304.17	1
09AA009	Watson River	0.16	14.3	1150	30.5	140.00	2
	sub basin	0.40	35.7	1510	40.0	69.54	3
	Out flow	1.12		3775		301.99	4
Marsh							
	from Tagish	6.71	96.4	16171	93.0	418.03	4
	sub-basin	0.52	3.4	1114.1	7.0	195.40	3
09AA011	Tagish Creek	0.01	0.1	76.9	0.5	120.81	2
09AB008	M'ClintockR.	0.301		1700		177.06	2
	Out flow	7.54		17389		400.26	4

1: Environment Canada, Historical Streamflow Summary: British Columbia. Ottawa: Inland Water Directorate, Water Resources Branch, Water Survey of Canada, 1990.
2: Environment Canada, Historial Streamflow Summary: Yukon and Northwest Territories. Ottawa: Inland Water Directorate, Water Resources Branch, Water Survey of Canada, 1990.
3: Estimated as the same method in Kirkland, R.A. and C.B.J. Gray. Reconnaissance of the Chemical and Biological Limnology in Fur Large Lakes of the Yukon River Basin. HHRI Paper No. 33, 1986.
4: Carmack, E. E. Marles, and Ri Wigand. A limnological transect of the southern lakes of the Yukon River system. In prep.
*: Glacier fed inflow (Brown, 1976; Energy, Mines and Resources Canada 1988, 1990).

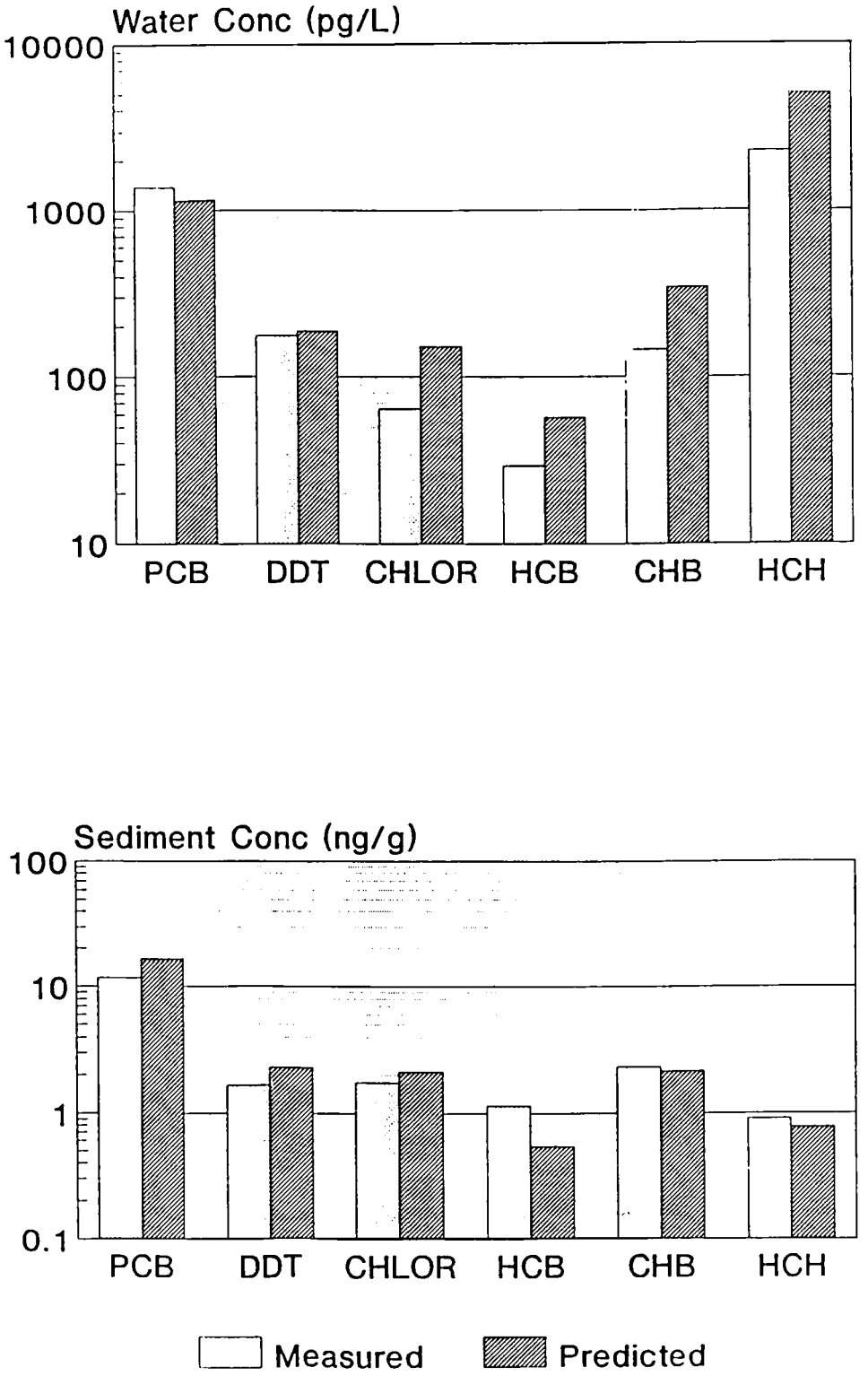
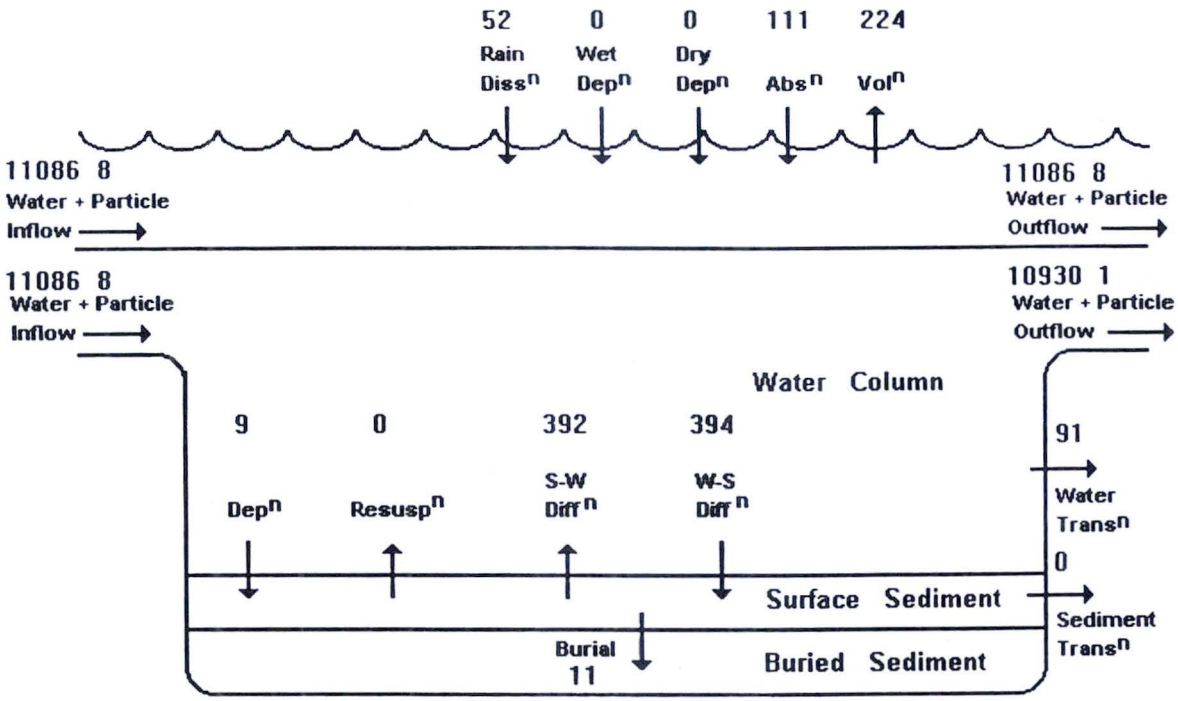


Figure 1. Measured versus predicted organochlorine concentrations in Amituk Lake water and sediment. Predicted values were obtained with empirical partition coefficients



Annually averaged mass balance for α-HCH in milligrams per year for Amituk lake as calculated from the single-species steady-state model.

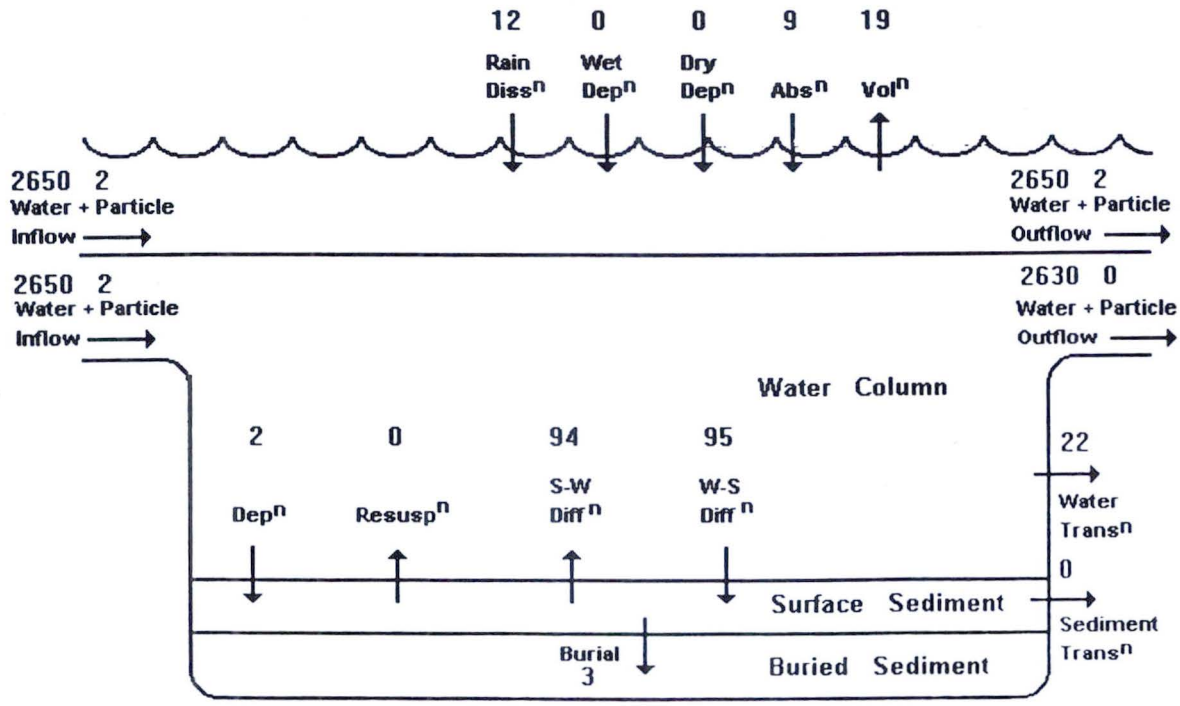


Figure 2. Annually averaged mass balance for γ–HCH in milligrams per year for Amituk Lake as calculated from the single-species steady-state model

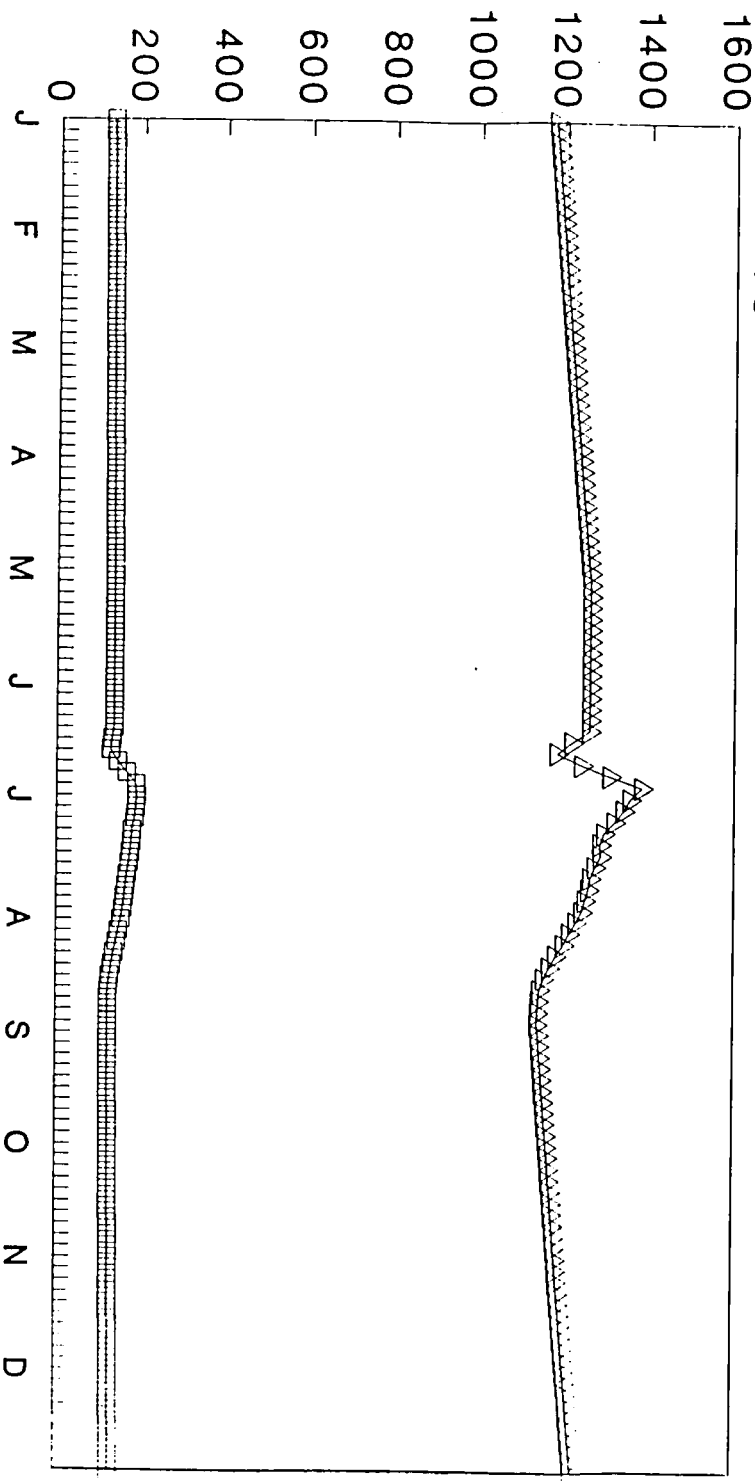


Figure 3. Seasonal water column concentrations for HCB and PCB as calculated by the unsteady-state model

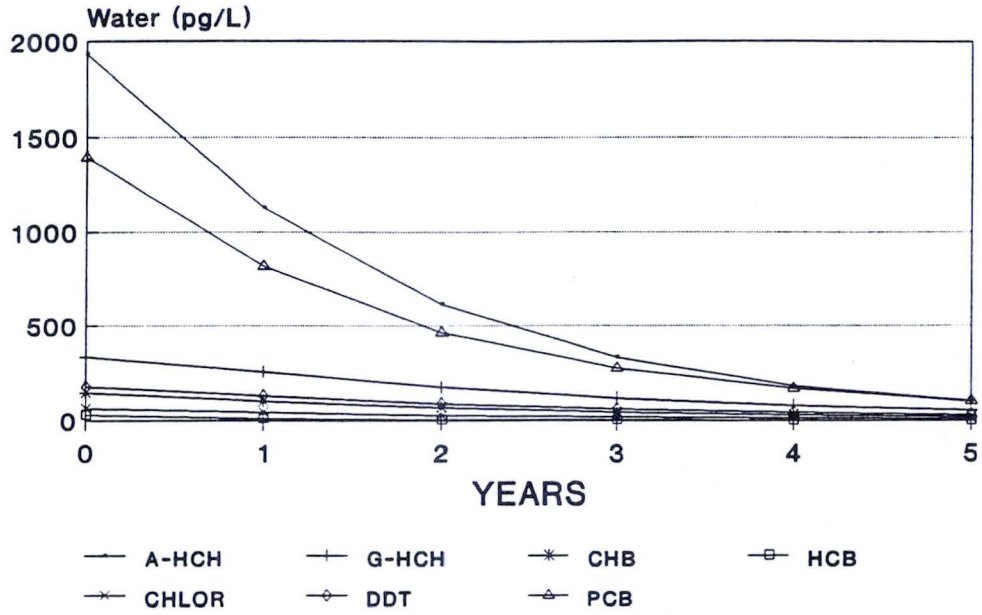


Figure 4a. Changes in current water column concentrations with eliminated chemical loadings as calculated by the unsteady-state model

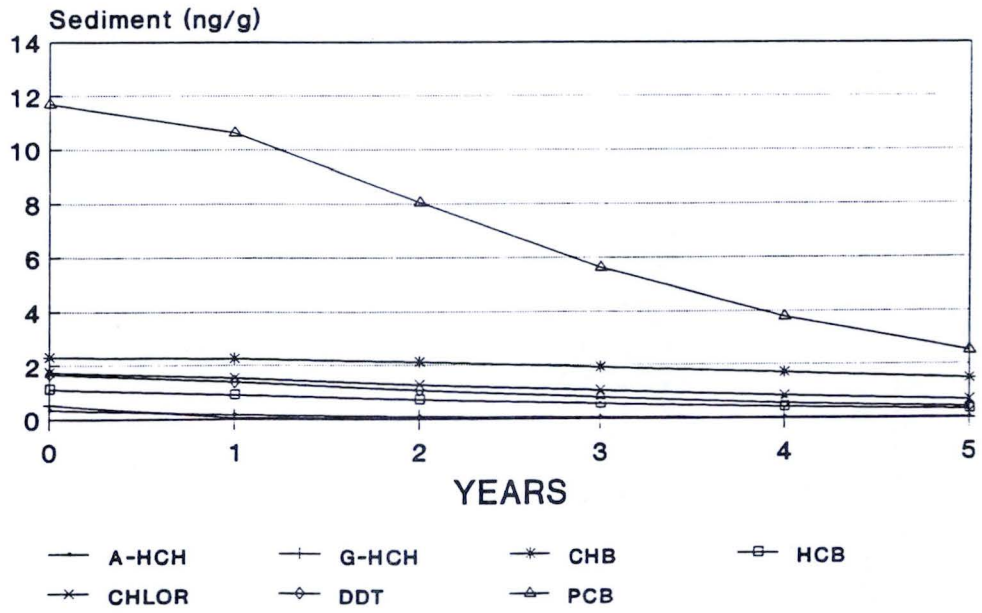


Figure 4b. Changes in current sediment concentrations with eliminated chemical loadings as calculated by the unsteady-state model

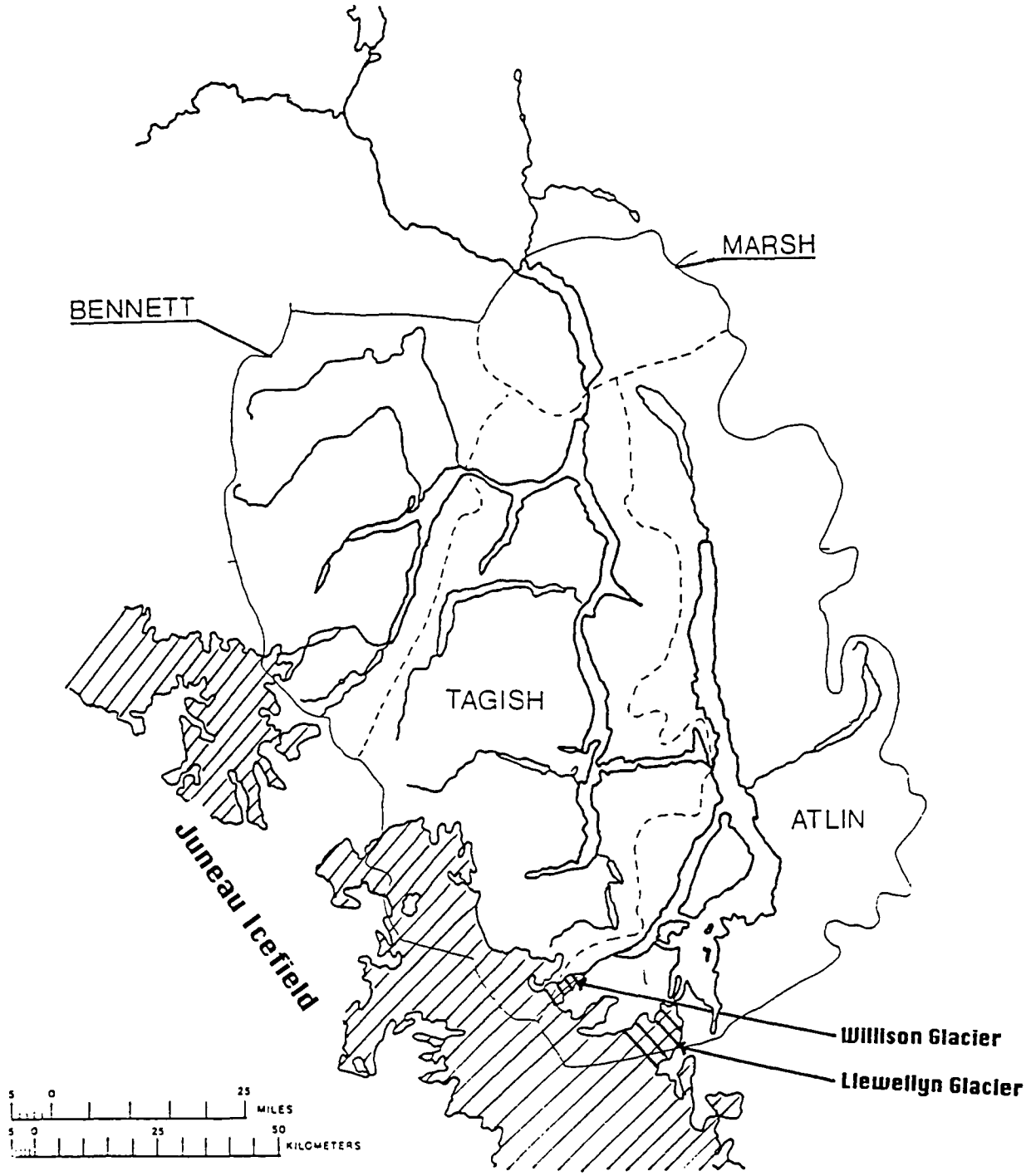


Figure 5. Glacier and icefield located at the upper Yukon River basin. Source: U.S. Geological Survey (1956)

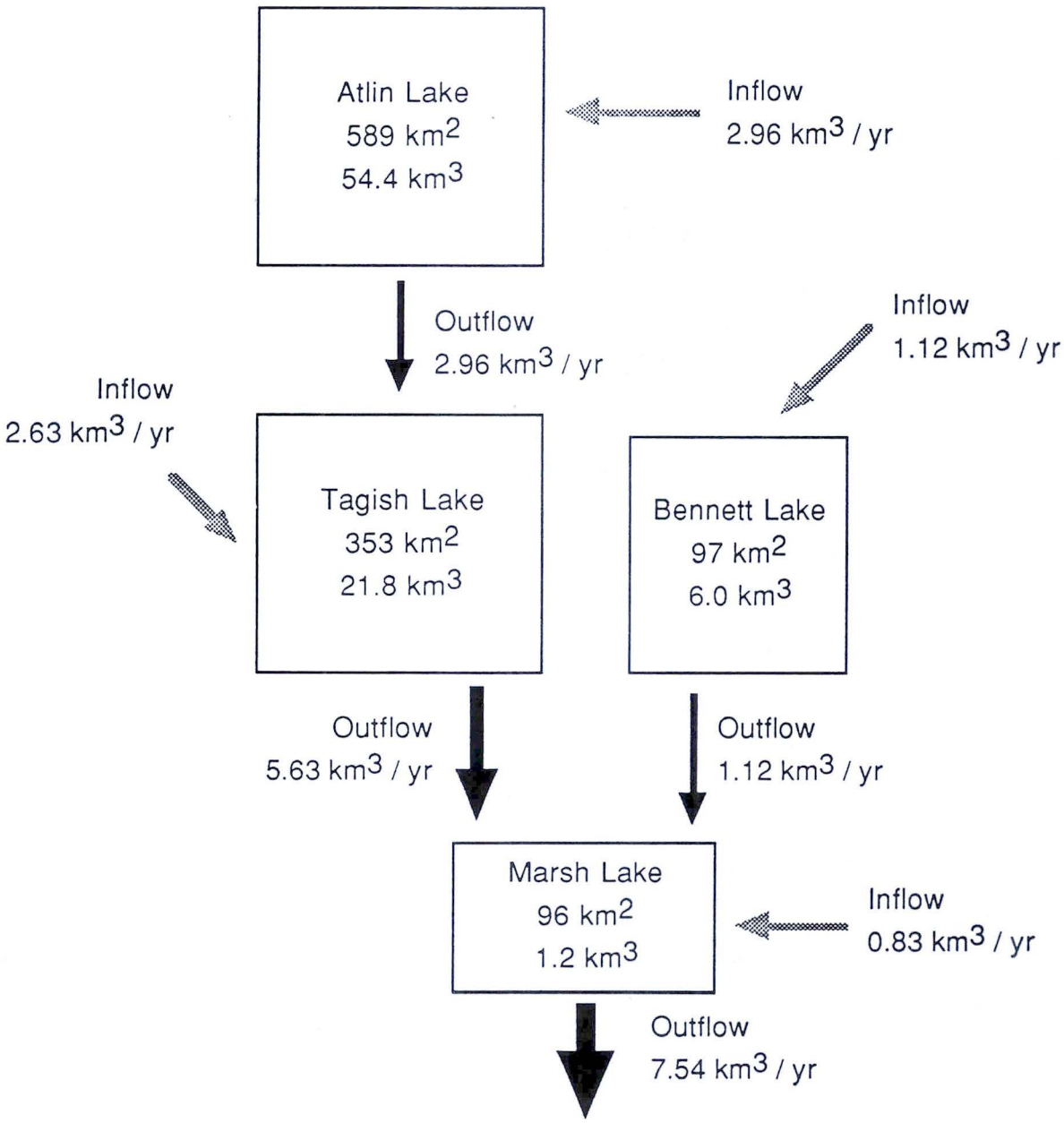


Figure 6. Illustrative model of water flow

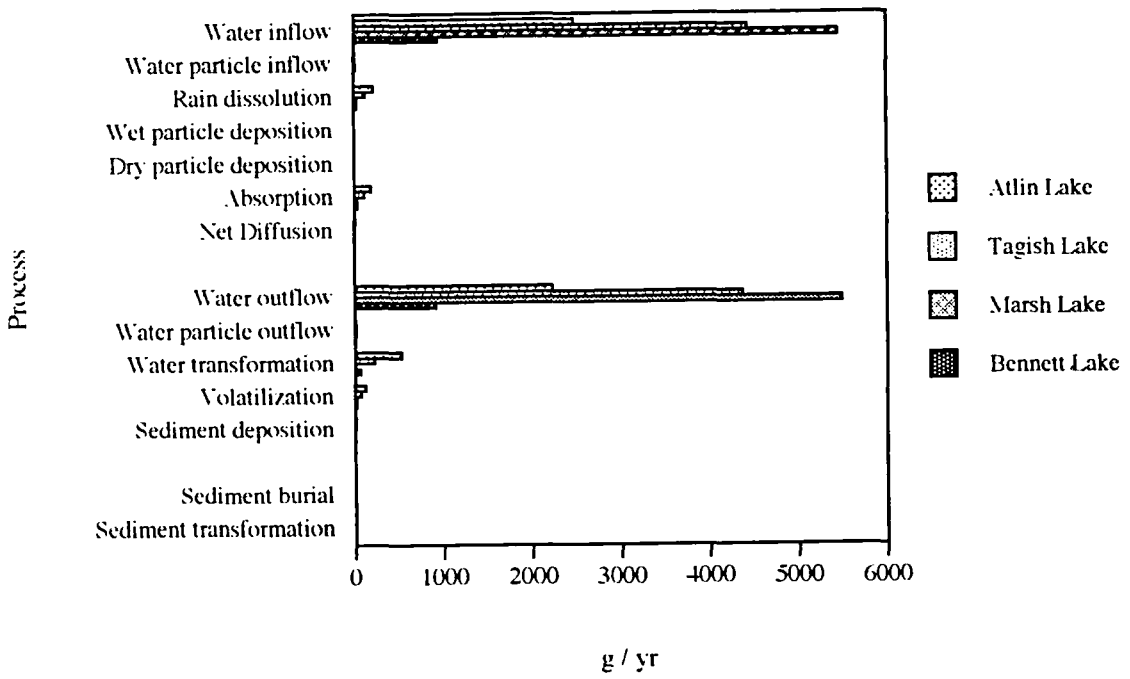


Figure 7. Estimated movement of α–HCH in lake modelled

II ECOSYSTEM CONTAMINANT UPTAKE AND EFFECTS

ECOSYSTEM CONTAMINANT UPTAKE AND EFFECTS
NEW FINDINGS

1) Belugas sampled in the eastern and western Arctic had regional mean mercury concentration in muscle tissue of 0.94±0.44 and 1.34±0.67 µg/g wet wt, respectively, exceeding significantly the Canadian guideline (0.5 µg/g wet wt) for mercury in consumable and exportable fish. In muktuk of belugas the mean mercury concentrations in the western Arctic (0.79±0.41 µg/g wet wt) and the eastern Arctic (0.59±0.22 µg/g wet wt) were approximately at the level of the guideline. Ringed seals had mean concentrations in muscle, of 0.39±0.17 and 0.41±0.29 µg/g wet wt, in the eastern and western Arctic, respectively, clearly below the guideline.

The mean mercury concentration in the liver of belugas in the western Arctic was higher by a factor of 3, than the mean for belugas in the eastern Arctic. The corresponding mercury mean for ringed seals in the western Arctic was higher by a factor of 4 than that for the eastern Arctic. A spatial trend for total mercury in Canadian Arctic marine mammals, decreasing from west to east, is indicated. This difference between the western and eastern arctic largely reflects the different environmental background concentrations of mercury in the western and eastern Arctic, dictated by the different geological settings in the eastern and western Arctic.

2) The comparatively low levels of contaminants (organochlorine, metal and radionuclides) detected in caribou in the NWT, 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 have conducted a human health risk assessment on the complete organochlorine, heavy metal and radionuclide data set from all 10 sites, which indicated that caribou meat safe to eat in unlimited quantities.

3) Studies of caribou across the Arctic indicate that PCDDs, PCDFs and non-ortho PCBs are unlikely to pose a threat to either caribou or their human consumers. The levels observed are likely background concentrations.

4) Levels of organochlorines in breast muscle of birds in the Yukon are generally quite low. The most commonly detected residues were ΣPCBs, ΣDDT, ΣChlordanes and ΣChlorobenzenes with ΣHCH also prevalent in diving species. Those species which feed at a lower trophic level, such as ptarmigan, grouse and geese, contained lower organochlorine levels than most of the ducks.

5) Contrary to predictions, there is no evidence of a declining trend in contaminant levels in arctic-breeding peregrine falcons and their prey species at Ranking Inlet, NWT. The local terrestrial environment is essentially free of organochlorine contaminants. Therefore, the contaminants found in peregrines and their prey must originate elsewhere. Levels of contaminants in Rankin Inlet peregrines are higher than in their Alaskan and Greenland counterparts. Given that these three populations overwinter in the same region in Latin America suggests that the differences are not due to diet on the wintering grounds. The difference is explained by the diet on the summer breeding grounds in the Arctic. Oldsquaw is the most heavily contaminated waterfowl species surveyed in the NWT and it forms a major part in the diet of the Rankin Inlet peregrines, while it is missing from the diets of the Alaskan and Greenland populations.

6) Recent studies show that non-ortho and mono-ortho PCBs comprise a significant proportion of total TCDD toxic equivalents in Arctic fish and marine mammals. CB 126 is by far the most prominent toxic PCB congener in almost all samples.

7) Burbot liver samples from Great Slave Lake contain significantly higher concentrations of toxaphene and ΣPCB than those from Fort Good Hope. Levels of all major OCs in Great Slave Lake burbot liver were, however, much lower (10x for ΣPCBs) than in burbot liver from Lake Laberge in the Yukon.

8) Relatively high concentrations of most organochlorines were found in both Beaufort Sea and Cumberland Sound turbot. Toxaphene was the predominant organochlorine (376±28 ng/g in Beaufort Sea samples). Concentrations of toxaphene and other OCs in turbot liver were generally lower than in muscle despite higher lipid content (mean of 24% in liver vs 16% in muscle).

9) Levels of mercury in lake trout in Peter Lake, NWT are generally higher than the guideline limit for commercial fish of 0.5 µg/g (wet wt). Arctic char from this lake had much lower levels of mercury than lake trout. Mercury concentrations are also relatively high in lake trout and pike from the Nunavik region of northern Quebec.

10) Levels of ΣPCB in female ringed seals from the Canadian Arctic archipelago or in male beluga from the southern Beaufort Sea do not appear to have declined

significantly over a 7 to 10 year period. There are indications of a decline in ΣDDT in ringed seals in the eastern Canadian Arctic, but surprisingly little decline in ΣPCB and, especially ΣDDT over a 10-20 year period in belugas in the western Arctic.

11) The accumulation of cadmium in Yukon wildlife appears to vary widely among species and individuals. Levels in some Yukon animals, such as moose (>200 ppm dry wt in kidney), Finlayson caribou, beaver (129.7±99.1 ppm dry wt in kidney) and some individuals of grouse (80.0±232.1 ppm dry wt in kidney) and ptarmigan (143.0±68.4 ppm dry wt in kidney), are higher than in other geographical regions. Studies suggest that the high levels of cadmium seen in some Yukon wildlife result from local natural mineralization.

12) In a study of traditional foods in Nunavik (Northern Quebec), levels of OCs in the species sampled were generally low. For mercury, the Northern Pike, the Lake Trout and the Walleye were the most contaminated species (>0.7 mg/kg). Among fish-eating birds, the Herring Gull and the Common Loon showed the highest mercury and OC concentrations. The Northern Pintail, the Green-winged Teal and the American Black Duck contained relatively elevated concentrations of lead (~0.3 mg/kg). Beluga meat showed the highest mercury (2.6 mg/kg) concentrations and beluga blubber showed the highest total OC concentrations of Nunavik country foods sampled.

13) Hexachlorocyclohexanes, cyclodienes, isomers of DDT and its metabolites and congeners of PCBs and toxaphene (PCCs) have been detected in seawater, under-ice epontic particulate matter and tissue samples of marine biota from lower trophic levels of the Arctic Ocean. This distribution of toxaphene among organisms in the marine food web shows biomagnification between predators and prey. Biomagnification factors (BMFs) (predator:prey toxaphene concentrations) were highest (65) for the potential transfer link between ringed seals to the benthic scavenging amphipod *Eurythenes gryllus,* and zooplankton to arctic cod and char (37).

14) Mercury levels in ringed seal muscle in both 1993 and 1994 were below guideline levels (0.5 ppm), but in the liver the mean levels in the samples were 20 to 40 times the guideline. The liver is also high in cadmium, as is the kidneys. Most commonly eaten are the muscle, blubber or muktuk (in beluga); it is much rarer for people to eat the liver or kidneys.

15) The down-core profiles in sediments of Yukon Lakes have indicated much less fallout of metal contaminants, in comparison with natural geological background levels, than in eastern Canada. In the east, for example, lead found in the top slices of cores typically exceeds that in the bottom. This is not the case in the Yukon lakes, with the exception of Fox Lake, which is likely contaminated by nearby road traffic rather than by long-range atmospheric transport.

In contrast, atmospheric fallout is suggested to be the cause of elevated levels of toxaphene in fish from Yukon lakes.

16) Contaminant levels in NWT mink are low in comparison with other mink studied in North America. Many of the pesticides and PCB congeners detected were found at very low levels. Heavy metal residues are also comparatively low, with the exception of total mercury, which was at moderate levels (community means of 0.12-3.30 µg/g wet wt in liver samples) Mercury levels were highest in Fort Rae, Fort Smith and Fort Good Hope mink livers.

17) There appears to be a sharp gradient in ΣPCB levels in bears from the Arctic Ocean (Prince Patrick Island), through M'Clure Strait and Viscount Melville Sound to Barrow Strait: 20.7, 10.1 and 4.4 mg/kg.

18) "In a recent study of OC kinetics in female polar bears, the estimated rate of transfer of ΣChlordane and ΣPCB from females to cubs in the autumn of their first year was in the range of 0.4 to 1.1 mg/d, which is approximately 0.5% of the female's body burden per day. The rate of OC excretion by pregnant females during the 6 month denning period appears to be in the same order, approximately 0.15 mg/d, based on the estimated 32 mg PCB difference in body burdens before and after denning. Most of the 32 mg PCB was probably transferred to the fetuses and cubs. This suggests that there is little or no excretion of OCs during fasting."

SOURCES AND SINKS OF ORGANOCHLORINES IN THE ARCTIC MARINE FOOD WEB

Project Leader: B. Hargrave, Fisheries and Oceans Canada (DFO), Bedford Institute of Oceanography

Project Team: G. Philips, W. Vass, G. Harding, R. Conover, H. Welch (DFO); T. Bidleman, L. Barrie, Environment Canada

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 to assess input of organochlorines to arctic marine 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 (Muir *et al.* 1992a, Harding 1986).

Many OCs have a low water and high lipid solubility. Bioaccumulation (the partitioning of compounds between an aqueous phase and tissues of organism) 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. Biomagnification (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 (Harding 1986). Biomagnification should be favoured in arctic marine ecosystems where there is a summer maximum of lipid synthesis and storage (Hargrave *et al.* 1989a).

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 winter months 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.* 1992a). Measurements from the Canadian Ice Island between 1986 and 1989 (Hargrave *et al.* 1992) were restricted to summer months due to difficulties in sampling throughout the year. The main objective for the POLARPRO project was to provide

the first seasonal measurements of OCs in seawater and lower trophic level marine organisms in any arctic marine location. The sampling area (Barrow Strait/ Resolute Bay) was chosen because logistic support was available throughout the year through the Polar Continental Shelf Project and a DFO laboratory (South Camp) located in 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.* 1992, 1989b, 1988) over a restricted range of seasons can be compared with the new data set covering a full annual period.

ACTIVITIES IN 1994/95

Sample Analysis

Samples of seawater and lower trophic level organisms collected during the 12-month study in Barrow Strait between January and December 1993 were analysed for 16 OC pesticides, including toxaphene, and for PCBs by congener during 1994. Analyses of all seawater (1 and 50 m depth) samples extracted from XAD-2 resin columns, epontic particulate matter, various size classes and species groups of planktonic and benthic crustaceans and fish were completed. Sample collection was co-ordinated with other DFO studies (H. Welch, R. Conover) to allow comparisons of biomass and productivity of plankton and benthos in the Barrow Strait/Resolute Bay area over the annual cycle. Data for hydrographic variables (temperature, salinity, dissolved nutrients), chlorophyll *a*, zooplankton biomass, lipid content and species composition have been summarized at monthly or more frequent intervals for comparison of levels of OCs in various sample types. The data set is unique in providing seasonal observations of marine food web dynamics over an annual cycle for comparison with seasonal changes in OC levels in lower trophic level biota.

Methods

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 concentrate dissolved and colloidal OCs from 150 to 350 L of seawater. Seawater was pumped (150 mL 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 amount 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. Zooplankton were collected in solvent cleaned plankton nets. By using nets of different mesh sizes and solvent clean stainless steel sieves, plankton were separated into various size classes. Scavenging amphipods were collected by deployment of baited traps with protected bait on the bottom. Fish *(Boreogadus saida)* were collected by a trap net moored across leads or from the shore in Resolute Bay. Excess water was removed from biota by blotting and samples 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.* (1992 and 1989b).

Procedures for sample extraction, OC analysis, identification, quantification and QA/QC follow methods used by Axys Analytical Services (AAS) Ltd. (formerly Seakem Oceanography Ltd.), Sidney, B.C. The methods, described in Hargrave *et al.* 1988, are the same as those used in studies from the Canadian Ice Island (Hargrave *et al.* 1989b). 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 analysed by two commercial laboratories (OceanChem Ltd., Dartmouth and AAS) and two DFO laboratories— The Bedford Institute of Oceanography (BIO) and the Freshwater Institute (FWI)—were consistent for seven major OC groups or compounds.

Data Processing and Management

Approximately half of the samples (from alternate months over the annual period) were delivered to AAS in February 1994. The remaining samples (approximately 80%) were then selected to complete annual coverage in the data. Funding for 1994/95 allowed OC analysis for these additional samples to be completed during the latter part of 1994. A final report of results was available (hard copy and Lotus spread sheets) in December 1994 and results were transferred to a DOS relational database (Alpha Four v 4.) in early 1995.

RESULTS

Five classes of compounds (hexachlorocyclohexanes, cyclodienes, isomers of DDT and its metabolites and congeners of PCBs and toxaphene (PCCs)) have been detected in seawater, under-ice epontic particulate matter and tissue samples of marine biota from lower trophic levels of the Arctic Ocean (Table 1). PCCs, PCBs, isomers of DDT and DDE, chlordane, dieldrin, α–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, pelagic and benthic crustaceans are also present in the Arctic atmosphere, particulate and dissolved fractions of snow, ice melt water and seawater samples (Hargrave *et al.* 1988). Small-bodied organisms which are short-lived and generally have a lower lipid content for storage of OCs than larger sized animals, have lower OC levels in their tissues. 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 under-surface of the ice.

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). 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).

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.

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Table 1. Ranges of concentrations ($\mu g.g^{-1}$ lipid) of various organochlorine (OC) pesticides and PCBs in lower trophic level arctic marine biota, fish and marine mammals summarized from Hargrave *et al.* 1989b, 1992, 1993 and other sources indicated. Zooplankton in the smaller size class were dominated by *Pseudocalanus* and copepodites of *Calanus hyperboreus* with adults of the latter species in the larger size class. Pelagic amphipods were *Pseudalibrotus litoralis* and *Gammarus wilkitzki.* Benthic amphipods included *Onisimus sp., Tmetonyx cicada, Anonyx nugax* and *Eurythenes gryllus.* Data from Arctic cod (*Boreogadus saida*), Arctic char (*Salvelinus alpinus)* and Arctic eelpout (*Lycodes frigidus)* represent whole body, liver and gonad tissues. ND - not detected (sample size may have been insufficient for quantitative determination).

OC	Epontic Particles	Zooplankton 25-215 mm	Zooplankton >509 mm	Amphipods Pelagic	Amphipods Benthic	Fish[5]	Ringed Seal[5]	Beluga[5,6]	Narwhal[7]
PCCs	ND	0.01-0.89	0.02-1.36	0.46	1.5-34.8	0.01-0.16	0.13-0.48	1.38-5.78	2.44-9.16
ΣPCB[1]	0.04-0.36	0.01-0.49	0.01-0.11	<0.44	1.6-22.5	0.003-0.93	0.51-11.6	<0.5-4.91	2.70-5.18
ΣDDT[2]	0.02-0.07	0.008-0.15	0.01-0.06	<0.35	3.46-23.8	0.003-0.04	0.15-1.62	0.67-6.83	2.54-5.92
ΣChlor[3]	0.01-0.04	0.005-0.15	0.01-0.05	0.43	1.4-4.0	0.002-0.17	0.26-0.71	0.62-2.38	1.40-1.92
ΣHCH[4]	0.01-0.28	0.002-0.20	0.01-0.28	0.50	0.05-0.08	0.001-0.11	0.06-1.41	0.15-0.39	0.16
HCB	0.006-0.03	0.001-0.10	0.01-0.10	0.17	0.09-0.14	0.001-0.11	0.028[8]	0.50-0.96	0.39-0.55

[1] as Aroclor 1254 equivalents
[2] sum of *p,p'*-DDT + *p,p'*-DDE + *o,p'*-DDE
[3] sum of *cis*- +*trans*-chlordane + *cis*-nonachlor + oxychlordane + heptachlor + heptachlor epoxide
[4] sum of α– + β– + γ–HCH
[5] includes data from Hargrave *et al.* (1992) and Muir *et al.* (1992a)
[6] range of data for blubber from *Delphinapterus leucas* collected in Cumberland and Jones Sound, 1983-1984 (Muir *et al.* 1990)
[7] mean values for blubber from male and female *Monodon monoceros* from Pond Inlet, 1982-1983 (Muir *et al.* 1992b)
[8] blubber from male *Phoca hispida* from Barrow Strait 1984 (Muir *et al.* 1988)

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

Project Leaders: D. Muir and G. Stern, Freshwater Institute (FWI), Fisheries and Oceans Canada (DFO), Central and Arctic Region

Project Team: G. Stern and M. Loewen , University of Manitoba

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, a complex pesticidal mixture consisting primarily of chlorinated bornanes (CHBs), was widely used in the US, Canada and other parts of the world before its ban in the early 1980s (Saleh 1991). Its primary use was as an insecticide for cotton and soybean crops, and briefly as a pesticide in the late 1950s and 1960s. It is well known that toxaphene residues extracted from biotic and abiotic samples do not resemble the technical material as analysed by High Resolution Gas Chromatography (HRGC), but instead consist of a more limited number of hexa-, hepta-, octa- and nonachlorobornanes (Muir *et al.* 1995). The GC–ECNIMS selected ion chromatograms of ringed seal blubber and technical toxaphene are shown in Figure 1. In previous work (Stern *et al.* 1992, 1993), we structurally identified the two major CHB congeners, T2 (2–*exo*,3–*endo*,5–*exo*,6–*endo*,8,8,10,10–octachlorobornane) and T12 its nonachloro- analog (2–*exo*,3–*endo*,5–*exo*,6–*endo*,8,8,9,10,10– nonachlorobornane) found in beluga blubber. We report here the isolation of three more environmentally significant CHB congeners, TS2, TS3 and TS4, extracted from ringed seal blubber, and their structures as determined by mass spectrometry (GC–ECNIMS (CH_4), low resolution EIMS, and linked field scanning).

This work forms part of an M.Sc. project (M. Loewen, Deptartment of Chemistry, University of Manitoba). Characterization of three major CHBs has been accomplished and the results presented at the 43rd Mass Spectrometry and Allied Topic Conference in Atlanta Georgia (Loewen *et al.* 1995).

ACTIVITIES IN 1994/95

Samples

Ringed seal blubber (10 kg) collected at Arviat (NWT) was extracted (hexane) using polymeric film dialysis and HPLC as described by Stern *et al.* (1992).

Mass Spectrometry

GC–EIMS, GC–ECNIMS and linked field scanning were performed on a Kratos Concept high resolution mass spectrometer (EBE geometry) controlled using a Mach 3X data system. EI mass spectra were scanned from 35 to 450 daltons at a scan rate of 1 sec per decade. The ion source was maintained at a temperature of 220°C, the trap current was 500 uA, the ion accelerating voltage was 8 kV and the electron energy was adjusted for maximum sensitivity (~ 50 eV) . Decompositions of selected ions in the first field region were identified by a series of linked-field scans (B/E, B^2/E and CNL(daughter and parent)). Ion decompositions were enhanced by collisional activation by introducing argon into the collision cell at a pressure to give approximately 50 % attenuation of the m/z 231 ion of PFK. Selected ion ECNIMS was performed at a spectrometer resolution of $M/\Delta M$ ~14000. Methane was used as the moderating gas and PFK as the mass calibrant. Optimum sensitivity was obtained at a gas pressure of ~2 x 10^{-4} torr as measured by the source ion gauge. The electron energy was adjusted for maximum sensitivity (~180 eV), the accelerating voltage was 5.3 kV and the ion source temperature was 120°C. The following characteristic ions were monitored from the $(M\text{-}Cl)^-$ isotopic cluster of the hexa- to nonachlorobornane homolog groups; Cl_6 308.9352, 310.9323; Cl_7 342.8962, 344.8933; Cl_8 376.8573, 378.8543; Cl_9 410.8183, 412.8154.

Gas Chromatography

GC separations were performed on a Hewlett Packard model 5890 Series II gas chromatograph using a 60m x 0.25mm i.d. DB-5ms fused silica column (Chromatographic Specialities), which was connected directly to the ion source of the mass spectrometer. He was used as the carrier gas. Samples were run using splitless injection (2 min.) with the injector at 260°C. The initial column temperature was 80°C; at 2 minutes the oven was ramped at 20°Cmin^{-1} to 200°C, then at 2°Cmin^{-1} to 230°C then at 10°Cmin^{-1} to a final temperature of 300°C and held for 8 minutes. Electronic pressure programming was used to increase the pressure during the injection cycle and then to maintain a constant flow of 1 ml min^{-1} during the remainder of the run. All injections were made by a CTC A200SE autosampler under data system control.

RESULTS

Gas chromatographic analysis of seal blubber extracts (with ECNIMS detection) shows major peaks between T2 and T12 (Figure 1). From ECNIMS we have determined that TS2, 3 and 4 are octachlorobornanes. Electron ionization (EI) mass spectra for two of the three compounds are shown in Figure 2. Three major ion degradation pathways in the EI spectra can be used to identify a given CHB congener. First, is the loss of a $C_2H_2Cl_2$, C_2H_3Cl or C_2HCl_3 after an initial loss of HCl or Cl_2 from the molecular ion. This gives rise to an even mass odd-electron ion that is characteristic of the number of chlorine atoms located on C2–C3 and C5–C6. Elimination of a neutral fragment comprised of C7 and its two attached substituents yields information regarding the bridging group's (C8 and C9) chlorine content. Observation of decomposition involving the elimination of $\cdot CH_2Cl$ or $\cdot CHCl_2$ (e.g. [M–CH_2Cl]) provides evidence as to the identity of the substituted chloromethyl groups on C7, while the presence of CH_2Cl^+ or $CHCl_2^+$ ions at m/z 49 and 83, respectively yield information with regard to the chlorine substitution on C10.

In the EI positive ion mass spectrum of TS2, the even mass odd-electron ion at m/z 244 is the result of two processes: successive losses of Cl_2 and $C_2H_2Cl_2$ or HCl and C_2HCl_3 from the molecular ion. The even mass odd-electron ion at m/z 278 results from successive losses of HCl and $C_2H_2Cl_2$ also from the molecular ion. The observation of these decompositions indicate that there must be five chlorine atoms on the ring, two on one side and three on the other. The exact positioning of these ring chlorines, however, with the exception of the one which must be located in the 2-*exo* position (Hainzl *et al.* 1994), could not be determined using mass spectrometry. An ion giving rise to a peak at m/z 195 results from the loss of $C_3H_4Cl_2$ from [M–Cl_2–Cl]$^+$ (m/z 305), indicating there is a total of two chlorines on C8 and C9. The observed losses of $\cdot CH_2Cl$ from M$^{+\cdot}$ and [M–Cl_2]$^{+\cdot}$, and not of $\cdot CHCl_2$, suggest the presence of two monochloromethyl substituents on C7. The remaining chlorine atom must be positioned on C10.

The peak observed at m/z 278 in the positive ion mass spectrum of TS3 results from the successive losses of HCl and $C_2H_2Cl_2$ from the molecular ion. Loss of only $C_2H_2Cl_2$ and not for example, C_2H_2Cl, C_2HCl_3,suggest a total of four ring chlorines, two on each side. In the mass spectra of T2 and T12, competitive losses of Cl· and HCl from the molecular ion, were observed while those of toxicants A and B (2,2,5–*endo*,6–*exo*,8,8,9,10/8,9,9,10–Octachlorobornane and 2,2,5–*endo*,6– *exo*,8,9,10–Heptachlorobornane, respectively), showed an enhanced elimination of a chlorine from the molecular ion (Stern *et al.* 1993). It was suggested that the enhanced HCl elimination from the molecular ions in T2 and T12 with respect to that of toxicants A and B was to be expected from the greater acidity of the 5–*endo* and 6–*exo* hydrogen of T2 and T12 relative to the 5–*exo* and *endo* hydrogens of toxicant A and B, due to the electron-withdrawing properties of the 5–*exo* and 6–*endo* chlorines. This competitive loss of HCl and Cl· from the molecular ion is also observed in the mass spectrum of TS3. This result along with conclusions drawn by Hainzl (1994) with regard to relevant structures of CHBs suggest that TS3, like T2 and T12, has a 2–*exo*,3–*endo*,5–*exo*,6–*endo* ring conformation. Loss of the neutral fragment $C_3H_4Cl_2$ from [M–HCl–Cl]$^+$ indicates the presence of two chlorine atoms on C8 and C9. Loss of $\cdot CH_2Cl$ from the molecular ion and [M–HCl]$^{+\cdot}$ and the absence of losses involving $\cdot CHCl_2$ verify that both substituents located on C7 are monochloromethyl groups. The remaining two chlorine atoms must be positioned on C10. Support for a dichloromethyl group at C10 is shown by the presence of a peak corresponding to $CHCl_2^+$ at m/z 83. The postulated structure for TS3 is thus 2–*exo*,3–*endo*, 5–*exo*,6–*endo*,8,9,10,10–octachlorobornane.

A significant feature of the positive ion mass spectrum of TS4 is the very low relative abundance of the even mass odd-electron ion at m/z 278 which results from the loss of $C_2H_2Cl_2$ from [M–HCl]$^{+\cdot}$. As with TS3, the observed loss of only $C_2H_2Cl_2$ indicates the presence of two chlorines on each of the C2–C3 and C5–C6 sides of the ring. Lack of a predominant even mass odd-electron ion would be consistent with a ring structure having a geminal dichlorosubstitution and an adjacent unchlorinated carbon. Elimination of HCl in this case would be less likely while loss of ·Cl would be favoured.

We cannot, however, verify the actual chlorine substitution pattern on the ring using mass spectrometry. Loss of $C_3H_3Cl_3$ is observed from $[M–HCl–Cl]^+$ (m/z 339). This confirms the presence of three chlorine atoms on C8 and C9. Decompositions involving the loss of $\cdot CH_2Cl$ and $\cdot CHCl_2$ from the molecular ion and $[M–HCl]^{+\cdot}$ indicate the presence of a dichloromethyl and monochloromethyl substituent on C7. The remaining chlorine must be located on C10.

Recently, Parlar *et al.* were successful in isolating and characterizing a number of CHBs in the technical mixture using mass spectrometry and H1 NMR (Parlar *et al.*, unpublished data). Based on GC retention times and by comparison of full scan Positive ion EI spectra, we found TS2, TS3 and TS4 to correspond to Parlar#39 (2,2,3–*exo*,5–*endo*, 6–*exo*,8,9,10–octachlorobornane), Parlar#40 (2–*exo*,3–*endo*, 5–*exo*,6–*endo*,8,9,10,10–octachlorobornane), and Parlar#42, which is a mixture of 2,2,5–*endo*, 6–*exo*,8,8,9,10–octachlorobornane and 2,2,5–*endo*, 6–*exo*,8,9,9,10–octachlorobornane, respectively. Since these two compounds would likely give the same mass spectrum we cannot conclude whether we have a single compound or a mixture of the two compounds. Structures of the three compounds are shown in Figure 3.

CONCLUSIONS AND UTILIZATION OF RESULTS

We have isolated five major chlorinated bornanes present in ringed seal and structurally identified three of them, TS2, TS3 and TS4 (Figure 2). The latter congener, also denoted as toxicant A, is thought to be the most toxic component of the technical mixture (Saleh 1991). Characterization of these congeners will contribute to an assessment of their toxicological significance and increases to five (T2, T12, TS2, TS3 and TS4) the total number of fully characterized CHBs found to bioaccumulate in marine mammals and fish. If an accurate method of quantitation for this class of compounds is to be achieved, it is imperative that as many as possible of the environmentally significant toxaphene components be structurally identified.

GC retention times and mass spectral results enabled us to verify that the two major CHBs observed in human milk samples (Stern *et al.* 1992) correspond to T2 and T12. Work regarding the arctic air component of the project was not completed but will continue in 1995/96. Additional work will also be carried out to identify toxaphene congeners in Lake Laberge sediments.

Expected project completion: March 31, 1996.

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

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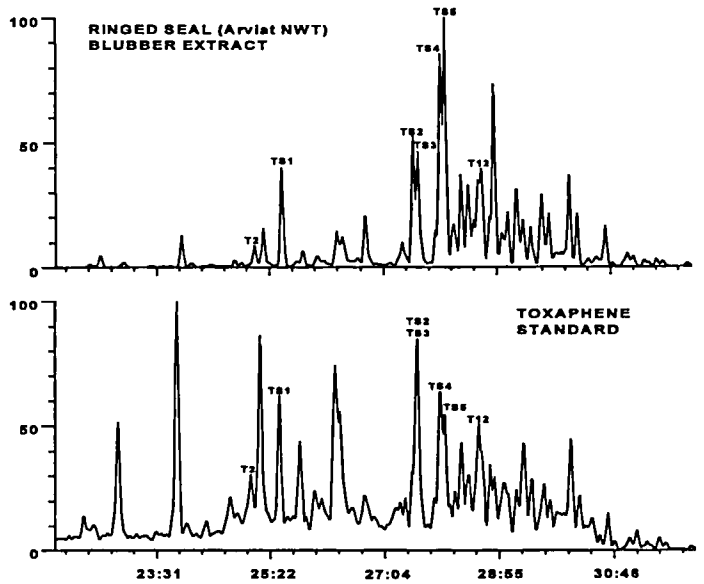

Figure 1. GC-ECNIMS chromatograms of ringed seal blubber and toxaphene standard on a 60 m DB5 column. Sum of ions for hexa- to nona-chlorobornanes.

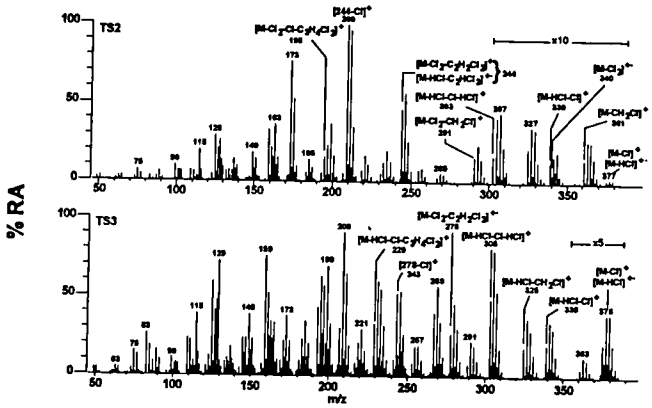

Figure 2. Electron ionization mass spectra of two octachloro-bornanes isolated from seal blubber

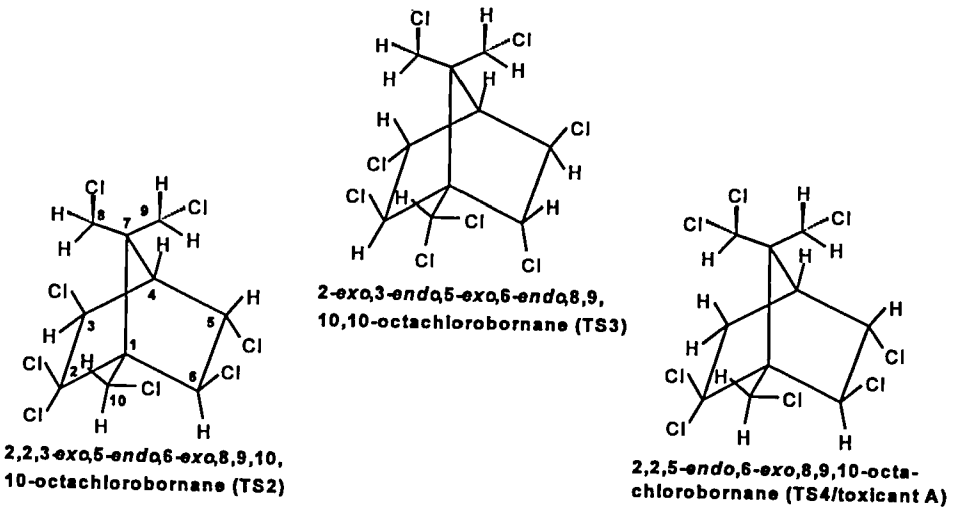

Figure 3. Postulated structures of three major chlorinated bornanes isolated from ringed seal blubber from Arviat (NWT)

SPATIAL AND TEMPORAL TRENDS OF ORGANOCHLORINES IN ARCTIC MARINE MAMMALS

Project Leader: D. Muir, Freshwater Institute, Fisheries and Oceans Canada (DFO)

Project Team: D. Tretiak, K. Koczanski, R. Stewart, S. Innes, G. Stern, DFO

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 in the Canadian Arctic and for use by the Arctic Monitoring and Assessment Programme (AMAP).

DESCRIPTION

Surveys have shown the presence of a wide range of organochlorine contaminants in arctic marine mammals throughout the Arctic. As a result of this project (Muir 1992, 1993, 1994) and work by Addison (Addison 1994, Beck *et al.* 1994), there is relatively complete data on organochlorine levels in seals and beluga in the Canadian Arctic (especially for northern Quebec, west Hudson Bay, Baffin Island, and the southern part of the Arctic archipelago) for samples collected in the mid- to late-1980s. There is limited information on geographic trends in some 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 Addison has reported results beginning in 1972.

The information on levels and on spatial and temporal trends is needed to inform people in arctic coastal communities, who consume marine mammals as part of their traditional diets, about risks of exposure to organochlorine contaminants.

The specific objectives for 1994/95 were (1) analysis of ringed seals from Resolute, Eureka and Arctic Bay in order to improve the spatial coverage and allow comparison with previous work (Muir *et al.* 1988), and (2) to analyse blubber and muktuk from beluga whales in the Beaufort Sea and Hudson Bay in order to examine spatial/temporal trends in this species.

ACTIVITIES IN 1994/95

Samples

Ringed seal samples were collected at Eureka by S. Innes (DFO) following consultation with the Grise Fiord Hunters and Trappers Association (HTA). Ringed seal samples collected at Resolute (B. Welch, DFO) during 1992 and the winter of 1993 were sexed using the polymerase chain reaction for amplification of sex chromosome DNA (Palsbøll *et al. 1992*) and aged. Ringed seals were also obtained from the Arctic Bay area (S. Innes, DFO). Beluga were obtained from the 1994 hunt in the Mackenzie Delta (D. Metner, DFO) and from the hunts at Sanikiluaq, Lake Harbour and Pangnirtung (R. Stewart, DFO). Fat biopsy samples from beluga captured at Churchill, Manitoba were provided by S. DeGuise (Université de Montréal). Additional ringed seal samples were provided by B. Doidge of Makivik Corp. (Kuujjuaq). Muktuk samples were prepared from blubber/skin samples from Mackenzie delta beluga by slicing off most of the attached fat.

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 list in Muir 1993). 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 60m 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 27 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 1994/95, the laboratory participated in the intercomparison on PCB congeners and organochlorines in a lipid-free seal blubber extract conducted by J.-P. Zhu for the Northern Contaminants Program.

RESULTS

Mean concentrations of major OC groups are listed in Table 1 for the 122 blubber and 18 muktuk samples analysed in 1994/95. As has been found in other surveys total PCBs (ΣPCB) were the major organochlorines in ringed seal blubber while toxaphene was present in the highest concentrations of all the major OCs in beluga tissues.

Blubber of female ringed seals from Eureka, the most northerly sampling site, had significantly higher (t-test $p<0.05$) concentrations of ΣPCB and ΣDDT than samples from Resolute and Arctic Bay (Table 1). Sample size from females at Arctic Bay and Eureka is limited and further comparison awaits analysis of additional samples. The analysis of samples from Resolute and Arctic Bay enabled temporal trends in ringed seals to be examined because samples from these locations were analysed during the mid-1980s (Muir *et al.* 1988). These comparisons were made with females because OC concentrations in females do not increase with age. There are indications of a significant decline in concentrations of ΣDDT at Admirality Inlet and Resolute over a nine- to ten-year period but no change is seen at Pangnirtung (seven-year interval). Little change is observed in ΣPCB at all three sites. Although Addison (1992) reported significant declines over the period 1972 to 1989, most of the decline occurred during the 1970s. So these results are not in disagreement with the Holman Island study.

Beluga whale blubber and muktuk were analysed from three locations on the Beaufort Sea coast in the Mackenzie delta area with most samples available from Hendrikson Island. Concentrations of major organochlorines were similar at these three locations. Blubber from male beluga from Sanikiluaq (Belcher Island area in southern Hudson Bay) had significantly higher levels of PCBs and toxaphene ($p<0.05$) than the Hendrickson Is. males. Spatial comparisons are best made with male beluga because they show little variation of organochlorine levels with age (Stern *et al.* 1994). Concentrations in fat biopsy samples from beluga in western Hudson Bay (Churchill) were also higher than in Beaufort Sea animals, but similar to levels in the Sanikiluaq animals, when compared on a lipid basis.

Blubber from male beluga in the southern Beaufort Sea collected in 1989 and 1983 had been analysed previously. Also available were results for ΣDDT from Addison and Brodie (1973) for Mackenzie delta beluga. The results (Figure 2) show few changes in ΣDDT levels over a 20-year period. It should be noted that Addison and Brodie (1973) used different methodology for DDT determination than this study and could have had some interferences from PCBs. The results also show few changes in ΣPCB over a 10-year period in the Beaufort Sea population.

Concentrations of organochlorines in muktuk from the southern Beaufort Sea belugas were, of course, much lower than in blubber. Average lipid content of the muktuk was about 4%. Concentrations are likely to vary depending upon how much fatty tissue remains on the skin. Concentrations of the major organochlorines in muktuk were similar to levels found by Stern *et al.* (1994) in beluga from west Greenland.

CONCLUSIONS AND UTILIZATION OF RESULTS

Results of the project during 1994/95 have added to the spatial and temporal information available on ringed seals from the Canadian Arctic archipelago and for belugas in the southern Beaufort Sea. Levels of ΣPCB do not appear to have declined significantly in female ringed seals or in male beluga over a seven- to ten-year period in these areas. There are indications of a decline in ΣDDT in ringed seals in the eastern Canadian Arctic (two out of three locations) but surprisingly little decline in ΣPCB and, especially ΣDDT over a 10- to 20-year period in belugas in the western Arctic. Future temporal trend work planned for 1995/96 will examine narwhal and beluga in eastern Arctic locations (southeast Baffin, Pond Inlet). We also hope to have ringed seals from Grise Fiord and walrus from the Thule region of Greenland. Results of the work have been provided to Health Canada, presented at Northern Contaminants

Program review workshops and provided directly to northern residents 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 Inuvialiut Settlement Region.

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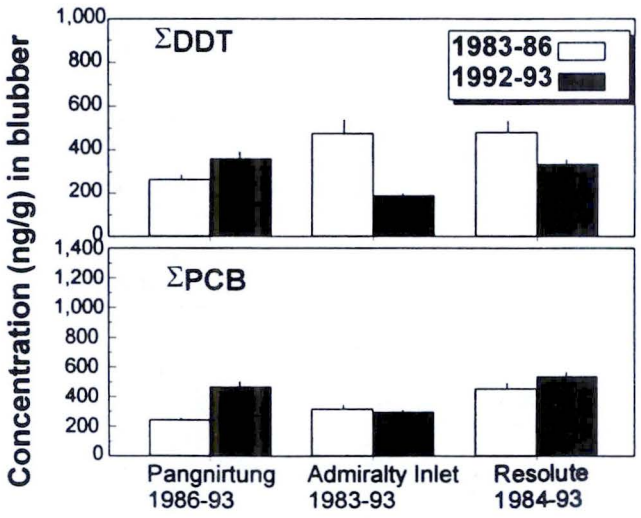

Figure 1. Temporal trends in ΣPCB and ΣDDT in female ringed seals. Vertical bars represent standard errors.

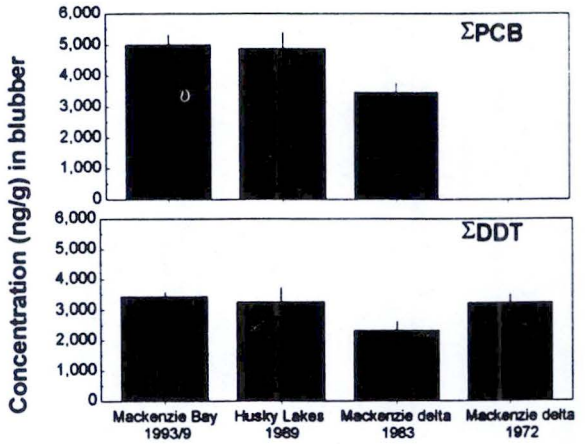

Figure 2. Temporal trends in ΣPCB and ΣDDT in male beluga from the Mackenzie delta area

Table 1. Concentrations (ng/g wet weight) of Major Organochlorine Groups in Marine Mammal Tissues Analysed during 1994/95.

Species	Location	Sex	N	Lipid (%)	Σ-CBZ	Σ-HCH	Σ-CHLOR	Σ-DDT	Σ-PCB	Toxaphene	Dieldrin
Ringed seal blubber											
	Arctic Bay	F	5 mean	93.0 ± 1.2	74.4 ± 12.4	194.0 ± 53.2	476.5 ± 265.9	305.5 ± 143.0	462.7 ± 226.0	286.1 ± 207.6	56.9 ± 12.4
			range	91.5 - 94.1	57.0 - 87.2	129.3 - 275.9	237.1 - 828.3	196.2 - 514.8	270.9 - 805.1	114.0 - 549.0	39.9 - 68.5
	Arctic Bay	M	10 mean	91.5 ± 3.1	107.8 ± 46.4	243.2 ± 97.4	981.2 ± 1013	1206 ± 1812	1119 ± 1221	418.5 ± 431.8	109.0 ± 58.9
			range	84.1 - 95.4	50.0 - 193.4	127.2 - 424.0	195.8 - 2793	125.8 - 5831	201.8 - 3662	74.8 - 1519	44.2 - 188.8
	Arviat, NWT	M + F	6 mean	93.9 ± 4.2	46.7 ± 4.5	255.8 ± 86.3	1291 ± 846.4	1347 ± 839.6	1729 ± 1011	305.1 ± 195.2	89.2 ± 36.0
			range	89.4 - 99.6	41.7 - 54.0	171.3 - 414.7	275.5 - 2385	201.5 - 2279	411.9 - 3076	39.8 - 496.0	53.3 - 151.9
	Eureka	F	7 mean	91.5 ± 2.1	187.4 ± 96.2	255.5 ±108.1	612.8 ± 188.9	672.6 ± 261.1	1267 ± 314.8	441.4 ± 136.4	96.1 ± 30.2
			range	88.3 - 94.9	60.2 - 347.6	120.6 - 405.7	460.4 - 1101	400.4 - 1239	761.3 - 1678	208.4 - 636.3	56.5 - 140.6
	Eureka	M	9 mean	90.8 ± 1.9	185.0 ± 80.8	301.9 ± 120.8	999.9 ± 344.2	1033 ± 266.3	2055 ± 707.0	561.0 ± 226.0	129.7 ± 44.2
			range	87.2 - 94.2	102.2 - 371.8	142.3 - 545.4	595.2 - 1579	580.6 - 1424	1457 - 3433	267.3 - 900.5	62.6 - 183.8
	Resolute Bay	F	10 mean	92.7 ± 0.9	87.7 ± 26.8	310.0 ± 141.1	465.5 ± 119.1	334.3 ± 108.2	535.3 ± 154.1	146.4 ± 47.3	71.5 ± 29.9
			range	91.5 - 94.1	55.1 - 143.1	167.0 - 614.0	287.6 - 702.8	152.0 - 471.5	338.3 - 826.0	86.1 - 239.8	35.2 - 120.8
	Resolute Bay	M	10 mean	92.9 ± 1.1	102.7 ± 19.0	383.5 ± 101.8	478.2 ± 155.6	365.3 ± 167.7	655.0 ± 183.9	163.4 ± 97.1	93.9 ± 37.9
			range	91.5 - 95.1	66.7 - 123.1	250.4 - 541.8	313.9 - 773.7	138.1 - 684.0	343.3 - 931.6	67.5 - 380.2	60.8 - 182.4
Beluga blubber											
	East whitefish	M	7 mean	92.0 ± 1.8	92.0 ± 1.8	987.4 ± 80.6	2596 ± 142.2	3419 ± 506.3	6293 ± 681.2	7777 ± 1214	421.4 ± 63.6
			range	90.6 - 96.0	90.6 - 96.0	939.1 - 1166	2408 - 2820	3029 - 4334	5400 - 7467	6814 - 10261	313.5 - 522.9
	Hendrickson Is.	F	5 mean	87.8 ± 4.2	861.9 ± 108.5	394.7 ± 174.1	2456 ± 328.6	3503 ± 563.1	5299 ± 1460	6171 ± 1673	436.0 ± 139.7
			range	84.2 - 92.6	702.1 - 994.7	213.1 - 664.8	2062 - 2868	2736 - 4321	3489 - 6786	4280 - 8641	342.4 ± 671.8
	Hendrickson Is.	M	20 mean	89.2 ± 2.1	910.0 ± 134.1	320.8 ± 49.9	2431 ± 416.7	3506 ± 929.5	4882 ± 1878	5900 ± 2333	397.1 ± 131.5
			range	84.5 - 93.0	692.1 - 1180	241.3 - 447.3	2023 - 3449	1787 - 6080	3026 - 9037	3525 - 11401	18.5 - 687.1
	Paulatuk		3 mean	91.2 ± 0.5	1177 ± 59.5	466.2 ± 42.2	2409 ± 60.2	2460 ± 123.1	3903 ± 217.1	5320 ± 199.1	386.3 ± 81.6
			range	90.7 - 91.7	1142 - 1246	432.8 - 513.7	2365 - 2478	2335 - 2581	3693 - 4126	5146 - 5537	297.6 - 458.0
	Sanikiluaq	F	5 mean	93.1 ± 1.8	294.2 ± 109.2	334.9 ± 86.9	1450 ± 943	1697 ± 1391	2185 ± 1559	8331.5 ± 3503	202.3 ± 306.1
			range	90.9 - 96.2	164.4 - 444.5	229.4 - 541.8	333.6 - 3116	182.5 - 4004	352.2 - 4384	3547.5 - 13769	646.5 - 61.3
	Sanikiluaq	M	5 mean	94.8 ± 0.7	366.8 ± 203.7	441.6 ± 133.2	4167 ± 1585	11205 ± 8231	6768 ± 2346	15414 ± 8157	407.8 ± 982.1
			range	94.3 - 96.0	219.7 - 650.1	307.9 - 698.7	2362 - 6456	2074 - 21660	3521 - 9080	8992 - 28906	1639 - 686.5
	Pangnirtung	F	5 mean	93.8 ± 2.6	275.0 ± 175.9	254.7 ± 107.5	2208 ± 1430	4025 ± 3730	4007 ± 2689	8157 ± 5407	293.7 ± 441.0
			range	90.5 - 96.5	81.8 - 458.3	155.5 - 395.1	704.8 - 3877	575.3 - 9833	1111 - 7477	2848 - 15020	747.1 - 142.6
	Pangnirtung	M	5 mean	93.3 ± 2.4	762.1 ± 312.8	509.6 ± 162.2	3144 ± 793.3	3685 ± 1575	4631 ± 1105	11819 ± 2922	279.8 ± 869.9
			range	89.5 - 95.8	464.3 - 1231	366.5 - 698.7	2362 - 4160	2074 - 6021	3521 - 6317	8301 - 15758	1300 - 612.4
	W. Hudson Bay[1]	F	5 mean	39.0 ± 16.9	276.7 ± 118.9	197.4 ± 69.4	1323 ± 264.8	1149 ± 237.0	1570 ± 293.1	4583 ± 1066	356.7 ± 138.0
			range	11.0 - 54.0	148.9 - 414.8	120.5 - 273.9	941.8 - 1630	839.7 ± 1479	1171 - 1973	3153 - 6086	218.8 - 510.8
	W. Hudson Bay	M	5 mean	38.0 ± 19.9	336.8 ± 85.2	209.8 ± 56.9	1594 ± 328.5	2230 ± 894.7	2213 ± 386.2	5537 ± 815.3	470.1 ± 148.3
			range	16.0 - 63.0	249.9 - 449.0	152.2 - 290.4	1268 - 2077	1419 - 3712	1743 - 2658	4758 - 6567	237.1 - 630.9
Beluga muktuk											
	East Whitefish	M	44 mean	3.9 ± 0.0	28.4 ± 16.7	19.0 ± 11.9	119.5 ± 82.2	179.6 ± 142.2	213.9 ± 132.7	351.3 ± 253.4	20.5 ± 13.2
			range	0.0 - 0.0	3.6 - 52.7	8.7 - 36.9	15.5 - 260.1	10.3 - 442.6	34.8 - 441.1	83.5 - 821.1	4.2 - 41.2
	Hendrickson Is.	F	5 mean	3.8 ± 0.6	35.6 ± 6.3	19.5 ± 3.5	120.3 ± 33.3	169.4 ± 81.1	218.5 ± 60.3	312.8 ± 136.4	22.3 ± 8.2
			range	3.2 - 4.5	28.6 - 43.1	13.4 - 22.2	97.7 - 179.2	100.6 - 301.9	168.2 - 308.7	197.6 - 548.4	15.2 - 36.3
	Hendrickson Is.	M	6 mean	4.2 ± 1.9	40.4 ± 11.5	23.2 ± 10.2	162.7 ± 41.3	271.6 ± 71.6	316.9 ± 96.1	467.8 ± 104.6	29.0 ± 8.9
			range	2.9 - 7.4	27.3 - 56.3	13.6 - 42.1	132.7 - 223.3	213.5 - 371.0	227.8 - 482.8	360.1 - 652.4	21.8 - 44.9
	Paulatuk	M + F	3 mean	4.9 ± 0.9	29.7 ± 6.2	24.9 ± 9.2	119.4 ± 25.5	159.8 ± 73.7	212.5 ± 59.7	318.6 ± 119.7	23.7 ± 5.6
			range	4.4 - 6.0	22.6 - 33.9	18.5 - 35.5	90.7 - 139.4	94.5 - 239.8	149.9 - 268.8	195.0 - 433.9	17.4 - 28.2

LONG-TERM TRENDS IN ORGANOCHLORINE (OC) RESIDUES IN EASTERN AND WESTERN ARCTIC SEAL BLUBBER.

Project Leaders: R.F. Addison, Institute of Ocean Sciences (IOS), Fisheries and Oceans Canada (DFO), T.G. Smith Pacific Biological Station, DFO

Project Team: Local hunters (Holman Inuit Co-operative)

OBJECTIVES

In general, the objective of this study is to measure trends in levels of PCBs, the DDT-group and other organochlorines from the early 1970s to the present in arctic seals. Secific objectives for 1994/1995 are:

1. To compare analyses of "biopsy" and "bulk" blubber samples, and to assess the feasibility of detecting trends in OC concentrations in seal blubber without killing animals;

2. To re-analyse samples from the early 1980s to present using identical procedures, equipment and standards in the same lab, by one operator to verify the trends implied by previous studies (which compared analyses done at different times);

3. To continue the sampling of ringed seals at Holman, NWT, and to continue the time series that began in the early 1970s. As well as blubber, samples of liver will be frozen for analysis of CYP 1A using immunochemical probes;

4. To analyse CYP 1A concentrations in Holman ringed seal liver (since CYP 1A has repeatedly been shown in other biota to be a reliable indicator of both contaminant exposure and effect, as its induction is essential to the production of reactive intermediates), correlating these CYP 1A concentrations with OC residue burdens or concentrations.

DESCRIPTION

Organochlorine (OC) residues are introduced to the Arctic by various routes, including 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 concern because these animals are used by native populations as a food resource. Previous analyses by Fisheries and Oceans Canada (DFO) have suggested that the OC concentrations observed in western arctic ringed seals may be declining. The main object 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.

ACITIVITES IN 1994/95

A comparison of DDT-group, PCB and other OC concentrations in blubber sampled by biopsy sampling and by "bulk" sampling after sacrifice of the animal was completed.

A paper submitted to *Arctic* in 1993 on long-term changes in OC concentrations in arctic ringed seals required some revision, which led to a need for further analysis. A suite of 35 ringed seal blubber samples (males and females from 1981 and 1992 sampling at Holman, NWT) were reanalysed by contract. Results are now being compared with previous (DFO) analyses and it is intended that a comparison of trends in major OC concentrations in Holman ringed seals between 1972, 1981, 1989 and 1992 be published.

A further suite of ringed seal blubber samples, together with the relevant biological data (age, size, sex and condition) was collected at Holman in spring 1994 by contract with the Holman Co-operative.

An attempt was made to analyse CYP 1A concentrations in frozen livers from Holman ringed seals. However, freezing in a domestic freezer led to too much deterioration of cytochrome P-450 to P-420 to allow reliable immunodetection of CYP 1A.

RESULTS

Mean concentrations of a range of OCs (DDT–group, PCBs, HCB, HCH, oxychlordane, *trans*-nonachlor) analysed in biopsy samples (approx 100 mg tissue) were 97.7 ± 6.24% (mean ± s.d. of 7 analyses in 10 animals) of the concentrations measured in bulk blubber samples. In other words, biopsy sampling seems to yield as representative samples as bulk blubber samples.

Preliminary digestion of the reanalysed samples from temporal trend studies shows that the decline in PCBs noted between 1972 and 1981 has levelled out between 1982 and 1989; concentrations observed in 1992 are not significantly different from those in 1989. DDT-group concentrations (notably *p,p'*–DDE fell less rapidly than those of PCBs over the same interval. We expect to have these conclusions published in 1995/96.

Holman ringed seal samples from 1992 have been archived at the Institute of Ocean Sciences (IOS).

DISCUSSION/CONCLUSIONS

Biopsy sampling of blubber has been shown to yield representative samples of "bulk" blubber, which can be used for trend analysis.

Temporal trends in PCB and DDT-group concentrations in arctic ringed seal blubber, which were identified during previous analyses, appear to be confirmed.

A further 1994 sample of Holman arctic ringed seal blubber together with associated biological data has been archived at IOS.

Domestic freezing of ringed seal liver samples leads to too much deterioration to allow reliable detection of CYP 1A.

Expected project completion date: March 31 1996.

MODELLING AND EVALUATION OF CONTAMINANT ACCUMULATION AND EFFECTS IN MARINE MAMMALS

Project Leader: M. Kingsley, Fisheries and Oceans Canada

Project Team: B. Hickie, Environmental and Resource Studies Program, Trent University;
D.C.G. Muir, Dept of Fisheries and Oceans Canada

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 (OCs) and some metals) from background and local sources. In many parts of the Canadian Arctic, they are esteemed food species and 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 relating contaminant levels in marine mammals to those in other components of their food web.

ACTIVITIES IN 1994/95

The population-level models previously developed were used to study two aspects of the dynamics of persistent fat-soluble (OC) contaminants in marine mammals.

The model developed for the beluga (*Delphinapterus leucas*) was used to examine the factors controlling the ratios of PCB congeners in whales over time, with an emphasis on the estimation of relative metabolic indices and clearance rates for arctic beluga populations. Data on over 70 organochlorines for over 140 West Greenland belugas was used with a data set for arctic cod (*Boreogadus saida*) from the Canadian high Arctic, which included congener-level data to study the relative clearance rates of different OCs, by comparing their relative bioconcentration factors. This was examined in the light of previously established classifications of PCBs according to their level of substitution in the *meta*-positions.

A second examination of OC dynamics was to use the population-level model with longer-term data on OC levels in the American eel (*Anguilla rostrata*) and other possible prey in the St. Lawrence to back-calculate a time trend in the contaminant level in St. Lawrence belugas. Recorded levels in other biota were used to reinforce the data set for time trends of PCB levels in eels, and population-level model runs were used to track the effects of these temporal changes in eel contamination on the levels in the St. Lawrence belugas.

RESULTS

Whole body clearance rates for 17 prominent PCB congeners were estimated from the model by repeatedly running the model with different trial values of clearance rate until the modelled concentration ratio, relative to CB138, (for which the clearance rate was set to zero), matched the data value. The clearance rates were compared with metabolic indices generated from the Arctic-cod-beluga data by the method of Tanabe *et al.* (1988), who derived indices for the metabolism of PCB congeners by Dall's porpoise (*Phocoenoides dallii*) by looking at the relative bioconcentration from prey to predator. A good agreement was obtained between the clearance rate predicted by the model and the empirical metabolic indices (Figure 1).

The results of the time-trend analysis of the St. Lawrence beluga with respect to changing levels in eels shows that for a certain range of diet compositions, predicted PCB levels in belugas can approximately track the recent slight observed changes.

The sensitivity analysis of the population-level model of time trend of contaminant levels showed that changes over time are affected by the trends in concentration in the diet, that they are very sensitive to clearance rates, and that the parameters of the individual growth curve are also quite important. Additional factors, which figure in the description of the life history of the female, are the birth rate and the efficiency with which contaminants are transferred from her fat to her milk.

DISCUSSION AND CONCLUSIONS

The agreement between the model predictions of relative contaminant clearance rate and Tanabe's metabolic index is not very surprising, as both are derived from empirical data using ratios of bioconcentration factors. However, the model has provided a quantitative estimate of relative clearance rate (relative to CB 138) which allows Tanabe's MIs to be calibrated in terms of clearance rate or biological half-life. As can be seen in Figure 1, the results confirm that unchlorinated M-regions are important in permitting PCBs to be metabolized by at least some cetaceans, because the PCBs with no unchlorinated M-regions are all down at the low end of the scatter of points. PCBs with unchlorinated M-regions are also the ones that Muir *et al.* (in prep.) have found to be much reduced, in fact almost completely absent, from St. Lawrence belugas.

The results of these modelling exercises confirm the results of the senstitivity analysis of previous years, that clearance rate is a major determinant of body burden in long-lived Arctic marine mammals. A similar point was made by Reijnders (1988): that position on the food chain is less important than the balance of intake and clearance in determining body burdens or concentrations of persistent contaminants.

We could use the population-level model to carry out the same sort of analysis of congener-level data for ringed seals, since a large data set for this species does exist. However, it has a mixed diet that includes both invertebrates and fish, and complex annual energetic cycles in which it strips off, and then replaces, considerable blubber reserves. The interaction of these annual changes in the body proportion of fat with the dynamics of congener-specific metabolic rates would be complex to model, but would provide interesting results for comparing the metabolic patterns for a pinniped with those that are becoming established for cetaceans.

The modelling exercises for the temporal trend in contaminant content of eels confirms that eels may be a component vector for contaminants reaching belugas. They are the only species for which there is good evidence that contaminant burdens have decreased with time, and there is a slight indication (Muir *et al.* submitted) that PCBs, at least, may be declining in St. Lawrence belugas. The observed burdens and the way they change with time is consistent with model runs in which eels compose 2% to 5% of the annual food intake of belugas; ranges which may be plausible.

Expected project completion date: 31 March 1997.

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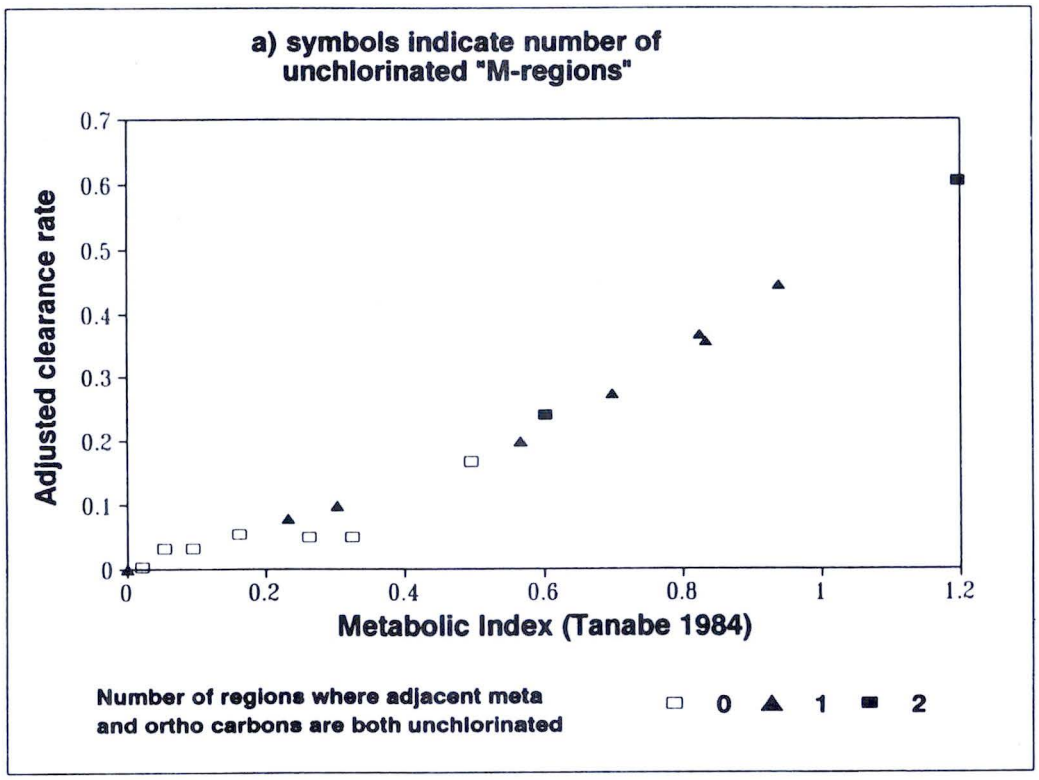

Figure 1. Relation of clearance rate predicted by the model to the Metabolic Indices developed by Tanabe (1984). a) keyed by number of unchlorinated meta-regions: congeners without such regions are refractory; b) keyed by number of chlorinated ortho carbons: no monotonic relationship with M.I. or clearance rate is evident.

PLANAR PCBS, CHLORINATED DIOXINS/FURANS AND RELATED COMPOUNDS IN ARCTIC MARINE MAMMALS AND FISH

Project Leader: D. Muir, Fisheries and Oceans Canada, Freshwater Institute, Winnipeg, Manitoba

Project Team: D. Muir, C. Ford, B. Rosenberg, 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, Muir 1993, 1994) have shown that co-planar and mono-ortho PCBs, are present in fatty tissues of marine mammals, and in freshwater and marine fish, in the Canadian Arctic. 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 modes of action: induction of hepatic mixed function oxidase (MFO) enzymes, immunotoxicity, teratogenicity and embryotoxicity (Safe 1990). Chlorinated dioxins and furans (PCDD/F) are also present, but co-planar PCBs account for most of the "TCDD equivalents (TEQs)" in arctic diet samples using the toxic equivalent factors (TEFs) of Safe (1990) or Ahlborg *et al.* (1994). Sample numbers and spatial and temporal trends for TEQs are limited compared with results for other organochlorines. The general objectives of this work are 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 as well as to provide support for biomarker studies in fish and marine mammals. For 1994/95 we planned to analyse co-planar PCBs in additional samples from the Yukon and from Great Slave Lake and to undertake a major study of non-ortho-PCBs in blubber of ringed seal from Arviat, which had been analysed for total PCBs, and which also had hepatic mixed function oxidase (MFO) enzyme induction measurements in liver.

Mono-ortho PCBs, which have a single chlorine in the 2-position, also have MFO enzyme induction potencies that 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 IN1994/95

Samples

Four samples of burbot liver from Fox Lake and eight from Lake Laberge were extracted and the extracts were split for co-planar PCB and for regular PCB/OC pesticide analysis. Extracts of 30 ringed seal blubber samples (2g) from Arviat were chromatographed by automated gel permeation chromatography to remove lipid prior to co-planar PCB and PCDD/F analysis.

Analytical methods

The analytical procedure for non-ortho PCBs is described by Ford *et al.* (1993) and in previous synopsis reports (Muir 1993, 1994). Mono-ortho PCBs in Fox Lake burbot livers were determined by high resolution GC-ECD as described in our other reports in this volume. For 1994/95 the carbon column elution was modified to include PCDD/Fs followed by analysis of non-ortho PCBs and PCDD/Fs by GC with high resolution mass spectrometry (GC-HRMS). This procedure was based on the work of Moisey and Norstrom (Unpublished method, CWS, Hull) with minor modifications. But work on method development is incomplete at this time because of the departure of C. Ford during 1994/95.

Quality Assurance

The National Institute of Standards and Technology (NIST) cod liver oil SRM 1588 was used as an internal control sample. An interlab comparison of non-ortho PCB in cod liver oil was made with D.E. Wells (Scottish Office, Agriculture and Fisheries Dept., Aberdeen Scotland).

RESULTS

An interlaboratory study with the lab of D.E. Wells (Aberdeen) showed relatively good agreement (±20%) between the two labs on the analysis of the non-ortho PCBs in cod liver oil.

We have previously reported levels of co-planar PCBs in fish from Lake Laberge and Kusawa but not from Fox Lake. Mean levels of CB 77, 126 and 169 in 4 samples of burbot liver from Fox Lake (Table 1) were much lower than in Lake Laberge burbot where concentrations of CB 126 and 169 exceeded 1000 pg/g (Muir 1993). The proportions of total PCB represented by each co-planar congener were similar in the two lakes. Concentrations of co-planar PCBs in Fox Lake were also similar to those found in burbot liver from Great Slave Lake (Muir 1994). CB126 comprised most of the TEQs for the non-ortho and mono-ortho PCBs.

Forty-one samples of ringed seal blubber from Arviat were selected for co-planar PCB and PCDD/F analysis from existing extracts already analysed for other organochlorines, and from a group of 52 animals in which liver mixed function oxidase enzyme activity had been determined (Lockhart and Ferguson 1994). Results for co-planar PCB and PCDD/F are incomplete at this time but mono-ortho PCB data are available and have not been reported previously for these animals. Major mono-ortho PCB congeners in seal blubber were CB 118, 156 and 105. (It should be noted that CB 105 was separated from CB 132 and 153 by HRGC in this work). Total TEQs for the mono-ortho PCBs (based on TEFs from Ahlborg *et al.* 1994) were correlated with age of male seals of >0.1 years old ($r = 0.677$, $p < 0.01$, $N=23$) but not with females ($p>0.05$). Ethoxyresorufin–O–deethylase (EROD) and TEQs were weakly correlated ($p < 0.06$) in combined males + females ($N=41$) but not in males ($p<0.10$). EROD was weakly correlated with age of males and females ($p<0.05$, $N=41$). Results are illustrated in Figure 1. We conclude that any correlation of EROD and TEQs, or individual PCB congeners, must take into account the confounding effect of positive correlations between TEQs and age.

CONCLUSIONS AND UTILIZATION OF RESULTS

Results from the 1994/95 work combined with our previous studies show that non-ortho and mono-ortho PCBs comprise a significant proportion of total TCDD toxic equivalents in Arctic fish and marine mammals. CB 126 is by far the most prominent toxic PCB congener in almost all samples. Future monitoring of PCBs in biological samples in the Arctic should focus on this congener. Unfortunately, results from 1994/95 are incomplete because of delays in converting to a new method which would determine mono-ortho PCBs and PCDD/Fs in the same sample using the high resolution GC-MS instrument now in use in our labs. Although the work has relatively little financial support in 1995/96 resulting from cuts in the Northern Contaminants Program, work on the outstanding samples will continue and we anticipate having results for ringed seals and burbot for next year's Northern Contaminants Program report.

Co-planar PCB and PCDD/F results for walrus and ringed seals from northern Quebec, previously reported in Northern Contaminants Program reports (Muir 1994) were recently accepted for publication in the journal Environmental Pollution and should be in print by the fall of 1995. Results will be provided to the Contaminants Committees in Yukon and NWT and to Health Canada.

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Table 1. Concentrations of non-ortho PCBs in Fox Lake burbot liver.

PCB	Concentration (pg/g wet wt)	Proportion of ΣPCB (%)	TCDD TEQs (pg/g)[1]
CB81	2.9 ± 2.7	0.008 ± 0.007	<0.001
CB77	5.7 ± 3.7	0.015 ± 0.009	0.003
CB126	24.8 ± 19.7	0.065 ± 0.053	2.38
CB169	11.5 ± 3.1	0.032 ± 0.013	0.12
Σmono-ortho PCBs (ng/g wet wt)	2.71± 0.81	—	0.32
ΣPCBs (ng/g)	38.1 ± 11.0	—	—

[1]TEFs from Ahlborg *et al.* (1994).

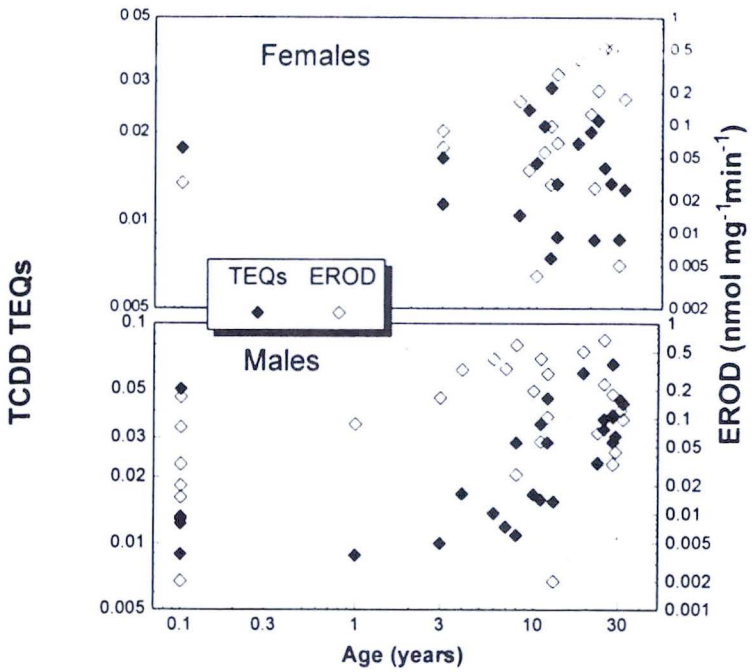

Figure 1. Relationship of TEQs (based on mono-ortho PCBs) and EROD in ringed seal blubber from Arviat (NWT) with age.

METHYLMERCURY AND HEAVY METALS IN TISSUES OF NARWHAL, BELUGA AND RINGED SEALS

Project Leader: R. Wagemann, Freshwater Institute, Fisheries and Oceans Canada

Project Team: R. Wagemann, G. Boila, H. Kozlowska (contractor), E. Trebacz (contractor)

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 by toxic metals in ringed seals and other arctic marine mammals;

3. To provide a data base on methylmercury in arctic marine mammals exhibiting high total mercury concentrations.

DESCRIPTION

This project is aimed at providing information on metals and methylmercury 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 metals exposure calculations. Past information on metals, especially methylmercury, has been sparse for arctic marine mammals, and nonexistent for muktuk. This report attempts to address some of these information gaps. High metal levels in some marine mammals have been reported sporadically. 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 Federal Guideline limit of 0.5 ppm (µg/g wet weight) for the consumption and exporting of fish. Lead was reported higher in belugas from Hudson Bay than from the MacKenzie Delta, and was very high in dolphins off the eastern Atlantic coast (Muir *et al.* 1988) and in some ringed seals from the Strathcona Sound area in the NWT (Wagemann, 1989), although the latter were likely 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 report, *Environmental Studies No. 72, 1993/94*, significant data on methylmercury and total metals in ringed seal tissues from the western Arctic, and some data on methylmercury for narwhal in liver and muscle, and metals in muktuk were presented.

This report deals with mercury in ringed seals and belugas from across the Arctic in a systematic fashion, and provides an overview of the available data for these species in the Canadian Arctic. It analyses the data for spatial and temporal trends, and provides regional levels of mercury in tissues of these species for dietary exposure calculations. The conclusions in this report are based, for the most part, on large sample sizes of animals, and the report uses pertinent data from the literature for comparison and temporal trend analysis.

ACTIVITIES IN 1994/95

Samples

Analyses for total mercury of tissue samples from belugas and ringed seals already in hand from across the Arctic were performed and these data have been incorporated in the present report. Some analyses for methylmercury of tissue samples already in hand (narwhal, belugas, ringed seals) from across the Arctic have been performed, but have largely been deferred pending the completion of an overview report on total mercury. The highest priority has been given to methylmercury analyses and the production of a substantial data set for this substance in marine mammals from across the Arctic. In the next one to two years, samples already in hand will be analysed for methylmercury, and new samples will only be obtained when absolutely necessary to fill a serious gap in the sampling grid, or when analyses are requested on an urgent basis by government agencies or outside interests. In the future, time and effort will be directed exclusively toward the production of an overview report on methylmercury in marine mammals from across the Arctic and sub-Arctic using inventory tissue samples.

Methods

Marine mammal tissues were analysed for total mercury by cold-vapour flameless AA, for other metals (lead, cadmium, selenium, zinc and copper) by direct-current plasma emission spectrometry or Zeeman graphite furnace AA or flame AA, depending on tissue concentration, and for selenium by atomization in a heated quartz tube and analysis by AA. Lead and cadmium in some tissues required pre-concentration by complexing (diethyldithiocarbamate) and extraction (butyl acetate). Methylmercury was determined by two methods. The first method was used for the analysis of hepatic tissue. The method of Uthe *et al.* (1972) was used in the preparative stages of the analyte. The tissue, homogenized with acidic, aqueous cupric sulfate and sodium bromide solution, was extracted with toluene, which was in turn extracted with sodium thiosulfate. The thiosulfate extract was back-extracted with toluene, dried with anhydrous sodium sulfate and analysed by capillary GC with ECD. Certified reference materials (DORM-1, DORM-2, NRC, Canada) were analysed along with the samples with good results. The second method was used for muscle tissue. In this method, methylmercury was determined by cold-vapour AA as for total mercury, after extraction of the aqueous tissue homogenate with a mixture of organic solvents (dichloromethane/hexane), and digestion of the organic extract with mineral acids (sulfuric/nitric).

Quality assurance

Certified reference materials (Bovine liver, NBS; DOLT, NRC; DORM, NCR) 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. For methylmercury analysis, only high-purity, distilled-in-glass organic solvents were used.

RESULTS

This is an overview report focusing primarily on summarizing the recent and past data on mercury in belugas and ringed seals from across the Canadian Arctic, produced under the Northern Contaminants Program. It provides a comprehensive basis for evaluating risk to consumers via consumption of marine mammal tissues in the eastern and western Arctic. This report also addresses the question of spatial and temporal trends of mercury in beluga and ringed seal tissues by adducing pertinent, earlier data from the literature on mercury in marine mammals.

Rationale for Pooling Data

In the eastern Arctic, as in the western Arctic, there was some variation in the mean mercury concentration among groups of belugas and ringed seals form the various sampling sites, reflected as a relatively large standard deviation of the overall means of the respective regions (Table 1 and 2). However, these differences among sites were, for the most part, not significant, except in the east; belugas from the St. Lawrence and Sanikiluaq had higher mercury concentrations in their tissues than belugas at other sampling sites in the eastern Arctic. In the western Arctic, there were no significant differences among sites sampled in 1993/1994. Data from the various sites in the eastern and western Arctic were combined into eastern and western Arctic means for belugas and ringed seals (Tables 1 and 2). The St. Lawrence data were not included in the eastern Arctic mean. Even with the inclusion of the higher Sanikiluaq levels in the eastern mean, the western mean for mercury concentration was significantly greater than that for the east. The lack of mercury differentiation among sites in the eastern and western regions of the Arctic, may indicate that individual stocks of animals did not maintain proprietary feeding areas, or that the level of mercury contamination in prey organisms was similar at all sites in the respective areas.

Hg Levels Relative to the Consumption Guideline

Belugas sampled recently in the eastern and western Arctic had regional mean mercury concentrations in muscle tissue of 0.94±0.44 and 1.34±0.67 µg/g wet wt. respectively (Table 1), exceeding the Canadian Federal Government Guideline Limit (0.5 µg/wet wt.) for mercury in consumable and exportable fish. Total mercury in liver tissue of belugas was significantly, positively correlated with the age of animals. By four years of age, the belugas (all locations and years combined) had mercury levels in muscle ≥0.5 µg/g wet wt. Similar, high concentrations of mercury in muscle have been found

in belugas caught off West Greenland. Hansen *et al.* (1990) report a median value for muscle tissue of 1.31 µg/g wet wt. for belugas ≥ 14 years of age. In muktuk of belugas, the mean mercury concentrations exceed only slightly the Federal Government Guideline, both in the western and eastern Arctic (Table 1). Although mercury concentrations in muscle, liver, and kidney of Arctic cetaceans have previously been reported (Hansen *et al.* 1990, Wagemann *et al.* 1990, and Wagemann *et al.* 1983), information on mercury in muktuk (a most valued food) was lacking until recently.

Ringed seals had mean concentrations in muscle of 0.39±0.17 and 0.41±0.29 µg/g wet wt. in the eastern and western Arctic, respectively—clearly below the Federal Guideline Limit (0.5 µg/g wet wt.) for mercury in fish. Total mercury in liver was positively correlated with selenium. In the west, mercury concentrations in the liver of ringed seals and belugas were relatively high, and correspondingly, selenium concentrations in the liver were also high. The rationale for this correlation has been discussed elsewhere (Wagemann and Stewart, 1994). Most of the mercury in the liver was inorganic mercury, possibly associated with selenium in the form of mercuric selenide (HgSe), presumed to be a biologically inert form of mercury (Martoja and Berry 1980), and seemingly non-toxic to the animals in question but not necessarily to consumers.

Spatial Trend

The mean mercury concentrations in liver of belugas caught recently in the western Arctic (1993 and 1994) (27.1± 24.7 µ/g wet wt) were significantly higher (by a factor of 3) than in liver of belugas sampled in the eastern Arctic (1992–1993) (8.40 ± 8.45 µg/g wet wt) (Table 2). The mean ages of the two groups were, however, not equal (19.3 and 11.8 years for the western and eastern Arctic respectively). Robust linear regression analysis of mercury on age of animals showed that the higher age of the western Arctic group could account for only 22% of the difference in mercury between the two groups, and 78% was attributable to the different environmental background concentrations of mercury in the western and eastern Arctic.

For ringed seals, as for belugas, the mean concentration of mercury in liver was also significantly higher in the western Arctic (32.6 ± 35.2 µg/g wet weight) than in the eastern Arctic (8.34 ± 7.03 µg/g wet weight), and the ages of the two groups were practically the same (7.4 and 6.1 years for the western and eastern Arctic, respectively) (Table 2). In this case, the difference in the mean mercury concentration between the western and eastern Arctic was almost entirely attributable to different environmental background concentrations in the eastern and western Arctic; only 6% was due to age differences.

Uptake of mercury appears to be related to the geology of the drainage basin that drains into the ocean where belugas and ringed seals feed. The eastern Arctic consists essentially of pre-Cambrian igneous and metamorphic rocks (gneiss, granite, greenstone), i.e. the Canadian Shield (Geological Survey of Canada, 1969). Whereas to the west of the Canadian Shield the rocks are younger, post-Cambrian, largely unmetamorphosed sedimentary (sandstone, dolomite, calcite, shale). The geological settings are such that higher background concentrations of mercury are present in rocks in the western Arctic (40–400 ng/g), than in the eastern Arctic (4–40 ng/g) (Handbook of Geochemistry, 1978). Mercury concentrations in near-shore surficial coastal marine bottom sediments in the western Arctic (Beaufort Sea) were also higher (68–243 ng/g dry wt.) than in the eastern Arctic (40–60 ng/g dry wt.) (sources cited in Wagemann *et al.* 1995). In surficial water, mercury was also higher in the Beaufort Sea (11–29 ng/L) than in the eastern Arctic (3.7 ng/L) (sources cited in Wagemann *et al.* 1995). These differences in the environmental background concentration of mercury in the eastern and western Arctic are seemingly reflected in the tissues of marine mammals in the two regions.

Eastern and western Arctic stocks are separated by heavy ice in the central Arctic. Indeed, observation on belugas suggests that east-west migration across the central Arctic is rare, even by individuals. Otherwise, any difference in the mercury level in belugas and ringed seals, between the eastern and western Arctic would have been obliterated by mixing through migration. The spatial trend of higher levels of mercury in belugas and ringed seals in the western relative to the eastern Arctic, and the intermediate level at Eureka would appear to be largely due to the different geological settings in these regions (Wagemann, *et al.* 1995). The mean mercury concentration in the liver of ringed seals at Eureka (26.5 ± 36.9 µg/g wet weight), was significantly different from that for the eastern Arctic but similar to that for the western Arctic. Although, geographically, Eureka is in the eastern Arctic, geologically this area is quite distinct from the Canadian Shield, and is more similar to the western Arctic, i.e. consisting of post-Cambrian, unmetamorphosed sedimentary rocks (Geological Survey of Canada 1969), perhaps accounting for the similar mercury levels in ringed seals in the two regions.

Temporal Trend

Belugas were sampled in the western Arctic approximately a decade apart (Table 1). The mean concentrations in tissues of the recently sampled animals was significantly higher (27.1 ± 24.7 µg/g wet weight, in the liver) compared with a decade ago (11.8 ± 12.1 µg/g wet weight in the liver). The recently sampled animals were, however, older. The age difference (19.3 and 13.9 years, respectively) can account for 31% of the increase as determined by robust linear regression of mercury on age. Most of the increase (69%) between 1984 and 1993-94 was due to a higher rate of mercury accumulation by the more recently sampled animals. The regression slope of the recently sampled animals was indeed significantly higher (approximately two-fold), than the regression slope for the animals sampled a decade ago (Table 3); the two slopes were significantly different at α=0.05. A similar increase was found for belugas in the eastern Arctic. The mean mercury concentration in the liver of belugas sampled recently (1993-94) in the eastern Arctic (7.59 ± 4.31 µg/g wet weight), was significantly higher than the mean of belugas sampled in 1984 (2.97 ± 2.20 µg/g wet wt.). The recently sampled animals were, however, older (12.69 ± 3.98 years) than those sampled in 1984 (7.76 ± 4.65 years). Based on robust regression analysis, 40% of the increase in the mercury concentration in the recently sampled group (1993-94) was due to the greater age of this group, and 60% was due to an increased rate of accumulation of mercury by this group. The regression coefficients for mercury in the liver on age of the two groups were significantly different; approximately twice as high for the recently sampled animals than for the animals sampled in 1984 (Table 3).

For ringed seals sampled in 1972, ages were available only for a limited number of animals (36). The mercury mean for this group (8.65 ± 7.48 µg/g wet wt.) was significantly lower than for the group sampled in 1987–1993 (32.6 ± 35.2 µg/g wet wt.). The mean ages of the two groups were not significantly different (8.57 ± 8.0 and 7.4 ± 5.1 years for 1972 and 1987–93, respectively), and the increase in the mercury concentration appeared to be due entirely to the recent increase in the rate of accumulation (approx. three-fold) (Table 4). Similar data for 1972 for ringed seals in the eastern Arctic were not available.

Both the western and eastern Arctic belugas have higher mercury levels in the liver than a decade ago, and a similar increase was found for ringed seals in the western Arctic. This indicates the existence of a positive temporal trend for mercury in belugas and ringed seals in the Canadian Arctic.

CONCLUSIONS AND UTILIZATION OF RESULTS

Belugas sampled recently in the eastern and western Arctic had regional mean mercury concentrations in muscle tissue of 0.94 ± 0.44 and 1.34± 0.67 µg/g wet wt., respectively, exceeding significantly the Canadian Government Guideline Limit (0.5 µg/g wet wt.) for mercury in consumable and exportable fish. In muktuk of belugas, the mean mercury concentrations in the western Arctic (0.79 ± 0.41 µg/g wet wt.) and the eastern Arctic (0.59 ± 0.22 µg/g wet wt.) were approximately at the level of the Guideline. Ringed seals had mean concentrations in muscle of 0.39 ± 0.17 and 0.41 ± 0.29 µg/g wet wt., in the eastern and western Arctic, respectively—clearly below the Guideline.

The mean mercury concentration in the liver of belugas in the western Arctic was higher, by a factor of three, than the mean for belugas in the eastern Arctic. The corresponding mercury mean for ringed seals in the western Arctic was higher by a factor of four than that for the eastern Arctic. A spatial trend for total mercury in Canadian Arctic marine mammals, decreasing from west to east is indicated. This difference between the western and eastern Arctic largely reflects the different environmental background concentrations of mercury in the western and eastern Arctic, dictated by the different geological settings in the eastern and western Arctic.

The levels of total mercury changed over time in both ringed seals and belugas. In belugas, the recent levels (1993–94) were significantly higher (approximately two times) than those of 10 to 14 years ago (1983–84), both in the western and eastern Arctic. Recent (1993–94) concentrations in ringed seals in the western Arctic were also significantly higher (approximately three times) than 15 to 20 years ago. A temporal trend of increasing mercury accumulation over time by these marine mammals of the Canadian Arctic is indicated. The temporal trend is superimposed on the spatial trend across the Arctic.

Expected project completion date: March 31, 1997.

Partners: Makivik Research Corp., Kuujuaq, Quebec; Inuit of NWT; Indian and Northern Affairs Canada; Fisheries and Oceans Canada; Health Canada; Native Hunters and Trappers Associations.

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Table 1. Comparison of mean mercury concentrations ± sd, (n), and concentration ranges (µg/g wet wt) in liver, kidney, muscle, and muktuk of western Arctic and eastern Arctic belugas collected between 1982 and 1994.

Year Sampled	Muktuk	Muscle	Liver	Kidney	Age (Years)
Western Arctic‡ 1981–1984	—†	1.07 ± 1.47 34 0.32 - 9.25	11.8 ± 12.1 42 1.23 - 48.6	2.83 ± 1.71 43 0.19 - 9.42	13.9 ± 5.5 43 2-42
Western Arctic 1993–1994	0.78 ± 0.41 65 0.19 - 1.93	1.34 ± 0.67 76 0.41 - 3.44	27.1 ± 24.7 77 0.31 - 116	4.91 ± 2.84 79 1.05 - 13.6	19.3 ± 6.6 71 7-35
Eastern Arctic 1984–1994	0.59 ± 0.22 45 0.32 - 1.37	0.94 ± 0.44 138 0.10 - 2.70	8.40 ± 8.25 139 0.011 - 41.0	3.10 ± 1.71 135 0.17 - 10.3	11.9 ± 6.0 143 <0.1 - 33
St. Lawrence‡ 1982–1987	—†	2.46 ± 1.46 9 0.89 - 5.54	33.6 ± 43.- 30 0.38 - 202	6.37 ± 9.16 30 0.32 - 49.2	18.1 ± 9.1 34 <-.1 - 30

‡ data from Wagemann *et al.* (1990), converted to wet wt basis using conversion factors given there.
† —muktuk tissue was not sampled at that time.

Table 2. Comparison of mean mercury concentrations ± sd, (n), and concentration ranges (µg/g wet wt) in liver, kidney, and muscle of ringed seals in the western Arctic, sampled between 1987 and 1993 and 1972 and 1973, the eastern Arctic, sampled between 1989 and 1993, and at Eureka in the central Arctic, sampled in 1994.

	Muscle	Liver	Kidney	Age (Years)
Western Arctic‡ 1972–1973	0.72 ± 0.33 80 —†	27.5 ± 30.1 80 —†	—†	12.8 (83)§ —†
Western Arctic 1987–1993	0.41 ± 0.29 133 0.049 - 2.02	32.6 ± 35.2 142 0.23 - 205	2.05 ± 1.34 144 0.25 - 7.15	7.4 ± 5.1 145 <0.1 - 38
Eastern Arctic 1989–1993	0.39 ± 0.17 61 0.054 - 1.03	8.34 ± 7.03 115 0.36 - 38.7	1.49 ± 0.58 35 0.64 - 2.88	6.1 ± 4.6 114 <0.1 - 22
Eureka 1994	0.66 ± 0.42 16 0.08 - 1.47	26.5 ± 36.9 18 0.42 - 143	3.17 ± 1.91 17 0.92 - 6.96	12.9 ± 12.2 18 <0.1 - 38

‡ data from Smith and Armstrong (1975).
† —concentrations ranges were not reported, and kidney was not sampled.
§ () the number of animals aged is not given, but the number of animals sampled was 83.

Table 3. Regression slopes (β, µg/[g•year]) of mercury in the liver on age of animals are compared (at α=0.05) for belugas in the western Arctic and belugas in the eastern Arctic, for belugas sampled 12 years apart in the western Arctic, and for belugas and ringed seals in the western Arctic. The large-number z-test was used to test for parallelism of two regression slopes. Numbers in parentheses (P) are the probabilities for the regression coefficients, and numbers in square brackets [n] are the sample sizes of the respective groups.

	Total Mercury in Belugas		
	Western Arctic		**Eastern Arctic**
	β, (P), [n]	**Outcome**	**β, (P), [n]**
Belugas 1981–1984	1.143 (P=0.0000) [30]	← ≠ →[§]	0.364 (P=0.0000) [56]
Outcome	↑ ≠ ↓		↑ ≠ ↓
Belugas 1993–1994	2.099 (P=0.0000) [67]	← ≠ →	0.623 (P=0.0000) [70]
Outcome	↑ =[‡] ↓		↑ = ↓
Ringed Seals 1987–1993	2.542 (P=0.0000) [127]	← ≠ →	0.750 (P=0.0000) [107]

§ '≠' means that there was a significant difference between the two regression slopes that the arrows are pointing to.

‡ '=' means that there was no significant difference between the two regression slopes that the arrows are pointing to.

Table 4. Regression slopes (β, μg/[g•year]) of mercury in the liver on age of animals are compared (at α=0.05) for ringed seals in the western Arctic and ringed seals in the eastern Arctic, for ringed seals sampled 20–25 years apart in the western Arctic, and for ringed seals at Eureka with ringed seals in the western and eastern Arctic. The large-number z-test was used to test for parallelism of two regression slopes. Numbers in parentheses (P) are the probabilities for the regression coefficients, and numbers in square brackets [n] are the sample sizes of the respective groups.

	Total Mercury in Ringed Seals		
	Western Arctic β, (P), [n]	**Outcome**	**Eastern Arctic** β, (P), [n]
Ringed Seals[1] 1972–1973	0.866 (P=0.0000) [36]	——	NA[2]
Outcome	↑[§] ≠ ↓		
Ringed Seals 1987–1993	2.542 (P=0.0000) [127]	← ≠ →	0.750 (P=0.0000) [107]
Outcome	↑ ≠ ↓		↑ ≠ ↓
Ringed Seals	1.174 (P=0.0000) [13] Eureka, 1994	← ≠ →	1.174 (P=0.0000) [13] Eureka 1994

[1] Ages of animals were determined by T.G. Smith, DFO, Nanaimo, BC, Canada.
[2] NA Data was not available from the eastern Arctic for these years.
[§] '≠'Indicates that there was a significant difference between the two regression slopes the arrows are pointing to.

ASSESSMENT OF ARCTIC ECOSYSTEM STRESS: EFFECTS ON POLAR BEARS

Project Leader: R.J. Norstrom, Canadian Wildlife Service, Environment Canada

Project Team: R. Letcher, Carleton University; M. Ramsay, S. Polischuk, University of Saskatchewan; S. Bandiera, University of British Columbia; A. Bergman, University of Stockholm; Inuit hunters; M. Mulvihill, 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 Fisheries and Oceans Canada (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

Because polar bears feed mainly on ringed seal, they are at the highest trophic level in the arctic marine ecosystem (Norstrom 1994), and accumulate high levels of chlordane and PCB compounds, although they do not biomagnify DDT compounds and toxaphenes (Norstrom and Muir 1994, Zhu *et al.* 1994a, Norstrom *et al.* 1988, Muir *et al.* 1988)). The polar bear is also a surrogate for exposure of the Inuit population that also consumes marine mammals (Dewailly *et al.* 1993, Zhu *et al.* 1995). This project focused on three areas of study:

Methylsulfone-PCBs and -DDE

Exposure of marine mammals and birds to persistent organochlorines (OCs) and their metabolites has been implicated as a causative factor in carcinogenicity, teratogenicity, sterility, growth retardation, immunologic dysfunction and reproductive abnormalities (Addison 1989, Sanderson *et al.* 1994). PCBs and DDT are the suspect compounds in a disease complex characterized by adrenocortical hyperplasia and other pathological abnormalities in grey and ringed seals in the Baltic Sea. There is evidence that some of the pathologies and reproductive failure in Baltic seals associated with PCB and DDT compounds are due to methylsulfone metabolites of these compounds, rather than the compounds themselves (Olsson *et al.* 1994). In a preliminary study, polar bear liver was found to contain µ/g levels of total methylsulfone-PCBs, and sub-µg/g levels of methylsulfone-DDE in lipid (Bergman *et al.* 1994). Research to identify and develop a method for determination of this class of metabolites in arctic biota was therefore undertaken.

Hepatic Cytochrome P450 Enzymes

The CYP450 enzymes, also known as mixed-function oxygenases (MFOs), are the major drug-metabolizing enzymes in liver and function in the primary oxidative biotransformation of a wide variety of lipophilic xenobiotic and endogenous compounds (Guengerich 1991). Induction of cytochrome P450 (CYP450) enzymes in liver is often used as a measure of exposure of an animal to specific classes of inducing chemicals. In many cases, degree of induction is correlated to toxic effects, which may or may not be directly related to the enzyme activity. Many OCs induce members of the CYP1A and CYP2B subfamilies in liver (Okey 1990). Induction of CYP450 can significantly affect the metabolism, bioaccumulation and toxicokinetics of xenobiotics and therefore alter the toxicological susceptibility of exposed animals. Furthermore, alteration of the MFO profile can lead to an imbalance of endobiotics, i.e. steroids, fatty acids, prostaglandins and other biological molecules (Okey 1990).

Induction of CYP1A has been recognized as a valid biomarker of exposure to xenobiotics with 2,3,7,8-TCDD-like toxicity, including certain non-ortho substituted ("co-planar") PCBs. Ethoxyresorufin-*O*-deethylase (EROD) and aryl hydrocarbon hydroxylase (AHH) bioassays are relatively specific markers of CYP1A1 isozyme activity and have been used as a measure of CYP1A induction in fish, birds and mammals (Stegeman *et al.* 1992, Boon *et al.* 1992). Hepatic polyclonal and monoclonal antibodies prepared against CYP450s of laboratory rodents and fish can be used to immunoquantitate specific CYP450 proteins (Goksøyr *et al.* 1992, Goksøyr *et al.* 1985, Watanabe *et al.* 1989, White *et al.* 1994). Immunoquantitation of CYP450 proteins can augment or replace enzyme assays as a more direct measure of CYP450 induction.

Immunoquantitation of specific CYP450s for the purpose of monitoring environmental contamination in Arctic species has been limited to CYP1A1 in beluga (*Delphinapterus leucas*) (White *et al.* 1994). There has been no research on MFO activity in ursids. Therefore we began by immunochemically characterizing the CYP450 enzyme system of the polar bear.

OC Kinetics in Female Polar Bears

Contaminant studies on free-ranging animals generally report on the concentration of compounds from a tissue sampled once. Usually, additional biological data from study organisms, such as body condition and percent body fat, are unknown. Organochlorine compounds, like PCBs, accumulate in lipid-rich tissues and the total body burden would presumably be affected by the historical nutritional status of the animal. Polar bears experience large changes in total-body adipose depots. Consequently, they may provide an ideal model to compare organochlorine concentrations and burdens with total body composition changes.

In western Hudson Bay, Canada, polar bears come ashore when the ice melts in summer and remain on land for four to five months until the Bay re-freezes. During their on-land stay they fast and live off their large adipose reserves that they have accumulated during the spring. Pregnant females do not return to the ice in autumn; they instead, find a den to carry out gestation, parturition, and lactation, which is done entirely while fasting. These females remain in their den for six to eight months, until late spring when they emerge with their cubs. The body mass of individual polar bears can more than triple over the period of hyperphagia and adipose tissue may constitute more than 50% of the total body mass (Ramsay *et al.* submitted). After extended fasting, adipose tissue depots may be reduced to less than 10% of body mass (Cattet 1990, Pond and Ramsay 1992). Mobilization of OC compounds from fat to target organs occurs in the female and fetus during gestation, and to the cubs via milk during the perinatal period.

ACTIVITIES IN 1994/95

A paper demonstrating the presence of a number of methylsulfone ($MeSO_2$-) metabolites of PCBs and two $MeSO_2$- metabolites of DDE was published (Bergman *et al.* 1994). A method for routine determination of $MeSO_2$-PCBs and DDE in biological tissues was developed and validated for whole fish, bird egg, adipose tissue and liver substrates. Using authentic standard supplied by Prof. Å. Bergman, University of Stockholm, virtually all of the $MeSO_2$-PCB congeners were identified. A paper has been submitted to *Analytical Chemistry* (Letcher *et al.* 1995a), and the method was presented at a special session on metabolites of halogenated compounds at the DIOXIN '94 conference in Kyoto Japan, November 1994 (Letcher *et al.* 1994a). A paper on the geographical distribution of $MeSO_2$-PCBs and -DDE in polar bear adipose tissue was also published (Letcher *et al.* 1995b).

Fresh liver samples were taken from a group of 12 polar bears near Resolute Bay in 1993 as part of an Inuit-sponsored study on half-life of the immobilizing drug used by polar bear researchers, Telazol, and preserved in liquid nitrogen. A further four samples were obtained in 1994. A paper reporting on the characterization of cytochrome P450 (CYP450) enzymes in livers of four

of these bears was published (Bandiera *et al.* 1995a). The testosterone metabolite profile was also determined. This part of the project was supported in part by a NSERC Strategic Grant to S. Bandiera at the University of British Columbia. Relationships between the hepatic levels of immunoreactive cytochrome P450 CYP1A and CYP2B isozymes in polar bear, alkoxyresorufin *O*-dealkylase activities and liver concentrations of OCs, including all those with TCDD-like activity and metabolites, were investigated. The influence of several CHCs on the induction of hepatic CYP450s in polar bear and the potential use of immunoassay quantitation as a bio-indicator of OC exposure was explored. A paper has been submitted on these studies (Letcher *et al.* 1995c), and the results were presented in part at a special session on the Arctic at the DIOXIN '94 conference in Kyoto Japan, November 1994 (Letcher *et al.* 1994b) and at the SETAC'94 conference in Denver, Colorado, November 1994 (Letcher *et al.* 1994c).

The two projects above form the major portion of the Ph.D. research of R. Letcher, Department of Chemistry, Carleton University. This research was supported in part by a NSERC Research grant to R. Norstrom, Carleton University.

The relationships between PCB concentrations in adipose tissue biopsies, body burdens, and percent body fat changes in 25 fasting females of differing reproductive classes and 8 cubs near Churchill Manitoba were determined, and rate of transfer of contaminants to cubs was estimated. A paper on the preliminary results was published (Polischuk *et al.* 1995), and the results were presented at a special session on the Arctic at the DIOXIN '94 conference in Kyoto Japan, November 1994 (Polischuk *et al.* 1994). This project forms part of the Ph.D. research of S. Polischuk, Department of Biology, University of Saskatchewan.

RESULTS

Methylsulfone-PCBs and -DDE

A simple column chromatography method was developed for separation and cleanup in the determination of chlorinated hydrocarbon contaminants and their methyl sulphone ($MeSO_2$-) metabolites in biological tissues (Letcher *et al.* 1995a, 1994a). A schematic diagram of the method is shown in Figure 1. Nineteen tetra- to heptachloro-, 3- and 4-$MeSO_2$-PCB metabolites of 10 PCBs, all chlorine substituted at the 2,5,4'- or 2,5,6,4'-positions, were positively identified in polar bear tissues by comparison to authentic standards (Table 1). Eight minor trichloro to hexachloro congeners, together constituting less than 5% of total $MeSO_2$-PCBs, remain to be identified. The method was validated using fifteen $MeSO_2$-PCBs, 3-$MeSO_2$-DDE, eleven polychlorinated biphenyls (PCBs), and tris(4-chlorophenyl)methanol spiked to polar bear liver and adipose tissue homogenates and contaminant-free lipid extracts. Recoveries of all analytes relative to the internal standard were approximately 100%, independent of analyte, substrate type and lipid weights up to ca 0.7 grams. There were no significant residual biogenic and xenobiotic interferences in the methylsulfone fraction of any substrate. Sensitivity and linearity of molar response of $MeSO_2$-PCBs and -DDE were tested for ECD and for electron-capture negative ion mass spectrometry (ECNI-MS), monitoring the total ion current (TIC) and the molecular ion (SIM) (Letcher *et al.* 1995a). Instrument detection limits were generally sub-picogram for all three techniques (Table 2), and were lower by an order of magnitude relative to those previously determined for SIM and TIC, which ranged from 2-6 pg and 30-88 pg for SIM and TIC, respectively. Method detection limits based on analysis of spiked substrates were in the 0.25 to 18 pg range for all three techniques, and increased in the order SIM<ECD≤TIC (Table 2).

ECNI mass spectral fragmentation patterns of 28 biologically relevant $MeSO_2$-PCB congeners were related to several features of congener structure. Indications of increasing tetra- to hepta-chlorination and 2,5,6-chlorine substitution versus 2,5-chlorine substitution on the $MeSO_2$- containing phenyl ring could be distinguished, as well as whether the $MeSO_2$- group was at the 3- or 4- position (Letcher and Norstrom, in prep.).

Hepatic Cytochrome P450 Enzymes

In the Resolute Bay male bears, PCBs classed as CYP1A and mixed CYP1A/CYP2B inducers accounted for approximately 25% of the total ΣPCBs (Letcher *et al.* 1995c, 1994b). CYP1A protein content correlated strongly with levels of Ah-receptor active PCBs, PCDDs (0.032 ± 0.018 ng/g lipid), and PCDFs (0.011 ± 0.007 ng/g lipid) and their corresponding toxic equivalents (TEQ, 0.377 ± 0.182 ng/g lipid, Fig. 2A). Mono-*ortho* CB-156, CB-157 and CB-105 were the predominant contributors to TEQ (Figure 2B). Backwards, stepwise, multiple regression was done between CYP2B protein content and liver residue levels of Σ*ortho*-PCBs, ΣMeSO$_2$-PCBs, ΣChlordane, ΣDDT, ΣHCH, dieldrin and Zolazepam (a component of the drug used to immobilize the bears at various times prior to death). *Ortho*-chlorine substituted PCBs (18.0 ± 5.1 μg/g lipid) and chlordanes (30.8 ± 25.4 μg/g lipid) were the major residues in liver, and the only significant contributors to CYP2B induction (Fig. 2C), although it is possible that Zolazepam may

have been involved as well. CYP1A and CYP2B content were therefore good indicators of CHC exposure in polar bear liver.

Ethoxyresorufin- (EROD), pentoxyresorufin- (PROD), and benzyloxyresorufin (BROD) *O*- dealkylase activities increased with CYP1A protein content, and did not correlate with CYP2B content, suggesting that all three activities were primarily CYP1A-mediated (Letcher *et al.* 1995c). About 90% of the EROD activity was inhibited by 10 mg anti-rat CYP1A1 IgG/nmole P450 (Figure 3B), proving that the activity was CYP1A-mediated. EROD activities levelled off at CYP1A protein levels of about 5 pmol/mg protein (Figure 3A). Therefore, immunoquantitated CYP1A and CYP2B isozymes are a more reliable measure of exposure to OC inducers than alkoxyresorufin activities in polar bear.

OC Kinetics in Female Polar Bears

In a preliminary study, adipose tissue and milk samples were analysed for two family groups, a female with a cub-of-the-year (COY) a female with a yearling (YRLG), and three solitary/pregnant females who gave birth in the winter and were with cubs the following spring (Polischuk *et al.* 1995). Females with cubs were sampled in the fall, approximately 30 days apart, and solitary/pregnant females were sampled once in the fall and once in March, when they were with three-month old cubs. Pregnant females enter dens in fall and emerge from these dens in spring with their cubs. Lactation provides a mechanism whereby large quantities of organochlorines can be transferred from one generation to the next. The mean amount of milk ingested per day is significantly greater for cub-of-the-year (469 g/day) than for yearling polar bears (131 g/day) (Arnould 1990). Estimated average daily consumption of five OC classes is shown in Figure 4 for the two cubs at the two sampling periods. Greater consumption of organochlorines by COYs is consistent with the higher concentration of OCs in the adipose tissue of the COY compared with the yearling.

In another study, the effect of fasting on concentrations and body burdens of OCs in females and cubs was studied (Polischuk 1994). The body composition of each animal was determined by using a two-step model that involves measurement of total body water *in vivo* by the dilution of deuterated (^2H) water (Reilly and Fedak 1990, Farley and Robbins, in review). Female polar bears emerging from dens in March showed a significant increase in mean PCB concentrations over pregnant females from the previous August-September (Table 3). The increase was proportional to the decline in mean percent body fat (Table 3), consequently the PCB body burdens did not change significantly, although the mean PCB level in March was 14% lower than six months previously. Among this group were two individuals sampled at both time periods. These two lost 28% and 7% of their body burdens, which may not be significantly different from the group mean of 14%, given the lack of information on precision of the determination in individuals. The data therefore suggest that there is minimal excretion of OCs by pregnant females during the 6 month fast prior to breaking out of the dens. The main mechanism of excretion of OCs is transplacental transfer and lactation, but this is minimal by March, when the cubs are still small.

DISCUSSION/CONCLUSIONS

Methylsulfone-PCBs and -DDE

The column chromatography-based extraction and cleanup method (Figure 1) is simple and non-destructive, and gives good precision and accuracy for determination of OCs in a wide range of animal tissue substrates. Although the method was not validated for all OC compound classes normally determined, the range in polarity (elution order from Florisil and alumina columns) was spanned by PCBs and TCPMeOH, and the method was extended to the even more polar aryl methyl sulphones. This method is therefore suitable for multi-residue, routine determination of OCs, including aryl methyl sulphones, in animal tissues. The method has significant advantages over those previously used for aryl methyl sulphones, which included laborious liquid-liquid partitioning steps, or saponification. The aryl methyl sulphones were cleanly separated from other OCs by chromatography on 1.2% water deactivated Florisil®. The same column has been used for OC separation and lipid removal from lipid extracts of 1.0 gram polar bear fat samples, although more fractions were taken (Norstrom *et al.* 1988). The aryl methyl sulphones require greater polarity solvent for quantitative elution. In the present study, a 7:93 methanol/CH_2Cl_2 solvent mixture eluted $MeSO_2$-PCBs and -DDE while retaining some residual coloured biogenic co-extractants.

SIM is the best detection technique if extremely high sensitivity is required. In spite of superior sensitivity, there was more inherent variability in the response factors for SIM at a given concentration (ca. 5% to 25% CV) than for ECD or TIC (1% to 2% CV), therefore ECD or TIC are recommended for quantitative analysis. In samples analysed to date, the separation of aryl methyl sulphones from potential interferences was so effective that ECD was chosen because of significantly lower cost.

The method is potentially expandable to isolate HO-PCBs. Phenolic PCBs partition into a basic 1M KOH ethanolic solution and are likely retained on the present alkaline silica gel column. Residual acidic biogenic material remaining in the OC fraction after GPC is also retained. Further research is currently underway to explore the possibility of eluting phenolic compounds from the KOH/silica gel column, followed by derivatization to methoxy-PCBs for GC analysis.

There were two unidentified $MeSO_2$-Cl_3CBs in polar bear tissues. These are likely 3- and 4-$MeSO_2$- 2,4',5-Cl_3CB. Based on the common structural elements for the occurrence of $MeSO_2$-PCB and - DDE metabolites identified so far in biota (Table 1), no other trichloro-PCB congener fits the pattern. Both 3-/ 4-$MeSO_2$-PCB pairs are usually present, although the relative amounts can be quite variable depending on the tissue and species. $MeSO_2$-PCBs found to persist in biota have no chlorines at either of the 3,4 positions and a minimum of 2,4',5 chlorine substitution. It is probable that the 2,5 chlorines stabilize the 3,4-epoxide formed in the primary metabolism step, preventing formation of monools and diols, the usual path for PCB metabolism. The epoxide is therefore subject to attack by cytosolic glutathione-S-transferase, the initial step in the mercapturic acid pathway eventually leading to methylsulfone formation. Chlorine is required at the 4' position to block epoxidation at the 3',4' position, which would lead to formation of readily conjugated and excreted monools and diols. Applying these rules to the commonly occurring PCBs in commercial mixtures, it is probable that the concentrations of the nineteen $MeSO_2$-PCBs congeners identified in polar bears represent >90% of the total $MeSO_2$-PCBs likely to be formed in biota.

Hepatic Cytochrome P450 Enzymes

Total CYP450 content has frequently been used as a crude measure of xenobiotic oxidation capacity of an animal. The total CYP450 content in polar bear liver was similar to that in laboratory rats (Bandiera *et al.* 1995) whereas marine mammals studied so far, have significantly lower levels (Goksøyr *et al.* 1992, Watanabe *et al.* 1989, Goksøyr *et al.* 1985), perhaps due to lower residue levels of OCs capable of CYP450 induction. For example, a total CYP450 content of approximately 0.300 nmol P450/mg and a concentration of approximately 500 ng/g lipid of Ah-receptor active PCBs has been reported for arctic beluga liver (White *et al.* 1994). In contrast, polar bear hepatic microsomes had a CYP450 content of 1 to 2 nmol/mg and a mean PCB concentration of approximately 4800 ng/g lipid for PCB congeners classed as CYP1A and mixed CYP1A/CYP2B inducers (Letcher *et al.* 1995a).

The mean hepatic EROD activity of 1165±454 pmol/min/mg protein in the polar bears was several orders of magnitude higher than observed in adult male hooded seals 30±7 pmol/min/mg, (Goksøyr *et al.* 1992), and approximately the same to the two-fold higher levels in adult whales. EROD activities in male arctic beluga (White *et al.* 1994), killer whale (Watanabe *et al.* 1989) and minke whale (Goksøyr *et al.* 1985) were 1255±651, 612±373 and 740±170 pmol/min/mg microsomal protein, respectively. These EROD activities generally correlate with the level of PCB exposure (Tanabe *et al.* 1994, Haraguchi *et al.* 1992). Assuming that the inter-lab EROD activities are comparable, CYP1A-mediated activity was elevated in polar bear. The correlation between EROD activity and CYP1A protein content up to the 5 pmol/mg level (Figure 3A) suggested CYP1A was the primary catalyst for EROD activities in polar bear. Furthermore, anti-rat CYP1A1 and CYP2B1 immunoinhibition results indicated that EROD activity (Figure 3B) was catalysed predominantly by CYP1A in polar bear.

There was a strong positive correlation between hepatic concentrations of PCBs known to be CYP1A-type inducers (77, 126, 169) or mixed CYP1A/2B-type inducers (37, 105, 118, 138, 170, 156, 157, 189) and CYP1A protein content (r^2=0.875, $p<0.0001$). White *et al.* (1994) recently concluded that high correlation between CYP1A content and Ah-receptor active PCB levels (37, 81, 77, 126, 169, 105, 114, 118 and 156) in arctic beluga liver indicated CYP1A induction by these compounds or compounds that co-vary with PCBs. Because of the high degree of correlation among potential Ah-receptor active and inactive aromatic CHCs in polar bear, cause-effect relationships cannot be established with certainty using these comparisons. However, the non-aromatic Σchlordane levels were two- to four-fold higher than the known Ah-receptor active PCBs but exhibited no correlation to CYP1A content (r^2=0.024, $p<0.6$) suggesting that the structure- activity rules for CYP1A induction in polar bears are similar to those in other mammals.

The average TEQ of 0.4 ng/g in polar bear was consistent with values found for terrestrial mammals, which are generally much lower than marine mammals (Tanabe *et al.* 1994). CYP1A isozyme content and TEQs were strongly correlated (r^2=0.857, $p<0.0004$) in polar bear liver. These results suggested CYP1A isozyme content was a good measure of exposure to xenobiotic compounds that are Ah-receptor active inducers.

The TEQ contribution order was mono-*ortho*-PCBs >>> non-*ortho*-PCBs > PCDDs > PCDFs in polar bear regardless of the TEF used for CB-118 (Figure 2B).

Using the TEF values of Safe (1994), the dominant TEQ contributions in polar bear were mono-*ortho*-CB-156 (32±6.9%), and CB-157 (29±8.4%). Mono-*ortho*-CB-118 and CB-105 generally dominate the TEQ in marine mammals and terrestrial mammals including humans (Tanabe *et al.* 1994). Furthermore, the TEQ contribution of non-*ortho*-CB-126 is usually more important. CB-126 contributed 20-50% to the TEQ in narwhal, ringed seal and beluga (Ford *et al.* 1993), but only 6.9±3.8% in polar bear. The TEQ contribution of CB-156 in marine and terrestrial mammals generally accounts for less than 20% (Tanabe *et al.* 1994). It therefore appears that polar bears have a greater CYP1A-type capacity to metabolize non-*ortho*- and mono-*ortho*-PCBs with 3,4-chlorine substitution on one phenyl ring than most mammals. A greater rate of CYP1A-type metabolism of CB-105, CB-118 and CB-126 was also indicated by a 10-fold lower ratio to CB-153 in polar bear liver relative to their diet of ringed seal (Letcher *et al.* 1995c). Metabolism of mono-*ortho*-PCBs in seals appears to occur only with high PCB exposure, presumably via CYP1A induction. For example, CB-118 was not detectable in Baltic adult ringed seal with high PCB levels (Haraguchi *et al.* 1992), whereas CB-118 levels were biomagnified from cod without apparent metabolism by arctic ringed seal with low PCB levels (Muir *et al.* 1988).

The structural diversity of CYP2B-type inducers known to activate expression of the CYP2B subfamily is much greater than the rigid, planar, TCDD-like structural requirement for CYP1A induction (Okey 1990). Several OCs known to be CYP2B-type inducers in laboratory animals (Waxman and Azaroff 1992) such as *ortho*-chlorine substituted PCBs and chlordanes, were significant residues in polar bear liver. However, PCBs classed as pure CYP2B-type inducers and CYP2B content were not correlated (r^2=0.266, $p<0.08$) suggesting that PCBs were not the most important CYP2B isozyme inducers in polar bear. Correlation of $\Sigma MeSO_2$-PCBs and CYP2B content was slightly higher (r^2=0.326, $p<0.05$), and there was no better correlation for Σ3-$MeSO_2$-CB and Σ4-$MeSO_2$-PCB. The 3-$MeSO_2$-PCB congeners have been shown to induce hepatic microsomal CYP2B in rats, whereas 4-$MeSO_2$-PCBs had little effect (Kato *et al.* 1994), but they do not appear to be important in polar bears.

ΣChlordane, ΣDDT and Zolazepam (the tranquilizer component of Telazol) correlated with CYP2B content (r^2=0.755, $p<0.0002$, r^2=0.506, $p< 0.02$, r^2=0.810, $p<0.00004$, respectively). There were significant non-zero intercepts in all of the above regressions, suggesting that there are multiple inducers of CYP2B activity in the polar bear. Although the stepwise, backward, multiple linear regression indicated that only ΣPCB and ΣChlordane contributed significantly to the CYP2B activity, there was still a non-zero intercept of 9.4 pmol/mg (Figure 2C). Zolazepam had the highest correlation of the individual chemicals, but it was probably dropped from the regression because of colinearity with ΣChlordane. Preliminary research on the effect of Telazol on the rat hepatic CYP450 system demonstrated an increase in CYP2B-type activities with increasing doses of Telazol (Bandiera *et al.* 1995, unpublished results). Contributions of Zolazepam to CYP2B induction can therefore not be ruled out, but there is a strong indication that the major residues, *ortho*-PCBs and Chlordane compounds (mainly the metabolite oxychlordane) are the principal inducers of CYP2B in the polar bear.

Immunological quantitation of CYP1A and CYP2B isozyme protein is generally not affected by physiological factors that can affect catalytic activity (Goksøyr 1991) and therefore would be more reliable than MFO activity for bio-monitoring of OC exposure in polar bear. Other assays such as testosterone hydroxylase may be more appropriate for measuring CYP2B isozyme activity. We recommend that the immunoassay of CYP1A and CYP2B isozymes be done in conjunction with catalytic assays to provide an additional measure of quality assurance against sample degradation or possible enzyme activity inhibition by high levels of environmental contaminants. Quantitation of western blots of CYP1A and CYP2B could supplant catalytic assays in standard environment contaminant monitoring.

OC Kinetics in Female Polar Bears

Because bear cubs are born in a notably altricial state and experience a lengthy period of lactation (Ramsay and Dunbrack 1986), the transfer of organochlorine contaminants in milk from mother to young occurs at a crucial point in the growth and development of polar bear cubs. Younger cubs are more susceptible to organochlorine loads than older cubs because they consume greater amounts of milk than do yearlings. The estimated rate of transfer of ΣChlordane and ΣPCB from females to cubs in the autumn of their first year was in the range 0.4 to 1.1 mg/d (Figure 4), which is approximately 0.5% of the female's body burden/d (Table 3). The rate of transfer to yearling cubs was about 10-fold lower, 0.06 to 0.13 mg/d (Figure 4).

The rate of OC excretion by pregnant females during the six-month denning period appears to be in the same order, approximately 0.15 mg/d, based on the estimated 32 mg PCB difference in body burdens before and after denning (Table 3). Most of the 32 mg PCB was probably transferred to the fetuses and cubs. This suggests that

there is little or no excretion of OCs during fasting. Because there is no significant effect of age on OC levels in fat of either adult male or female polar bears, including non-lactating females (Norstrom *et al.* 1995), there must be some mechanism of excretion to balance intake from the diet which is fast enough to allow approximate steady-state to occur. It is probable that excretion of unmetabolized OCs occurs mainly during periods of active feeding by partitioning into gut lumen contents. This has interesting implications to the overall dynamics. Pregnant females from the western Hudson Bay population studied here represent the extreme in fasting (up to eight months a year). In some areas of the high Arctic, males fast only when forced by weather or lack of suitable hunting conditions. More detailed temporal information is required to understand OC dynamics in polar bears.

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Table 1. $MeSO_2$-PCB and -DDE congeners identified in polar bear tissues (from Letcher *et al.* 1995a).

Substituted biphenyl/DDE Formula	Compound Abbreviation§
3-CH_3SO_2-2,2',4',5-Cl_4	3-$MeSO_2$-CB49
4-CH_3SO_2-2,2',4',5-Cl_4	4-$MeSO_2$-CB49
3-CH_3SO_2-2,4',5,6-Cl_4	4-$MeSO_2$-CB64
4-CH_3SO_2-2,4',5,6-Cl_4	4-$MeSO_2$-CB64
3-CH_3SO_2-2,3',4',5-Cl_4	3-$MeSO_2$-CB70
4-CH_3SO_2-2,3',4',5-Cl_4	4-$MeSO_2$-CB70
3-CH_3SO_2-2,2',3',4',5-Cl_5	3-$MeSO_2$-CB87
4-CH_3SO_2-2,2',3',4',5-Cl_5	4-$MeSO_2$-CB87
3-CH_3SO_2-2,2',4',5,5'-Cl_5	3-$MeSO_2$-CB101
4-CH_3SO_2-2,2',4',5,5'-Cl_5	4-$MeSO_2$-CB101
3-CH_3SO_2-2,2',3',4',5,6-Cl_6	3-$MeSO_2$-CB132
4-CH_3SO_2-2,2',3',4',5,6-Cl_6	4-$MeSO_2$-CB132
3-CH_3SO_2-2,2',3',4',5,5'-Cl_6	3-$MeSO_2$-CB141
4-CH_3SO_2-2,2',3',4',5,5'-Cl_6	4-$MeSO_2$-CB141
3-CH_3SO_2-2,2',4',5,5',6-Cl_6	3-$MeSO_2$-CB149
4-CH_3SO_2-2,2',4',5,5',6-Cl_6	4-$MeSO_2$-CB149
4-CH_3SO_2-2,2',3',5,5',6'-Cl_6	4-$MeSO_2$-CB151
3-CH_3SO_2-2,2',3',4',5,5',6-Cl_7	3-$MeSO_2$-CB174
4-CH_3SO_2-2,2',3',4',5,5',6-Cl_7	4-$MeSO_2$-CB174
2-CH_3SO_2-DDE	2-$MeSO_2$-DDE
3-CH_3SO_2-DDE	3-$MeSO_2$-DDE

§ Based on IUPAC numbering of precursor PCB congener. CB stands for Chloro Biphenyl.

Table 2. Ranges in Mean Instrumental (IDL) and Method (MDL) Detection Limits and Mean Practical Quantitation (PQL) Limits for determination of $MeSO_2$-PCBs and 3-$MeSO_2$-DDE using three different gas chromatography (GC) detection methods (from Letcher *et al.* 1995a).

	GC/ECD	GC/ECNI-MS(SIM)	GC/ECNI-MS(TIC)
IDL ± SD (pg)‡			
low	0.16 ± 0.03	0.04 ± 0.01	0.60± 0.02
high	0.31 ± 0.05	0.14 ± 0.02	1.82±0.10
MDL ± SV (pg)*			
low	4.21 ± 1.66	0.25 ± 0.11	6.80 ± 2.79
high	7.51 ± 2.62	1.01 ± 0.40	17.54 ± 2.62
Mean PQL (pg)§	24.2 ± 4.6	2.1 ± 0.9	44.4 ± 17.1

ECD = electron capture detector; ECNI-MS = electron capture negative ion mass spectrometry, SIM = single ion monitoring, TIC = total ion current monitoring.

‡ n=3 replicate analysis.

* SV = significance of variation of MDL for analysis at n mass levels, i.e. n=7 for GC/ECD and GC/ECNI-MS(SIM) and n=6 for GC/ECNI-MS(TIC).

§ Mean PQL = the mean of ten times the SV for each congener, ±SD.

Table 3. Mean concentration of PCBs (µg/g lipid weight), PCB body burden (mg), and percent body fat in female polar bears and their cubs before and after a period of fasting. Values in parentheses designate standard deviation.

Reproductive Class	Date Sampled	n	PCB conc. (ug/g lipid)	PCB body burden (mg)	Body fat (%)
Pregnant females with spring cubs	Aug/Sep'93	7	1.9 (0.8)	236 (89)	41.9 (2.4)
	Mar'94	5	*4.4 (1.2)	204 (71)	*27.0 (3.9)
Females with cubs	Aug/Sep'93	6	4.4 (3.8)	275 (201)	30.4 (3.8)
	Oct/Nov'94	7	6.1 (6.2)	216 (117)	24.7 (5.5)
Cubs	Aug/Sep'93	3	4.0 (1.8)	177 (109)	29.8 (2.8)
	Oct/Nov'94	5	7.1 (4.9)	175 (122)	25.8 (1.9)

* Significantly different, ($p<0.05$), from previous date sampled

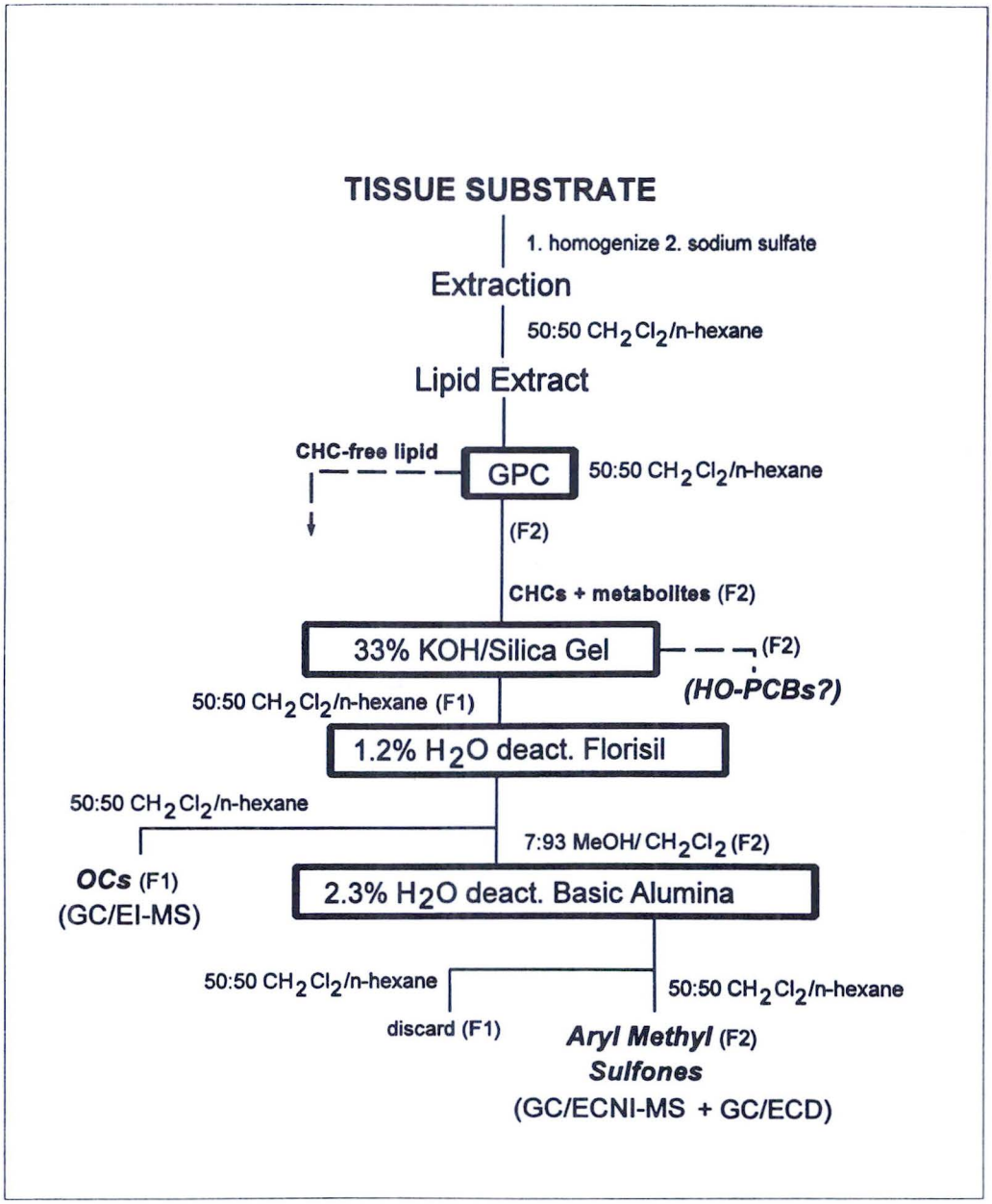

Figure 1. Schematic diagram of the analytical method for determination of OCs and methylsulfone metabolites in polar bear tissues (from Letcher *et al.* 1995a and Letcher *et al.* 1994a)

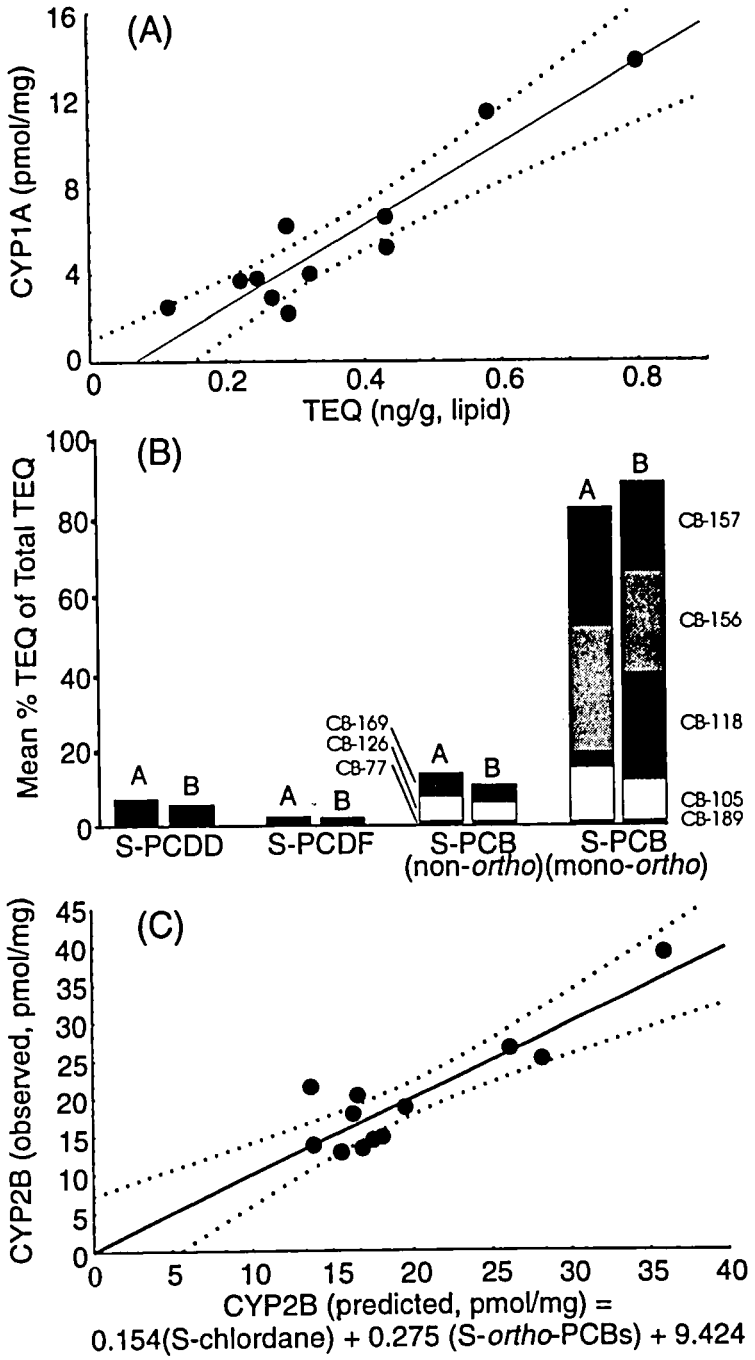

Figure 2.

(A) Correlation between CYP1A1+CYP1A2 content in male polar bear hepatic microsomes versus 2,3,7,8-TCDD toxic equivalents (TEQs) using the TEF indices given by Safe (1994,1990).

(B) Mean contributions of non-ortho- and mono-ortho-PCBs, PCDDs and PCDFs to the total TEQ composition of 13 polar bear livers using a TEF for CB-118 of 0.0001, left bars (Safe 1994), or a TEF of 0.0001, right bars (Safe 1990).

(C) Correlation between observed CYP2B content in male bear hepatic microsomes versus levels of CP2B predicted from ortho-substituted PCBs and total chlordane levels (mainly oxychlordane) by backwards, stepwise, multiple linear regression. The regression was highly significant, $r^2=0.784$, $p<0.0005$. Data are from Letcher *et al.* (1995c).

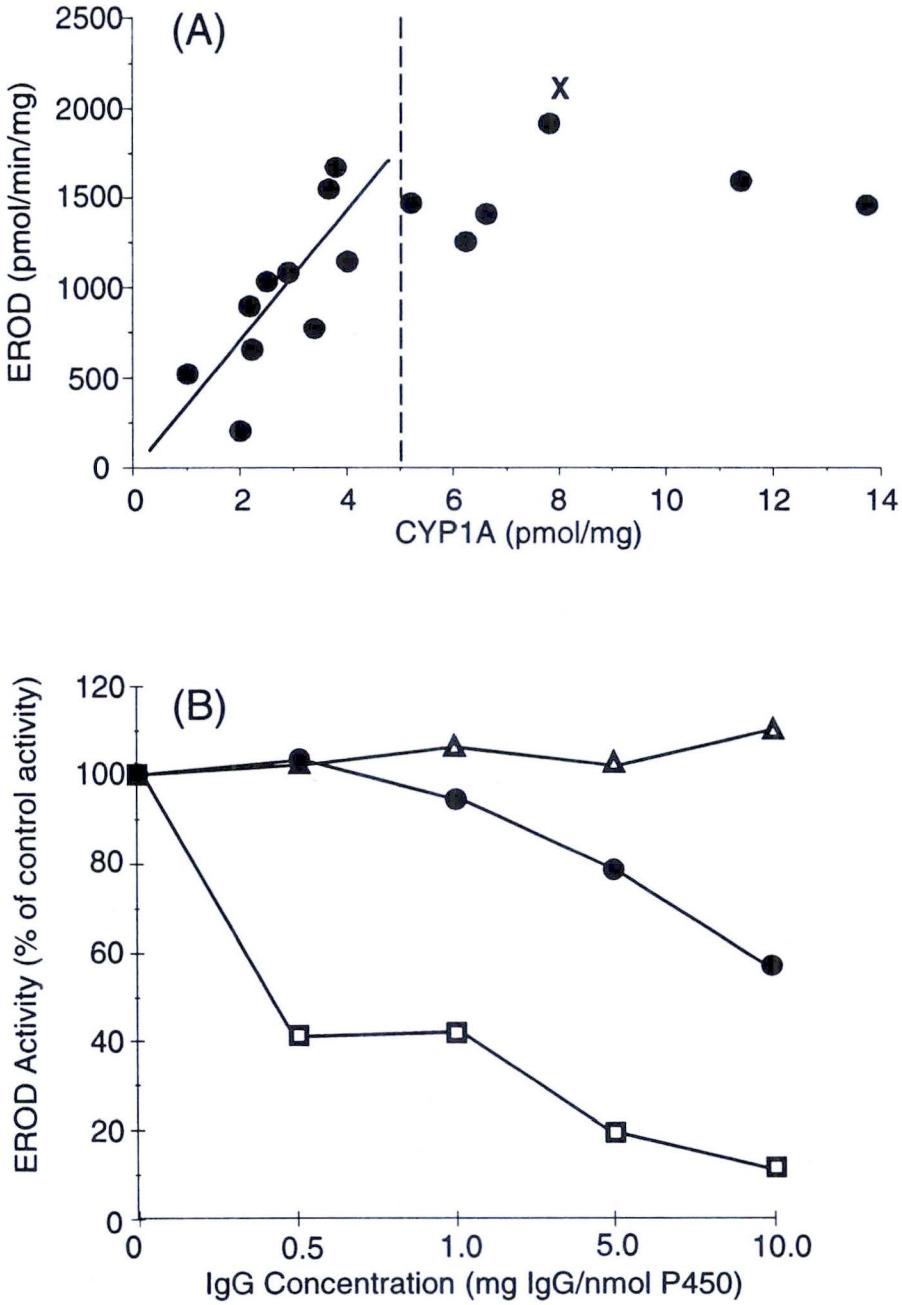

Figure 3.

(A) Correlation between ethoxyresorufin-O-deethylase (EROD) activity in polar bear hepatic microsomes versus CYP1A1+CYP1A2 protein content. The dashed line gives the approximate onset of maximal EROD activity.

(B) Antibody inhibition of EROD activity in hepatic microsomes of a single bear by control IgG (triangles, anti-rat CYP1A1 IgG (squares) and anti-rat CYP2B1 IgG (circles). Data are from Letcher *et al.* (1995c).

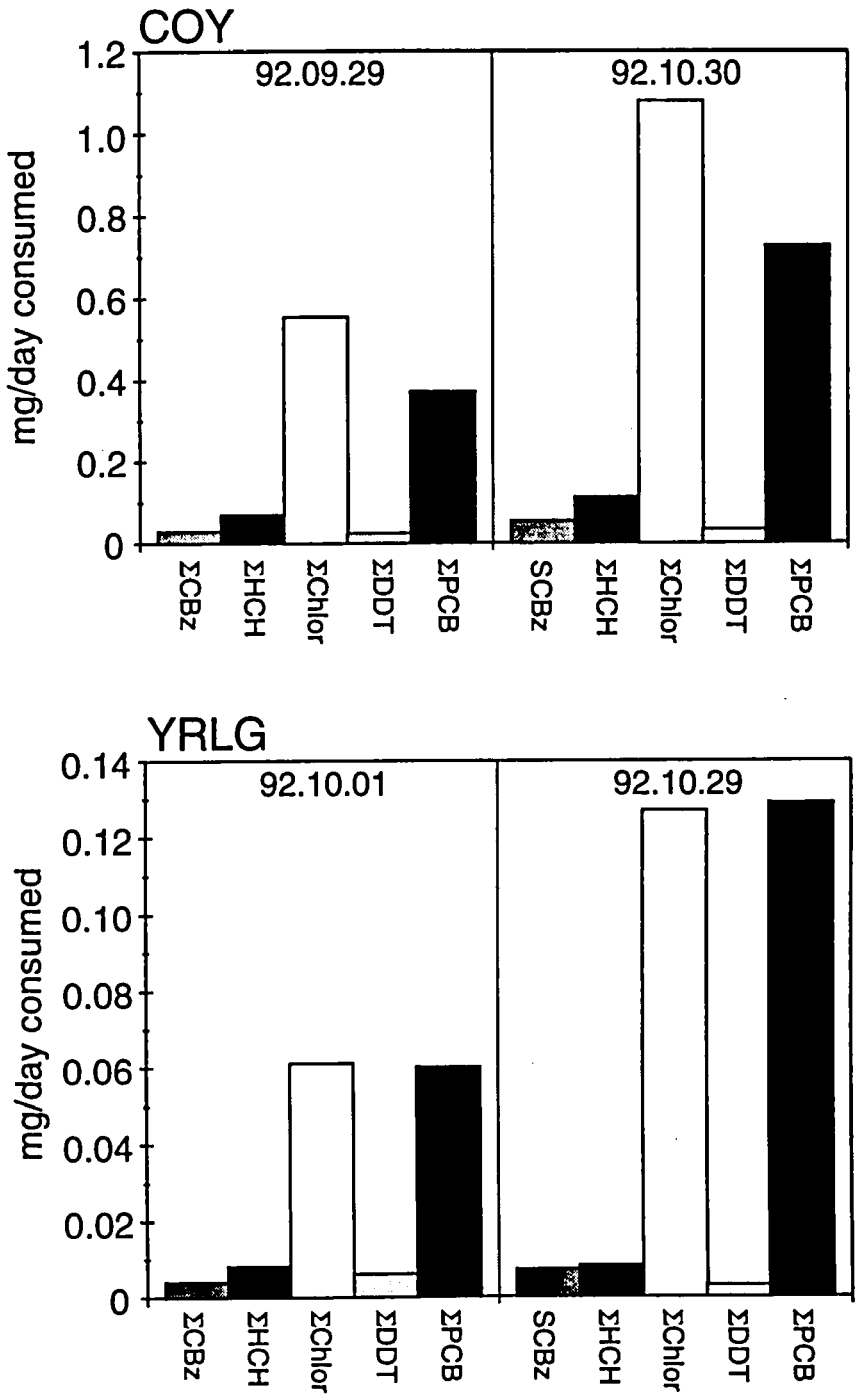

Figure 4. Estimated daily intake of OCs by two individual bear cubs, a cub-of-the-year (COY) and a yearling cub (YRLG) at two different times in the Autumn of 1992 approximately one month apart. Intake is based on estimated milk consumption for cubs of that size (Arnould 1990), and OC concentration in milk of the cub's mothers at the time of sampling.

CONTAMINANT TRENDS IN POLAR BEARS

Project Leader: R.J. Norstrom, Canadian Wildlife Service, Environment Canada

Project Team: M. Simon, M. Mulvihill, Environment Canada; R. Letcher, J. Zhu, Carleton U.; I. Stirling, Canadian Wildlife Service (CWS) and University of Alberta; M. Ramsay, University of Saskatchewan

OBJECTIVES

Short-term

1. To extend data base on circumpolar geographic distribution of persistent organochlorine contaminants in the polar bear to areas not included in the previous survey in Canada, Russia and across the pole;
2. To publish the circumpolar survey;
3. To apply multivariate statistics to examine geographic differences in polar bear bioaccumulation patterns;
4. To determine the influence of season and sex/condition of the bear on interpretation of trends;
5. To extend retrospective analysis of contaminant levels in archived polar bear samples to determine temporal trends, from 1982 to present, in more areas of the Canadian Arctic;
6. To determine structures of, and quantify, unidentified chlordane and toxaphene contaminants in arctic biota, including humans.

Long-term

1. 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

There are mg/kg concentrations of a number of OCs in the blubber of Arctic cetaceans and polar bear (Norstrom and Muir 1994), and levels of PCBs are about two to ten times higher in milk of Inuit women from northern Québec than in the southern population (Dewailly *et al.* 1994). Knowledge of the circumpolar distribution and temporal trends in concentrations of organochlorines is therefore important in determining the sources and potential significance of these contaminants to arctic marine and maritime wildlife and the humans that consume them.

The polar bear is an excellent biomonitor for the Arctic marine environment. Polar bears are the principal mammalian predators at the top of the arctic marine food chain, they are distributed widely throughout the Arctic and Subarctic circumpolar regions (Norstrom and Muir 1995; Norstrom *et al.* 1988), and they are distributed into relatively discrete populations (Taylor and Lee 1995, Bethke *et al.* 1995). The Polar bear is at trophic level 5 compared to particulate organic matter in seawater (Hobson and Welch 1992). Biomagnification factors of OCs are in the order of three to seven per trophic level on a lipid weight basis (Norstrom 1994), therefore biomagnification factors from particulate matter to polar bear lipid can be as high as $7^5 \cong 17{,}000$. This is illustrated for CB-153 (2,4,5,2',4',5'- hexachlorobiphenyl) in Figure 1.

A circumpolar survey of OC contamination in polar bear fat was initiated by the Canadian Wildlife Service (CWS) in collaboration with conservation managers and research biologists from Canada, the US, Greenland, Russia and Norway. Samples were collected by necropsy or biopsy between the Spring of 1989 and the Spring of 1993 from 18 regions in the Western Hemisphere from Alaska in the west through the range of the bear in Canada and eastern Greenland to Svalbard in the east—a span of 200°L encompassing the Western Hemisphere Arctic. These samples were

analysed for concentration of thirty five individual organochlorines (OCs) using the method of Zhu *et al.* (in prep.). The results for the other OCs were summed according to membership in three OC classes: 19 polychlorinated biphenyl congeners (ΣPCB), 12 chlordane related compounds and metabolites (ΣChlordane), and *p,p'*-DDT + *p,p'*-DDD + *p,p'*-DDE (ΣDDT). Geographical distribution of these OCs among the regions sampled was reported in 1992/93. Biopsy samples were also collected by US Fish and Wildlife Service biologists from female polar bears emerging from dens on Wrangel Island, Russia and in the Chukchi Sea, and by Ian Stirling, CWS, in the Arctic Ocean near Prince Patrick Island.

ACTIVITIES IN 1994/95

Biopsy samples from Wrangel Island (21) and Prince Patrick Island (25) were analysed for OCs to enlarge the earlier geographical distribution data base. The additional information was incorporated into the circumpolar survey, and a publication is in final draft stage (Norstrom *et al.* 1995). Further polar bear biopsy samples from the Arctic Ocean were collected by M. Ramsay during the US-Canada trans-polar ice-breaker expedition. These will be analysed in 1995/96. A review on contaminants in arctic marine mammals was published (Norstrom and Muir 1994). A presentation on chlorinated hydrocarbon contaminants in the arctic marine environment, in which mean OC levels in the food chain were related to trophic levels determined from published ^{15}N stable isotope data, was presented at Dioxin'94 in Kyoto, Japan (Norstrom 1994). A paper on the geographical distribution of methylsulfone-PCBs and -DDE was published (Letcher *et al.* 1995). Two papers on toxaphene were published: one identifying congeners in polar bear and comparing them with ringed seal (Zhu *et al.* 1994a) and the other on fractionation of the technical toxaphene mixture (Zhu *et al.* 1994b). Polar bear fat tissue was analysed by GC/ECNI-MS, and 21 minor chlordane components were identified. Photoheptachlor was synthesized and levels determined in ringed seal blubber, polar bear fat and human plasma (Zhu *et al.* 1995).

RESULTS

Geometric mean levels of OCs in polar bear adipose tissue biopsies from the two newly sampled areas: Wrangel Island, Chukchi Sea and Prince Patrick Island, Canadian High Arctic Ocean, Canada are presented in Table 1 along with previously reported data for neighbouring regions of the Alaskan and western Canadian Arctic. Levels of ΣPCB in adipose tissue of female bears with cubs emerging from dens on Wrangel Island tended to be higher than other bears in the Chukchi and Bering Seas, while levels of ΣChlordane tended to be lower. Polischuk *et al.* (1994) found that ΣPCB concentrations in adipose biopsies from females emerging from dens with cubs after a six-month fast were approximately twice those in the summer and autumn, and possibly other times of the year when actively feeding. If the Wrangel Island ΣPCB levels were divided by two, they would be similar to those in surrounding areas in the Bering, Chukchi and Beaufort Seas. The Canadian High Arctic Ocean samples from near Prince Patrick Island also include some bears from M'Clure Strait. These bears had the highest levels of ΣPCB, ΣChlordane and ΣDDT of any region in the Canadian Arctic. The levels were similar to those found in polar bears from the east side of Greenland and in Svalbard (Norstrom *et al.* 1995).

DISCUSSION/CONCLUSIONS

The most pronounced geographical variation in the new data was the significantly higher level of ΣPCB in the Arctic Ocean polar bears. The level of 20.7 mg/kg lipid wt. is equivalent to those in polar bears from Scoresby Sound in eastern Greenland, 23.5 mg/kg and from Svalbard, 22.7 mg/kg (Norstrom *et al.* 1995). There appears to be a sharp gradient in ΣPCB levels in bears from the Arctic Ocean, through M'Clure Strait and Viscount Melville Sound to Barrow Strait: 20.7 mg/kg, 10.1 mg/kg, 4.4 mg/kg. Results from bears sampled in 1982–84 also indicated a somewhat elevated level of ΣPCB, 8.3 mg/kg, in pooled adipose tissue from eight bears in Viscount Melville Sound, compared to nearby areas, which had ΣPCB levels in the range of 4-6 mg/kg (Norstrom *et al.* 1988).

It is tempting to conclude that the similarity in OC levels in the Arctic Ocean and North Atlantic bears is due to ocean current transport from the Greenland Sea. However, there is no direct surface water flow between the two areas along the northern coasts of Greenland and Ellesmere Island. Instead, surface waters near Prince Patrick Island are more likely to be directly influenced by flow from the East Siberian Sea via the Beaufort Gyre (Barrie *et al.* 1992). Koerner (1994) found no significant difference in ΣPCB levels in snow pack on a transect through the North Pole from Russia along 80°E latitude to the Canadian Archipelago along 100°W longitude, apart from high levels of homologues with eight to ten chlorines at 84°N and 86°N on the Russian side of the transect. There is therefore no indication that high rates of ΣPCB deposition to snow may coincide

with high levels in polar bears in the Arctic Ocean. Similarly, the ΣPCB concentration in seawater at an ice island situated near the coast of Axel Heiberg Island in the Arctic Ocean in 1986 (Hargrave *et al.* 1988) was similar or lower than that observed in the Bering and Chukchi Seas in 1989-90 (Iwata *et al.* 1993).

There may be an ecological explanation for the high ΣPCB levels in the Arctic Ocean and Viscount Melville Sound. Welch *et al.* (1992) noted that energy flow at the lowest trophic levels in Lancaster Sound was dominated by phytoplankton and pelagic feeding copepods. They suggested that ice algae and under-ice amphipods were more important in areas where there was multi-year ice, such as the Arctic Ocean near Prince Patrick Island. Faunal composition of multi-year ice of the polar basin is dominated by sympagic Gammarid amphipods (e.g., *Gammarus wilkitzkii*), which remain associated with the under-ice year round (Gulliksen and Lønne 1989). The relative importance of ice algae and amphipods versus phytoplankton and copepods in the food chain may influence bioconcentration of CHCs (and heavy metals). If ice algae dominate, concentrations of contaminants in the top few meters of water under the ice, including snow and ice melt water, are probably more important to bioconcentration than those in deeper waters. Thus, it is possible that the exaggerated levels of ΣPCB and other CHCs in Arctic Ocean bears compared with surrounding regions are due to a more under-ice based feeding ecology of ringed seals. There is little information on regional variability in ringed seal feeding ecology, but higher levels of Cd in ringed seal and polar bear from the western Arctic have been attributed to a greater proportion of hyperiid amphipods in the ringed seal diet (Braune *et al.* 1991, Macdonald and Sprague 1988). Polar bears from M'Clure Strait also had exceptionally high levels of mercury in liver compared to nearby regions (Braune *et al. 1991*). If the source of mercury in M'Clure Strait was biogeochemical rather than long-range transport, this finding supports the idea that polar bear feeding ecology in this region may differ from other areas in some respect.

A comparison of ΣPCB levels in the present study with previous results from analysis of pooled adipose tissue in equivalent regions in 1982-84 indicates no consistent pattern (Norstrom *et al.* 1988). Levels were higher in four areas, lower in five areas, and the same in three areas in 1982-84 than in 1989-93. The mean (± SD) ΣPCB level among 11 regions in 1982-84 was 5.6 ± 1.9 mg/kg. The mean level in the corresponding regions in 1989-93 was 5.8 ± 1.9 mg/kg. ΣChlordane levels in polar bear adipose tissue pooled without regard to sex and age, were higher and more variable in 1982-84 (3.7 ± 1.7 mg/kg, Norstrom *et al.* 1988) than the present results from the same areas in 1989-91 (2.1 ± 0.32 mg/kg, Norstrom *et al.* 1995). The most notable differences between the two time periods were three fold lower levels of ΣChlordane in northern and western Hudson Bay in 1989-90 than in 1982-84. Southeastern Hudson Bay was not sampled in 1982-84. In 1990/91 levels in southeastern Hudson Bay were higher than in other regions in Hudson Bay, but still not as high as in northern and western Hudson Bay in 1982-84. In spite of the difficulties in comparing the two data sets because of age and sex differences in composition, ΣChlordane levels appear to have declined slowly throughout the Arctic in the 1980s, but perhaps fastest in Hudson Bay.

Expected project completion date: March 31 1997

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Table 1. Geometric mean levels of OC contaminants in polar bear adipose tissue, mg/kg lipid wt. basis, from the Alaskan, eastern Russian and western Canadian Arctic. Most recent data from analysis of biopsy samples are highlighted in bold. Levels of ΣChlordane, ΣDDT and ΣPCB in female samples have been corrected for effects of sex by standardizing to male levels.

Region	Males	Females	SPCB	SChlordane	SDDT	Dieldrin
Wrangel Island	**1**	**16**	**7.95**	**0.72**	**0.27**	**0.03**
Bering/Chukchi Sea	3	6	2.76	1.00	0.08	0.05
Arctic Ocean	**11**	**14**	**20.26**	**2.96**	**0.29**	**0.15**
Amundsen Gulf	3	8	5.19	1.45	0.07	0.09
Melville Sound	9	12	8.63	1.95	0.11	0.10
Queen Maud Gulf	4	9	4.56	2.14	0.05	0.15
Barrow Strait	8	2	4.28	1.77	0.11	0.16

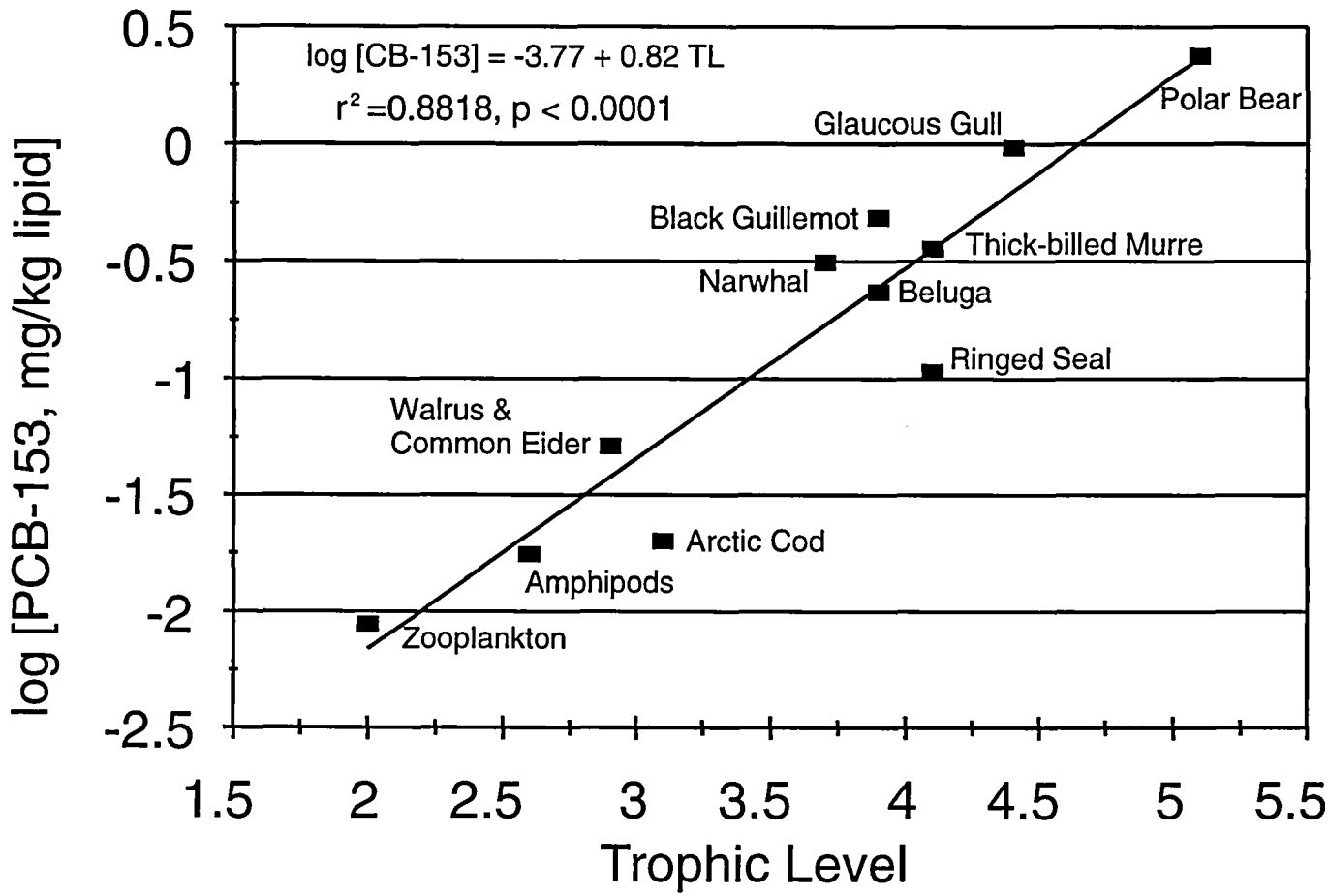

Figure 1. Correlation between logarithm of CB-153 concentration on a lipid wt. basis and trophic level in the arctic marine food web. Trophic level data are from Hobson and Welch (1992). The trophic level of walrus was assumed to be the same as for common eider because both are primarily molluscivores. The trophic level of arctic cod was assumed to be an average of large and small fish (Hobson and Welch 1992). CB-153 data are derived from Hargrave *et al.* (1992) for ringed seal, beluga and polar bear, and from Muir et al. (1992a) for Narwhal. Walrus data were for Hall Beach and Igloolik in northern Foxe Basin (Muir *et al.* 1992b). Data for common eider, black guillemot, thick-billed murre and glaucous gull are from Braune et al. (1994). The CB-153 levels for zooplankton and amphipods were estimated from the total PCBs assuming that the ratio of CB-153/total PCBs was the same as in arctic cod (Muir et al. 1988). Total PCBs for pelagic amphipods were assumed to be one-half the detection limit (Hargrave *et al.* 1992).

MERCURY AND OTHER INORGANIC CONTAMINANTS IN COUNTRY FOODS IN EASTERN HUDSON BAY

Project Leader: M. Kingsley, Fisheries and Oceans Canada (DFO)

Project Team: W.L. Lockhart, Freshwater Insttitute, DFO; D.W. Doidge, Resource Development Division, Makivik Corporation, Kuujjuac, Québec; C. Metcalfe, Trent University, Peterborough, Ontario

OBJECTIVES

1. To evaluate baseline levels of mercury and other heavy metals in country foods available to native people in communities on the Eastmain; and

2. 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 program on the major marine and freshwater country food species, including marine shellfish, marine and freshwater finfish, and marine mammals. 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 1994/95

A sampling program was arranged with the cooperation of Makivik Corporation to collect samples of beluga whale (*Delphinapterus leucas*), ringed seal (*Phoca hispida*), Greenland cod (*Gadus ogac*), brook trout (*Salvelinus fontinalis*) and Arctic char (*Salvelinus alpinus*) from the communities of Kuujjuaraapik and Umiujaq. The following samples were obtained and analysed for metals: beluga whales (10), ringed seals (32), brook trout (2), and Arctic char (9). For all other species muscle tissue was analysed, for all marine mammals liver and kidney, for belugas muktuk, and for ringed seals heart as well.

All tissue samples were analysed for the target metals—cadmium, mercury, and selenium. We obtained results for total mercury, and methylmercury analyses on selected tissues are under way at the moment.

RESULTS

As in 1993, levels of all metals in fish muscle samples were not high enough to cause concern. Mean mercury was 0.06 ppm wet weight, about one-tenth guideline levels, with little evident difference between species.

The results obtained from the 1994 sampling program for marine mammal tissues are summarised in Table 1; levels obtained from the 1993 samples are given for comparison in Table 2. Marine mammal liver samples were both high on average, and highly variable, for all metals; this is common, but indicates that sampling should be extensive, and interpretation cautious. The highest mercury levels in ringed seal liver were over 100 ppm. High mercury in liver was often associated with high levels of selenium: correlation between these two metals was especially high (0.93) in ringed seal liver, where, also, the levels of both metals were very variable. The correlation was less marked, but still significant, in beluga liver. In muscle tissue, or in ringed seal kidney, where selenium levels were relatively constant, the correlation with mercury vanished. Mercury levels in

ringed seal heart, determined in 1994, are not different from the levels in other muscle.

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, although its presence in other tissues confirms that belugas are exposed to it.

Kidney was not sampled in 1993, when the sampling was directed specifically toward species and organs used as food. Kidney, from any species, is not much consumed as food in northern communities. However, some metals concentrate in kidney, so it is a useful tissue as an indicator and tracer. In view of the high levels of some metals found in some tissues in 1993, kidney was collected and analysed in the 1994 program. Mercury and selenium levels were higher in kidney than in muscle, but not as high as in liver. However, cadmium levels in kidney, especially of ringed seal, were very high indeed. Most levels were over 10 ppm wet weight, and several over 100; the 1994 maximum value was 183.

DISCUSSION AND CONCLUSIONS

Metal levels in these country foods need to be examined in the light of local food preferences and customs. For example, in most parts of the Canadian Arctic ringed seal is commonly eaten, and in some places the liver is very highly esteemed. In both years of sampling, mercury levels in ringed seal muscle were below guideline levels (0.5 ppm), but in the liver the mean levels in the samples were 20 to 40 times the guideline. The highest level was 200 times the guideline. It would appear that while ringed seal meat and fat are innocuous, some caution should be applied in using the liver as food. Ringed seal liver is also high in cadmium. So is ringed seal kidney, but it is not eaten as often as the meat, the liver and the heart.

Kidney cadmium has been measured at high levels in many, or most, samples of marine mammals in the Arctic. In many cases, individual levels have been measured that were so high as to raise questions about how the kidney continues to function with such levels. This phenomenon has also been observed, although not in the same degree, in Arctic terrestrial mammals as well.

The parts of beluga that are usually eaten are the muscle and muktuk. It is much rarer for people to eat the liver, kidneys, or heart. Both muscle and muktuk are close to, or over, guideline levels for mercury. Relative to its content of cadmium and mercury, beluga muktuk has high levels of selenium.

All the results we obtained on metal levels in marine mammal tissues are broadly in line with results obtained in other areas of the Arctic.

All the fish tested were at 10% to 20% of guideline levels for mercury.

Expected project completion date: 31 March 1997.

Table 1. Concentrations of Cadmium, Mercury and Selenium in Marine Mammal Tissues from eastern Hudson Bay in 1994.

	Beluga		Beluga		Ringed seal	
	Mean	C.V.(%)	Mean	C.V. (%)	Mean	C.V. (%)
			Liver (wet wt. 10^6)			
Cd			8.0	98	18.9	69
Hg			8.3	106	18.5	124
Se			6.8	58	12.1	71
	Muktuk (wet wt/10^6)		Muscle (wet wt/10^6)			
Cd	0.00	56	0.04	94	0.15	101
Hg	0.42	62	1.66	79	0.21	65
Se	8.76	44	0.38	13	0.43	19
			Kidney (wet wt/10^6)			
Cd			21.6	94	55.7	76
Hg			2.6	95	1.1	52
Se			2.4	26	2.2	21

Table 2. Concentrations of Cadmium, Mercury, and Selenium in Country Foods from Eastern Hudson Bay, 1993.

			Metals (parts per million, wet wt)		
Species	**Tissues**	**#**	**Cadmium**	**Mercury**	**Selenium**
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	muscle	3	0.009-0.201	0.058-0.093	0.54-0.69
(Gt. whale)	liver	3	0.871-5.839	0.441-2.68	2.04-2.9
Ringed seal	muscle	26		0.054-0.349	
(Belcher Is.)	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.

CONTAMINANT TRENDS IN FRESHWATER AND MARINE FISH

Project Leaders: D. Muir and W.L. Lockhart, Fisheries and Oceans Canada (DFO) Central and Arctic Region, Winnipeg

Project Team: J. Gibson, K. Koczanski, B. Grift, B. Rosenberg, R. Hunt, K. Ramlal

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 (NWT) and northern Québec;

2. To provide information on contaminants to evaulate current risks of human exposure to PCBs, PAH and chlorophenols via fish consumption.

DESCRIPTION

When this project was initiated in 1991, 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 was nonexistent (Lockhart *et al.* 1992, Muir *et al.* 1990). The initial objectives of the project were therefore to determine levels of organics and metals in fishes from a broad range of remote lakes in northern Québec and NWT to 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, as well as to 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 northern Québec. The results for 1991-93 have been summarized in previous reports (Muir and Lockhart 1993, 1994) and presented to the people of the NWT and the Yukon at numerous workshops and public meetings. This report deals with results generated during 1994/95.

ACTIVITIES IN 1994/95

Samples: Fish samples were collected by DFO personnel from Winnipeg (Doug Chiperzak, Ross Tallman, Jim Reist and John Babaluk) or Yellowknife (Dave McKenna, Anne Wilson) from various locations in the NWT. Samples from Great Slave Lake were obtained from DFO Fish Inspection (M. Hendzel, Winnipeg). Species from NWT waters were Arctic char *(Salvelinus alpinus)*, burbot (*Lota lota*), lake trout (*Salvelinus namaycush*) and greenland halibut (*Reinhardtius hippoglossoides*). Arctic char muscle from the Kola Peninsula (Russia) was provided by Dr. T. Savinova (Murmansk Marine Biological Institute). A variety of species collected from Northern Québec (brook trout, sculpin, lake trout, burbot, lake whitefish) were provided by B. Doidge of Makivik Corp. (Kuujjuaq,QC).

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 (using ootoliths) were determined for all NWT samples. Age was not available for northern Québec samples. Generally, samples were selected to give three to six 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 i.d. 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 on a Kratos Concept high resolution mass spectrometer (EBE geometry) controlled using a Mach 3X data system.

Heavy metals (Hg, Cd, Pb, As) were determined in fish muscle by atomic absorption (AA) spectrophotometry (Hendzel and Jamieson 1976, Vijan and Wood 1974). Hg was determined by hot block digestion followed by cold vapour AA. Cu and 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 and duplicate samples were run approximately every 10 samples to check contamination of reagents and glassware and reproduciblity. During 1994 the laboratory participated in the intercomparison on PCB congeners in standards and in a ringed seal extract for the Northern Contaminants Program. The lab also participated in an international study of organochlorines in mussels carried out by the Marine Environmental Laboratory of Monaco.

RESULTS

Organochlorines: Amongst freshwater fish muscle samples, highest concentrations of all persistent organochlorines were found in lake trout and lowest in walleye. With the exception of results from Peter Lake (discussed below) concentrations in lake trout were within the range reported in other reports (see Table 1, Muir and Lockhart 1994). As has been observed previously, toxaphene was the major OC contaminant in lake trout and other species (Table 1). Results for toxaphene are reproducible but only approximate the actual chlorobornane concentrations because the technical standard was used for quantitation rather than individual standards. Nevertheless our lab has obtained results similar to other labs using GC-ECD or GC-MS (negative chemical ionization) in various interlab comparisons. Toxaphene patterns varied between species but were generally dominated by two major peaks, an octachlorobornane (T2) and a nonachlorobornane (T12). PCBs (sum of 90 congeners) were generally present at 1.5 to 2-fold higher levels than DDT- or chlordane-related compounds and at about 50% to 75% of toxaphene levels in lake trout. Hexachlorocyclohexanes (sum of α–, β– and γ–HCH isomers) and chlorobenzenes were present at much lower concentrations than the four major organochlorines.

Higher concentrations of toxaphene and PCBs were found in lake trout from Great Slave Lake than in the same species in smaller western NWT lakes (Raddi, Fish, Colville, Gordon, Belot) but further data analysis is needed to confirm this. This data analysis, planned for 1995/96, will involve correcting for effects of lipid and age using an Analysis of Covariance similar to recent work by Hebert and Keenleyside (1995).

Burbot liver samples from Great Slave Lake had significantly higher (t-test $p<0.05$) mean concentrations of toxaphene and ΣPCB than those from Fort Good Hope (Table 1). Concentrations of all major organochlorines in Great Slave Lake burbot liver were, however, much lower (10x for ΣPCBs) than in burbot liver from Lake Laberge in the Yukon.

Lowest concentrations of organochlorines were found in walleye from Hay River. Levels of toxaphene were <1 ng/g in walleye muscle. These are the lowest toxaphene levels ever found by our laboratory in fish from NWT, the Yukon or northwestern Ontario.

Levels of toxaphene in Peter Lake lake trout and arctic char were much lower than found in a previous set of samples reported last year (Muir and Lockhart 1994). These samples were part of a new set collected by Dr. Ross Tallman (DFO Winnipeg) in July 1994 and were much smaller and younger than the trout analysed previously. There seems to be a strong size to concentration relationship of toxaphene and ΣPCB in lake trout (Fig. 1). The two largest trout were also much older (40 and 48 yrs, respectively) than all other trout analysed. The variation in results illustrates the difficulty of reporting a single mean concentration of any organochlorine unless a narrow size/age range is selected. This is less of a problem in other lakes analysed since 1991 where most lake trout have been <4 kg. Nevertheless, concentration differences even in

lake trout of similar size are common in the NWT fish dataset. 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)(Kidd *et al.* 1995).

Greenland halibut (or turbot) muscle and liver samples from two arctic locations were analysed for the first time. The Beaufort Sea turbot are thought to migrate from the Greenland Sea/northern North Atlantic Ocean while adult turbot in Cumberland Sound are thought to be year long residents (D. Chiperzak, DFO Winnipeg, personal communication). Turbot is a bottom feeder which preys on benthic fish and invertebrates. Relatively high and remarkably uniform concentrations of most organochlorines were found in both Beaufort Sea and Cumberland Sound animals. Toxaphene was the predominate organochlorine in turbot (376 ± 28 ng/g in Beaufort Sea animals) (Table 1). Concentrations of toxaphene and other OCs in turbot liver were generally lower than in muscle despite higher lipid content (mean of 24% in liver vs 16% in muscle).

Concentrations of toxaphene and ΣPCB in arctic char muscle from the Kola Peninsula in Russia were similar to levels in samples from the Canadian Arctic. Unlike whitefish samples from the Ob River in central Russia (reported in Muir & Lockhart 1994) these char had higher concentrations of toxaphene than ΣPCB.

High Hg levels (ranging from 0.26 to 1.85 µg/g fresh wt) were previously reported for muscle of lake trout from Peter Lake (Muir and Lockhart 1994). Analysis of additional lake trout showed that Hg levels varied with size (and age) of the lake trout (Figure 2) but were generally higher than the guideline limit for commercial fish of 0.5 µg/g (wet wt). Arctic char from Peter Lake had much lower levels of Hg than lake trout (Table 2). Hg concentrations were also relatively high in lake trout and pike from the Nunavik region of northern Québec. The exact location of the samples is not known but this information will be available for the next Northern Contaminants Program report.

The analysis of burbot liver from Fort Good Hope, where sampling had been carried out previously during the 1980s permitted the first temporal trend information on toxaphene in fish in NWT. The results (Figure 3) show a significant decline between 1986 and 1994 for toxaphene and smaller declines in ΣPCB, ΣDDT and chlordane-related compounds.

CONCLUSIONS AND UTILIZATION OF RESULTS

The results for Peter Lake indicate that data on organochlorines and metals in fish from Arctic lakes must be viewed with caution until a reasonably representative sample (by age/size) is obtained. This project is gradually providing data on contaminants for most regions of NWT but there are still major gaps in spatial trend information. Additional temporal trend data would also be useful to determine if concentrations are increasing or decreasing. In the case of Hg, lake sediment cores suggest levels are increasing. In addition to the results reported here, the laboratory collaborated with the project of M. Evans (NHRI Saskatoon) on the analysis of fish from Great Slave Lake and with K. Kidd on the analysis of fish from Yukon lakes. These results are reported elsewhere in this volume. For 1995/96, additional samples of both lake trout and arctic char will be collected in the Keewatin region to follow up the results from Peter Lake. Further sample collections are planned for other major lakes and rivers in NWT in cooperation with DFO Fish Inspection and NWT Natural Resource officers including Baker Lake.

Expected project completion date: March 31, 1997.

Partners: DFO Fish Inspection (M. Hendzel), J. Reist and R. Tallman (DFO Winnipeg), D. McKenna (DFO Yellowknife), M. Swiripa (INAC, Water Resources, Yellowknife).

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Table 1. Concentrations (ng wet wt ± SD) of Major Organochlorine Groups in Marine and Freshwater Fishes Analysed in 1994/95.

Location	Species		N	Lipid (%)	ΣCBz	ΣHCH	ΣCHL	ΣDDT	ΣPCB	Toxaphene
Beaufort Sea	turbot	msc./skin	10 mean	1.46 ± 3.2	45.3 ± 3.3	12.7 ± 1.2	108 ± 7.4	120 ± 9.7	189 ± 14.8	376 ± 28.2
(Banks Is.)			range	11.0 - 21.1	38.7 - 50.3	10.1 - 14.6	95.9 - 119	105 - 133	163 - 216	318 - 408
Cumberland Sound	turbot	msc/skin	10 mean	16.6 ± 3.7	44.8 ± 4.3	17.0 ± 1.8	143 ± 15.4	145 ± 14.5	185 ± 20.8	376 ± 39.4
(Baffin Is.)			range	10.9 - 24.7	36.8 - 51.4	13.1 - 19.2	111 - 163	111 - 163	140 - 216	282 - 427
	turbot	liver	15 mean	24.4 ± 5.8	14.6 ± 3.8	18.9 ± 6.3	59.2 ± 14.6	67.9 ± 24.8	136 ± 57.5	340 ± 109
			range	12.6 - 34.5	6.6 - 20.6	8.0 - 31.0	25.9 - 86.4	28.1 - 113	43.9 - 291	160 - 589
Peter Lake	arctic char	msc./skin	6 mean	3.2 ± 1.5	3.1 ± 1.3	1.3 ± 0.69	4.4 ± 3.0	2.2 ± 1.1	11.4 ± 3.5	4.0 ± 2.8
(near Rankin In.)			range	1.1 - 5.7	1.2 - 5.3	0.61 - 2.6	1.6 - 10.2	0.87 - 3.8	7.5 - 18.1	2.0 - 9.5
	lake trout	msc./skin	12 mean	1.2 ± 0.7	1.3 ± 0.3	0.6 ± 0.3	5.8 ± 2.6	3.3 ± 2.7	19.0 ± 14.1	15.0 ± 15.7
			range	0.3 - 2.6	1.0 - 2.0	0.2 - 1.1	1.9 - 11.4	0.5 - 8.2	4.8 - 58.8	1.0 - 41.1
Raddi Lake	lake trout	msc./skin	6 mean	4.0 ± 2.9	1.7 ± 0.9	1.6 ± 0.60	12.0 ± 4.4	17.1 ± 7.0	33.5 ± 9.9	42.8 ± 18.2
(Banks Is.)			range	0.8 - 8.7	0.72 - 3.1	0.89 - 2.3	7.3 - 19.5	8.2 - 24.5	23.7 - 45.8	24.5 - 72.1
Fish Lake	lake trout	msc./skin	5 mean	4.2 ± 1.9	2.4 ± 0.85	1.6 ± 0.4	13.5 ± 6.3	14.3 ± 3.9	31.9 ± 15.5	50.6 ± 27.8
(Banks Is.)			range	1.3 - 7.4	1.8 - 3.8	1.1 - 2.1	6.4 - 22.4	10.0 - 19.9	16.9 - 53.4	21.6 - 88.1
Fort Good Hope	burbot	liver	11 mean	31.0 ± 13.7	12.8 ± 3.4	9.1 ± 3.3	24.5 ± 6.0	39.6 ± 19.6	56.6 ± 18.1	169 ± 60.5
(Mackenzie River)			range	10.0 - 53.0	8.4 - 19.8	2.8 - 13.2	12.2 - 34.0	8.7 - 75.7	33.7 - 92.2	65.0 - 282
Great Slave Lake	burbot	liver	10 mean	27.3 ± 8.7	7.5 ± 3.1	3.5 ± 1.6	64.8 ± 8.6	30.4 ± 1.7	114 ± 23.2	311 ± 48.3
			range	17.9 - 46.9	3.2 - 12.4	2.0 - 6.8	54.1 - 82.7	28.0 - 33.9	79.1 - 145	248 - 415
	lake trout	msc./skin	10 mean	11.0 ± 3.0	3.3 ± 0.6	3.9 ± 0.7	15.9 ± 4.8	7.7 ± 2.3	31.1 ± 11.0	86.3 ± 15.4
			range	6.9 - 16.8	2.7 - 4.5	2.9 - 5.1	7.7 - 24.2	3.6 - 11.2	14.6 - 49.5	60.7 - 103
Hay River	walleye	msc./skin	3 mean	1.2 ± 0.5	0.24 ± 0.06	0.16 ± 0.08	0.65 ± 0.20	0.61 ± 0.26	1.4 ± 0.32	0.40 ± 0.19
			range	0.9 - 1.8	0.18 - 0.28	0.09 - 0.24	0.49 - 0.87	0.34 - 0.85	1.0 - 1.6	0.21 - 0.59
Murmansk	arctic char	muscle	3 mean	4.1 ± 0.8	4.16 ± 0.44	2.92 ± 0.84	3.01 ± 0.74	5.65 ± 0.77	26.6 ± 2.65	35.4 ± 14.0
(Russia)			range	3.6 - 5.0	3.90 - 4.67	2.12 - 3.79	2.51 - 3.86	5.12 - 6.53	25.0 - 29.6	26.5 - 51.5

Table 2. Mean concentrations of metals in muscle of freshwater and marine fish (µg/g wet weight) analysed during 1994/95.

Location	Species	N	[Hg] mg/g	[Se] mg/g
Peter Lake	Arctic char	11 mean	0.096 ± 0.036	na
		range	0.058 - 0.181	na
	Lake trout	17 mean	0.681 ± 0.450	na
		range	0.152 - 1.850	na
N. Québec (Nunavik)	brook trout	22 mean	0.106 ± 0.050	0.332 ± 0.197
		range	0.030 - 0.208	0.195 - 1.183
	lake trout	8 mean	0.368 ± 0.113	0.362 ± 0.025
		range	0.197 - 0.531	0.328 - 0.397
	pike	3 mean	0.530 ± 0.079	0.277 ± 0.048
		range	0.443 - 0.596	0.242 - 0.332
	salmon	25 mean	0.049 ± 0.034	0.277 ± 0.050
		range	0.019 - 0.152	0.181 - 0.387
	sculpin	25 mean	0.137 ± 0.037	0.337 ± 0.063
		range	0.076 - 0.237	0.234 - 0.511
	sucker	15 mean	0.231 ± 0.100	0.242 ± 0.024
		range	0.100 - 0.438	0.199 - 0.281
	whitefish	31 mean	0.164 ± 0.098	0.274 ± 0.056
		range	0.067 - 0.501	0.150 - 0.387

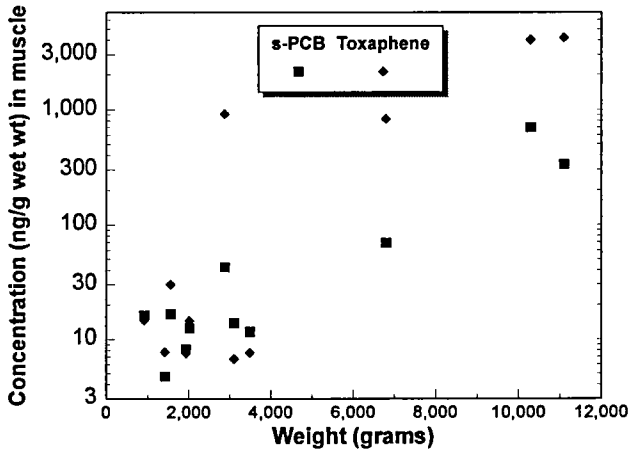


Figure 1. Relationship of ΣPCB and toxaphene concentrations with weight of lake trout from Peter Lake (near Rankin Inlet, NWT)

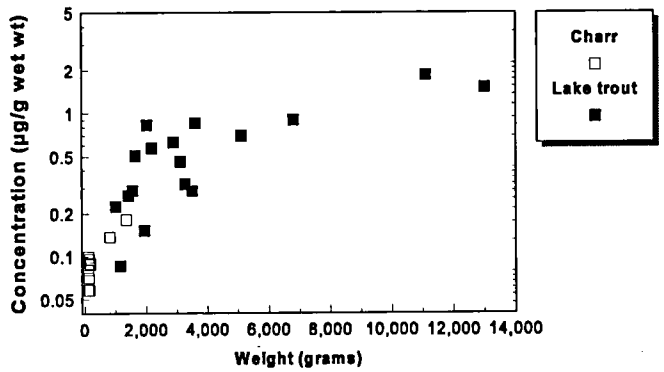


Figure 2. Variation of total mercury in muscle with size of Arctic char and lake trout from Peter Lake

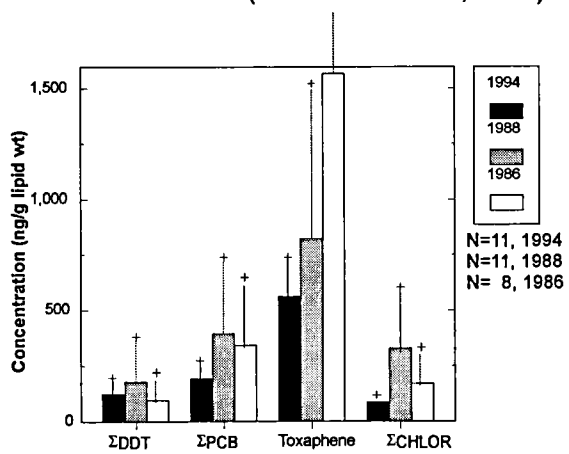


Figure 3. Temporal trends in concentrations of organochlorines collected in the Mackenzie River at Fort Good Hope, NWT

SOURCES, PATHWAYS AND LEVELS OF CONTAMINANTS IN FISH FROM YUKON WATERS

Project Leaders: Yukon Technical Committee on Contaminants in Northern Ecosystems and Native Diets (Contact: Mark Palmer, Chair)

Project Team: Government of Yukon Fisheries; Fisheries and Oceans Canada; Indian and Northern Affairs Canada; Environmental Protection Branch, Environment Canada Council for Yukon Indians

OBJECTIVES

Short-term

1. To collect contaminant fish data to complement that gathered in the 1991, 1992 and 1993 seasons by sampling additional lakes;

2. To collect icontaminant fish data to confirm that information gathered in the 1991, 1992 and 1993 seasons addresses concerns raised by health advisories based on existing data; and

3. To determine spatial variability in 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 and Atlin lakes (1991 and 1992, respectively). 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 limited on Atlin Lake. This has affected the various fisheries on the lakes, and generated considerable concern from residents who use 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 northerners. Additional lakes are being added to the monitoring program in an attempt to put confidence back in consuming country foods.

ACTIVITIES IN 1994/95

The 1994/95 sampling program was reduced substantially from previous years. Several lakes were sampled on request from local consumers. The sampling program also focused on filling in data gaps, especially in the area of burbot livers. The following lakes were sampled as part of the 1994/95 sampling program:

Little Salmon Lake
Klukshu Lake
Big Kalzas Lake
Jackfish Lake
Quiet Lake
Wellesley Lake
Kusawa Lake

RESULTS

The samples collected in 1993/94 have been sent to Axys Analytical Services in British Columbia for analysis. The results are being verified and will be sent to Health Canada for an assessment.

Table 1 summarizes the results from the previous four years of sampling; Figure 1 indicates the location of the lakes.

DISCUSSION/CONCLUSONS

- DDT is higher at Lake Laberge and Watson Lake, areas where extensive spraying of DDT for mosquito control was carried from the 1940s to the 1960s.

- PCBs appear to be higher in Lake Laberge, this is probably related to past use and disposal practices in the area.

- The three species of salmon, despite different marine feeding areas had similar levels of organochlorines with toxaphene being the dominant organochlorine.

- In addition to the results in Table 1, lake trout and whitefish eggs, livers and stomachs were sampled. In general, for the same fish the organochlorine levels were found in proportion to the lipid content of the body parts.

The results collected during the 1994/95 sampling season will be added to the Yukon fish database. All results will be sent to Health Canada for an assessment. The objective is to allow northerners to consume their country foods with confidence. Duplicate samples have been archived for use in future years.

The information will also be used in determining the sources and fate of a wide range of contaminants in Yukon lakes. All data will be presented at a series of Contaminants Workshops scheduled to be held throughout the Yukon in 1995/96.

Expected project completion date: March 31, 1997

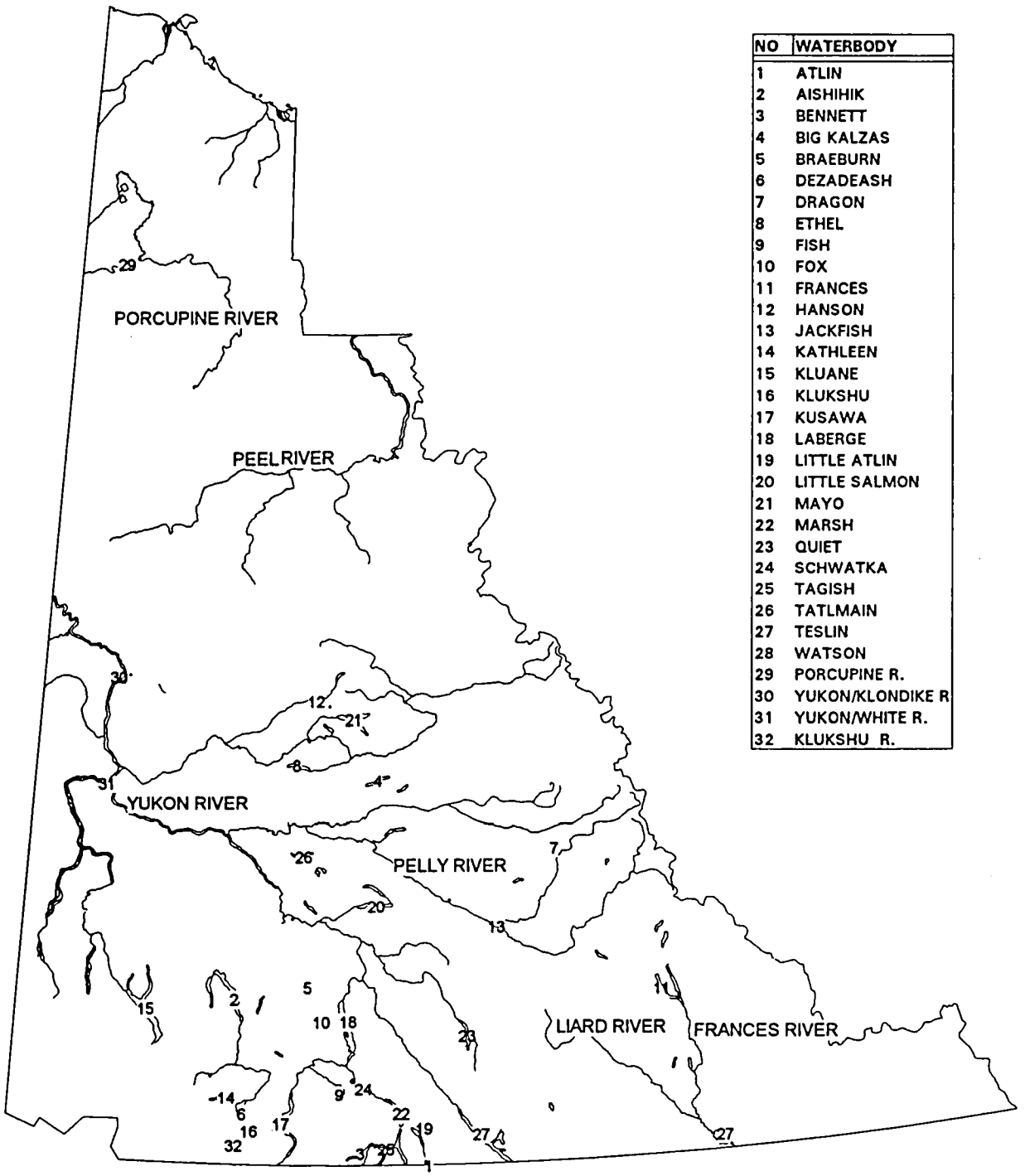
Table 1. Organochlorines in Yukon Fish, 1990-1993. Ranges of means for each location.

Species/ Tissue type	Location (number of lakes/rivers)	Sample Sizes[1]	Lipid[2] %	Toxaphene[2] (ppb)	ΣPCB[2] (ppb)	DDTs[2] (ppb)	Chlordane[2] (ppb)	Notes
burbot liver	Laberge	35	44	2301	1267	3433	217	Burbot liver was consistently the highest in OCs of any fish tissue sampled. By contrast,burbot muscle, sampled for Laberge, was extremely low in OCs.
	Atlin	6	33	1533	136	105	138	
	other (11)	2 - 8	27 - 47	54 - 945	50 - 579	21 - 272	10 - 183	
lake trout muscle	Laberge	27 P	6.1	344	448	458	30	Watson Lake trout were elevated in DDT only, while Laberge trout were high in all OCs.
	Watson	2P	5.2	<12.9	38	3427	2.2	
	other (20)	2 - 15 P	1.2 - 7.1	4.6 - 296	3.5 - 128	14 - 403	1.2 - 2.1	
whitefish muscle	Laberge	3 P	3	33.8	61	212	8.5	While DDT and PCBs stand out as high in Laberge, Ethel Lake whitefish fish had higher toxaphene levels. Watson Lake whitefish were elevated in DDT only. Old Crow whitefish had the highest lipid levels and yet had the lowest overall OC levels.
	Watson	2 P	2.2	<11.7	6.9	464	2.7	
	other (15)	2 - 5 P	0.3 - 3.6	0.2 - 52	0.3 - 8.3	0.2 - 6.6	0.1 - 5.1	
chinook salmon	Whitehorse Klukshu	2 - 6	0.9 - 1.0	35 - 43	7.1 - 14	9.0 - 13	2.0 - 3.9	All samples reported here are of muscle tissue. Egg samples had slightly higher lipid and proportionately higher OCs. The three species of salmon spend most of their lives in the Pacific Ocean or Bering Sea. Toxaphene was the dominant OC.
chum salmon	Porcupine	3	1.2	21	2.3	1.8	0.9	
sockeye salmon	Klukshu	3	1	9.3	3.1	3.1	0.9	
arctic grayling muscle	Laberge	6	1.7	25	21	22	1.8	All samples had very low or non-detectable OC levels. Laberge samples were about an order of magnitude higher in OC levels.
	other (3)	3 - 6	0.7 - 1.7	<0.2 - 2.7	<0.5 - 1.1	<0.3 - 0.7	<0.2 - 0.4	
northern pike muscle	Laberge	5P	1.8	48	90	247	14	All samples except Laberge were below detection or very low in organochlorines, including Hansen Lakes, which were treated with toxaphene as a piscicide 30 years ago.
	other (2)	3-6 P	0.4 - 0.6	<0.1 - 1.2	<0.2 - 1.1	<0.2 - 2.5	<0.1 - 0.5	

[1] Sample sets marked with a 'P' are all, or mainly pooled samples, usually with about six fish per sample. Other samples are mainly of individual fish.

[2] Values of lipids and organochlorines are ranges of mean values for each location. All values are wet weights.

YUKON FISH SAMPLING LOCATIONS



NO	WATERBODY
1	ATLIN
2	AISHIHIK
3	BENNETT
4	BIG KALZAS
5	BRAEBURN
6	DEZADEASH
7	DRAGON
8	ETHEL
9	FISH
10	FOX
11	FRANCES
12	HANSON
13	JACKFISH
14	KATHLEEN
15	KLUANE
16	KLUKSHU
17	KUSAWA
18	LABERGE
19	LITTLE ATLIN
20	LITTLE SALMON
21	MAYO
22	MARSH
23	QUIET
24	SCHWATKA
25	TAGISH
26	TATLMAIN
27	TESLIN
28	WATSON
29	PORCUPINE R.
30	YUKON/KLONDIKE R
31	YUKON/WHITE R.
32	KLUKSHU R.

FOOD CHAIN ACCUMULATION, BIOLOGICAL EFFECTS AND SEDIMENT CONTAMINATION IN LAKE LABERGE AND OTHER YUKON LAKES

Project leaders: L. Lockhart and D. Muir, Dept. of Fisheries and Oceans, Freshwater Institute

Project team: D. Metner; B. Billeck, P. Wilkinson, R. Danell, J. Gibson, B. Grift, G. Stern, K. Koczanski, B. Rosenberg, K. Kidd

OBJECTIVES

1. To determine temporal trends in organochlorines and PAHs via the analysis of dated sediment cores and analysis of archived fish tissues;

2. 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;

3. To contribute to studies of food chain contamination of organochlorines in Yukon lakes.

DESCRIPTION

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 fishes in 1990/91, and examining historical trends in these contaminants in Yukon lakes. The elevated levels of toxaphene, DDT and PCBs in fishes from Lake 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, when used as an *in vitro* assay, has been shown 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 have been shown to be an excellent tool for examining temporal trends in the deposition of particle-reactive contaminants such as PCBs, toxaphene, PAH, and heavy metals in lakes. Last year we reported, for the first time, detailed profiles of DDT, PCBs and PAH in dated sediment cores from lakes Laberge, Fox and Kusawa, in the Yukon (Muir and Lockhart 1994). The results for Lake Laberge clearly showed historical contamination, during the 1940-50s with DDT and PCBs, and much lower inputs in the 1980s.

In 1994/95, the major emphasis was on the collection, dating and analysis of lake sediments for organochlorines and PAHs from other Yukon lakes. Work also continued on the correlation of bone hydroxyproline with toxaphene and other organochlorine concentrations in fish.

ACTIVITIES IN 1994/95

Sample collection

Fish samples were collected from lakes Laberge, Fox and Kusawa in 1993 and 1994 by Ph.D. student K. Kidd (Univ. Alberta) in cooperation with Yukon government biologists. Weight, length and sex of the lake trout, burbot and whitefish were recorded. Ootoliths 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 analysed.

Sediments were collected from Lindeman, Bennett and Marsh lakes in March 1994. Cores were sliced at 0.5 cm intervals and the sediments placed in "WhirlPak" bags. Additional sediment cores were taken from Hansen and Watson Lakes in February 1995.

Sample analysis

PCBs and other organochlorines in fish tissues: Procedures for the analysis of fish muscle and liver samples are described in this volume by Muir and Lockhart (1995) and further details on the extraction and cleanup steps are given by Muir *et al.* (1990).

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 (10g) 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 compounds, chlordane-related compounds, 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. The biogenic compounds, perylene and retene, were also determined.

Toxaphene in sediments was analysed by GC-electron-capture negative ion mass spectrometry (ECNIMS) using a Kratos Concept high resolution mass spectrometer and a HP5890 GC with a 60 m x 0.25 mm i.d. DB-5MS column (He carrier gas). Two ions from the M^- (m/z 342.8962 + 343.9041) and $M\text{-}Cl^-$ (m/z 308.9352+310.9323) cluster for Cl_6 bornanes and two from the $(M\text{-}Cl)^-$ cluster for the Cl_7 (m/z 342.8962,344.8933), Cl_8 (m/z 376.8573, 378.8543) and Cl_9 (m/z 410.8183, 412.8154) components were monitored at 10,000 resolution.

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 . Firstly, 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 hydrolysed at 115°C for six hours and then calcium was determined by the method of Gitelman (1967) using Sigma Scientific Kit # 586 (Sigma Scientific, St. Louis MO).

Quality assurance

The laboratories located at the Freshwater Institute in Winnipeg participated in Northern Contaminants Program interlab quality assurance program on PCBs in a ringed seal extract during 1994/95. Certified reference sediments from NRC (Marine Analytical Standards Program) were used routinely for checking accuracy of PAHs and PCB determinations in sediments.

RESULTS

PCB and organochlorine pesticide concentration in fishes: Results for burbot liver, and lake trout muscle from Fox Lake and Lake Laberge, as well as lake whitefish from all three lakes are presented in Table 1. The large number of samples analysed (60) represents the combined efforts of K. Kidd, who conducted the majority of the samples as part of her Ph.D. work, and J. Gibson and K. Koczanski (DFO Winnipeg). The fish were analysed for 130 organochlorines (OCs), but only totals for major groups are reported. The entire dataset is available on disk and has been provided to the Yukon Contaminants Committee and to Health Canada. With a few interesting exceptions, mean concentrations of major OCs were similar to those found in the smaller sample set analysed in 1992/93 and 1993/94 (Muir and Lockhart 1993, Muir and Lockhart 1994) and in line with those found in ongoing studies by the Yukon Contaminants Committee (Palmer 1994, Eamer 1991). The exceptions are ΣDDT, toxaphene and ΣPCB in lake trout from Lake Laberge, which had much lower concentrations than observed previously. The difference may be partly explained by the lower lipid content (4.9%) of trout collected in 1993 compared with those from 1992 (8.4%) and earlier. ΣDDT concentrations in six lake trout collected in 1992 and analysed by our laboratory were 937.8±1184 ng/g wet wt (range 44-3010 ng/g), while 1993 samples averaged 139±81 ng/g wet wt. However, the 1992 samples included two animals with high concentrations, 1710 and 3010 ng/g, along with others having concentrations similar to those from 1993. Results reported by Palmer (1994) for ΣDDT in lake trout from Laberge averaged about 1000 ng/g but much of this work was on pooled samples. Although ΣDDT, toxaphene and ΣPCB levels are much lower in lake trout in the 1993 samples, mean concentrations of these organochlorines in whitefish and burbot liver did not differ significantly (t-test, $p<0.05$) from previous results (see Muir and Lockhart 1993, 1994). Therefore we conclude that there is a wide range of organochlorine concentrations in lake trout, which can lead to high variability between years. This variability needs to be monitored by analysing individual fish as much as possible.

Lake sediments: Two examples of the lead-210 and cesium-137 are given for two cores from Lindeman Lake and two from Marsh Lake (Figure 1). In all instances the lead-210 slice dates place the cesium-137 peaks in the mid-1960s, lending credence to the dates. The sedimentation rates estimated for Lindeman Lake were unusually high at 1500 to 2000 g m^{-2} yr^{-1}, while those at Marsh Lake were more in line with experience elsewhere (386 and 595 g m^{-2} yr^{-1}). Lindeman Lake receives input from a large glacier and probably much of the sediment contributing to the high sedimentation rate is derived from the glacier.

Previous analyses of organochlorines in Lake Laberge sediments (Muir and Lockhart 1994) that used GC-ECD analysis showed relatively high historical levels of ΣDDT and ΣPCB and showed the presence of toxaphene (<1 ng/g dry wt). Analysis of the extracts by GC-ECNIMS revealed low (pg/g) concentrations of chlorinated bornanes in post-1940 slices. The concentration profile of toxaphene in four lakes using a single dated core from each lake is shown in Figure 2. Highest toxaphene concentrations were found in Fox Lake (maximum 2 ng/g or 2000 pg/g). The profile of chlorinated bornanes in Fox Lake sediments suggests that the lake received a small quantity of technical toxaphene. In work done on sediments from Alberta lakes treated with toxaphene during the 1960s, we have found that the toxaphene profile contains more hexa- and heptachlorobornanes than untreated lakes (Miskimmin *et al.* 1995). Fox Lake has a similar profile of chlorinated bornanes. Kusawa and Lindeman show no evidence of this "technical toxaphene" profile; they have mainly octa- and nonachlorobornanes. Lake Laberge sediments have an intermediate pattern with some hexa- and hepta-chlorobornanes but mainly more highly chlorinated congeners.

Sediments from Lindeman Lake were also analysed for PCBs and other organochlorines (Figure 3) as well as for PAHs and heavy metals. Lindeman sediment core 1 had a very high sedimentation rate, which gave rise to almost year-by-year resolution for the period 1976-1993. Concentrations of organochlorines are low in Lindeman compared with other Yukon Lakes, due to dilution by high natural sedimentation. The results show higher recent fluxes of ΣPCBs and ΣDDT. However, we have not yet analysed slices from the 1950-60s which should have higher levels if the profile at Lindeman is similar to other lakes. Most of the cores have now been analysed for a series of heavy metals often associated with pollution, notably lead, cadmium and mercury. The lead profiles for some Yukon cores are shown in Figure 4 and they are much less striking than those from eastern lakes. The profiles are quite variable but show a general long-term tendency to increase slightly. Fox Lake, in contrast to the others, showed a striking increase in the top few slices, probably due to the road. Lead inputs to lakes in North America have generally been declining in recent years since the conversion to unleaded gasoline.

Bone collagen and hydroxyproline

The biological implications of toxaphene for the fish are not known. One observation on fish exposed experientially to toxaphene has been decreased concentrations of collagen in bone (Mehrle and Mayer 1975, Mayer *et al.* 1977). In a comparison of bone samples from lake trout from lakes Laberge, Kusawa Lake and Lake 260 in northwestern Ontario in 1992, it appears that the fish from Lake Laberge had significantly lower levels of hydroxyproline and collagen than lake trout from Kusawa or from northwestern Ontario. However, when additional fish from Kusawa and Laberge were analysed in 1993, and also fish from Fox Lake (Figure 5) the picture was much less clear. Fish from Laberge had higher levels of bone collagen than those measured in 1992, and Fox Lake fish, where toxaphene residues are lower, had lower levels of collagen than those from Laberge in that year. Some of the fish in Lake 260 were treated with a single intraperitoneal dose of 7 μg/g toxaphene, tagged and returned to the lake (Delorme 1994). No differences were found between treated and untreated fish in that lake.

CONCLUSIONS AND UTILIZATION OF RESULTS

The most recent analysis of the results for toxaphene in fish suggests that atmospheric fallout of this material followed by food chain accumulation is sufficient to explain the high levels. That is, there does not appear to be a need to find a localized source of toxaphene to explain the levels found. The question of the effects of toxaphene on the fish, however, remains open. Administration of technical toxaphene as done in the laboratory experiments cited does not necessarily reflect the toxicology of the depleted mixture found in fish from Lake Laberge. There appears to be a need for exposures of experimental animals to the mixture actually found in the fish, not to the original source mixture.

In the Yukon lakes, the down-core profiles of several metals have indicated much less fallout of metal contaminants, in comparison with natural geological background levels, than in eastern Canada. In the east, for example, lead found in the top slices of cores typically exceeds that in the bottom by several fold. That is not the case in the Yukon lakes studied, with the exception

of Fox Lake, where the source appears more likely to be road traffic than long-range atmospheric transport.

Expected project completion date: No future sampling is planned for this project because of funding cuts. But analysis of sediment cores collected in 1994 and 1995 is expected to continue over the next several years.

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Table 1. Concentrations (ng/g wet wt ±SD) of major organochlorine groups in fishes from the Yukon analysed during 1994-95.

Lake	Species/tissue[1]		Year	N		Lipid (%)	ΣCBz	ΣHCH	ΣCHL	ΣDDT	ΣPCB	Toxaphene	dieldrin
Fox	Burbot	L	1993/94	11	Mean	31.4 ± 7.2	10.3 ± 5.1	9.7 ± 6.6	33.0 ± 22.9	47.4 ± 35.9	40.8 ± 17.3	42.5 ± 37.0	2.5 ± 1.7
					range	18.0 - 44.8	4.6 - 18.6	1.6 - 21.4	12.6 - 77.0	12.3 - 125	18.7 - 80.0	2.6 - 105	0.42 - 5.8
Fox	Lake Whitefish	M	1993/94	10	Mean	0.9 ± 0.5	0.28 ± 0.15	0.35 ± 0.29	0.50 ± 0.34	3.6 ± 2.3	3.6 ± 4.5	5.0 ± 5.4	0.09 ± 0.06
					range	0.5 - 1.9	0.16 - 0.63	0.01 - 1.0	0.15 - 1.3	0.81 - 8.0	1.1 - 16.3	0.33 - 18.5	0.02 - 0.21
Fox	Lake Trout	M	1993/94	7	Mean	1.3 ± 0.5	0.43 ± 0.22	0.6 ± 0.29	1.6 ± 1.1	5.8 ± 4.5	5.3 ± 2.9	7.9 ± 5.5	0.22 ± 0.12
					range	0.5 - 2.2	0.15 - 0.70	0.05 - 0.86	0.3 - 3.3	1.6 - 12.8	1.9 - 9.6	0.65 - 15.6	0.10 - 0.44
Kusawa	Lake Whitefish	M	1993	11	Mean	1.3 ± 0.8	0.55 ± 0.32	0.41 ± 0.32	2.1 ± 1.7	15.6 ± 18.1	20.6 ± 21.7	16.1 ± 14.7	0.09 ± 0.06
					range	0.4 - 2.7	0.16 - 1.2	0.12 - 1.1	0.44 - 6.5	1.1 - 59.4	2.2 - 69.1	2.7 - 55.0	0.02 - 0.21
Laberge	Lake Trout	M	1993	4	Mean	4.9 ± 1.7	2.2 ± 0.82	2.1 ± 0.66	20.6 ± 7.9	139 ± 80.9	99.0 ± 49.8	243 ± 143	0.73 ± 0.52
					range	2.8 - 7.0	1.4 - 3.1	1.4 - 2.9	13.3 - 29.3	65.7 - 217	53.6 - 144	112 - 403	0.02 - 1.3
Laberge	Lake Whitefish	M	1993	4	Mean	3.1 ± 1.9	0.88 ± 0.58	0.9 ± 0.57	7.3 ± 3.1	75.4 ± 47.2	53.1 ± 29.9	46.6 ± 24.6	0.24 ± 0.16
					range	0.9 - 5.0	0.13 - 1.5	0.20 - 1.5	3.0 - 9.7	25.6 - 138	22.6 - 92.6	10.8 - 65.4	0.07 - 0.44
Laberge	Burbot	L	1993	13	Mean	42.6 ± 10.1	33.5 ± 17.8	39.7 ± 23.1	203 ± 124	2230 ± 1290	1380 ± 816	2710 ± 1730	17.8 ± 10.2
					range	23.0 - 55.5	14.6 - 68.1	18.6 - 77.2	57.6 - 501	545 - 5470	338 - 3330	1100 - 7440	7.6 - 40.2

[1] M= muscle + skin; L = liver

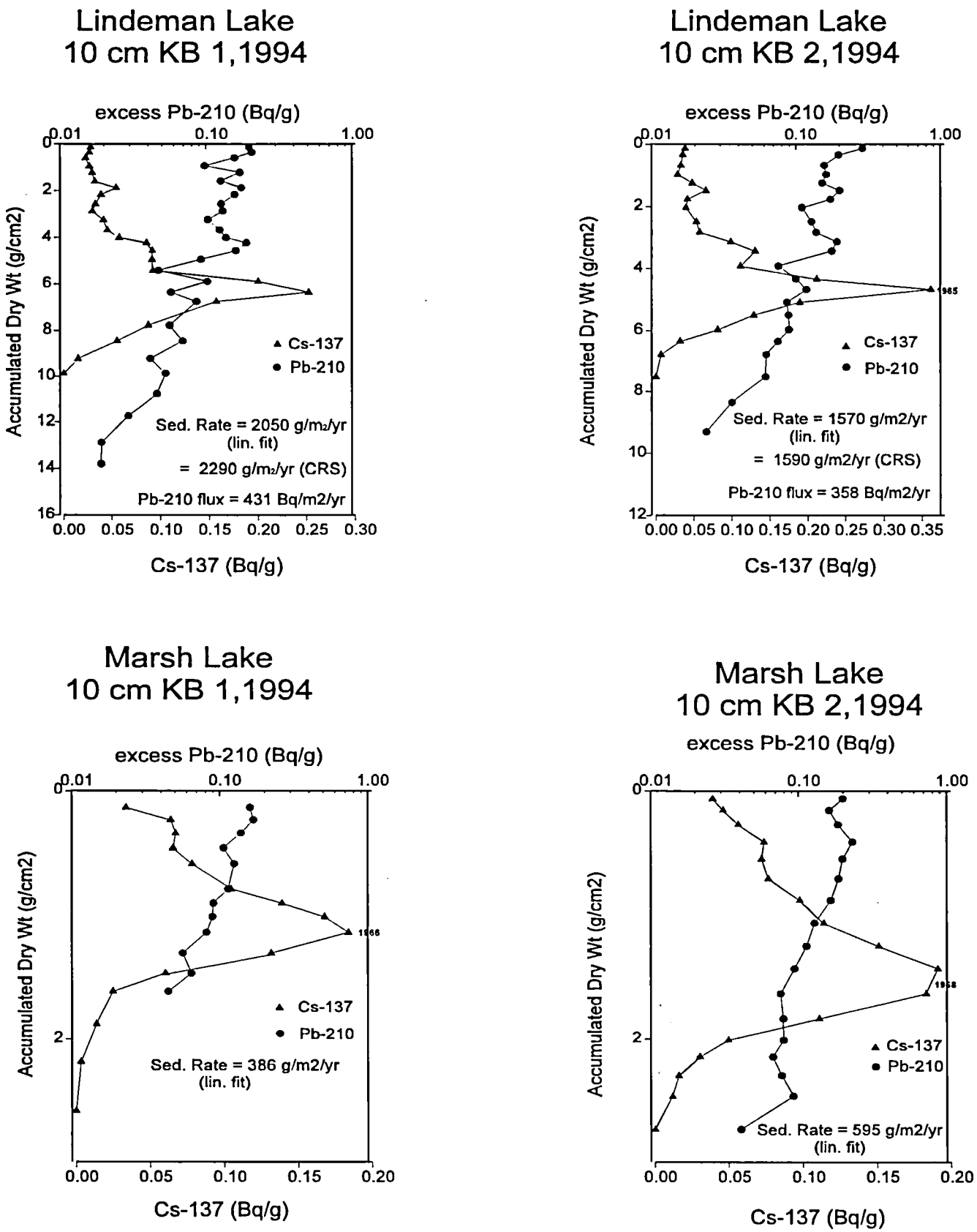

Figure 1. Lead -210 and cesium-137 from two cores from Lindeman Lake, BC, and in two from Marsh Lake, Yukon Territory

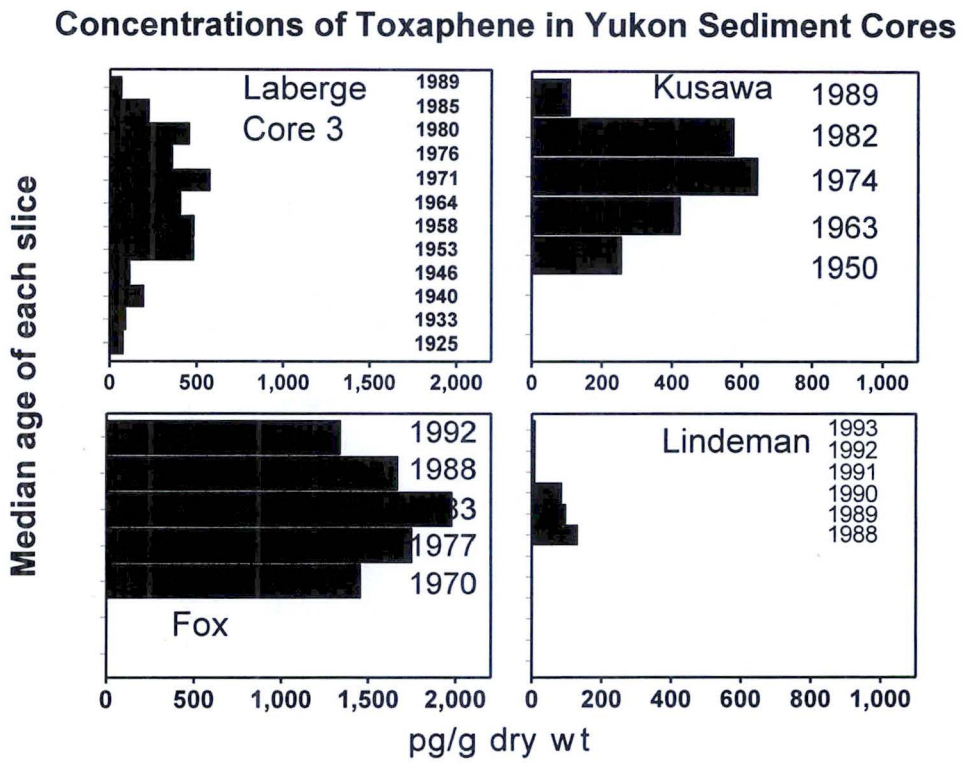

Figure 2. Concentrations of toxaphene in dated slices of sediment cores from several Yukon Lakes

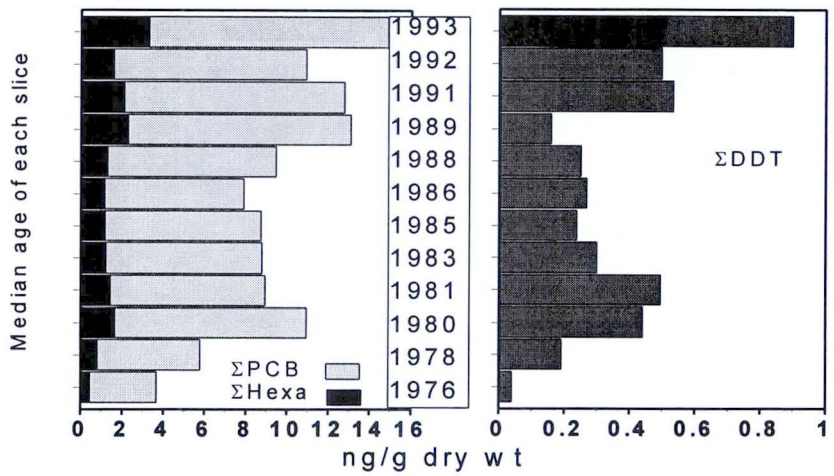

Figure 3. PCBs and DDT in slices of core 1 from Lindeman Lake, BC

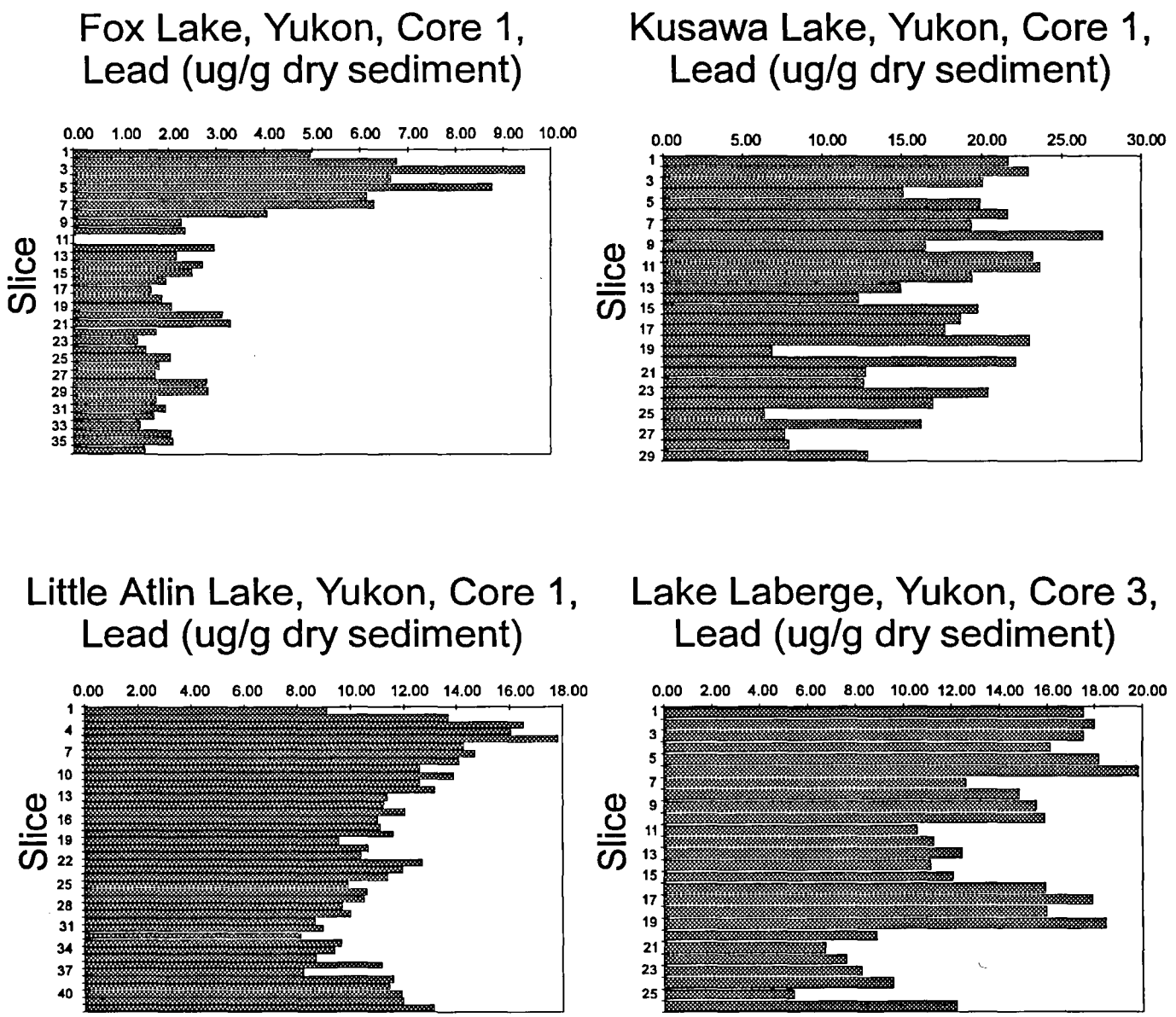

Figure 4. Down-core profiles of lead in sediments of several Yukon lakes

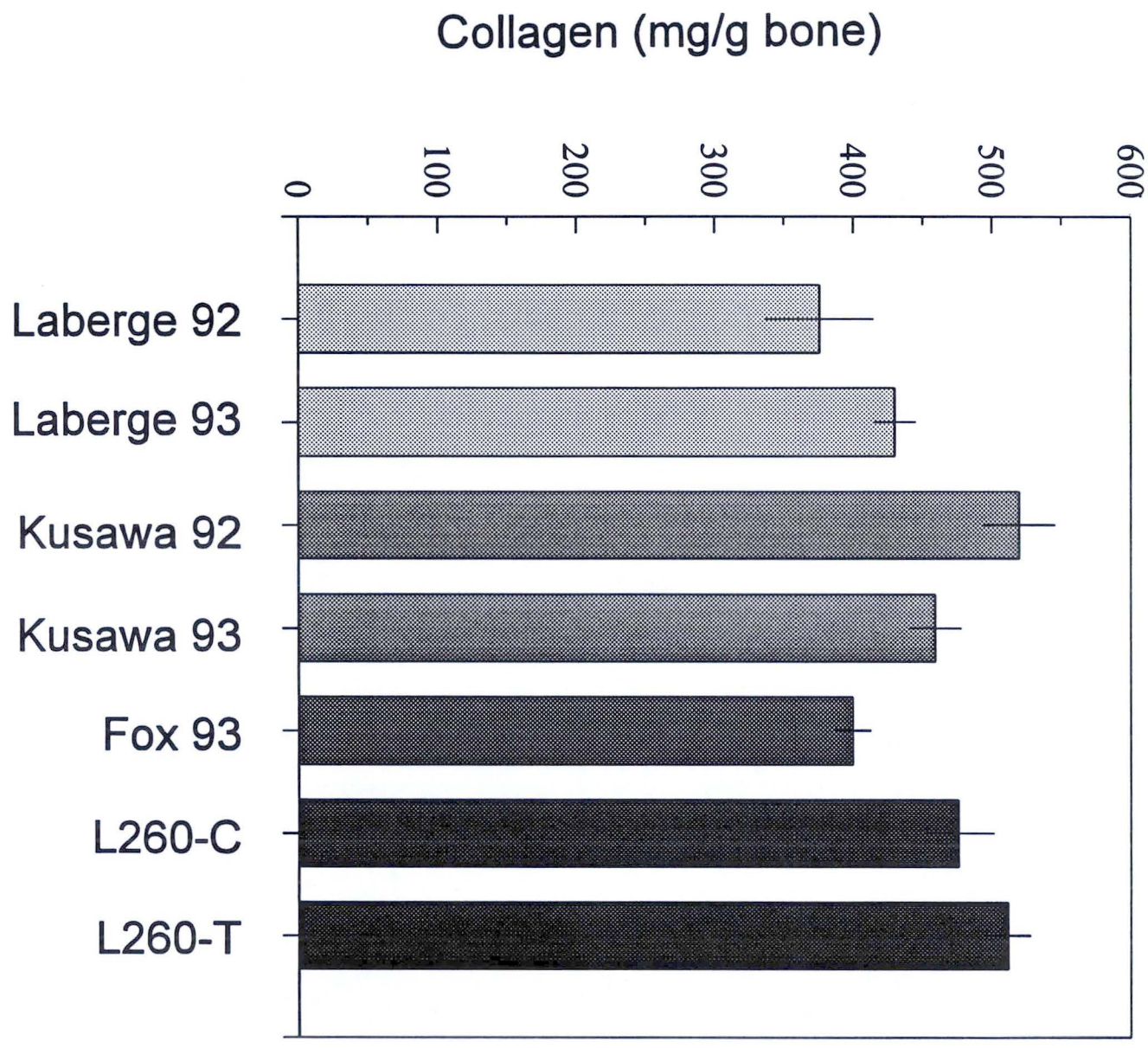

Figure 5. Collagen in Lake trout vertebrae from Yukon lakes (1992 and 1993) and comparison with treated lake trout in CLA L260

THE BIOMAGNIFICATION OF ORGANOCHLORINES THROUGH THE FOOD WEB OF LAKE LABERGE AND OTHER YUKON LAKES

Project Leaders: K.A. Kidd, D.W. Schindler, University of Alberta; D.C.G. Muir, R.H. Hesslein, Fisheries and Oceans Canada

Supporting Agencies: Fisheries and Oceans Canada (DFO); Indian and Northern Affairs Canada (INAC); Environment Canada; Northern Research Institute; Ta'an Kwach'an First Nation; Yukon Contaminants Committee; Yukon Territorial Government Fisheries Branch; Arctic Institute of North America and Canadian Circumpolar Institute, Alberta

OBJECTIVES

1. To examine the biomagnification of persistent organic pollutants through the food webs of Laberge, Fox and Kusawa Lakes, Yukon Territory (YT);

2. To examine factors underlying variable contaminant burdens in the lakes' top predators.

RATIONALE

Elevated concentrations of the pesticide toxaphene (chlorobornanes, CHBs) were found in lake trout and burbot from Lake Laberge, YT in 1990/91. Levels were significantly higher in fish from Laberge than those found in the same species from other Yukon lakes (Kidd *et al.* 1993), and resulted in a consumption advisory being issued by Health Canada. Other organochlorines, including PCBs and DDT, were also highest in fishes from Laberge (Kidd and Schindler 1994, Schindler and Kidd 1993, Muir and Lockhart 1992,1993, 1994, Yukon Contaminants Committee, in preparation). As a result, the commercial, sport and native subsistence fisheries on Lake Laberge have been closed.

Previous studies of Lake Laberge have found that the fish community structure is different from other lakes; the percentage of lake trout and lake whitefish are low while the percentage of burbot and longnose sucker are unusually high (de Graff and Mychasiw 1994). The lake trout are also high in lipids 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. A longer-than-normal food chain was hypothesized to be one possible cause for the contamination of fishes in Laberge. With only this exception, there are no known point sources of toxaphene in the Canadian Arctic. It is therefore suspected that the origin of toxaphene is atmospheric. It is known that one lake in YT was treated with toxaphene in 1963 (Minister of Indian Affairs and Northern Development 1993).

Sediment cores were collected by Muir and Lockhart (1994) from Laberge, and two reference lakes, Fox and Kusawa, to examine historical inputs of CHBs, PCBs and DDT. The results for CHBs indicate that both the contemporary and historical fluxes to Laberge were comparable to other regional lakes and considerably lower than those found in lakes previously treated with toxaphene (Miskimmin *et al.*, in press). Whereas elevated historical inputs of DDT and PCBs from local sources are evident in the core from Laberge, CHB inputs appear to be due to long-range atmospheric transport and deposition.

The main focus of this study was to examine the foodchain structure in Laberge and other regional lakes, and its relationship to the elevated levels of persistent organic pollutants in the lakes' fishes. We characterized the trophic relationships of biota in Laberge, Fox and Kusawa lakes using tissue stable nitrogen ($^{15}N/^{14}N$; $\delta^{15}N$) and carbon ($^{13}C/^{12}C$; $\delta^{13}C$) isotope analyses, and measured the levels of persistent organic pollutants in organisms from various trophic levels. 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 (Fry and Sherr 1984). The heavier isotope of nitrogen (^{15}N) is generally enriched three to five 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).

Research in 1992/93 and 1993/94 on Laberge, Fox and Kusawa lakes has resulted in the following conclusions:

- Lake trout, burbot and lake whitefish from Lake Laberge feed at a higher trophic level (as determined by $\delta^{15}N$) than the same species from Fox and Kusawa lakes, a factor that has resulted in higher contaminant burdens in the top predators from Laberge.
- Levels of CHBs, DDT and HCH in biota are significantly correlated to their $\delta^{15}N$ through the food web of Lake Laberge. The slope of this relationship appears to be a function of the biomagnification potential of these persistent organic pollutants.

ACTIVITIES IN 1994/95

For the final field season, between May and July, samples of benthic invertebrates (mainly chironomids (Chironomidae), snails (Lymnaeidae, Valvatidae and Planorbidae), tricopterans, and amphipods (*Gammarus* sp.)) and zooplankton were collected from Laberge, Fox and Kusawa lakes. These samples were collected using benthic grabs, shore sampling and verticle tows. Invertebrates were sorted and blotted to remove surficial water, and then frozen shortly after collection.

Invertebrate samples were pooled to obtain adequate masses (>4 g wet weight for organochlorine and <100mg wet weight for stable isotopes analyses). Laboratory analyses of fishes and invertebrates were completed on samples collected in 1994 and 1995. Subsamples of muscle and whole invertebrate samples were dried in an oven (50°C). These dried samples were ground to a fine powder and used for the stable isotope analyses described below.

Stable Isotope Analyses

To remove external carbonates from the invertebrates and to dissolve snail shells, HCl (1M) was added to ground invertebrate samples prior to analyses. Analyses were completed using a VG Optima automated mass spectrometer. Samples were combusted in a Carlo Erba NA1500 elemental analyzer and introduced directly into the mass spectrometer with a helium carrier. Carbon and nitrogen isotope ratios were 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

Briefly, wet tissues (fish muscle, whole fish (round whitefish only) and whole invertebrates were homogenized with dry ice. After CO_2 sublimation, 5 - 20 g were 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).

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. CHBs were quantified using a single response factor based on the areas of 20 peaks in the standard (Muir *et al.* 1992).

RESULTS AND DISCUSSION

Total concentrations of HCH, chlordanes, DDT, PCBs and CHBs in invertebrates and fishes from Laberge, Fox and Kusawa lakes are presented in Table 1 (see also Muir and Lockhart, this issue). Concentrations of CHBs in biota were significantly correlated with their trophic position, as established by $\delta^{15}N$ for all three lakes (Kidd *et al* 1995a). Further, the slopes of CHBs versus $\delta^{15}N$ in the three lakes were not significantly different, indicating a broad regional similarity in the biomagnification of this contaminant through the food chain. A significant relationship between other persistent organic pollutants and $\delta^{15}N$ has also been found for these three lakes (Kidd *et al.* 1995b, Kidd, unpublished data).

Relative trophic positions of the biota from these lakes, as determined using stable isotope ratios, are shown in Figure 1. Lake trout, burbot and lake whitefish from Lake Laberge feed at a significantly higher trophic position, as indicated by $\delta^{15}N$, than the same species from Fox and Kusawa (Kidd *et al* 1995a). While pelagic $\delta^{13}C$ (zooplankton) was comparable between lakes, the benthic $\delta^{13}C$ (for example the $\delta^{13}C$ of chironomids) was much lighter in Fox than the other two lakes, indicating

some differences in carbon cycling in this food chain. Also, $\delta^{13}C$ of lake trout and burbot from Laberge indicated that these fishes fed more on the pelagic food chain than the same species from Fox and Kusawa. Pelagic cisco have higher concentrations of CHBs than those benthic feeders, such as round whitefish, at the same trophic level (see Table 1 and Figure 1). A greater reliance on a more contaminated pelagic food chain may also contribute to the higher tissue CHBs in the fishes from Laberge.

CONCLUSION

Results from this study and those of Muir and Lockhart's indicated that an unusually long food chain, and not elevated inputs of CHBs to Lake Laberge, is responsible for the high concentrations of CHBs in fishes from this lake. Lake trout, burbot and lake whitefish from Laberge feed at a higher trophic level than the same species from other regional lakes. Elevated PCBs and DDT in fishes from Laberge also appears to be due to a food-chain phenomenon because contemporary inputs of these contaminants to Laberge are comparable to other regional lakes. $\delta^{13}C$ indicated that lake trout from Laberge also fed more heavily on pelagic organisms which have higher concentrations of CHBs. This factor may also contribute to the higher levels of CHBs in these fish. These results suggest that the highest contaminant levels are found in fishes from lakes with unusually long food chains, and that $\delta^{15}N$ is a useful technique to identify such lakes.

Expected project completion date: September 1995

ADDITIONAL SOURCES OF FUNDING

Arctic Institute of North America - Lorraine Allison Scholarship
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Table 1. Mean (SD) of ΣHCH, ΣChlordane, ΣPCB, ΣDDT and ΣCHB (toxaphene) concentrations (ng g^{-1} wet weight; N.D. - non-detectable <0.01 ng g^{-1}) and % lipid in biota collected from Fox, Kusawa and Laberge Lakes between 1992 and 1994. See Muir and Lockhart (1994) for lake trout, burbot and lake whitefish data.

	n	ΣHCH	ΣChlordane	ΣPCB	ΣDDT	ΣTox.	%lipid
Fox Lake							
Chironomidae	4	0.52(0.24)	1.53(0.60)	8.95(6.13)	2.43(0.50)	3.31(2.46)	1.30(0.28)
Zooplankton	4	1.36(1.17)	1.95(1.87)	4.31(5.20)	2.20(2.23)	11.55(12.28)	3.00(0.41)
Gammarus sp.	4	0.39(0.18)	0.38(0.27)	1.03(0.38)	0.80(0.37)	1.01(0.57)	1.18(0.69)
Tricoptera	5	0.40(0.23)	0.25(0.24)	1.74(2.21)	0.62(0.76)	1.09(1.12)	1.54(0.75)
Lymnaeidae	2	0.21	0.09	1.91	0.58	N.D.	0.96
Valvatidae/ Planorbidae	4	0.44(0.22)	0.31(0.17)	2.54(0.76)	1.19(0.69)	1.67(1.15)	0.60(0.53)
Grayling	4	0.64(0.49)	0.31(0.08)	0.98(0.30)	0.97(0.36)	1.92(0.51)	1.75(1.60)
Northern Pike	8	0.09(0.04)	0.12(0.07)	0.43(0.29)	0.54(0.31)	0.49(0.63)	0.28(0.09)
Round Whitefish	8	0.69(0.35)	0.37(0.17)	1.11(0.23)	0.90(0.42)	1.75(0.87)	1.81(0.87)
Kusawa Lake							
Chironomidae	4	0.58(0.16)	0.89(0.45)	7.46(3.19)	0.68(0.58)	2.70(0.71)	1.49(0.40)
Lymnaeidae	5	0.74(0.52)	0.80(0.49)	2.76(1.27)	0.41(0.27)	5.12(3.17)	1.93(0.68)
Valvatidae/ Planorbidae	2	1.05	0.60	2.27	0.51	4.17	1.60
Tricoptera	2	0.39	0.34	3.71	0.33	3.06	0.84
Zooplankton	4	0.44(0.30)	0.62(0.2)	1.19(0.29)	0.37(0.35)	2.88(1.13)	1.34(2.27)
Longnose Sucker	6	0.34(0.08)	1.56(0.53)	10.53(5.92)	10.28(3.59)	9.34(3.62)	1.24(0.36)
Round Whitefish	6	0.67(0.20)	1.70(0.88)	2.26(0.71)	1.27(0.52)	15.32(8.53)	2.31(0.58)
Lake Laberge							
Chironomidae	6	1.43(0.89)	1.075(0.52)	8.31(3.06)	14.61(10.00)	5.35(2.90)	2.89(0.89)
Lymnaeidae	4	0.29(0.14)	0.36(0.20)	1.19(0.50)	0.63(0.29)	1.09(0.19)	1.17(0.47)
Valvatidae/ Planorbidae	3	0.55(0.67)	0.25(0.06)	4.25(2.30)	1.42(0.57)	3.20(1.96)	0.24(0.08)
Tricoptera	5	0.35(0.25)	0.63(0.35)	2.57(1.35)	2.29(0.93)	2.11(1.14)	0.78(0.55)
Zooplankton	4	1.24(0.87)	1.32(0.91)	5.08(0.76)	4.09(1.54)	15.04(7.74)	1.48(1.04)
Lake Cisco	7	1.60(1.12)	6.33(3.83)	20.71(8.57)	31.76(15.70)	68.28(36.21)	5.00(2.89)
Round Whitefish	7	0.92(0.43)	3.24(2.01)	17.01(9.67)	22.57(11.00)	25.76(11.89)	2.14(0.61)
Northern Pike	8	0.12(0.04)	0.94(0.31)	7.20(3.12)	8.35(2.74)	9.68(3.86)	0.41(0.09)

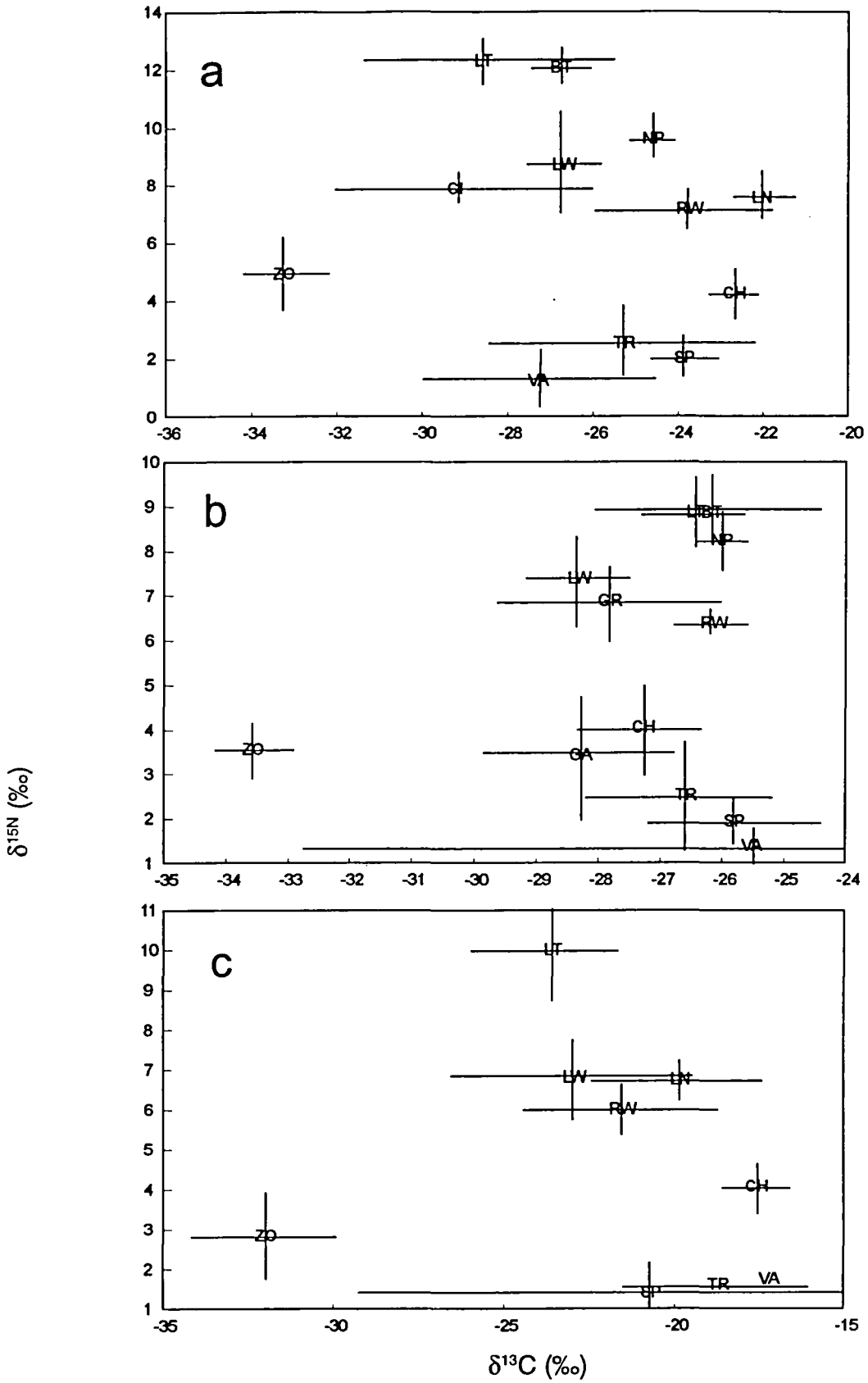

Figure 1. Mean (+/-SD; n=2 to 20) δ15N and δ13C of fish muscle and pooled whole invertebrates from a) Laberge, b) Fox, and c) Kusawa lakes, YT. LT-lake trout, BT - burbot, LW—lake whitefish, RW—round whitefish, GR—grayling, LN—longnose sucker, CI—lake cisco, NP—northern pike, CH—Chironomidae, TR—Tricoptera, VA—Valvatidae/Planorbidae, SP—sphaeriidae, GA—Gammarus sp. and ZO—zooplankton

BIOMAGNIFICATION OF PERSISTENT ORGANIC CONTAMINANTS IN GREAT SLAVE LAKE

Project Leader: M.S. Evans, National Hydrology Research Institute, Environment Canada

Project Team: D. Muir and W.L. Lockhart, Freshwater Institute, Fisheries and Oceans Canada

OBJECTIVES

Short-term

1. To determine organic contaminant concentrations in plankton, mysids, and amphipods collected from two regions of Great Slave Lake, i.e., an area strongly influenced by the Slave River delta region (Fort Resolution in the West Basin) and a second, more isolated "control" area (Lutsel' K'e in the East Arm). Compare these data with data collected from other subarctic and Arctic regions;

2. To determine stable isotope ($\delta^{13}C$, δ^{15}) composition in plankton, mysids, amphipods, lake whitefish muscle, lake trout muscle, and burbot muscle collected from the Slave River delta region and Lutsel K'e. With these data, investigate food web pathways and the role of trophic level in the biomagnification of organic contaminants in lake trout and burbot;

3. To investigate the spatial pattern in sediment deposition relative to the Slave River plume outflow with a special focus on the West Basin. As time allows, collect a series of cores in the East Arm;

4. To complete dioxin and furan analyses of fish collected in 1993/94;

5. To conduct limited limnological sampling of the Slave River plume. As time allows, collect a series of sediment trap samples in the plume region.

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.

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 is also 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 1994/1995

Two field trips were conducted in 1994/95. In August 1994, a ten-day sampling trip was conducted in Great Slave Lake by chartering a privately-owned, 49-foot steel-hull boat. In March 1995, a 1-week sampling study was conducted to collect sediment cores in the West Basin and East Arm. A twin otter was chartered for this work.

The primary goal of the August 1994 cruise was to obtain plankton, mysids, and amphipods for organic contaminant and stable isotope analysis. Sampling was conducted in Resolution Bay (near the Slave River outflow) and near Lutsel K'e. A preliminary series of plank-

ton and amphipod samples were also collected offshore of Hay River as part of our equipment testing program. Suckers and cisco were obtained from a local fisherman at Hay River. We were also able to obtain a limited collection of small fish (primarily burbot and sculpins) which were caught during our mysid/amphipod bottom sled collections made in Resolution Bay and Lutsel K'e. *Chara* and leaf litter were prevalent in our sled tows at Lutsel K'e and were retained for analyses. A sediment trap was set in 15 m of water offshore of the Slave River mouth with duplicate traps set at 5 m and 12 m and left in place for 10 days. Two surficial sediment samples were collected in the vicinity of Lutsel K'e and one in Resolution Bay. Samples were and are being analysed for persistent organochlorine contaminants (including toxaphene and PCB congeners) and PAHs.

In general, the August sampling was successful. However, we were unable to obtain a sufficient biomass of mysids from the East Arm for organic contaminant analysis. Nor did we have sufficient time to conduct baseline limnological sampling in the Slave River region (except for one temperature, oxygen, pH, conductivity, turbidity profile at the sediment trap site) nor in the East Arm. The data which we did obtain have been sufficiently well analysed to allow us to present the results at the November 1994 annual meeting of the Society of Environmental Contaminants and Toxicology (Evans *et al. 1994*). These data were also presented at the January Northern Contaminants Program (NCP) workshop in Sydney, British Columbia.

The two sediment cores collected in August 1993 were collected in non-depositional areas and were not suitable for further analysis for organic contaminants. However, four of the five core sites sampled in March 1994 (with Northern River Basin Study [NRBS] funding and in collaboration with R. Bourbonniere, National Water Research Institute [NWRI]) were in regions with a good depositional history record. Funding was received (16K from the Department of Indian Affairs and Northern Development, Yellowknife: J. Peddle and J. Witteman) to analyse some of these core sections for dioxins and furans. PAH and organochlorine analyses were conducted with NCP and NRBS funding. These analyses are near completion.

In March 1995, we broadened our collections of sediment cores in Great Slave Lake. We designed our study to obtain a series of core samples in the East Arm with limited sampling in the West Basin in regions not covered by the March 1994 sampling. However, we were only able to obtain one core of marginal quality in the East Arm despite sampling four sites and using two days of aircraft time. More background work will be conducted during our August 1995 study to better pinpoint suitable sites for coring in the East Arm. Two aircraft days were used to complete our core collections in the West Basin. One day of aircraft time was provided by the Department of Indian and Northern Affairs, Yellowknife. Cores will be dated using Northern River Basin funding.

RESULTS

The analysis of the majority of samples collected in August 1995 are near completion. Moreover, core samples collected in March 1995 have been freeze-dried and preliminary decisions made on the sequence of sample analysis. A brief summary of the organochlorine contaminant data and the stable isotope data are presented in the following paragraphs.

Cisco and suckers obtained from Hay River have been analysed for organochlorine contaminants (Table 1). Toxaphene was the most abundant organochlorine contaminant followed by ΣPCB, Σchlordane and ΣDDT. Organic contaminant levels were similar in both species of fish.

Toxaphene tended to be the predominate organic contaminant in biota caught in the Slave River delta region (Table 1). ΣPCB, ΣChlordane, and Σ-DDT were predominate compounds. Organic contaminant concentrations tended to be higher in amphipods than mysids: this has also been observed in the Great Lakes (Borgmann and Whittle 1983, Evans *et al.*1991). Organic contaminant concentrations were higher in whitefish muscle than in invertebrates and still higher in lake trout muscle and burbot liver. Contaminant levels were substantially lower in burbot muscle than burbot liver and in burbot muscle than lake trout muscle. Similar trends were observed for biota collected from the Lutsel K'e region.

Stable isotope analyses were conducted to infer carbon sources to the Great Slave ecosystem and food web pathways. There was remarkably little variation in carbon isotopes for the food web investigated in Resolution Bay (Fig. 1). This suggests that plankton production was the primary carbon source for the food web in the West Basin, i.e., there was no obvious river input of terrestrial carbon. The carbon isotope data were substantially more variable at the Lutsel K'e study site suggesting that there were a variety of carbon sources. *Chara* and possibly leaf litter may have been additional important carbon sources to the Great Slave Lake food web in the East Arm, particularly in the shallow water where the invertebrate collections were made. In addition, lake

trout, burbot, and whitefish appeared to be feeding on substantially different carbon sources in the East Arm than in the West Basin. Differences were particularly large for whitefish.

Nitrogen was used to infer trophic relations. Plankton and mysids had similar $\delta^{15}N$ values in the Slave River delta region. Moreover, there was a progressive enrichment to amphipods, whitefish, and lake trout, reflecting trophic feeding. Burbot muscle had slightly lower $\delta^{15}N$ values than lake trout muscle, possibly reflecting different food sources for the two species of fish inhabiting the West Basin. Similar trends were observed at Lutsel K'e although $\delta^{15}N$ values were lower in plankton and amphipods than in the Slave River delta region.

Organic contaminant concentration was strongly associated with trophic level as inferred from the $\delta^{15}N$ and toxaphene data (Figure 2). There were regional differences in the relationship between organic contaminant concentration and $\delta^{15}N$, i.e., the intercept and the slope of the calculated regression line differed between the two study sites. The primary factor accounting for these differences was the fact that toxaphene concentrations tended to be higher in plankton and amphipods collected from the East Arm than the Slave River delta region. In addition, the regression was also affected by the fact that $\delta^{15}N$ values tended to be lower for amphipods and plankton collected from the East Arm than the West Basin.

Organic contaminant concentrations in the sediment traps set in the Slave River mouth were low and comparable to concentrations observed offshore of the Stark River mouth in the East Arm (Table 1). ΣPCB concentrations in sediment were higher than in amphipods in contrast to previous research on Lake Michigan where the reverse trend has been observed (Evans *et al.*1991).

DISCUSSION/CONCLUSIONS

Initial results of our study indicate that most organochlorine contaminants occur in relatively low concentrations in Great Slave Lake food webs. To date, there is no indication that organic contaminant concentrations are higher in the vicinity of the Slave River mouth than in the East Arm. In fact, organic contaminant levels tended to be somewhat higher in biota collected from the East Arm than the West Basin.

The biomagnification of organic contaminants in Great Slave Lake whitefish muscle, lake trout muscle, and burbot liver appears to be directly linked to trophic feeding as inferred from the $\delta^{15}N$ data and as shown by previous researchers. However, some care must be used in the interpretation of these data because some of the data are based on whole body burdens (invertebrates), some on muscle (whitefish, lake trout) and some on liver (burbot). Carbon pathways appear to differ between the West Basin and the East Arm and may be especially complex in the East Arm where the high water clarity and sheltered embayments allow for the establishment of a significant *Chara* community and the probable retention of leaf litter blown into the lake.

Organic contaminant levels in Great Slave Lake biota were within the general range of values observed for other Yukon and Territorial lakes (Muir and Lockhart 1993, Kidd *et al. 1994*). ΣPCB, ΣDDT and toxaphene values were lower in the Great Slave Lake plankton than in Lake Laberge plankton (Kidd *et al. 1994*). DDT and toxaphene concentrations were also lower in Great Slave Lake lake trout than Lake Laberge lake trout. In contrast, toxaphene values were higher in amphipods in Great Slave Lake than benthos collected from Lake Laberge. Toxaphene appeared to occur in similarly high concentrations in Great Slave Lake and Lake Laberge lake whitefish. ΣPCB occurred in higher concentrations in burbot liver from Great Slave Lake than burbot caught from Trout and Alexis lakes, ΣDDT and toxaphene concentrations were lower than in Lake Laberge burbot liver.

Expected project completion date: March 1997

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Table 1. Organochlorine contaminant concentrations (ng•g-1 wet wt) and percent lipid of biota collected in Great Slave Lake, August 1994. Also shown are fish data from 1993/94 sampling and sediment trap and surficial sediment data from August 1994.

Location	Sample Type	% Lipid	ΣCBZ	ΣHCH	ΣChlordane	ΣDDT	ΣPCB	ΣToxaphene	Dieldrin
Hay River	Cisco - whole fish	5.88 ± 1.56	1.00 ± 0.40	1.12 ± 0.40	8.25 ± 1.04	2.68 ± 0.61	8.44 ± 1.58	50.8 ± 7.32	0.85 ± 0.26
	Sucker - muscle	3.14 ± 2.8	1.19 ± 0.32	0.84 ± 0.23	9.23 ± 4.66	6.08 ± 4.62	13.8 ± 8.00	33.8 ± 20.6	0.84 ± 0.23
Fort Resolution	Sediment trap	n.d.	0.28 ± 0.00	0.21 ± 0.04	0.19 ± 0.13	0.17 ± 0.07	2.87 ± 0.06	0.39 ± 0.01	0.07 ± 0.03
	Plankton	10.2 ± 1.12	0.14 ± 0.01	0.90 ± 0.14	0.61 ± 0.11	0.81 ± 0.10	4.46 ± 2.02	1.20 ± 0.08	0.10 ± 0.04
	Mysids	36.7 ± 2.33	0.06 ± 0.01	0.74 ± 0.03	0.69 ± 0.06	0.23 ± 0.13	1.83 ± 1.26	3.69 ± 0.45	0.05 ± 0.07
	Amphipods	10.8 ± 15.0	0.10 ± 0.08	1.65 ± 0.71	0.84 ± 0.29	0.39 ± 0.15	2.13 ± 0.95	3.94 0.48	0.15 ± 0.03
	Whitefish muscle	6.04 ± 1.77	2.08 ± 1.26	1.68 ± 0.35	5.34 ± 4.29	1.51 ± 1.15	4.21 ± 4.93	23.5 ± 19.8	23.5 19.8
(Hay River)[1]	Lake trout muscle	12.8 ± 3.06	2.58 ± 0.89	2.02 ± 0.64	10.2 ± 4.8	5.79 ± 3.38	13.9 ± 7.19	48.5 ± 24.3	0.79 ± 0.30
	Burbot muscle	4.2 ± 0.28	0.18 ± 0.04	0.07 ± 0.01	0.33 ± 0.02	0.33 ± 0.20	1.61 ± 0.26	0.81 ± 0.12	0.09 ± 0.02
	Burbot liver	23.4 ± 9.5	10.5 ± 2.1	6.5 ± 1.7	61.2 ± 16.2	26.7 ± 5.5	74.5 ± 16.9	244 ± 89.8	5.1 ± 1.2
Lutsel K'e	Sediment (Stark R.)	n.d.	0.43	0.22	0.19	0.51	4.90	1.01	0.14
	Plankton	9.87 ± 2.72	0.15 ± 0.05	1.50 ± 0.66	1.0 ± 0.50	0.78 ± 0.13	4.68 ± 1.00	5.69 ± 1.96	0.17 ± 0.08
	Amphipods	24.9 ± 2.31	0.09 ± 0.03	2.60 ± 0.62	1.90 ± 0.3	0.93 ± 0.04	2.63 ± 0.99	17.5 ± 0.96	0.33 ± 0.03
	Whitefish muscle	2.75 ± 1.19	1.36 ± 0.63	0.82 ± 0.50	4.54 ± 2.26	2.09 ± 1.02	5.58 ± 2.78	33.1 ± 17.4	0.58 ± 0.28
	Lake trout muscle	7.63 ± 3.94	3.22 ± 2.17	2.61 ± 1.32	16.8 ± 9.9	9.58 ± 7.15	24.9 ± 18.5	151 ± 102	1.13 ± 0.57
	Burbot muscle	6.10 ± 0.28	0.43 ± 0.08	0.20 ± 0.03	0.97 ± 0.23	0.55 ± 0.11	2.60 ± 0.49	4.04 ± 1.53	0.15 ± 0.08
	Burbot liver	30.0 ± 7.85	16.5 ± 4.24	10.8 ± 5.19	93.5 ± 34.7	51.2 ± 25.7	138 ± 52.2	762 ± 298	9.66 ± 3.93

[1] Lake trout caught near Hay River are assumed to be representative of lake trout in the Fort Resolution area. Lake trout are rare near the Slave River mouth.

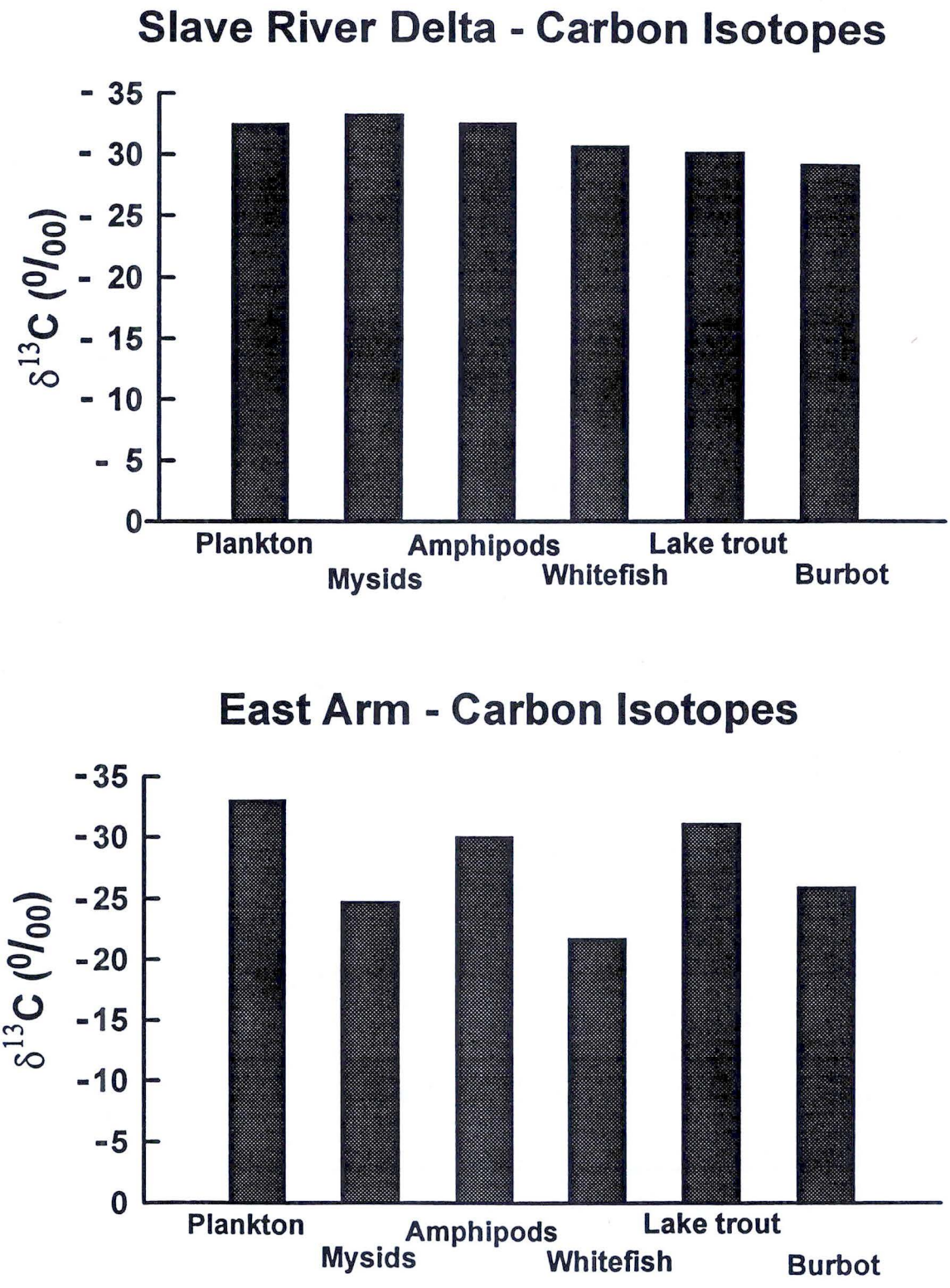

Figure 1. Carbon isotopic composition in biota collected from the Slave River delta (Resolution Bay) and the East Arm (Lutsel K'e) region. Invertebrate values are based on whole body while fish values are based on muscle

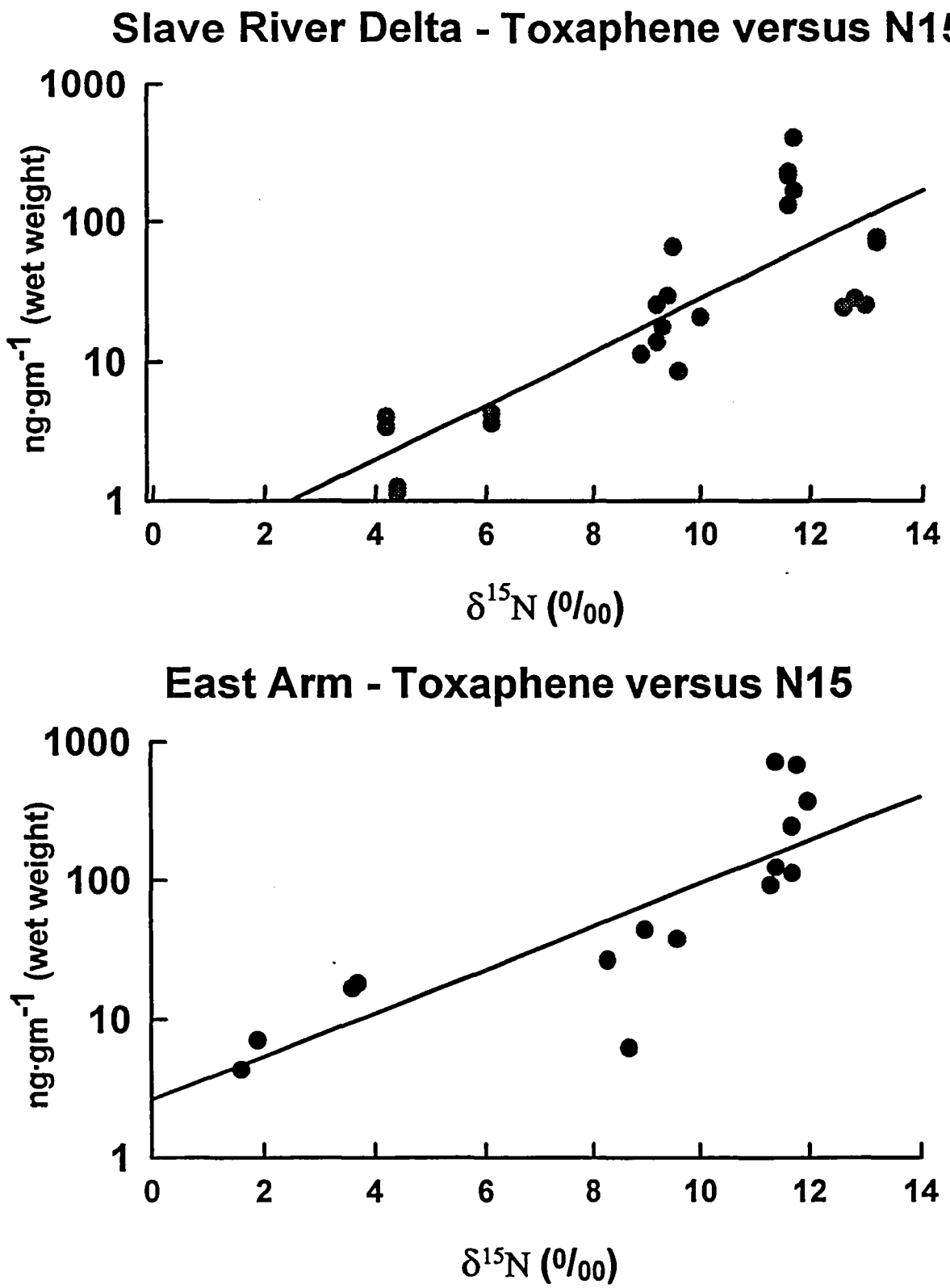

Figure 2. The relationship between toxaphene concentrations and $\delta^{15}N$ composition for biota collated from the Slave River delta (Resolution Bay) and the East Arm (Lutsel K'e). Data are presented as individual values. Burbot contaminant data are based on the liver while δN^{15} is based on muscle

EVALUATING THE UTILITY OF "BIOMARKERS" TO INDICATE THE BIOLOGICAL EFFECTS OF CONTAMINANTS ON ARCTIC MARINE MAMMALS AND FISH.

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Project Team: D. Metner, DFO, Winnipeg, Manitoba; P. Bullock, DFO, IOS

OBJECTIVES

1. The main objective of this project is to relate activity of the hepatic enzymatic detoxification system (mixed function oxidases: MFO) and DNA adduct formation to concentrations of organic contaminants through use of co-ordinated sampling and analysis.

DESCRIPTION

This work is a pilot project to assess the usefulness of biomarker measurements by relating these to contaminant concentrations in a limited range of biota from a few sites. The relationship between contaminants and effects in arctic biota will be compared with that established for biota in the south. "Biomarkers" are measurements of biological changes that apparently occur in response to environmental stress. While conventional chemical analyses define the amount of contaminant present in a fish or a seal, the effect of this contaminant can only be assessed by some measure of biological response. Within the last decade or so several sensitive and sub-lethal effects measurements have been developed—the biomarkers. It is now well established that chemical contaminant concentrations are well correlated with some biomarker changes.

The biomarker, which is best established as a measure of contaminant effect, is induction of the mixed function oxidase (MFO) enzyme system in vertebrate liver. During the process of degrading (and eventually excreting) certain organic contaminants the MFO system may form "reactive intermediates," which bind covalently with DNA to form DNA adducts. This step is believed to be a key reaction in liver tumour formation in vertebrates in general. There is so far no way of assessing the impact of liver tumour development (or of other intermediate biochemical changes) on reproductive capacity, or on population or community structure. Other field evidence also points to a correlation (though not necessarily a cause-effect relationship) between the presence of contaminants and either reproductive or health effects in seals. None of these field studies (which have been carried out in lower latitude environments) proves the causal link between contaminant exposure, MFO induction, and either DNA adduct formation and tumourigenesis, or a disruption of reproductive physiology whose mechanism is not clear. Nevertheless, taken together, the cumulative evidence suggests that MFO induction and related measurements may be an early warning of effects on individuals or on populations, mediated through disease or reproductive disruption.

In this pilot project a limited suite of biomarkers (all based on MFO induction or DNA adduct formation) are analysed in beluga whales and in lake trout. (Both are high trophic level organisms and accumulate high contaminant burdens and so may be most at risk). The species are sampled by one investigator and samples will be distributed to other team members.

ACTIVITIES IN 1994/95

Twenty-one Beluga whales were collected in Kugmallit Bay, NWT during June and July 1994. Samples of skin and blubber, liver, muscle, and kidney were removed for chemical analyses (metals and organics). Further liver samples were taken for mono-oxygenase measurements, and all of the above tissues plus brain were taken for DNA adduct measurements. Samples were preserved appropriately for the subsequent analyses. Size, age and sex of the individual whales were recorded.

The following analyses have now been performed on these samples:

Concentrations of total cytochrome P-450, and of cytochrome P-450 1A (CYP 1A) and its associated enzyme activity, ethoxyresorufin O-de-ethylase (EROD) have been measured in liver at IOS. Activities of pentoxy- and methoxyresorufin O-de-ethylases (PROD and MROD) (indicators of CYP 2B) were also measured.

Concentrations of DNA adduct in liver and brain, testosterone in blood, acetylcholinesterase (AChE) activity in brain and of Vitamin A in liver are being analysed by DFO St. John's, Newfoundland.

Concentrations of major organochlorines and metals have been analysed in various tissues by DFO, Winnipeg. EROD was also measured in liver samples.

RESULTS

EROD activities were detectable in all liver samples, indicating that the method of preservation was successful in retaining at least some mono-oxygenase activity. Microsomal activities of PROD were generally similar to those of EROD, suggesting that pentoxyresorufin was functioning as an inefficient substrate for CYP 1A rather than indicating concentrations of CYP 2B as it does in other mammals. Testosterone concentrations in male beluga were analysed to see if there was any correlation with contaminant distribution. Testosterone was in the low ng/ml range. AChE, which is inhibited by various organic contaminants, notably organophosphates and carbamates, was also detectable in preserved beluga brain tissue. DNA adducts were detectable in liver, but showed no great variation from sample to sample.

The only statistical analyses carried out so far between biomarker measurements (EROD, measured at FWI) and contaminant distribution suggest correlations between EROD activity and PCB concentrations are weaker than those observed previously in beluga from Husky Lakes (Lockhart and Stewart 1992). In that previous analysis, the whales were starving and this may have increased circulatory concentrations (and hence effects) of PCBs.

Beluga whale blood contained high concentrations of mercury: about one-third of the samples had mercury concentrations above the 100 ng/g "risk threshold" estimated for human blood. This raises concerns about the susceptibility of the whales to high Hg concentrations, and their significance as a vector of contaminants to people.

DISCUSSION/CONCLUSIONS

Indicators of mono-oxygenase activity (EROD and CYP 1A) were present in all beluga liver samples. Preliminary analyses suggest that EROD activities were not well correlated with PCB concentrations.

Other biochemical studies (testosterone, brain AChE and DNA adduct distribution) showed that all these variables were detectable in beluga tissue, but as yet no clear correlation exists between them and contaminant distribution.

Expected project completion date: March 31 1996.

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TRENDS AND EFFECTS OF ENVIRONMENTAL CONTAMINANTS IN ARCTIC SEABIRDS, WATERFOWL, AND OTHER WILDLIFE: CONTAMINANTS IN WATERFOWL: NATIVE HARVEST IN THE YUKON

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Project Team: B. Wakeford, CWS, Hull; J. Hawkings, CWS, Whitehorse; D. Mossop, Yukon Renewable Resources; M. Gamberg, contractor, Watson Lake

OBJECTIVES

1. To determine the levels and geographical distribution of contaminants in arctic wildlife with particular emphasis on avian species;

2. To provide Health Canada with a data set on contaminants in waterfowl and other game birds that are potential food sources for native people, so that potential health risks to the human consumer may be evaluated.

DESCRIPTION

There is only limited information available on contaminants 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 describe spatial and temporal trends, or the degree of contamination of those species. This study will lead to a better understanding of the contribution of specific contaminants to the native diet, and it will also enable the assessment of effects of contaminants on birds and other wildlife at the top of the arctic food web. In addition, the information gathered will 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 human health risks resulting from consumption of harvested waterfowl. The Nunavik survey was followed by surveys in Labrador in 1992/93, in the Northwest Territories in 1993/94, and in the Yukon Territory in 1994/95.

In 1994/95, the specific objectives were to collect birds and eggs commonly harvested and consumed by native people in the Yukon Territory, to undertake chemical analyses of these samplings, and to submit the resulting data to Health Canada for evaluation of human health risks related to consumption.

ACTIVITIES IN 1994/95

Collections of birds and eggs representative of the hunted/harvested population in the Yukon Territory were requested. Eggs were collected by hand and adult birds were shot and gathered. Samples were collected under permit by local native hunters, enforcement officers and territorial biologists. Collection, storage, and analytical protocols as specified by the National Wildlife Research Centre (NWRC), Hull, Quebec, were followed. All tissues were processed by the Laboratory Services Section of the Canadian Wildlife Service (CWS) at NWRC. Breast muscle was chosen as the tissue most representative of the edible portion of the bird. Where adequate tissue is available, samples of breast muscle will be sent to the Radiation Protection Bureau of Health Canada for radiocesium analyses. As well, samples have been sent to the Norwegian Institute for Nature Research in support of an international study on metals in Willow Ptarmigan.

Breast muscle and egg contents are being analysed for PCBs, organochlorines, mercury, cadmium, lead and selenium at the CWS laboratories at NWRC. 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 analysed.

RESULTS

A total of 3 collections of 3 species of eggs and 62 collections of 17 species of birds commonly harvested and consumed by native people were gathered from six general areas in the Yukon Territory in 1994 (Table 1). Organochlorine residue data available to date (1988-1994 inclusive) for the Yukon Territory are presented in Table 2. Organochlorine residues in harvested eggs are presented in Table 3. The results for metals are not yet available.

Residue levels of organochlorines found in breast muscle were generally quite low (Table 2). The most commonly detected residues were ΣPCBs, ΣDDT, ΣChlordanes and ΣChlorobenzenes with HCH also prevalent in the diving species. Those species which feed at a lower trophic level, such as ptarmigan, grouse and geese, contained lower organochlorine levels than most of the ducks. Since most of the waterfowl harvest occurred in the spring, variation in organochlorine levels found among the species is probably linked to the different overwintering grounds further south.

Organochlorine levels in eggs were generally low and did not vary greatly among the three species analyzed (Table 3). Residue levels in the Yukon herring gull eggs were up to an order of magnitude lower for some compounds than levels found in herring gull eggs collected from northern Quebec in 1991 (Braune 1993) and the Great Lakes in 1993 (CWS, unpubl. data). The probable use of the Great Lakes for overwintering by the northern Quebec gulls is likely a contributing factor to the organochlorine levels found in those birds.

DISCUSSION/CONCLUSIONS

All chemical data collected from both the Yukon and Northwest Territories in the period from 1993 to 1995 will be submitted to Health Canada by fall 1995 for evaluation of human health risks related to consumption of harvested birds and eggs. Health Canada has issued its report with recommendations for earlier residue data (1988-92) for samples collected from the N.W.T., Yukon and northern Quebec. These recommendations have been forwarded to the appropriate local 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

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Table 1. Harvested Birds and Eggs sampled in Yukon during 1994.

	Species Sampled			Species Sampled	
Location	**Birds**	**Eggs**	**Location**	**Birds**	**Eggs**
Old Crow area	Willow Ptarmigan		**Whitehorse area**	Ptarmigan sp.	
	Spruce Grouse			Ruffed Grouse	
	Mallard			Spruce Grouse	
	Green-winged Teal			Mallard	
	Wigeon			Green-winged Teal	
	Canada Goose			Wigeon	
	Northern Pintail			Northern Pintail	
	Lesser Scaup				
	Common Goldeneye		**Teslin-Tagish area**	Willow Ptarmigan	Mallard
	Barrow's Goldeneye			Spruce Grouse	Herring Gull
	Surf Scoter			Malard	Ring-billed Gull
	White-winged Scoter			Green-winged Teal	
				Bufflehead	
Dawson Area	Spruce Grouse			Common Goldeneye	
	Ruffed Grouse			Barrow's Goldeneye	
	Rock Ptarmigan			Oldsquaw	
	Willow Ptarmigan				
	Mallard		**Watson Lake area**	Ruffed Grouse	
	Northern Pintail			Spruce Grouse	
	Northern Shoveler			Canada Goose	
				Green-winged Teal	
Champagne-Aishihik area	Spruce Grouse			Northern PIntail	
	Canada Goose			Ring-necked Duck	
	Wigeon			Bufflehead	
	Northern Pintail			Common Goldeneye	
	Green-winged Teal			Lesser Scaup	
	Ring-necked Duck			Surf Scoter	
	Lesser Scaup			White-winged Scoter	
	Barrow's Goldeneye				

Table 2. Mean Levels of Organochlorines in Breast Muscle of Birds Harvested in the Yukon, 1988-1994.

			mg/kg (ppm) wet weight							
	#	%	ΣCB	ΣHCH	OCS	ΣChlord	ΣDDT	Mirex	Dieldrin	ΣPCB
BROWSERS										
Rock Ptarmigan	3	2.3	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Willow Ptarmigan	12	1.5	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.002
Ptarmigan *sp.*	6	1.6	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Ruffed Grouse	4	2.9	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Spruce Grouse	24	3.9	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
GRAZERS										
Canada Goose	8	3.2	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	<0.001	<0.001
SURFACE-FEEDING DUCKS										
Mallard	42	2.4	<0.001	<0.001	<0.001	0.001	0.043	<0.001	0.001	0.001
Northern Pintail	27	3.4	0.006	<0.001	<0.001	0.002	0.036	<0.001	0.001	0.014
American Wigeon	17	3.0	<0.001	<0.001	<0.001	<0.001	0.009	<0.001	<0.001	<0.001
Northern Shoveler	3	2.5	0.015	<0.001	0.002	0.010	0.507	<0.001	0.001	0.115
Green-winged Teal	26	2.8	0.012	<0.001	<0.001	0.005	0.146	<0.001	0.001	0.025
DIVING DUCKS										
Ring-necked Duck	2	2.8	<0.001	<0.001	<0.001	0.001	0.051	<0.001	<0.001	0.002
Lesser Scaup	26	3.3	0.002	<0.001	<0.001	0.003	0.053	<0.001	<0.001	0.064
Common Goldeneye	14	3.4	0.002	0.001	<0.001	0.002	0.010	<0.001	<0.001	0.005
Barrow's Goldeneye	8	3.7	0.003	0.002	<0.001	0.002	0.005	<0.001	<0.001	0.004
Bufflehead	11	2.7	0.002	0.001	<0.001	0.001	0.007	<0.001	<0.001	0.005
Oldsquaw	3	3.9	0.008	0.027	<0.001	0.008	0.003	<0.001	0.004	0.003
White-winged Scoter	24	4.0	0.002	0.001	<0.001	0.001	0.004	<0.001	<0.001	0.004
Surf Scoter	15	3.9	0.006	0.001	<0.001	0.003	0.077	<0.001	<0.001	0.054

Residue values in table are weighted means factoring in the number of birds in each pooled analysis.

Browsers–eat mainly terrestrial vegetation
Grazers– eat terrestrial and aquatic vegetation
Surface-feeding Ducks– eat mainly aquatic vegetation
Diving Ducks– eat more animal matter than surface-feeding ducks; goldeneye, bufflehead, oldsquaw and scoter eat primarily molluscs and crustaceans.

ΣCB = Sum Chlorobenzenes (1,2,3,5- & 1,2,3,4-tetracholrobenzene, pentachlorobenzene and hexachlorobenzene)
ΣHCH - Sum of α–, β–, and γ-hexachlorocyclohexanes
OCS = octachlorostyrene
ΣChlord - Sum Chlordanes (*oxy-, trans-* & *cis*-chlordane, *trans-* & *cis*-nonachlor and heptachlor epoxide)
ΣDDT - Sum of *pp'*-DDE, *pp'*-DDD and *pp'*-DDT
Σ Mirex = Sum of photo-mirex and mirex
ΣPCB - Sum of PCB congeners 28, 31, 44, 52, 60, 66/95, 87, 97, 99, 101, 105, 110, 118, 138, 141, 146, 153, 170/190, 171, 172, 174, 180, 182/187, 183, 194, 195, 201, 203, 206.

Table 3. Levels of Organochlorines in Eggs Harvested in the Yukon During May 1994.

Species	N	Location	% Lipid	mg/kg (ppm) wet weight ΣCB	ΣHCH	OCS	ΣChlord	ΣDDT	ΣMirex	Dieldrin	ΣPCB
Mallard	5	Teslin Lake	16.0	0.019	0.002	ND	0.023	0.379	0.004	0.016	0.248
Ring-billed Gull	5	Teslin Lake	9.6	0.015	0.007	ND	0.029	0.351	0.002	0.007	0.279
Herring	5	Tagish Lake	9.9	0.025	0.018	0.002	0.043	0.517	0.009	0.011	0.334

ΣCB = Sum Chlorobenzenes (1,2,3,5- & 1,2,3,4-tetracholrobenzene, pentachlorobenzene and hexachlorobenzene)
ΣHCH - Sum of α–, β–, and γ–hexachlorocyclohexanes
OCS = octachlorostyrene
ΣChlord - Sum Chlordanes (*oxy-*, *trans-* and *cis*-chlordane, *trans-* and *cis*-nonachlor and heptachlor epoxide)
ΣDDT - Sum of *pp'*-DDE, *pp'*-DDD and *pp'*-DDT
ΣMirex = Sum of photo-mirex and mirex
ΣPCB - Sum of PCB congeners 28, 31, 44, 52, 60, 66/95, 87, 97, 99, 101, 105, 110, 118, 138, 141, 146, 153, 170/190, 171, 172, 174, 180, 182/187, 183, 194, 195, 201, 203, 206.

TEMPORAL TRENDS IN CONTAMINANT LEVELS OF THE PEREGRINE FALCON AND ITS PREY IN THE KEEWATIN DISTRICT OF THE NORTHWEST TERRITORIES

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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 and compare two top avian carnivores as an indicator of arctic ecosystem health.

DESCRIPTION

Court *et al.* (1990) assessed the contamination of 14 avian species breeding around Rankin Inlet in the Keewatin District of the NWT and concluded that significant amounts of organochlorine pesticides and ΣPCB residues were accumulated by 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 Tundra Peregrine Falcons *(Falco peregrinus tundrius).* Eggshell thinning, levels of DDE residues in eggs, and the levels of contaminants found in some prey species were all close to the critical levels considered to result in decreased production for the peregrine falcon (Court *et al.* 1990, Peakall and Kiff 1988, Peakall *et al.* 1990).

This study was initiated to establish the present level of contamination in 10 common avian prey species, two mammalian prey species and the same population of tundra peregrines as Court *et al.* (1990). Information regarding contamination of the avian component of terrestrial ecosystems in the North is limited and is mainly based on raptors and waterfowl (Thomas *et al.* 1992). Secondly, we assessed the biological significance of these contaminants; whether or not contaminant levels in lower trophic level species are within ranges known to interfere with reproductive success in the tundra peregrine, a top avian carnivore of the Arctic ecosystem. By adopting the same protocol as Court *et al.* (1990) and the same study population, we were also able to assess temporal trends in contaminant levels between the early 1980s and the 1990s. 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). To identify whether the source of contamination is distant or local we compared residue levels of two avian top carnivores, the Tundra Peregrine Falcon which preys upon migratory birds and also lemmings, and the Rough-legged Hawk *(Buteo lagopus),* which eats non-migratory small mammals.

ACTIVITIES IN 1994/95

Data and samples were collected between May 10 and September 1 of 1994 around Rankin Inlet, Keewatin District, NWT. Eight whole peregrine eggs, eggshell fragments from 20 nests and plasma samples from 70 peregrines were collected. Plasma samples were also collected from ten juvenile rough-legged hawks. Production of the Rankin Inlet peregrine population and other standard population parameters were measured throughout the field season.

The 1994 field season represented the fourth and final year of sampling at Rankin Inlet. Toxicological analysis of all the samples collected between 1991 and 1994 was completed at the Health of Animals Laboratory, Agriculture and Agri-Food Canada, Saskatoon in early 1995. The thickness of peregrine eggshell was measured using an optical micrometer at the Department

of Engineering, University of Alberta, Edmonton. The complete contaminant residue data set was analyzed and interpreted during 1994/95. Re-analysis of the provisional residue levels published in the 1993/94 Northern Contaminants Program Synopsis of Research Report demonstrated an error in tabulation and these levels have been corrected. A paper detailing the complete toxicological assessment undertaken during the study period 1991-1995 is in final preparation and will be submitted for publication in July 1995.

RESULTS

Contaminant Levels

Analysis of our sample showed the continuing contamination of arctic-breeding avian species by organochlorines. ΣPCB, DDE, dieldrin, and heptachlor epoxide residues were detected in most avian species (Table 1). Variation in residue levels appeared related to the habitat occupied, i.e. terrestrial vs. aquatic, and the trophic level of the species, not to migration range as has been previously hypothesized. For example, Oldsquaw, a diving duck feeding mainly on invertebrates, recorded the highest mean organochlorine residue levels of all prey species consumed by peregrines in the study area.

Two mammalian species, Arctic ground squirrels *(Spermophilus parryi)* and Collared lemmings *(Dicrostonyx groenlandicus),* were also collected for analysis. Unlike the avian prey species, they are non-migratory. Any residue levels in these mammals will reflect the contamination of the local environment. We found little evidence suggesting contamination of the local environment. Organochlorine residues were recorded at detectable levels in just one of 13 whole body homogenates of lemmings. Though exposure to PCBs around Rankin Inlet is possible, direct exposure of lemmings to DDE and DDT is unlikely. The single contaminated lemming specimen may be explained by an omnivorous diet; the inclusion of tundra nesting bird's eggs in its diet could explain the high levels found in this one lemming relative to the rest of the sample. However, this sample was collected within six km of the Rankin Inlet community, so it may also indicate a point source of local contaminants.

Contaminant levels of peregrines at Rankin Inlet are higher than other populations of *F. p. tundrius.* The mean residue levels of DDE in the plasma of post-laying after-second-year (ASY) females that we sampled are three to four times the levels found in post-laying ASY females breeding in Greenland and mean ΣPCB levels are three to five times higher than in Greenland (Jarman *et al.* 1994).

Rankin Inlet peregrines also show higher residue levels in egg contents than *F. p. tundrius* in Alaska (Swem 1994, T. Swem and S. Ambrose US Fish and Wildlife Service unpublished data). Mean DDE levels are similar between Rankin Inlet and Greenland populations (4.5 vs. 3.3 mg/kg wet weight) but maximum levels are much higher at Rankin Inlet (28.1 vs. 5.3 mg/kg wet wt.). None of the eggs from the Alaskan sample exceed critical levels whereas 10% of clutches from Rankin Inlet include eggs exceeding minimum critical levels (15-20 mg/kg, Peakall *et al.* 1990).

Another measure of the contamination of the immediate terrestrial environment around Rankin Inlet was gained from tissues of Rough-legged hawks, a species which preys mainly on small mammals. We took blood samples from Rough-legged hawk nestlings just prior to fledging. Having never migrated, any contaminants detected in nestlings would have been accumulated from local sources, though there may be some residual contamination from the egg contents. We did not record any organochlorines at detectable levels in plasma samples from seven Rough-legged hawk nestlings.

Biological Significance

Residue levels from whole body analysis of 10 avian species preyed upon by peregrines shows the presence of organochlorine contaminants. In most species, they were found at low levels and there is considerable variation in levels between species. A suite of measurements from the peregrine falcon, the top carnivore in the avian component of this arctic ecosystem, also showed the presence of organochlorine contaminants at detectable levels. What then is the biological significance of the presence of these contaminants? Do they occur in levels known to produce some lethal or sub-lethal effect on individuals and/or populations of the species concerned?

Peregrine falcons are extremely sensitive to organochlorine contaminants and are known to experience reproductive failure as a consequence of dietary intake of contaminants at relatively low levels. Organochlorine residue levels in some prey species at Rankin Inlet are consistent with levels previously shown to affect the reproductive success of peregrines (Table 1). Baril *et al.* (1990) concluded that only three residues in prey species—DDE, ΣPCB and dieldrin—are likely to affect reproduction in peregrines. We found that critical dietary levels of ΣPCB for peregrines (5 ppm, Baril *et al.* 1990) were exceeded in Oldsquaw *(Clangula hyemalis).*

Maximum detected levels of ΣPCB residues in Pintail *(Anas acuta)* also exceeded critical ΣPCB levels. Mean DDE residue levels in Oldsquaw exceeded critical levels (1 ppm, Baril *et al.* 1990), while our sample of Water Pipits *(Anthus spinoletta)* and Semipalmated Plovers *(Charadius semipalmatus)* included individuals with levels exceeding critical levels. Critical levels for dieldrin (0.1 ppm, Baril *et al.* 1990) were exceeded in Oldsquaw, Pintail, and some Semipalmated Plovers.

Residue levels in egg contents are consistent with the peregrines preying on a partly contaminated prey base (Table 3). Mean residue levels of 28 eggs, representing 20 clutches were below minimum critical levels, but 10% (two) of clutches included eggs with detected levels of ΣPCB, DDE and dieldrin exceeding minimum critical levels (Peakall *et al.* 1990).

The thickness of peregrine eggshell collected from Rankin Inlet concurs with the other data sets. The mean thickness of eggshell collected between 1991 and 1994 was 15% thinner than the pre-DDT shell thickness for peregrines from the Nearctic. Almost one-third of the sample included eggs with shells thinner than critical levels (Peakall *et al.* 1990).

Temporal Trends

Mean residue levels of dieldrin and ΣPCB in peregrine eggs have not shown any change between decades (Table 3). Mean DDE residues in eggs have decreased slightly but the difference is small and biologically insignificant. The proportion of eggs in the sample with DDE residues exceeding minimum critical levels has not changed between decades. That the changes in mean residue levels in eggs between decades are biologically insignificant is confirmed by measurements of eggshell thickness. We found no difference in the thickness of eggshell between decades. Residue levels in the blood plasma of adult males and chicks support trends found in egg residues and eggshell thickness. There has been no improvement in plasma DDE, dieldrin, or ΣPCB residue levels between decades, in fact ΣPCB residues in chicks have increased. The temporal trends in plasma residues of adult female peregrines do not concur with the rest of the data set. There has been no change in plasma ΣPCB residues in adult females, but DDE, dieldrin, and heptachlor epoxide residues have decreased between decades.

DISCUSSION/CONCLUSIONS

Contrary to predictions, we could find no evidence of a declining trend in contaminant levels in arctic-breeding peregrine falcons and their prey species at Rankin Inlet. The peregrine population must be considered representative of a population that, while productive, may still experience organochlorine-related reproductive failure. The lack of a decline is in direct contrast to populations of *F. p. tundrius* from both Greenland and Alaska, where residue levels have decreased within the last decade (Jarman *et al.* 1994, Swem 1994).

Most studies attribute continuing contamination of raptors to the use of prey species upon the breeding grounds that have accumulated contaminants while wintering in Latin America, or the use of contaminated resident species while the peregrines are on their wintering grounds in Latin America. Either way, Latin America, where organochlorine insecticides continue to be used, is indicated as a major source of contaminants. This study provides some evidence that not all pollutants originate from these areas.

The source of contaminants found in arctic breeding peregrines and their prey species must be distant to Rankin Inlet. Low or even nil residue levels from non-migratory mammals and the rough-legged hawk, an avian carnivore which exploits a mammalian prey base, suggest that the local terrestrial environment is essentially free of organochlorine contaminants. The contaminants found in peregrines and their prey must originate elsewhere.

The higher levels of contaminants recorded in Rankin Inlet peregrines relative to their Alaskan and Greenland conspecifics must be due to differences in dietary intake. Band returns and recent satellite tracking of *F. p. tundrius* from Alaska, Greenland and Rankin Inlet indicate that they share a common migratory route from the lower United States and also occupy similar wintering areas (T. Swem *pers comm.*, J. Dayton *pers comm.*, unpublished satellite telemetry data). Thus, any differences in contaminant levels between populations is not due to differences in diet while wintering in Latin America, but must reflect differences in dietary intake on the breeding grounds. Dietary studies of these three populations show that Oldsquaw are the missing element from Greenland and Alaskan peregrine prey species (Duncan 1993, Bradley and Oliphant 1991, Falk *et al.* 1986, Burnham and Mattox 1984, T. Swem pers comm.). It is the most heavily contaminated waterfowl surveyed in the Northwest Territories (Braune 1994), and is the most contaminated prey species taken by peregrines at Rankin Inlet. It is also the greatest single species contributor to the diet of peregrines here, accounting for up to 25% of the peregrine diet by biomass at the nestling stage (Duncan 1993). The Oldsquaw is also one of the least migratory species

preyed on by peregrines at Rankin Inlet, wintering in the Great Lakes and along the Atlantic Seaboard as far south as Chesapeake Bay (Godfrey 1986).

Continued reproductive problems of the top avian carnivore in this Arctic ecosystem appears as much related to the continued contamination of a species that spends most of its time within North America, particularly the Great Lakes ecosystem, as it is related to continued pesticide use in South America. We conclude that further decreases in organochlorine contamination of peregrines breeding at Rankin Inlet in the Northwest Territories are primarily related to declines of these contaminants in marine and aquatic ecosystems within North America, and secondarily to a decrease in use of organochlorines in Latin America.

Expected project completion date: July 1995

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Table 1. Selected organochlorine residues (mg/kg wet wt.) in prey species of Peregrine Falcons nesting at Rankin Inlet (1991-1994).

Species	N	Residues ΣPCB	DDE	Dieldrin
Oldsquaw *Clangula hyemalis*	5	6.88 (2.88- 18.88)	1.09 (0.61- 3.75)	0.51 (0.02- 4.02)
Black Guillemot *Cepphus grylle*	8	0.38 (0.13- 0.65)	0.17 (0.10- 0.24)	0 (0- 0.02)
Pintail *Anas acuta*	4	2.11 (0- 5.40)	0.47 (0.09- 0.91)	0.09 (0.03- 0.26)
Semipalmated Plover *Charadius semipalmatus*	5	0.40 (0- 2.06)	0.50 (0.10- 1.07)	0.02 (0- 0.11)
Semipalmated Sandpiper *Calidris pusilla*	3	0.03 (0- 0.10)	0.25 (0.04- 0.70)	ND
Water Pipit *Anthus spinoletta*	5	0.14 (0- 0.79)	0.69 (0-9.50)	ND
Horned Lark *Eremophila alpestris*	7	0.01 (0- 0.06)	0.07 (0- 0.17)	ND
Lapland Longspur *Calcarius lapponicus*	10	0.03 (0- 0.36)	0.01 (0- 0.02)	ND
Snow Bunting *Plectrophenax nivalis*	2	0.03 (0- 0.06)	ND	ND
Dunlin *Calidris alpina*	1	ND	0.04	ND
Mammals				
Arctic Ground Squirrels *Spermophilus parryi*	7	ND	ND	ND
Collared Lemmings* *Dicrostonyx groenlandicus*	13	0.06 (0- 4.17)	0.01 (0- 0.11)	ND

* Contaminants were only found in one collared lemming who had levels (mg/kg wet wt.) of ΣPCB 4.168, DDE 0.114, DDD 0.068, and DDT 0.080.
ND means that residues were not found at detectable levels.

Table 2. Geometric mean levels of selected organochlorine residues (mg/kg wet wt.) in the blood plasma of post-laying ASY female Peregrine Falcons sampled at Rankin Inlet.

	n	SPCB (range)	HCE (range)	DDE (range)	Dieldrin (range)
Females 1991-94	26	0.95 (0-6.82)	0.03 (0-0.18)	0.46 (0-4.23)	0.04 (0-0.37)

Table 3. Minimum critical residue levels and detected organochlorine residues (mg/kg wet wt.) in Peregrine Falcon eggs collected at Rankin Inlet during 1982 to 1986 and 1991 to 1994.

	Critical level[1]	1991-1994 (n=20) Range	1991-1994 (n=20) Geometric mean	1982-1986 Range	1982-1986 Geometric mean	n	Difference[2] between years (P)
PCB	> 40	1.67-45.63	8.31	1.95-47.76	8.74	36	0.72
HCB	> 4.0	0-0.17	0.03	0-0.15	0.03	22	0.7105
BHC		0-0.03	0.00	0	0	19	
OXY		0.04-0.91	0.21	0.08-0.80	0.21	21	0.5408
HCE	> 1.5	0.05-1.39	0.27	0.09-5.92	0.36	36	0.1038
DDE	15-20	0.76-28.05	4.45	1.79-29.27	7.59	36	0.0062
DIEL	> 1.0	0.05-1.80	0.36	0.13-1.66	0.41	36	0.1997
DDD		0-0.20	0.01	0-0.37	0	22	0.2026
DDT		0-0.03	0.00	0-1.41	0	36	0.0482
MRX		0.06-1.82	0.50			NM	

[1] Following Peakall *et al.* (1990)
[2] Students t-test on log-transformed values
NM= not measured

IDENTIFICATION OF BASELINE LEVELS AND SPATIAL TRENDS OF ORGANOCHLORINE, HEAVY METAL AND RADIONUCLIDE CONTAMINANTS IN CARIBOU *(Rangifer tarandus)*

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Project Team: S. Bohnet; R. Bethke; local Hunters' and Trappers' organizations

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 geographic 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 (Wong 1985, Thomas *et al.* 1992). The scarcity of metal or organic residue data for terrestrial mammals has been identified as a data gap in Arctic contaminant research (Wong 1985). 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.

Barrenground caribou are strict herbivores that have a winter diet consisting primarily of lichen (Kelsall 1968, Parker 1978). Lichens accumulate contaminants more readily than other vascular plants because of their large surface area, longevity, and ability to bind heavy metals. Lichen can accumulate atmospheric contaminants in a non-selective manner, resulting in a contaminant load similar to atmospheric input through long-range transport (Thomas *et al.* 1992). 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 barrenground caribou herds across the NWT also make it a good 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 1994/95 were (1) to complete caribou collections from all 10 herds, (2) to determine organochlorine, metal and radionuclide residues in several caribou tissues, and (3) to begin evaluating the results from all ten herds tested.

ACTIVITIES IN 1994/95

Field Sampling

In 1994/95, the last of the field collections of barrenground caribou were completed in cooperation with local Hunters' and Trappers' organizations at Fort Smith and Ndilo/Fort Rae. Collections had been conducted in previous years at Arviat, Cambridge Bay, Cape Dorset, Inuvik, Lake Harbour, Pond Inlet, Southampton Island, Taloyoak, and the Beverly herd (Figure 1). Twenty 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 site were analysed for organochlorine and metals 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 analysed for organochlorine residues, and metal analysis was conducted on kidney and liver samples. Muscle samples from 10 caribou at each location were also analysed for radionuclides at AECL Whiteshell Laboratories in Pinawa, Manitoba. Samples from the remaining 10 caribou at each site were banked for future use.

RESULTS

The contaminant data set from the first 5 caribou herds sampled was reported previously. Results from the last 5 herds tested (Cambridge Bay, Inuvik, Pond Inlet, Taloyoak, Beverly herd) are presented here, with reference to data previously reported from the other 5 sites. A wide range of organochlorine contaminants were detected, with most compounds found at low levels and with less toxic compounds predominating. Mean residue levels of the predominant organochlorine compounds found are given by community in Table 1. In general, organochlorine contaminant levels decreased from east to west and from south to north (Figure 2).

HCB and HCH were found to be the predominant organic residues present, as seen in other terrestrial herbivores in the Canadian north (MacNeil *et al.* 1987, Thomas *et al.* 1992, Salisbury *et al.* 1992). Total HCH ranged from 3.33 $ng \cdot g^{-1}$ lipid corrected in fat from Inuvik caribou to 39.78 $ng \cdot g^{-1}$ at Cape Dorset, and consisted almost entirely of α–HCH. HCB residues ranged from a mean of 20.29 $ng \cdot g^{-1}$ in fat of Taloyoak caribou to 129.41 $ng \cdot g^{-1}$ in Lake Harbour animals. HCB and α–HCH were detected in fat samples from all caribou at all ten sites. HCB and HCH have been shown to be the predominant organochlorine contaminants in arctic air (Hargrave *et al.* 1988, Patton *et al.* 1988, Gregor and Gummer 1988), which suggests a direct air-plant-animal pathway into the terrestrial food chain (Thomas *et al.* 1992).

Oxychlordane, a major metabolite of several compounds in the pesticide technical chlordane, was the major chlordane-related compound detected. Total chlordane levels ranged from 0.11 $ng \cdot g^{-1}$ in Inuvik caribou to 5.01 $ng \cdot g^{-1}$ at Cape Dorset, with oxychlordane and to a lesser degree heptachlor epoxide predominating. The extent of transformation of chlordane in caribou is evident by the fact that *cis*- and *trans*-chlordane were only minor contaminants in all fat samples, although they form a major proportion of technical chlordane. Total DDT, comprised largely of *p,p'*-DDE, was below detection limits in Inuvik caribou, and ranged form 0.11 $ng \cdot g^{-1}$ in Beverly caribou to 2.58 $ng \cdot g^{-1}$ at Cape Dorset. Total PCB (ΣPCB) residues (sum of 43 congeners) ranged from a mean of 1.02 $ng \cdot g^{-1}$ lipid corrected in fat of Inuvik caribou to 31.68 $ng \cdot g^{-1}$ at Cape Dorset. The PCB congener patterns were similar at all sites, with greater accumulation of more highly chlorinated congeners (Figure 3). PCB-153 was bioaccumulated to the greatest extent at all 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 cadmium were detected in caribou kidney and liver tissue from all sites (Figure 4). Levels in kidney tissue ranged from 7.49 $\mu g \cdot g^{-1}$ dry weight in Taloyoak caribou to 42.71 $\mu g \cdot g^{-1}$ at Inuvik, and levels in liver ranged from 0.98 $\mu g \cdot g^{-1}$ at Pond Inlet to 5.83 $\mu g \cdot g^{-1}$ at Inuvik. The levels detected are similar to levels found in caribou in the NWT and Yukon (Gamberg and Scheuhammer 1994), and are comparable to those found in caribou in northern Quebec and reindeer in Norway (Froslie *et al.* 1986, Scanlon *et al.* 1988, Crête *et al.* 1987 1989), and moose and white tail deer from Ontario and Newfoundland (Glooshenko *et al.* 1988, Brazil and Ferguson 1989). Mercury levels were generally low, with means in liver ranging from 0.16 $\mu g \cdot g^{-1}$ in Bathurst caribou to 0.92 $\mu g \cdot g^{-1}$ at Arviat. These levels were slightly higher than levels found in livers of reindeer from Sweden and Norway, which had levels in liver up to 0.19 $\mu g \cdot g^{-1}$ and 0.24 $\mu g \cdot g^{-1}$ respectively (Froslie *et al.* 1984, Erikson *et al.* 1992).

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 cesium-137, cesium-134 and potassium-40 (Figure 5). ^{137}Cs was the most predominant radionuclide, with activity ranging from 2.83 $Bq \cdot Kg^{-1}$ at Inuvik to 184.10 $Bq \cdot kg^{-1}$ in Lake Harbour caribou. Levels of ^{134}Cs ranged from <0.37 $Bq \cdot Kg^{-1}$ in Bathurst caribou to <0.71 $Bq \cdot kg^{-1}$ in Cambridge Bay animals. ^{137}Cs and ^{134}Cs are fission products, and most cesium in the Canadian Arctic originated from atmospheric testing of nuclear and thermonuclear devices that began in 1955 and peaked between 1961 and 1963. The levels of ^{137}Cs measured in caribou muscle during the 1960s and 1980s indicate that concentrations in caribou decreased considerably following the moratorium on atmospheric weapons testing reached in 1963 (Thomas *et al.* 1992). The results from this study are consistently at the lower range of values found from 1986 to 1988, consistent with the view

of declining Cs levels in the Arctic. The levels of ^{134}Cs in this study were very low, and most likely derived from the Chernobyl accident. ^{40}K, a naturally occurring radionuclide with a very long half-life, was also consistently found in all samples at levels similar to those reported for moose in southern Manitoba (Zach *et al.* 1989).

DISCUSSION/CONCLUSIONS

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 kidney and liver from caribou in the NWT are comparable with findings in other big game species in Canada, and are most consistent with long-range atmospheric transport (Elkin and Bethke 1994). The levels of ^{137}Cs, the predominant radionuclide in this study, support 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 have conducted a human health risk assessment on the complete organochlorine, heavy metal and radionuclide data set from all 10 sites, which indicated that caribou meat is safe to eat in unlimited quantities.

Expected project completion date: Field collections of barrenground caribou were completed in 1994/95. Collection of woodland caribou samples and completion of contaminant analyses will be done in 1995/96. Data evaluation/interpretation and community consultation/ communication of results will be completed by the end of 1996/97.

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Table 1. Arithmetic means ($ng \cdot g^{-1}$, lipid corrected [SE] of selected organochlorine residues in fat of caribou collected from five sites in the NWY. For each compound, site means having the same superscript were not significantly different ($p < 0.05$). ND is given where residues in all samples were below the detection limit.

Compound	Collection Sites				
	Inuvik	Beverly	Cambridge Bay	Taloyoak	Pond Inlet
n	9	9	10	10	10
% Lipid	84.39 (1.56)	81.20 (2.27)	81.45 (3.40)	95.03 (1.58)	88.01 (1.52)
HCB	26.00^{c} (1.95)	24.29^{c} (1.64)	41.29^{b} (6.15)	20.29^{c} (2.53)	82.78^{a} (5.72)
Dieldrin	ND^{c}	0.02^{c} (0.01)	ND^{c}	0.08^{b} (0.03)	0.24^{a} (0.04)
ΣHCH	3.33^{c} (0.28)	4.34^{c} (0.50)	15.52^{a} (2.21)	9.46^{b} (1.35)	13.98^{a} (1.42)
ΣChlordane[2]	0.11^{c} (0.02)	0.12^{c} (0.02)	0.80^{a} (0.11)	0.44^{b} (0.05)	0.61^{a,b} (0.08)
ΣDDT[3]	ND^{d}	0.11^{c} (0.03)	0.33^{b} (0.11)	0.18^{b} (0.02)	0.73^{a} (0.18)
ΣPCB[4]	1.02^{c} (0.06)	2.83^{b} (0.40)	6.64^{a} (1.06)	2.39^{b} (0.34)	6.52^{a} (1.06)

[1] ΣHCH = Sum of α–HCH, β-HCH and γ–HCH.
[2] ΣChlordane = Sum of *oxy-*, *cis-* and *trans*-chlordane, *cis-* and *trans*-nonachlor, and heptachlor epoxide.
[3] ΣDDT = Sum of *p,p'*-DDT, *p,p'*-DDE and *p,p'*-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-1, [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				
	Inuvik	Beverly	Cambridge Bay	Taloyoak	Pond Inlet
n	10	10	10	10	10
% Water	77.66 (0.82)	78.75 (0.36)	78.71 (0.89)	79.39 (0.70)	78.78 (0.41)
Al	0.36^{c} (0.06)	0.44^{c} (0.09)	$1.05^{b,c}$ (0.32)	$1.34^{a,b}$ (0.19)	2.78^{a} (0.33)
Cd	42.71^{a} (9.25)	30.96^{a} (4.23)	9.41^{c} (1.73)	7.40^{c} (0.68)	14.54^{b} (0.89)
Cr	0.23^{b} (0.03)	0.23^{b} (0.03)	0.44^{a} (0.34)	0.79^{a} (0.32)	0.71^{a} (0.04)
Cu	26.25^{b} (2.02)	24.53^{b} (0.53)	29.59^{a} (1.04)	25.99^{b} (0.84)	18.44^{c} (0.55)
Fe	262.82^{a} (38.25)	291.53^{a} (21.03)	271.26^{a} (35.54)	219.86^{a} (20.46)	234.94^{a} (19.19)
Mn	8.61^{b} (0.54)	6.63^{c} (0.21)	11.41^{a} (1.26)	8.33^{b} (0.29)	11.09^{a} (0.30)
Ni	0.10^{b} (0.00)	0.10^{b} (0.00)	0.31^{b} (0.10)	0.40^{b} (0.18)	0.53^{a} (0.03)
Pb	0.06^{b} (0.01)	0.10^{b} (0.04)	0.48^{a} (0.13)	0.32^{a} (0.04)	0.44^{a} (0.13)
Zn	121.82^{a} (4.68)	117.80^{a} (3.76)	110.58^{a} (3.50)	113.74^{a} (8.15)	124.71^{a} (2.86)
Hg	1.88^{a} (0.19)	2.16^{a} (0.19)	0.87^{b} (0.12)	1.05^{b} (0.15)	2.17^{a} (0.18)

Table 3. Arithmetic means of metal concentrations in liver of caribou collected from five sites in the NWT. All concentrations (µg•g-1, [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				
	Inuvik	Beverly	Cambridge Bay	Taloyoak	Pond Inlet
n	10	10	10	10	10
% water	69.71 (0.71)	70.16 (0.68)	70.78 (0.70)	71.10 (0.66)	71.06 (0.49)
Al	0.48^{c} (0.13)	0.71^{c} (0.29)	$1.36^{a,b}$ (0.20)	1.19^{b} (0.35)	2.20^{a} (0.12)
Cd	5.83^{a} (1.00)	3.42^{a} (0.27)	1.35^{b} (0.32)	1.06^{b} (0.08)	0.98^{b} (0.14)
Cr	0.20^{a} (0.00)	0.20^{a} (0.00)	0.09^{a} (0.05)	0.16^{a} (0.10)	0.59^{a} (0.04)
Cu	29.68^{c} (3.60)	75.39^{b} (15.11)	155.94^{a} (28.01)	$40.49^{b,c}$ (8.84)	$48.92^{b,c}$ (6.49)
Fe	1233.11^{b} (167.36)	$1502.08^{a,b}$ (231.21)	$2081.16^{a,b}$ (352.66)	$1534.70^{a,b}$ (290.69)	2647.19^{a} (617.98)
Mn	9.89^{b} (0.44)	$9.21^{b,c}$ (0.49)	11.54^{a} (0.42)	8.62^{c} (0.49)	$10.26^{a,b}$ (0.35)
Ni	$0.13^{a,b}$ (0.03)	$0.10^{a,b}$ (0.00)	0.07^{b} (0.03)	$0.12^{a,b}$ (0.04)	0.28^{a} (0.05)
Pb	0.12^{b} (0.04)	0.07^{b} (0.02)	0.61^{a} (0.13)	0.62^{a} (0.17)	0.56^{a} (0.13)
Zn	80.76^{a} (4.91)	86.96^{a} (9.71)	92.61^{a} (16.10)	93.05^{a} (8.99)	80.08^{a} (3.48)
Hg	0.49^{a} (0.06)	0.37^{a} (0.04)	0.22^{b} (0.02)	0.23^{b} (0.03)	0.39^{a} (0.05)

Table 4. Arithmetic means of radionuclide activities ($Bq \cdot kg^{-1}$ wet weight [SE]) in muscle of caribou collected from five sites in the NWT. Values indicated by '<' are reported as the minimum detectable limit.

Radionuclide	Colection Sites				
	Inuvik	Beverly	Cambridge Bay	Taloyoak	Pond Inlet
n	10	10	10	10	10
% Dry Weight	29.40 (1.65)		25.10 (0.29)	26.40 (0.27)	2940 (1.65)
^{137}Cs	2.83 (0.38)		20.30 (1.68)	14.80 (1.41)	36.50 (8.22)
^{134}Cs	<0.39		<0.71	<0.46	<0.40
^{40}K	99.30 (4.11)		92.40 (1.55)	112.00 (2.38)	108.00 (2.43)
^{232}Th	<1.26		<2.29	<1.47	<1.27
^{235}U	<1.99		<3.61	<2.32	<2.00
^{226}Ra	<1.05		0.57 (0.09)	0.64 (0.14)	0.81 (0.10)
^{60}Co	<0.57		<1.04	<0.67	<0.58

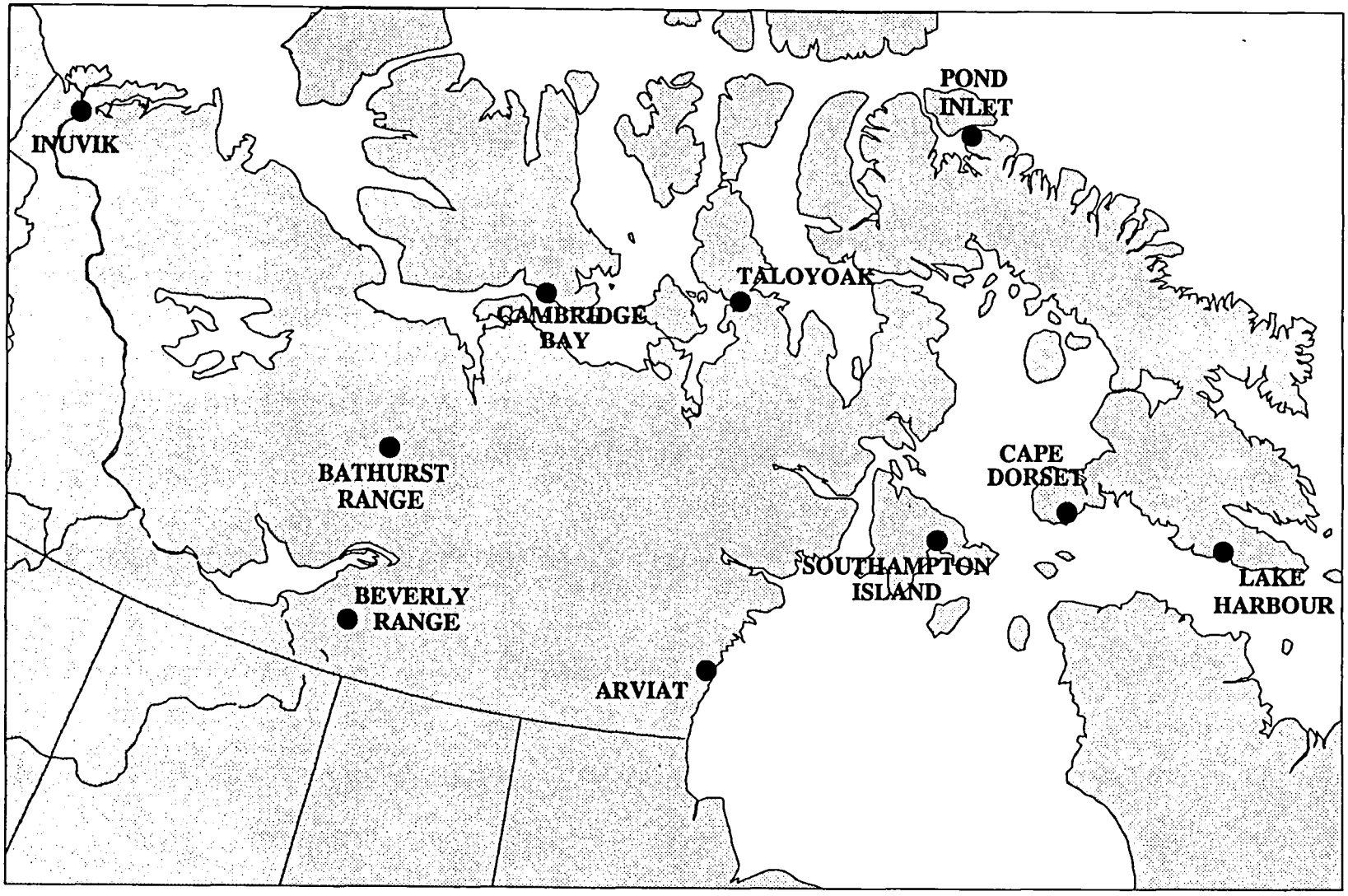

Figure 1. Sites in the Northwest Territories where caribou collections were conducted between 1991 and 1995. All collections were made within 100 km of the site

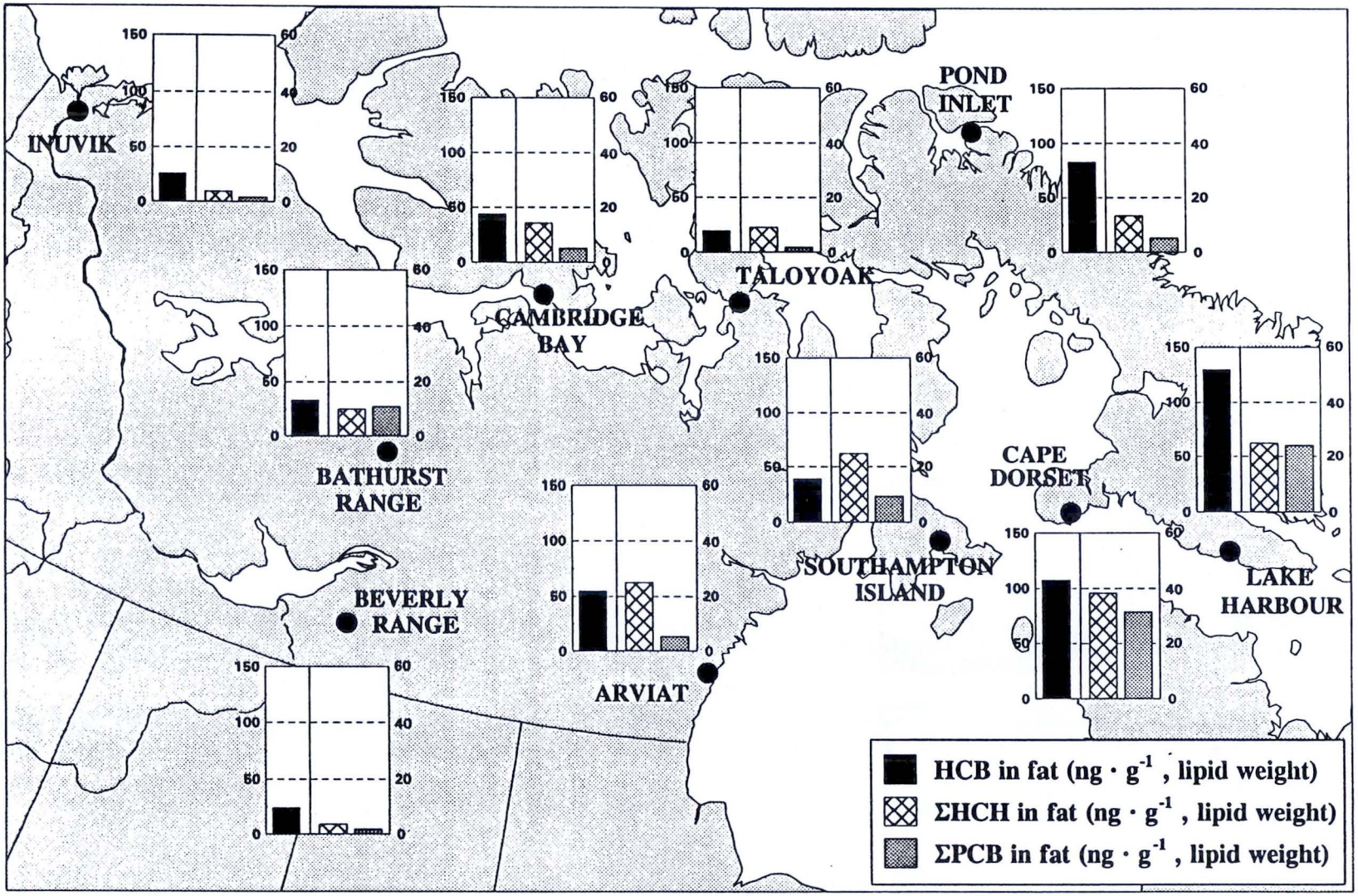

Figure 2. Concentrations of HCB, ΣHCH and ΣPCB in fat of caribou collected in the Northwest Territories, 1991-95

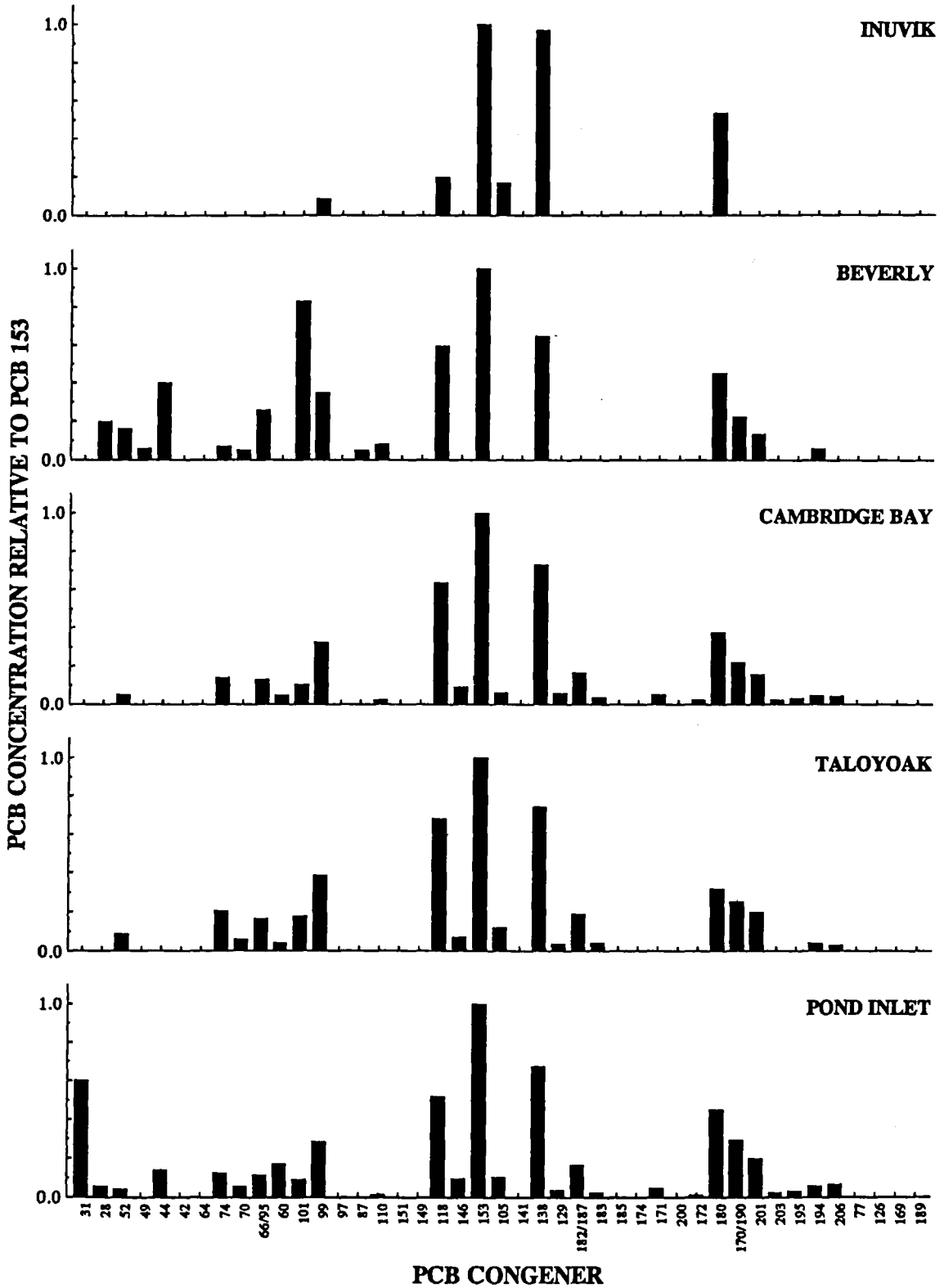

Figure 3. Pattern of PCB congeners (relative to PCB-153) in fat of caribou collected in the Northwest Territories, 1991-95

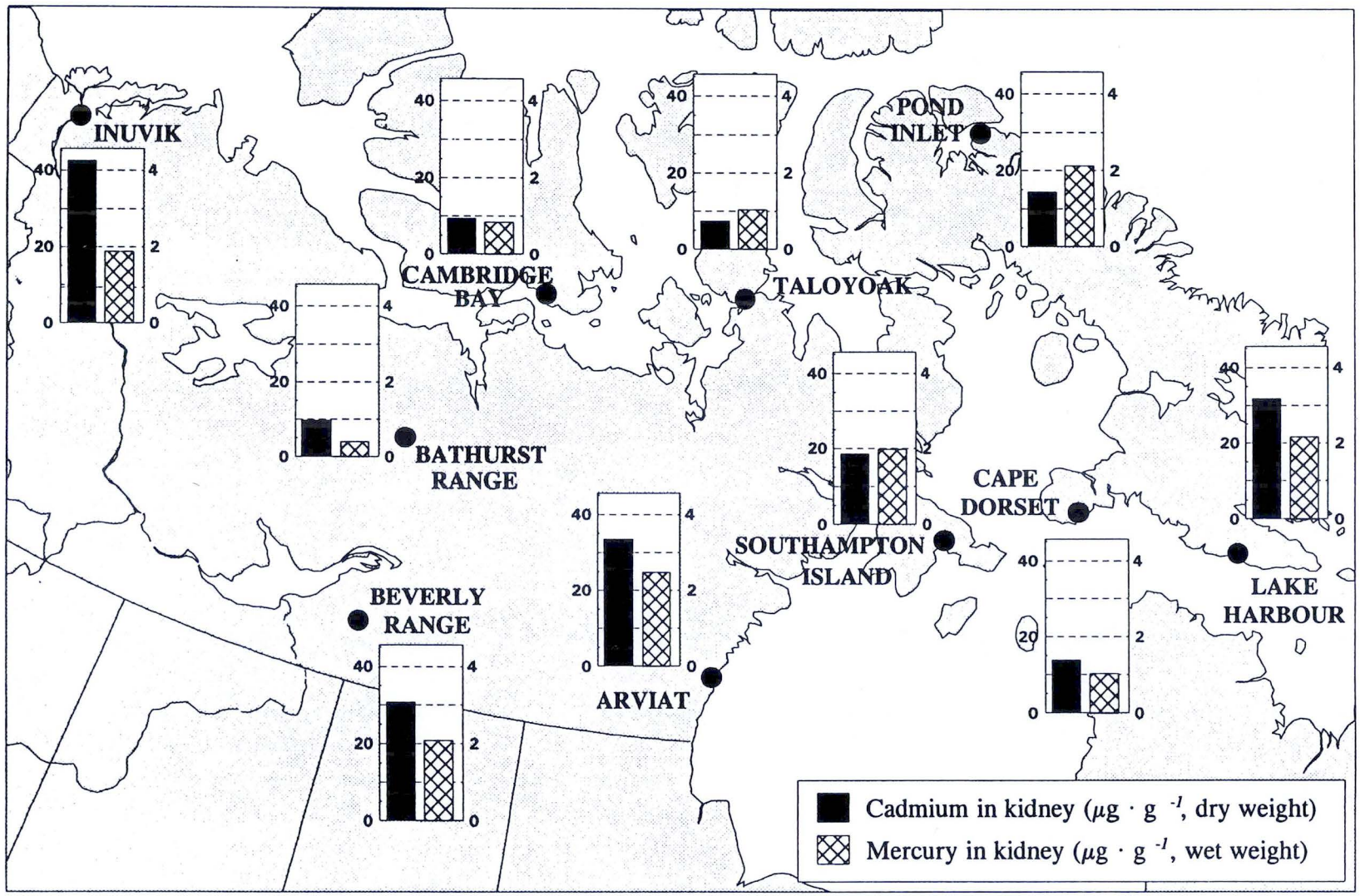

Figure 4. Cadmium (Cd, dry weight in kidney) and mercury (Hg, wet weight in kidney) levels in caribou collected in the Northwest Territories, 1991-95

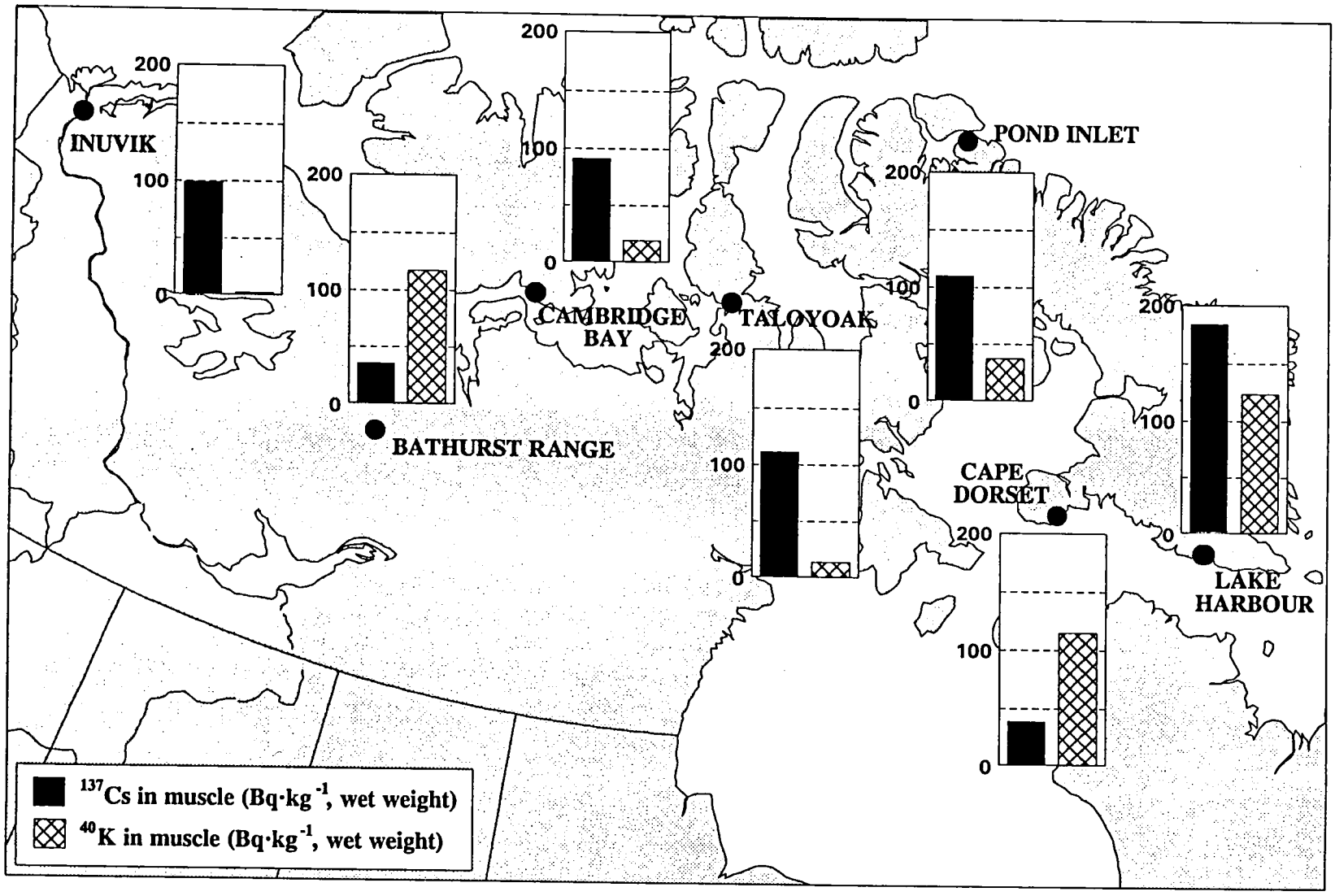

Figure 5. Cesium-137 and Potassium-40 (wet weight in muscle) activities in caribou collected in the Northwest Territories, 1991-95

ORGANOCHLORINE, HEAVY METAL AND RADIONUCLIDE CONTAMINANT TRANSFER THROUGH THE LICHEN-CARIBOU-WOLF FOOD CHAIN

Project Leader: B.T. Elkin, Department of Renewable Resources, Government of the 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 evaluate the transfer of these contaminants through the lichen-caribou-wolf food chain;

4. To determine spatial variations of contaminant exposure in the lichen-caribou-wolf food chain among three locations in the Northwest Territories (NWT).

DESCRIPTION

Information on contaminant exposure in caribou *(Rangifer tarandus)* and other terrestrial wildlife species in Canadian Arctic and sub-Arctic regions is 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 indicates 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 have 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 provides 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 allow for an examination of spatial variation in contaminant exposure or food chain dynamics. Samples were collected near Yellowknife (Bathurst herd), Cambridge Bay (Victoria Island herd) and Inuvik (Bluenose herd) (Figure 1).

ACTIVITIES IN 1994/95

This study was initiated in 1992/93; lichen, caribou and wolf collections have now been completed on the Bathurst, Bluenose and Victoria Island caribou herds. Field collections of barrenground caribou were conducted in cooperation with local Hunters' and Trappers' organizations from Cambridge Bay, Inuvik, and Ndilo/Fort Rae (Figure 1). Wolf carcasses were collected by local hunters from these communities, and were submitted frozen for processing and sampling. For both caribou and wolves, samples were collected from 20 animals. Stomach contents were collected from the caribou and wolves for diet analysis. Teeth were collected for ageing purposes, and a variety of biological and morphometric measurements were taken. Samples of three common lichen species *(Cladina mitis, Cladina rangiferina, Cetraria nivalis)*, which 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.

Lichen, caribou and wolf samples from all three sites were analysed 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 samples and muscle samples from caribou and wolves were also analysed for radionuclides at AECL Whiteshell Laboratories in Pinawa, Manitoba.

RESULTS AND DISCUSSION

The contaminant analyses of lichen, caribou and wolf samples from the Bathurst, Bluenose and Victoria Island samples were all completed in 1994/95. Data on the caribou collected at all three sites 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). The complete data set is currently being evaluated to assess and model contaminant transfer between the three trophic levels, and this analysis will be completed in 1995/96.

The relative tissue concentrations of the predominant organochlorine contaminants detected in lichen, caribou and wolf are given in Figure 2. Residue levels in caribou and wolf are for adipose tissue. A breakdown of the components of total HCH, total chlordane and total DDT is given for lichen, caribou fat and wolf fat in Figure 3. Concentrations of individual PCB congeners relative to PCB 153 for lichen, caribou fat and wolf fat are given in Figure 4. The data sets from all three locations are currently being evaluated, and detailed analysis will be available by the end of 1995/96.

Expected project completion date: Field collections and contaminant analysis of lichen, caribou and wolves were completed at all three sites in 1994/95. Data evaluation and interpretation, food chain modelling, human health risk assessment, and community consultation will occur in 1995/96.

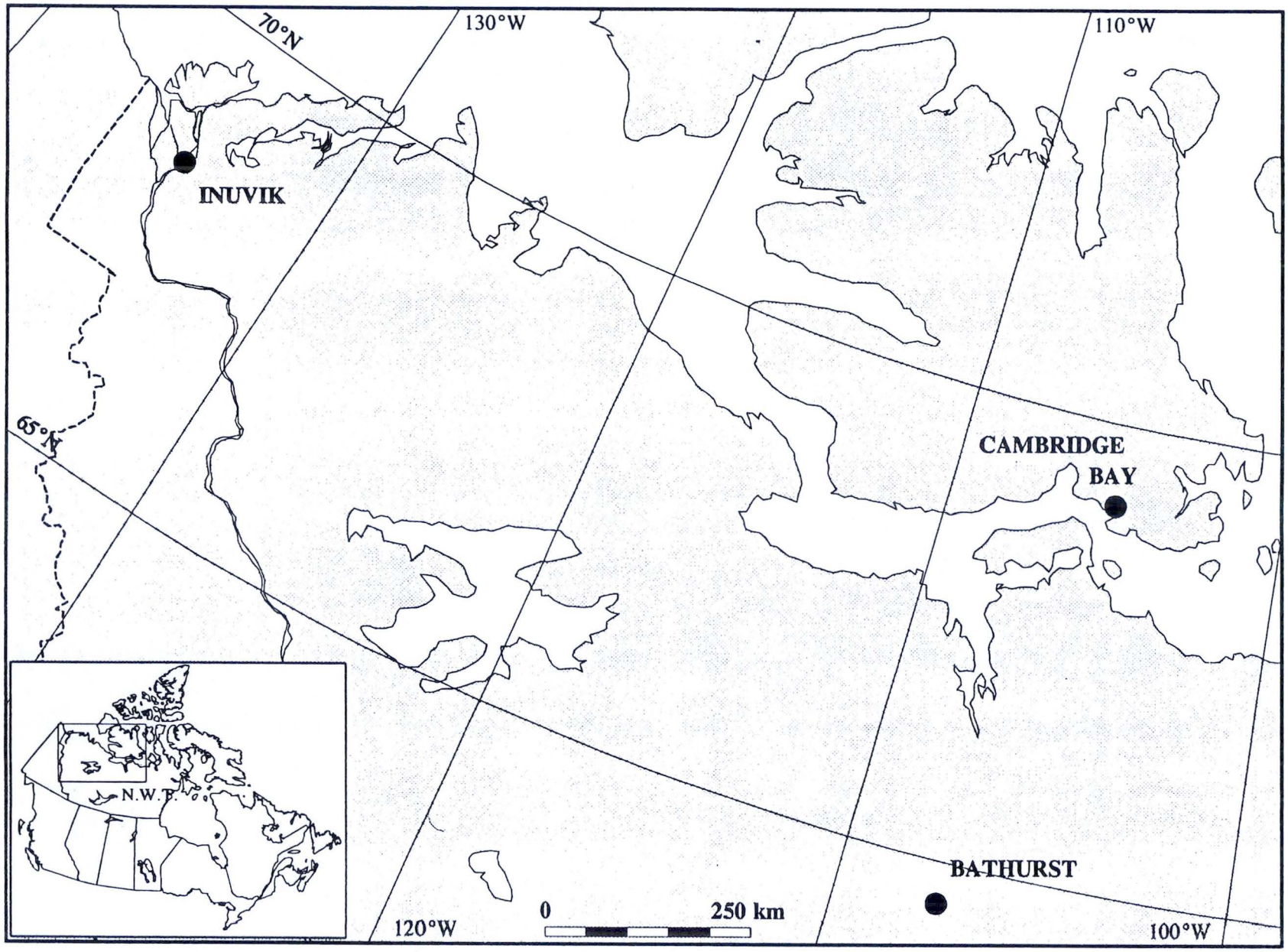

Figure 1. Sites in the Northwest Territories where the lichen-caribou-wolf food chain study was conducted. All lichen, caribou and wolf samples were collected within 100 km of the sites

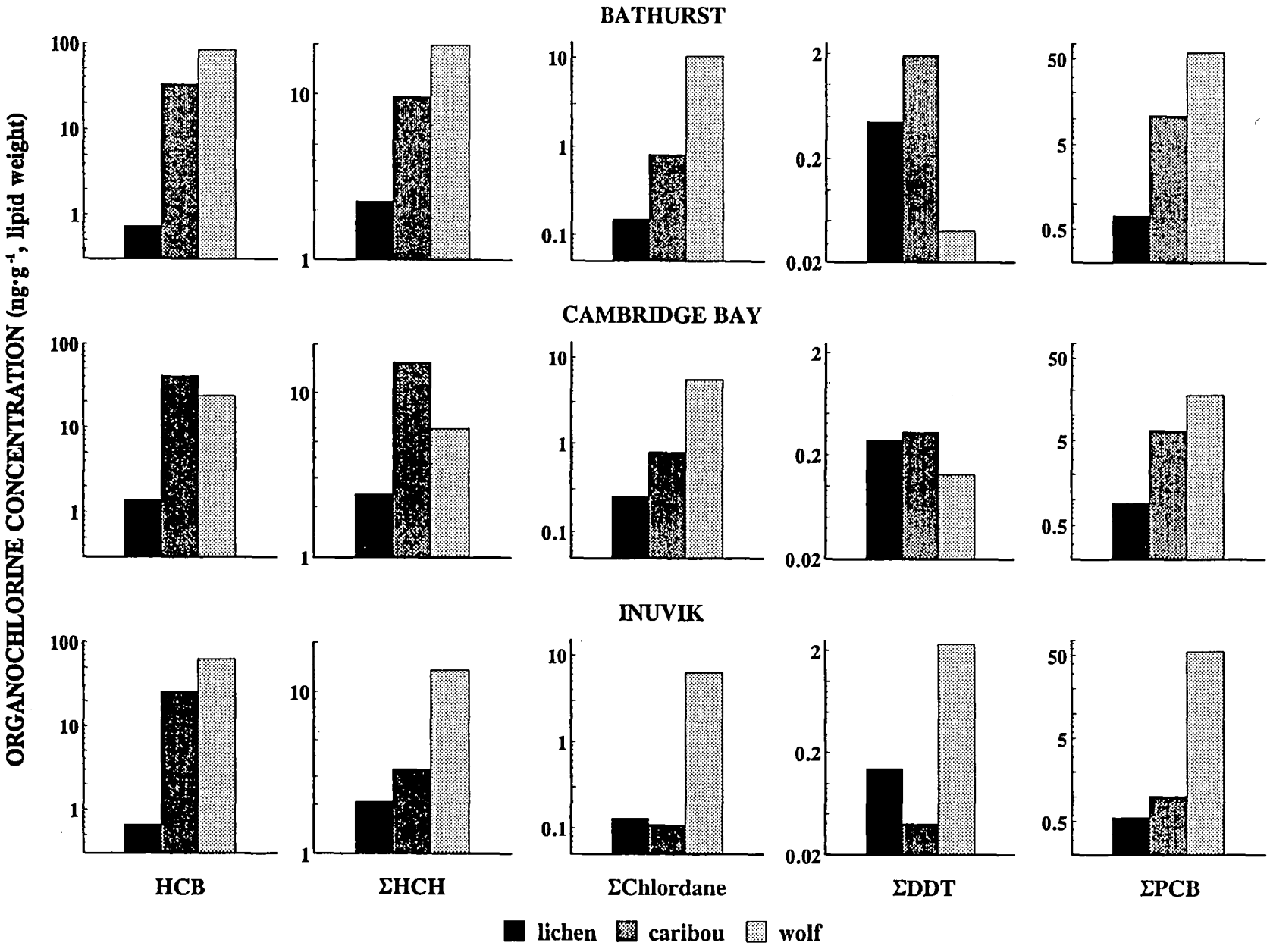

Figure 2. Concentrations (ng·g^{-1}, lipid weight) of selected organochlorine compounds in lichen, caribou fat and wolf fat collected from three sites in the Northwest Territories

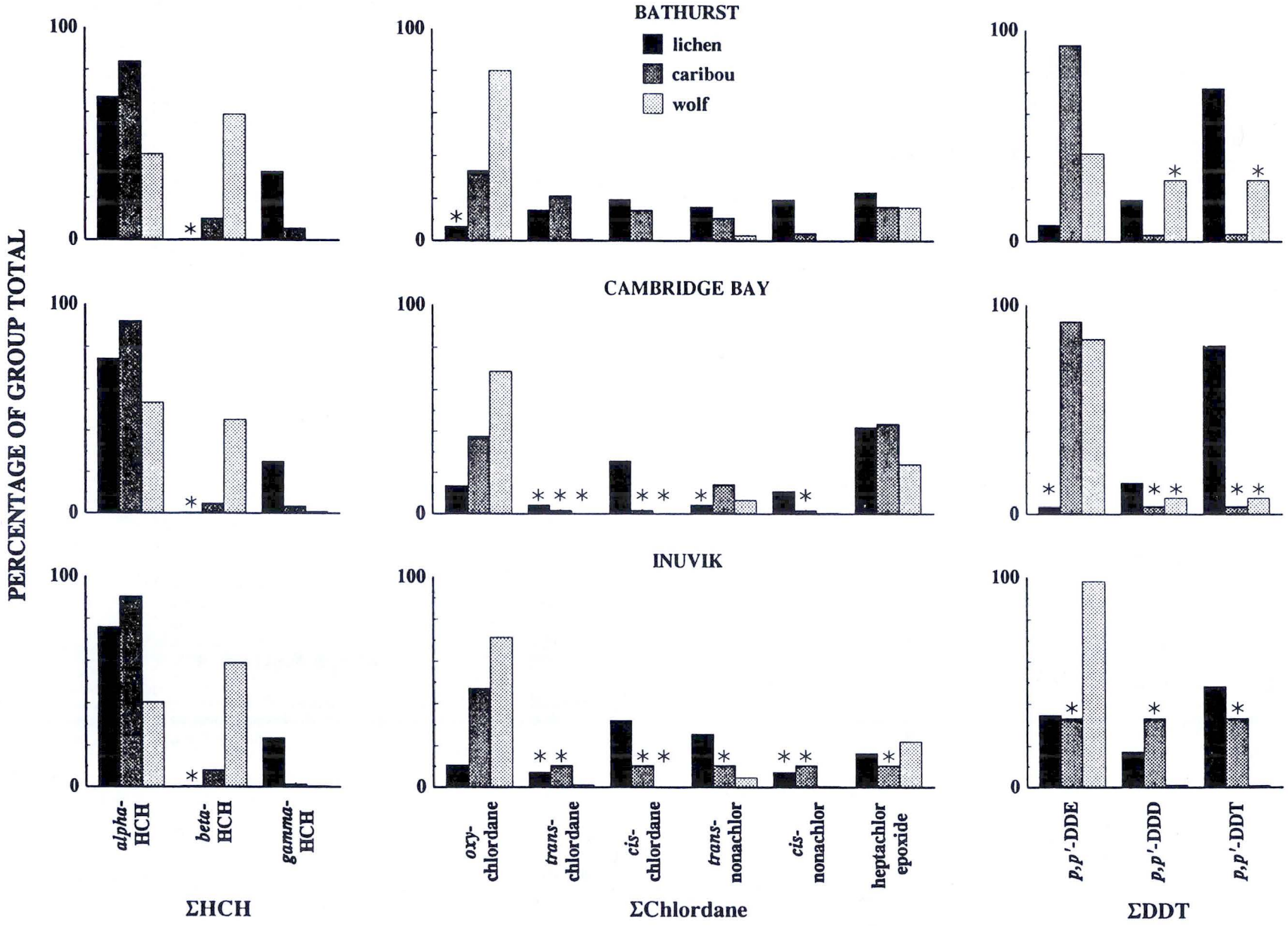

Figure 3. Distribution of constituent organochlorines within ΣHCH, ΣChlordanes and ΣDDT in lichen, caribou fat and wolf fat collected from three sites in the Northwest Territories

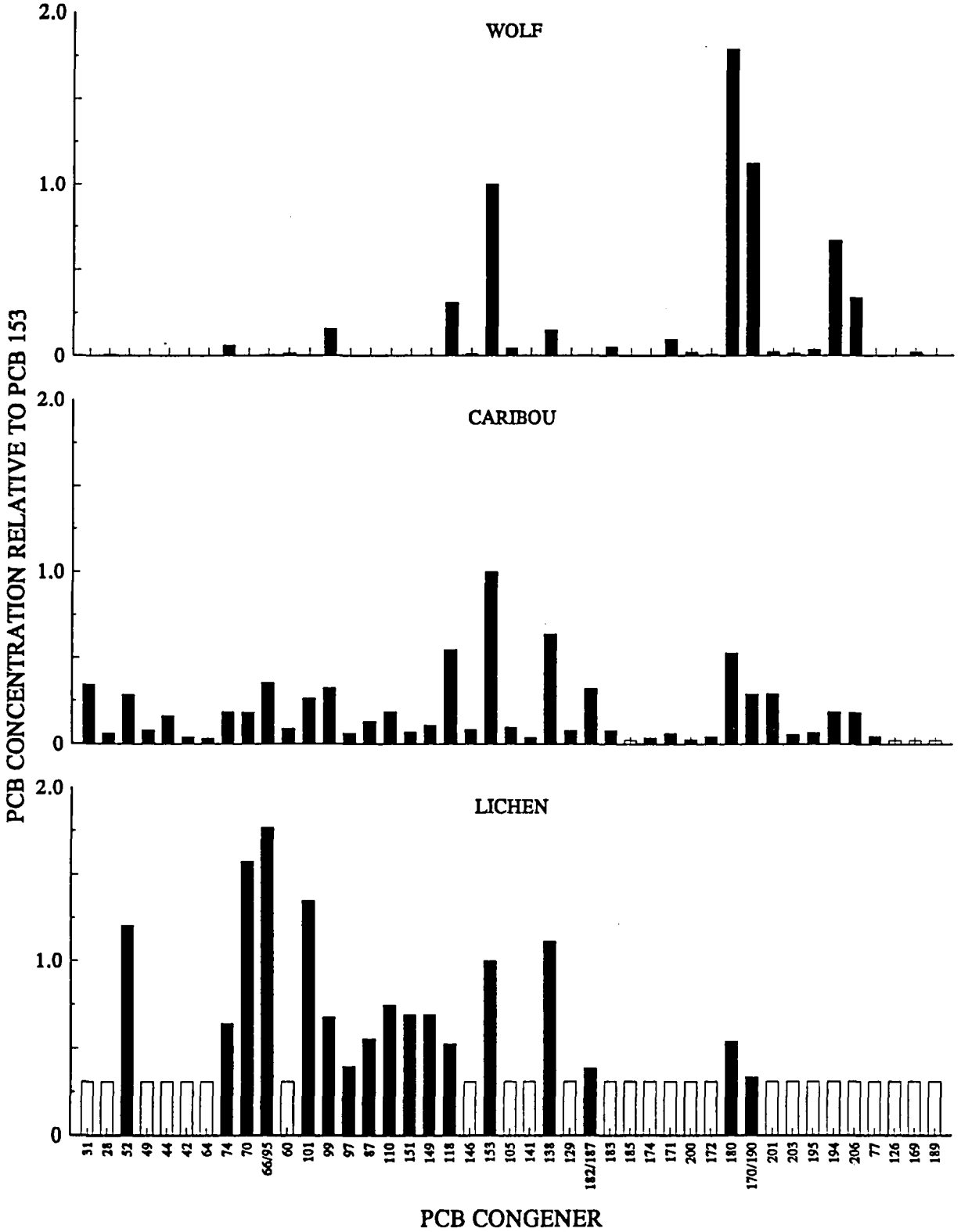

Figure 4. Pattern of PCB congeners (relative to PCB-153) in lichen, caribou fat and wolf fat collected from the Bathurst caribou herd range in the Northwest Territories

PCDD/PCDF RESIDUES IN CARIBOU FROM THE CANADIAN ARCTIC

Project Leader: C. Hebert, Canadian Wildlife Service, National Wildlife Research Centre

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. To determine levels of 2,3,7,8-TCDD equivalents in caribou tissue;

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

The broad distribution of persistent halogenated organic and heavy metal contaminants has been demonstrated in the Arctic physical environment (Barrie *et al.* 1992), the marine ecosystem (Muir *et al.* 1992) and the terrestrial environment (Thomas *et al.* 1992). The presence of these compounds in the environment is a concern because of their potential for adversely affecting the health of wildlife and human populations. Caribou *(Rangifer tarandus)* are an important food for many residents of the Arctic. Elevated levels of the heavy metal cadmium have been found in caribou kidney and liver from Québec, the Yukon and Northwest Territories (Crête *et al.* 1989, Gamberg and Scheuhammer 1994). Organochlorine contaminants are generally much lower in caribou (and the terrestrial ecosystem generally) than in marine mammals because of shorter food chains and lower fat content (Thomas *et al.* 1992; Gamberg *1993*; Elkin and Bethke 1995). Nevertheless, contaminants in caribou are of particular concern to those people who rely on these foodstuffs for a significant portion of their diet.

Among the most toxic contaminants found in the environment are the 2,3,7,8-chlorine substituted polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), and the 3,4,3',4'-chlorine substituted, non-ortho substituted polychlorinated biphenyls (NOPCBs). The mechanism of toxicity of this class of compounds is similar to that of 2,3,7,8-TCDD, but at varying potency, thus they may act in an additive fashion to exacerbate their impact on wildlife and humans. The additive effect is usually expressed as Toxic Equivalent (TEQ) concentrations of TCDD, which is the sum of the product of relative potency to TCDD times the concentration of each compound (Safe 1990). Few data exist documenting levels of these compounds or TEQs in Arctic terrestrial wildlife. Levels of PCDDs and PCDFs in arctic marine mammals are low, but NOPCBs may be of more concern (Ford *et al.* 1993, Norstrom *et al.* 1990). A systematic study to quantify concentrations of PCDDs, PCDFs and NOPCBs in caribou from across the Canadian North was therefore initiated in 1993.

The study made use of existing collections of subcutaneous back fat from female caribou in the Northwest Territories (Elkin and Bethke 1995). Only one sex was chosen to facilitate comparison among herds. The collections had been made from four herds on the following dates: Southampton Island (November 1991, n=5), Cape Dorset (April 1992, n=3), Lake Harbour (April 1992, n=4) and Bathurst (July and September 1992, n=7). Individual samples were pooled for chemical analysis. In addition, liver, muscle and subcutaneous back or kidney fat samples were taken from twenty female caribou shot from each of the Finlayson (n=15), Tay (n=13) and Bonnet Plume (n=14) herds from the Yukon Territory in March 1993. Fat samples from the Finlayson herd were analysed to determine if there was a relationship between age and contaminant 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). Pooled liver and muscle samples from the Finlayson Age 3 group were also analysed to determine tissue distribution.

ACTIVITIES IN 1994/95

Details regarding collection and processing procedures can be found in last year's summary (herbert 1994). With respect to the analytical methods, lipids were removed

by gel permeation chromatography and alumina column cleanup (Norstrom *et al.* 1986). Separation of PCDDs, PCDFs and NOPCBs from other contaminants was accomplished using a carbon/fibre column (Norstrom and Simon 1991, Ford *et al.* 1993). Separation of the PCDDs/PCDFs from the NOPCBs was completed using Florisil column chromatography. The samples were analysed by high-resolution mass spectrometry for twenty seven PCDD and PCDF congeners, including all of the fifteen 2,3,7,8-substituted toxic ones. By July 1994, all samples had been analysed using high resolution mass spectrometry. A large number of congeners was determined because it was hypothesized that non-2,3,7,8-substituted congeners, which predominate in the atmosphere, may accumulate in caribou because of the short air-lichen-caribou pathway. The NOPCBs determined were CB-37, CB-77, CB-81, CB-126 and CB-169. Accurate TEQs could be calculated only for caribou from the Northwest Territories because data for the mono-ortho-substituted PCBs, IUPAC #105 and #118, were available only from these herds (Elkin and Bethke 1995). Toxic equivalents (TEQs) were calculated for each congener by multiplying congener concentration (wet weight) by a congener-specific toxic equivalency factor (TEF) (NATO/CCMS 1988, Ahlborg *et al.*1994). The average contribution of CB-105 and CB-118 in the NWT herds was 12%. The TEQs from the Yukon herds were corrected by this percentage to account for the missing CB-105 and CB-118 data.

RESULTS/DISCUSSION

The results are reported in detail in Hebert *et al.* (1995). The data are summarized as total of each isomer group for PCDDs and PCDFs, and individual NOPCBs in Table 1. Sub-part per trillion (pg/g) detection limits on a lipid weight basis were achieved for individual PCDDs, PCDFs and NOPCBs in the great majority of analyses. Levels of PCDDs, PCDFs and NOPCBs were extremely low in animals from all herds. Only 2,3,7,8-substituted PCDDs were observed. TCDD was found in only two fat samples (Cape Dorset, 0.73 ppt and Lake Harbour, 0.14 ppt) at detection limits ranging from 0.02 to 0.43 ppt. OCDD was the only PCDD or PCDF that was found in the majority of fat samples, at levels ranging from <0.38 ppt to 4.69 ppt in the Cape Dorset sample. Among PCDF congeners, 1,2,4,7,8-PnCDF was present in all samples except Finlayson at levels ranging from 0.24 to 0.74 ppt. Five other non-2,3,7,8-substituted PCDF congeners, 2,3,6,8-TCDF, 2,3,6,7-TCDF, 1,2,4,6,8-PnCDF, 1,2,4,6,7,8-HxCDF and 1,2,4,6,8,9-HxCDF, were found only in the Lake Harbour sample at levels < 1 ppt .

The larger number of PCDD/PCDF congeners detected in two of the Northwest Territories herds may have reflected differences in the long-range atmospheric transport of these compounds to the western and eastern Arctic. This is consistent with the observation that OCDD was the predominant PCDD/PCDF congener found in all samples. Highly chlorinated dioxins, such as OCDD, are usually indicative of combustion-related sources (Broman *et al.* 1991), which probably arrived in the Arctic via long-range atmospheric transport (Norstrom *et al.* 1990). The finding of traces of non-2,3,7,8-PCDFs in the Lake Harbour sample is also consistent with an atmospheric signal.

Non-ortho PCBs were present at low concentrations in all of the caribou from the Yukon and Northwest Territories (Table 1). PCB congeners #126 and #169 showed some spatial variability with higher levels in the eastern Arctic. This result corroborates the findings of Elkin and Bethke (1995) who found higher concentrations of ortho-substituted polychlorinated biphenyl congeners in the eastern Arctic. Higher levels of these PCBs in the east are probably also the result of differences in atmospheric circulation patterns, thereby affecting the deposition of these contaminants via long-range atmospheric transport.

The relationship between age and lipid-normalized congener concentration was examined using linear regression analysis. Obviously, this could only be completed on congeners which were present at detectable levels in the majority of the Finlayson samples (OCDD and the five NOPCBs). There were no statistically significant relationships between age and OCDD/NOPCB levels in fat tissue from the Finlayson caribou ($p>0.1$ in all cases).

No detectable PCDDs or PCDFs were found in the Finlayson muscle sample. However, the detection limits were in the 2-18 ppt range because of the low lipid content of the sample (2%). On a lipid weight basis, significantly higher levels of CB-37 (213 ppt) and CB-77 (81 ppt) were found in muscle than fat (12 ppt and 7 ppt, respectively), whereas the other NOPCBs were not detected. CB-37 (176 ppt) and CB-77 (44 ppt) were also higher in liver than in fat, as was CB-126 (50 ppt). This indicates that the partitioning of these compounds to caribou tissue is not purely driven by the lipid content of the tissue (i.e. equilibrium partitioning) but that physiological processes may be important in regulating the preferential deposition of these compounds in muscle and liver. From a human consumption perspective, however, it is the wet weight concentrations which are of interest because all tissues are consumed on a wet weight basis.

TCDD TEQs on a wet weight basis were calculated for each pooled sample (Table 2). In three-year-old caribou from the Finlayson herd, TEQ levels are greater in fat tissue than in liver or muscle. However, the TEQ levels found in all of the caribou tissues are extremely low, generally less than 1 ppt, maximum 3.29 ppt. Only Cape Dorset and Lake Harbour samples exceeded 1 ppt. By comparison, TEQs in Arctic marine mammals, such as the beluga (Delphinapterus leucas) and narwhal (Monodon monoceros), range from approximately 100 to 500 ppt (Norstrom and Muir 1994). TEQ levels in ringed seal (Phoca hispida) are approximately one-tenth those observed in beluga and narwhal but are still an order of magnitude greater than those observed in caribou. The greatest contribution to overall TEQ levels in caribou was from the NOPCBs, with PCB #126 being of particular importance. Their mean contribution to TEQ levels in fat tissue from all of the herds was greater than 70%. These results are similar to those from previous studies which found that PCBs were the major contributors to overall TEQ levels in Arctic marine mammals (Daelemans *et al.* 1993; Ford *et al.* 1993).

CONCLUSIONS

These results indicate that PCDDs, PCDFs and NOPCBs are unlikely to pose a threat to either the caribou sampled in this study or to their human consumers. The levels observed can probably be considered to be background concentrations. TEQs in caribou fat are as low or lower than those reported in fat of domestic animals (Ryan and Norstrom 1991).

Project completion date: September 30, 1994

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Table 1. Concentrations (ng•kg-1 or ppt, lipid weight) of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and non-ortho substituted PCBs (NOPCBs) in female fat collected from three herds in the Yukon during 1993 and from four herds in the Northwest Territories during 1991/92. ND is not detected. Minimum detection limits corrected for percent lipid (MDLs) are provided for each compound or isomer group in each sample.

Location	Finlayson		Tay		Bonnet Plume		Bathurst		Southhampton Is.		Cape Dorset		Lake Harbour	
Pool	Age 2-6		Age 5.3		Age 6.6		Age 4.1		Age 3.6		Age 3.7		Age 4.3	
Sample Type	Fat		Fat		Fat		Fat		Fat		Fat		Fat	
% Lipid	84.2		84.2		83.8		43.0		92.3		19.2		80.4	
PCDDs	**Conc.**	**MDL**	**Conc.**	**MDL**	**Conc.**	**MDL**	**Conc.**	**MDL**	**Conc.**	**MDL**	**Conc.**	**MDL**	**Conc.**	**MDL**
Total TCDD	ND	0.45	ND	0.05	ND	0.11	ND	0.19	ND	0.15	0.73	0.31	0.14	0.02
Total PnCDD	ND	0.32	0.12	0.02	ND	0.13	ND	0.40	0.30	0.18	1.67	0.78	0.31	0.02
Total HxCDD	ND	0.74	0.08	0.08	ND	0.26	ND	0.64	0.10	0.38	1.77	0.40	0.57	0.08
Total HpCDD	ND	0.98	0.25	0.04	ND	0.20	0.33	0.18	ND	0.32	0.73	0.62	0.39	0.04
OCDD	0.38	0.19	1.09	0.04	0.66	0.01	2.14	0.02	1.65	0.04	4.69	0.05	1.13	0.01
PCDFs	**Conc.**	**MDL**	**Conc.**	**MDL**	**Conc.**	**MDL**	**Conc.**	**MDL**	**Conc.**	**MDL**	**Conc.**	**MDL**	**Conc.**	**MDL**
Total TCDF	ND	0.30	0.20	0.08	ND	0.48	ND	0.90	0.16	0.45	0.99	2.97	0.35	0.06
Total PnCDF	ND	0.58	0.52	0.20	0.25	0.55	0.74	0.95	0.63	0.33	1.77	0.50	0.77	0.10
Total HxCDF	ND	1.63	0.36	0.26	ND	0.70	ND	1.12	0.23	0.30	1.98	1.11	0.61	0.07
Total HpCDF	ND	0.80	0.23	0.03	ND	0.13	ND	0.23	ND	0.48	ND	0.93	0.22	0.03
OCDF	ND	0.20	0.25	0.04	ND	0.06	ND	0.26	ND	0.13	ND	0.21	0.25	0.04
NOPCBs	**Conc.**	**MDL**	**Conc.**	**MDL**	**Conc.**	**MDL**	**Conc.**	**MDL**	**Conc.**	**MDL**	**Conc.**	**MDL**	**Conc.**	**MDL**
IUPAC #37	6.06	1.10	3.98	0.70	3.93	1.58	7.70	1.49	2.60	1.30	15.10	5.47	2.64	0.95
IUPAC #77	3.41	0.46	3.04	0.59	2.92	0.36	5.14	0.23	6.45	0.85	10.31	0.89	5.52	0.75
IUPAC #81	0.50	0.44	ND	0.59	0.36	0.36	0.58	0.23	0.91	0.85	2.45	0.89	1.74	0.75
IUPAC #126	6.40	0.44	5.74	0.18	9.64	0.25	7.16	0.09	26.73	0.53	74.74	0.21	30.73	0.12
IUPAC #169	0.86	0.37	0.58	0.26	0.75	0.43	0.88	0.26	2.28	0.65	11.77	0.68	3.42	0.30

Table 2. 2,3,7,8-TCDD equivalents (TEQs) ($ng \cdot kg^{-1}$ or ppt, wet weight) in caribou from the Northwest and Yukon Territories. ND is not detected. *TEQs contributed by PCBs #105 and #118 were estimated for the Yukon caribou.

Herd	Tissue	PCDDs	PCDFs	NOPCBs	PCB 105 + 118	Total TEQs
Northwest Territories						
Lake Harbour	Fat	0.29	0.23	2.5	0.27	3.29
Cape Dorset	Fat	0.34	0.13	0.46	0.3	1.23
Southampton Is.	Fat	0.15	0.14	0.49	0.07	0.85
Bathurst	Fat	<0.01	ND	0.31	0.02	0.33
Yukon Territory						
Tay	Fat	0.06	0.12	0.49	*0.09	0.76
Bonnet Plume	Fat	<0.01	ND	0.82	*0.11	0.93
Finlayson Age 2	Fat	<0.01	ND	0.57	*0.08	0.65
Finlayson Age 3	Fat	<0.01	ND	0.62	*0.08	0.7
Finlayson Age 3	Liver	0.17	ND	0.21	*0.05	0.43
Finlayson Age 3	Muscle	ND	ND	<0.01	*<0.01	<0.01
Finlayson Age 4	Fat	<0.01	ND	0.63	*0.08	0.71
Finlayson Age 5	Fat	<0.01	ND	0.44	*0.06	0.5
Finlayson Age 6	Fat	<0.01	ND	0.48	*0.06	0.54

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 the 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)* are a top trophic level species that readily bioaccumulate 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 Fort 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 also were 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 1994/95

In 1994/95, 221 mink carcasses were collected from 27 trappers from Fort Liard near the Liard River, from Fort Smith and Fort Resolution near the Slave River, and from Fort Providence west of Great Slave Lake. This represented the fourth and final year of carcass collections for the study, and brings to 1025 the number of mink carcasses collected from NWT trappers in seven communities.

Liver and kidney samples from up to 26 mink collected at each site were analysed for organochlorine and heavy metal contaminants at the Great Lakes Institute in Windsor, Ontario. Analyses were conducted for three years in the Inuvik area to examine short-term temporal trends. 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 published in January 1995 in a special issue of STOTEN (Poole *et al.* 1995). Preliminary analyses of samples collected in 1993/94 have been completed, and are reported here. Analyses of samples collected in 1994/95 and an evaluation of the complete program is currently in progress.

RESULTS

A total of 804 mink carcasses were collected from 1991/92 to 1993/94, and contaminant analyses were conducted on 152 mink and 20 martens. Organochlorine levels given below are for liver samples. 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 and more highly chlorinated PCB congeners predominating. ΣPCB residues (sum of 43 congeners) in mink ranged from a mean of 4.94 $ng \cdot g^{-1}$ wet weight in the livers of Inuvik mink to about 25 $ng \cdot g^{-1}$ in mink from Forts Liard, Rae, Resolution and Smith, and 92.50 $ng \cdot g^{-1}$ in mink from Fort Providence (Table 1). The reason why ΣPCB levels in the Fort Providence samples were over three times higher than mink from any other community is unknown; Fort Providence mink did not have significantly higher residues of other groups of OCs, and mink diet did not differ from other collection sites (K. Poole, pers. data). ΣPCB averaged 37.35 $ng \cdot g^{-1}$ in the Fort Good Hope marten sample. Mean ΣPCB levels in Inuvik mink varied by two-fold over the three years of collection, but were the lowest detected in all communities (range of means 4.94 to 11.57 $ng \cdot g^{-1}$). ΣDDT ranged from 0.77 $ng \cdot g^{-1}$ in the 1991/92 Inuvik sample to 13.66 $ng \cdot g^{-1}$ in Fort Liard mink (Table 1). ΣDDT was composed primarily of DDE, with low levels of DDD, in all but two mink ($n = 152$) and two marten samples ($n = 20$), DDT levels were below detection limits. Of the more toxic non-ortho substituted PCB congeners, PCB-77 was detected in no mink samples and only two marten samples, 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. Dioxin/furans were not detected in any mink liver samples, and were detected in only three cases (at ≤ 0.005 $ng \cdot g^{-1}$) in Fort Good Hope marten liver samples. Ten pooled mink liver samples were examined for total toxaphene. Total toxaphene ranged from 1.8 to 7.9 $ng \cdot g^{-1}$ (wet wt.); there was no apparent temporal pattern. 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 0.12-3.30 $\mu g \cdot g^{-1}$ wet wt. 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 generally were 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.

In the final year of the study, collections conducted during 1994/95 will be analysed and a complete synthesis of the study will be prepared. Examination of contaminant levels in terrestrial prey species collected to date (snowshoe hares *[Lepus americanus]* and red-backed voles *[Clethrionomys rutilus]*) will be concluded. Emphasis will be on analysis and publication of the data set, and communication of the results to participating communities.

Expected project completion date: March 31, 1996

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Table 1. Arithmetic means (ng•g^{-1} wet wt. [SE]) of selected organochlorine residues in livers of mink and marten trapped in the NWT, 1991/92 to 1992/94.

Species/community	*n*	% lipid	SDDT[a]	SHCH[b]	HCB	SChlordane[c]	Dieldrin	SPCB[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)	11.57 (1.97)
Mink Inuvik94	20	4.5	1.58 (0.65)	0.04 (0.01)	0.26 (0.05)	1.77 (0.40)	0.07 (0.03)	4.94 (1.12)
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)	17.17 (3.25)
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)	24.70 (5.45)
Mink Fort Providence	21	5.54	10.86 (3.48)	0.05 (0.01)	0.38 (0.11)	2.20 (0.48)	0.23 (0.08)	92.50 (21.18)
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)	25.83 (7.36)
Mink Fort Resolution	7	6.2	7.41 (3.54)	0.03 (0.00)	0.31 (0.07)	0.61 (0.18)	0.16 (0.08)	25.15 (6.77)
Mink Fort Smith	26	4.5	3.75 (0.70)	0.11 (0.05)	0.52 (0.08)	3.48 (0.80)	0.74 (0.26)	23.51 (4.37)
Marten Fort Good Hope	16	4.5	2.43 (1.23)	0.35 (0.07)	3.47 (0.89)	13.60 (2.75)	6.97 (5.58)	37.35 (6.10)

[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*- and *trans*-nonachlor.
[d] ΣPCB = Sum of individual congeners.

Table 2. Metal concentrations from mink and marten trapped in the NWY, 1991/92 to 1993/94. All metals given in dry wt. in kidneys, except for total mercury (HG) given in wet wt. in livers

Species/ community	*n*	metal concentration (mg•g^{-1} [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 Inuvik94	10	2.51 (0.44)	0.20 (0.05)	0.30 (0.06)	15.18 (1.29)	788.1 (64.6)	2.13 (0.22)	0.12 (0.02)	0.09 (0.02)	67.97 (3.25)	1.35 (0.15)
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 Providence	10	3.17 (0.81)	0.20 (0.07)	0.31 (0.07)	11.76 (0.97)	835.1 (109.6)	2.59 (0.31)	0.13 (0.02)	0.20 (0.04)	77.97 (6.14)	1.07 (0.37)
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 (13.51)	1.45 (0.53)
Mink Fort Resolution	4	1.14 (0.30)	0.83 (0.32)	0.20 (0.00)	21.40 (1.90)	1005.5 (55.8)	3.19 (0.33)	0.10 (0.00)	0.22 (0.12)	100.65 (9.57)	0.12 (0.05)
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: Yukon Contaminants Committee
(Contact: Mary Gamberg, Gamberg Consulting, Watson Lake, Yukon)

Project Team: Yukon Territorial Government Renewable Resource Officers and Biologists;
Yukon First Nations

OBJECTIVES

1. To quantitatively determine use of country foods by Yukon First Nations;
2. To determine the presence and quantity of organic and inorganic contaminants in country foods used in the Yukon;
3. To identify potential health risks to members of the First Nations and others consuming country foods;
4. To identify potential health problems in wildlife populations as a result of contaminant loading;
5. To develop baseline data on levels of inorganic and organic contaminants in wildlife in the 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. Several studies on arctic caribou *(Rangifer tarandus)* have found high levels of cadmium in the livers and kidneys of these animals (Crête *et al.* 1989, Froslie *et al.* 1986). Subsequent work on Yukon caribou found similar levels in the Porcupine herd (Gamberg and Scheuhammer 1994), and considerably higher levels in the Finlayson caribou from the Ross River area (Gamberg 1993). This raised concern among members of the First Nations and others using the caribou as a food source, and also brought up the issue of contaminants in other food sources: other mammals, plants, birds and fish. This project was designed to work with the individual First Nations to address these concerns.

In 1993/94 a pilot study was conducted to measure contaminants in mammals used as country foods in the Southeastern Yukon. Sampling was restricted to mammals, and encompassed three communities: Watson Lake, Ross River and Teslin. Two additional communities were subsequently added to the study, but rather late in the hunting season, so few samples were obtained from those locations. Tissue samples from the following animals were collected and analysed for organic and inorganic contaminants: 5 moose *(Alces alces)*, 6 caribou, 4 mountain goats *(Oreamnos americanus)*, 5 Dall sheep *(Ovis dalli)*, 8 muskrat *(Ondatra zibethicus)*, 12 snowshoe hare *(Lepus americanus)*, 8 beaver *(Castor canadensis)*, 4 porcupine *(Erethizon dorsatum)*, and 5 ground squirrels *(Citellus parryi)*.

ACTIVITIES IN 1994/95

The quantitative determination of country foods used by Yukon First Nations has been incorporated into a Northern Contaminants Program project conducted by the Centre for Nutrition and the Environment of Indigenous Peoples, and so was not included in this study. Each of the 14 First Nations in the Yukon agreed to participate in the Country Foods project. A sampling list for each community was developed in consultation with the Band members, so that the resulting data would be applicable on a local level. Sampling was designed to take place over a calendar year, so that each food could be sampled at the time of traditional harvest. A coordinator was designated in each community to oversee collections, and the first to begin sampling did so in December, 1994. Liver, kidney, muscle and fat tissue were extracted from each animal carcass submitted and stored for analysis.

In addition to the sampling provided by First Nations, all Yukon hunters were requested to submit liver, kidney and muscle samples from moose and caribou taken during the 1994 hunting season. A tooth or incisor bar was also requested for aging purposes.

Liver, kidney and muscle tissues were analysed for a suite of 26 metals. Liver or fat tissue was analysed for organic contaminants including pesticides and PCBs (total and as Aroclors) and selected samples were also analysed for dioxins and furans. Samples analysed for organic contaminants were pooled to reduce costs.

RESULTS

As of March 1995, 6 snowshoe hare, 6 spruce grouse *(Dendragapus canadensis)* and 1 lynx *(Lynx canadensis)* had been collected from First Nations. Hunter-collected samples were obtained from 57 moose and 18 caribou (from various herds). Livers and kidneys were also obtained from 48 grouse and ptarmigan collected in the Yukon in 1994/95 as part of a Canadian Wildlife Service study of contaminants in birds. These included: 1 blue grouse *(Dendragapus obscurus)*, 3 ruffed grouse *(Bonasa umbellus)*, 24 spruce grouse, 2 white-tailed ptarmigan *(Lagopus leucurus)*, 4 rock ptarmigan *(Lagopus mutus)*, 8 willow ptarmigan *(Lagopus lagopus)* and 6 ptarmigan of undetermined species *(Lagopus* sp.*)*.

Levels of pesticides, PCBs, toxaphene, dioxins and furans were at or near detection limits for most samples analysed. The exception was one pool of fat from three porcupines from the Watson Lake area, which contained somewhat elevated levels of dioxins and furans (Table 1). A subsequent analysis of two of the three samples making up this pool indicated that these compounds were present at levels near or at the detection limits. All the fat tissue from the third porcupine had been used in the original analysis and was therefore unavailable for reanalysis.

Metal levels appeared normal in most cases, although for some species there were little or no existing data available for comparison. Mercury was elevated in some caribou kidneys and cadmium was high in kidneys and livers of several species including beaver, grouse, ptarmigan, porcupine (Table 2), caribou and moose (Figures 1 and 2). Cadmium levels were particularly high in moose kidney and liver, a point of concern because these organs are commonly used as food. Cadmium levels in muscle tissue of all animals were consistently low. All data have been submitted to Health Canada for a human health hazard assessment.

DISCUSSION/CONCLUSIONS

Levels of organic contaminants in the terrestrial birds and mammals tested were generally low and of no concern. Only one porcupine had dioxins and furans at levels above background, and even these were not exceptionally high. The same was true of metal levels, with the exception of mercury and cadmium. Although mercury was elevated in some caribou kidneys, previous work with the Finlayson caribou indicated that all mercury present was in the inorganic form, and is therefore of little concern (Gamberg 1993). Samples from animals showing elevated levels of mercury will be reanalysed for methyl mercury to confirm this assumption.

Cadmium levels in some Yukon wildlife are higher than in wildlife from other geographical areas. Cadmium levels in moose liver and kidneys are higher than levels reported in moose from Manitoba (Wotton and McEachern 1988), Québec (Crête *et al.* 1987), Newfoundland (Brazil and Ferguson 1989), Norway (Froslie *et al.* 1986, Scanlon *et al.* 1986) and Sweden (Frank 1986). However, moose from certain areas of Ontario (Glooschenko *et al.* 1988) and New Brunswick (Redmond *et al.* 1988) had levels of cadmium similar to those found in Yukon moose. Cadmium levels in the Porcupine caribou were similar to those in other arctic caribou (Gamberg and Scheuhammer 1994, Crête *et al.* 1989, Froslie *et al.* 1986), but concentrations in the Finlayson herd are considerably higher (Gamberg 1993). Beaver from the Yukon have higher levels of cadmium than beaver from the Sudbury mining area of Ontario, which are considered to have elevated levels (Hills and Parker 1993). Cadmium in Yukon grouse and ptarmigan are similar to levels found in rock ptarmigan and willow ptarmigan in Norway (Fimreite 1993), but some individuals from the Yukon had very high concentrations (up to 1200 ppm dry wt. in kidney). Few comparative data exist for porcupines, snowshoe hares and ground squirrels, but cadmium levels are quite high in porcupine, and in individual snowshoe hares. Muskrats, on the other hand, have uniformly low levels of cadmium.

The accumulation of cadmium in wildlife appears to vary widely among species and individuals. This may be the result of geographical variability, but low sample sizes in this study did not allow analysis of differences among locations. However, there did not appear to be high levels of cadmium particularly associated with industry (mining) or populated areas. Research conducted on cadmium in Yukon caribou included the study of plants, soil, air and water. Results suggest that the high levels of cadmium seen in Yukon wildlife are a result of natural mineralization that accumulates in some plants, and is in this way passed on to certain herbivores, depending on their dietary habits.

Work in 1995/96 will concentrate on increasing sample sizes of commonly used country foods, and ensuring that all parts of the Yukon are represented.

Expected project completion date: March 1996

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Table 1. Concentration of dioxins and furans (pg/g wet wt.) in a pool of porcupine fat from three individuals.

Dioxins		Furans	
T4CDD - Total	2.6	T4CDF - Total	ND
2,3,7,8	2.6	2,3,7,8,	ND
P5CDD - Total	20	P5CDF - Total	4.1
1,2,3,7,8	20	1,2,3,7,8	0.6
		2,3,4,7,8	3.5
H6CDD - Total	120	H6CDF - Total	23
1,2,3,4,7,8	11	1,2,3,4,7,8	7.5
1,2,3,6,7,8	87	1,2,3,6,7,8	10
1,2,3,7,8,9	23	2,3,4,6,7,8	5.1
		1,2,3,7,8,9	ND
H7CDD - Total	190	H7CDF - Total	16
1,2,3,4,6,7,8	190	1,2,3,4,6,7,8	16
		1,2,3,4,7,8,9	NDR (0.3)
O8CDD	160	O8CDF	NDR (0.2)

ND = not detectable.
NDR - Peak detected but did not meet quantification criteria.

Table 2. Cadmium concentration (ppm dry wt.) in birds and mammals from the Yukon Territory.

	Kidney				Liver			
Species	**N**	**X**	**±**	**SD**	**N**	**X**	**±**	**SD**
Muskrat	8	<0.2	±	0.1	8	<0.1	±	0.1
Arctic Ground Squirrel	5	15.3	±	6.3	5	5.1	±	3.0
Lynx	0	–	±	–	1	6.2	±	–
Snowshoe Hare	18	20.7	±	16.2	17	2.4	±	2.1
Grouse	34	80.0	±	232.1	28	8.1	±	12.4
Beaver	8	129.7	±	99.1	7	17.0	±	10.2
Ptarmigan	20	143.0	±	68.4	19	38.8	±	33.5
Porcupine	4	168.7	±	100.9	4	38.4	±	24.3

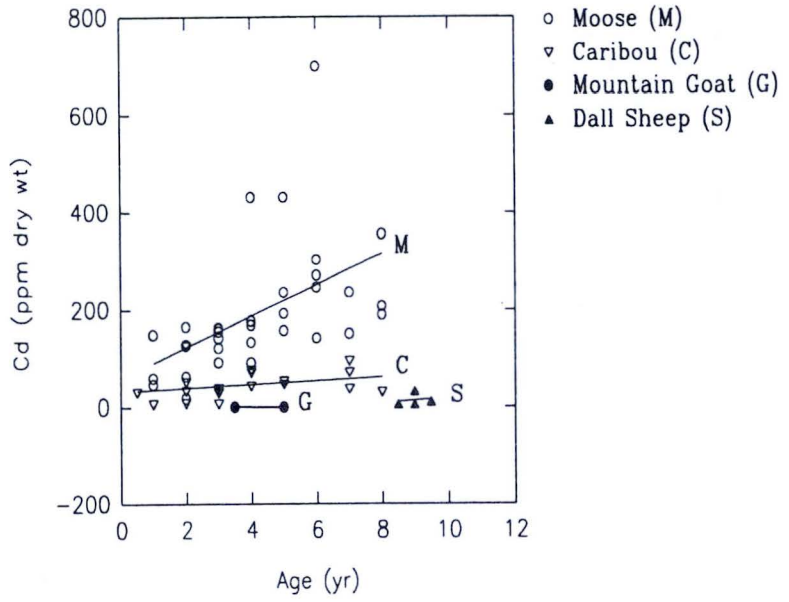

Figure 1. Cadmium concentrations in the kidneys of moose, caribou, mountain goats and Dall sheep from the Yukon.

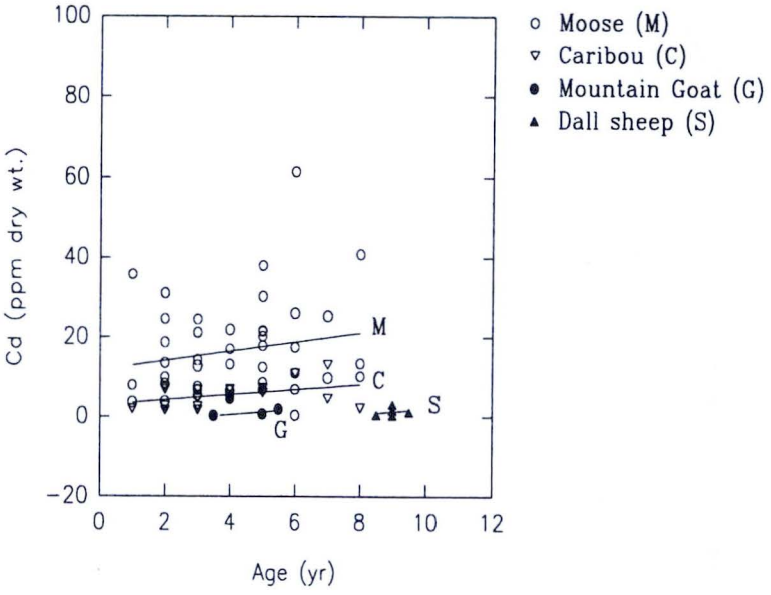

Figure 2. Cadmium concentrations in the livers of moose, caribou, mountain goats and Dall sheep from the Yukon

III HUMAN HEALTH

HUMAN HEALTH
NEW FINDINGS

1) In a study of the effects of food preparation on contaminant levels in traditional food, preliminary results suggest that total organochlorines in boiled or fried walrus blubber are lowered, but not significantly. However, the differences for individual homologues or pesticide groups may change significantly with cooking, and this may be related to evaporation of the more volatile compounds. For boiled blubber, lipid content decreases significantly and this may also lower contaminant concentrations. Total polyunsaturated fatty acids are not changed by food preparation.

2) For cadmium in caribou kidney, baking appears to have minimal effects on the amount of metallothionein-bound Cd.

3) Total mercury levels in cord blood of Inuit newborns from Nunavik (northern Quebec) averaged 68.8 nmol/L and was approximately 10-fold the levels (6.4 nmol/L) measured in newborns from Southern Quebec. The biological safe level of 150 nmol/L was exceeded in 18% of the Inuit newborns of Nunavik. Concentrations of lead in cord blood for Nunavik newborns (0.20 nmol/L) were also greater than those in Southern Quebec samples, and exceeded the intervention level of 0.48 nmol/L in 7% of the Inuit newborns.

4) In the NWT, extensive consultations have been conducted as part of the cord blood monitoring program. Sampling has been completed in the Mackenzie and Kitikmeot regions, and work is underway in the Keewatin and Baffin regions. Actual monitoring results are forthcoming, but were not available for inclusion in this report. Interim guideline levels for PCB, Hg, Cd and Pb in cord blood were developed.

5) A study conducted in Fort Resolution, NWT showed that although cadmium levels in caribou kidney and liver are elevated, human exposure to cadmium is well within safe limits due to the relatively infrequent annual intake of these tissues.

6) Preliminary results for consumption of marine mammals in Nunavik indicate that men and women have similar patterns of consumption: seal meat and seal fat are consumed most often on a monthly basis, followed by beluga skin, blubber and meat. On a yearly basis, fish is also prominent in the diet, while wildfowl is important primarily during the hunting season.

7) Traditional foods remain a large and important part of everyday diets of Sanikiluaq Inuit as shown by their widespread use among households and their thrice daily consumption. Seafood, birds and sea mammals are most often used, followed by berries and land mammals.

8) Caribou and whitefish are the principal traditional foods in Dene and Métis communities throughout the NWT. Moose and trout are also important, but consumption is geographically less uniform. A dietary study was conducted in the Yukon, but results were not available at time of publication of this report.

9) Nutrient analysis of traditional foods in Nunavik indicate that fish have the highest omega-3 fatty acid concentrations in meat, followed by marine mammals and waterfowl. Marine mammal and waterfowl meat also represent a good source of iron and zinc. Marine mammal blubber is high in omega-3 fatty acids and Vitamin A.

10) In Sanikiluaq, traditional foods were found to provide an average of 47% of daily energy requirements and 80% of protein, zinc, iron and niacin. Intakes of Vitamins A and C, and of calcium were low, often below the recommended amounts.

11) For people in Dene/Métis communities, a significant proportion of the required intake of protein, zinc and Vitamin A is supplied by the traditional diet , with dietary fat and energy also being important contributions. Calcium intake is lower than recommended and none of the traditional foods as consumed today represent a significant source of this mineral.

12) A pilot study has been completed which examines the feasibility of conducting research on contaminants effects on newborns. A variety of measures for assessment of child development were tested. Those which were culturally or linguistically inappropriate were eliminated, while others were modified or else their utility was validated. Measures which permit such a study to control for confounding factors were also validated, and a minimum sample size for statistical validity of such a study was determined (n=306).

13) With respect to biomarkers of contaminant exposure, no significant difference in placental EROD activity was found between Inuit women with high PCB body burden (as measured in cord plasma lipids) and a control

population of women in southern Quebec. Therefore, a preliminary assessment of results obtained to date indicates that the PCB body burden of Inuit women may not be high enough to induce EROD activity.

HUMAN CONTAMINANT TRENDS IN ARCTIC CANADA

Project Leader: J.E.B. Walker, Department of Health and Social Services, Government of the Northwest Territories

Project Team: L. Seddon, Regional Contaminants Coordinator, Mackenzie and Kitikmeot Health Regions; Mackenzie and Kitikmeot Consultation Working Groups on Environmental Contaminants, with representation from: Dene Nation, Métis Nation-NWT, Kitikmeot Inuit Association, Dogrib Renewable Resource Committee, regional Environmental Health Officers and Nutritionists, Medical Health Officer, health workers and GNWT Health and Social Services, Kitikmeot Health Board, Mackenzie Regional Health Service; Keewatin Regional Health Board (R. Kielly, R. Brown); Baffin Regional Health Board (D. Paradis, R. Allan); J. MacKinnon, GNWT Health and Social Services.

Collaborators: A. Gilman, Health Canada; É. Dewailly, Laval University

OBJECTIVES

1. To establish a baseline for selected metal and organochlorine contaminants in some residents of the Northwest Territories (NWT);
2. To investigate the relationship between contaminant levels in maternal blood with those in umbilical cord blood;
3. To assess the need for and feasibility of additional monitoring activities for environmental contaminants in NWT Northerners;
4. To compare the magnitude and range of these contaminant concentrations with those of other territorial, national and international jurisdictions;
5. To contribute to territorial, national and international databases.

DESCRIPTION

Evidence from a variety of environmental studies indicates widespread ecosystem contamination of the Arctic environment by organochlorine compounds and heavy metals. Previous work in the Baffin Region of the NWT and Arctic Quebec indicates that these contaminants may be found in elevated levels in some northerners, and that this may be as a result of traditional dietary habits. While health effects resulting from acute, high-level exposures to some contaminants are known, there is little known about health effects associated with chronic, lower-level exposures.

This project will establish a Territorial human contaminants exposure baseline, which will consist of data from each participating Health Region. This will be used to assess the need for additional monitoring, as well as define spatial trends. Temporal trends can then be established in future monitoring activities, if the necessary resources are available.

ACTIVITIES IN 1994/95

The following are Regional summaries of activities in 1994/95; these reports reflect the fact that regional participation in this work is at different stages. The Health Regions are identified in Figure 1.

Mackenzie Regional Health Service and Kitikmeot Health Board

Work in these regions has proceeded collaboratively and simultaneously through the efforts of the (shared) Regional Contaminants Coordinator and the Regional Contaminants Consultation Working Groups listed under project team above. Regular meetings, either face-to-face (in the Mackenzie Region), or via conference call (in the Kitikmeot Region), have resulted in the ongoing participation of regional/community representatives in the development and implementation of protocols for participant recruitment, sampling, and communications.

All Kitikmeot and Mackenzie mothers who planned to deliver their babies at Stanton Yellowknife Hospital were invited to participate in this program. Women met with their community Health Worker to discuss the project, and if they wished to participate, provided their informed consent in writing. Women were asked questions about their lifestyle choices, which may influence their exposure to various contaminants.

Participants are provided the opportunity of knowing their own test results for contaminants that have known guidelines (total PCBs [based on Aroclor 1260 standard], mercury, lead and cadmium). Additional information will accompany these results to assist participants with interpretation of their individual results. Summarized results will be provided to community and regional groups.

Consultations/Communications

Much of 1994/95 activities were devoted to maintaining links with Health Workers, participants, communities and Regional Consultation Working Groups.

Working Group activities focused on issue identification, and program development and implementation. These activities were achieved through the following:

- one joint meeting (October 1994);
- five Mackenzie Working Group meetings (July, November 1994; January, February, March 1995), including two meetings on fact sheet development with some members;
- six Kitikmeot Working Group teleconferences (May, July, August 1994; January, February, March 1995); and
- numerous presentations on program activities to various community agencies, including hamlet councils, school boards and Aboriginal organizations.

Communications with Health Workers included:

- weekly visits to Stanton Yellowknife Hospital (Obstetrics and Lab) to maintain current participant lists and monitor sampling kit availability;
- information sessions (in person and via teleconference) with Stanton Yellowknife Hospital (Obstetrics, Lab, Nursing Education) and community Health Workers; and
- monthly newsletters with program activities.

All communities in the Kitikmeot and Mackenzie Regions received program information and materials, including:

- environmental health posters (regionally commissioned);
- a 17-minute video entitled "Environmental Contaminants in the North";
- a one-page maternal and cord blood monitoring program flyer; and
- a two-page fact sheet on contaminants in the north.

Additionally, "Nedaa," a Yukon television show broadcast in the NWT, aired the video "Environmental Contaminants in the North" in early January 1995. All community groups and participants were informed of this broadcast in advance.

Protocol Development

Program forms (consent, separation, registration, survey) and information packages were finalized in November 1994, following a three-month trial period. Modifications to these forms were based on input received by Health Workers, Working Group members and Regional and Territorial health professionals. Selected program materials have been translated into Inuktitut, Innuinaqtun and Chipewyan, and additional translations are currently underway for South Slavey and Dogrib.

Sampling

As of 23 March 1995, 263 women were recruited into the program during the 1994/95 fiscal year. Of these 263 participants, 186 were from the Mackenzie Region, and 77 were from the Kitikmeot Region. Participant ethnicity was as follows: 76 Inuit, 45 Dene, 11 Métis and 131 non-Aboriginal. Participants were recruited into the program about two months (on average) prior to delivering their babies. Many women (140 or 53% of the 1994/95 recruitment) were recruited during the program's first three months (May-July, 1994). Blood samples were collected from May 1994 to June 1995.

Results

Total deliveries at Stanton Yellowknife Hospital were compared to program births for the months of May to August 1994. From this comparison, it appears that the program successfully recruited Inuit, Dene and non-Aboriginal women *in proportion* to the "population" of women who were eligible to participate (χ=2.972; p=0.226; df=2). Complete birthing statistics for the entire recruitment period will be collected to conduct a more comprehensive evaluation of recruitment success.

Centre du Toxicologie (L'Université Laval) has performed tests for organochlorinated pesticides and PCBs on 294 blood samples (not including duplicate testing). Tests

for cadmium, lead, mercury, copper, zinc and selenium have been performed on 300 samples (not including duplicate testing). Centre du Toxicologie has provided the Program Coordinator with available data in both computerized and hard-copy format, which was then entered into a regional contaminants database.

DISCUSSION/CONCLUSIONS

Consultation/Communications

Consultations will be ongoing with the Consultation Working Groups, Health Workers, Regional health agencies, communities and GNWT Health and Social Services. Strategies for results interpretation and communication to Health Workers, Participants and Communities will be formalized in early 1995/96. These strategies will be developed in full consultation with Regional Working Groups as part of cooperative risk management planning.

It is anticipated that participants will be provided the opportunity of knowing their own results in Fall 1995 by way of community Health Workers. Final results will be conveyed to community agencies immediately following notification of participants. Community visits will occur at the invitation of the community in late 1995/96, and perhaps continue into 1996/97.

Protocol Development

A final protocol document is being drafted for the Kitikmeot/ Mackenzie monitoring program. This protocol will include modifications to sampling procedures as well as new sections on database design and management, data analyses, and results communication. The protocol will be finalized in 1995/96.

GNWT Health and Social Services is working collaboratively with the Program Coordinator to develop territorial standards for maternal and cord blood monitoring. This protocol will be available to other regional health agencies to assist with program implementation in other NWT regions. This protocol will also be available to other national and international initiatives.

Sampling and Data Analysis

Recruitment of women into the program ceased in early June 1995, with all blood sampling completed at Stanton Yellowknife Hospital by early July 1995. Laboratory analyses of blood samples were completed in September 1995, and analyses of survey and lab data occurred in September/October 1995.

Evaluation

Evaluation of program materials and recruitment activities will occur in 1995/96. Evaluation of results communication activities will occur following implementation of the communication strategies.

Baffin Regional Health Board

Consultations/Communications

A workshop on Environmental Contaminants was hosted by the Environmental Health division of the Baffin Regional Health Board in Iqaluit in April 1994. Prior to the workshop a number of questionnaires were sent to each of the communities in the Baffin Region. Information from these questionnaires provided topics for discussion during the workshop on contaminant issues that related to community concerns.

Each community from the Baffin Region had two participants at the workshop. Participants included Community Health Representatives, local Health Committee members, Hamlet councillors and employees, and Hunter and Trapper Association Board members. Representatives from the Baffin Regional Inuit Association, Municipal and Community Affairs, Indian and Northern Affairs Canada (INAC), and the Chair of the Baffin Regional Health Board also participated.

There were six presentations: the first three were on contaminants in the Arctic, wildlife and people, and the second set discussed different issues on contaminants in the Baffin Region.

In September 1994, following a series of presentations to the Board, the Baffin Regional Health Board (BRHB) approved a contaminants monitoring program for Baffin residents. The Baffin Regional Inuit Association recommended that BRHB proceed with this activity prior to the September 1994 Board meeting.

Protocol Development

A workshop was held in December 1994 that was attended by nurses and/or Community Health Representatives (CHRs) from all but two Baffin communities. The purpose of this workshop was to discuss specific aspects of the Territorial maternal and cord blood monitoring program, update health workers on program progress and activities in other Regions, and identify areas in the existing monitoring protocol that would require modification prior to implementation. There was interest and enthusiasm expressed by health workers at this workshop about participating in contaminants

monitoring, although there were also concerns raised about current work loads and how these additional duties could be incorporated.

Discussion

Since mid-1994/95 there has been a 100% change in key Baffin Regional Health Board staff who were involved in consultation activities and protocol development. This has resulted in delays while these positions were staffed, and then while new staff were oriented.

Consultation activities expanded community awareness in the Baffin Region about contaminants issues, and were necessary precursors to more specific consultations about human contaminant monitoring activities in the Region.

Keewatin Regional Health Board

Consultation/Communications

To follow up on recommendations from the March 1994 Environmental Contaminants Workshop held in Rankin Inlet, community consultations were conducted in each community in the Keewatin Region during 1994/95. The purpose of these consultations was to provide opportunities for information exchange with Hamlet Councils, Hunter and Trapper Associations, Senior Administrative Officers, Renewable Resource Officers, and other community representatives about contaminants. These information exchanges included opportunities to discuss both local and long-range contaminant concerns, and were done in part to assist with 'setting the stage' for more detailed consultations about human contaminants monitoring activities.

As part of these community consultations, the video "Environmental Contaminants in the North" was shown in each community in Inuktitut or English. Copies of each version were left in Health Centres for future reference.

Activities/Results

Community representatives from Arviat, Baker Lake, Chesterfield Inlet, Coral Harbour, Rankin Inlet, Repulse Bay, Sanikiluaq and Whale Cove were able to raise their concerns about their local environment. Topics that were raised included those related to a lack of information exchange between researchers and the people that reside in the communities under investigation.

Other concerns were related to the health of traditional food species and the environment in which these animals live. Many people were interested in which kinds of traditional foods they should not eat because of high levels of contaminants. Representatives were troubled about the environmental impacts of sewage, garbage, and tailings ponds and their effects on the local wildlife. Concerns were also brought forward about pulp and paper mills in Alberta, incinerators used in Quebec, and the potential hazards from oil spills in the Arctic Ocean. Sanikiluaq participants expressed concerns about the proposed Great Whale Project, and the likelihood of environmental damage that could result if the project proceeds.

Questions about human baseline monitoring were also raised. These included whether compensation may be available for people that are found to have contaminants in them, how many people would be involved with this monitoring, and what ramifications there may be if the results of this monitoring show that there are high levels of contaminants in people.

Discussion

Concerns about mercury and toxaphene in fish at Peter Lake following a presentation of research results by Fisheries and Oceans Canada (DFO), INAC and GNWT Health and Social Services in April 1995 prompted a proactive response by the Keewatin Regional Health Board. The Board passed a resolution to implement human contaminants monitoring activities in the Keewatin Region. The community consultations that preceded this presentation about Peter Lake facilitated the Board's recommendation to continue contaminants investigations in the Keewatin Region, with an emphasis on Keewatin residents.

Inuvik Regional Health Board

There has been considerable activity in this Health Region in assessing communities' health and social services needs. At this time contaminants activities have not been defined as a priority by this Board.

Territorial Activities/Results

In June, 1994, the GNWT Department of Health and Social Services established an Ad Hoc Working Group of Canadian experts to develop NWT Interim Contaminants Blood Guidelines (Table 1). These Guidelines were developed to assist with interpretation of results from the Maternal and Cord Blood Monitoring program. The following blood guidelines are interim because of the sparse toxicological data available at the present time in this area, and the need for more consultation with international experts to agree formally on the usefulness of these levels. Standardizing blood guidelines, even for a limited number of contaminants, will enhance the ability of public health workers and others to respond

consistently and promptly in multiple jurisdictions. This is an important element of risk management and communication.

TERRITORIAL DISCUSSIONS/CONCLUSIONS

From the above information, it is apparent that progress in establishing a contaminants baseline for NWT residents is proceeding as is regionally feasible, given that each Region is required to address a wide range of health-related issues.

Protocols, information materials, and communication strategies developed by the Mackenzie and Kitikmeot Regions have been made available to other interested Regions, to avoid duplication of effort and ensure there are common elements to the Territorial baseline. GNWT Health and Social Services is a member of all Regional Contaminants Consultation Working Groups, and so participates in the definition, development and implementation of Regional activities.

There continue to be questions raised by Regional Health agencies and others about funding opportunities to continue the work begun under the Arctic Environmental Strategy for Northerners' health- related contaminants questions. This issue requires sustained effort to ensure that confidence in, and use of, traditional foods are not unnecessarily altered.

Expected project completion date: Baseline work in the Mackenzie and Kitikmeot Health Regions will be completed by 31 March 1997. Baseline work in the Baffin and Keewatin Health Regions is targeted for completion by 31 March 1997, however results communication activities may continue beyond this date.

It is anticipated that there will continue to be questions and concerns about contaminants in traditional foods beyond 31 March 1997.

Table 1. Interim NWT Contaminant Guidelines for Blood Levels for Women of Reproductive Age and for Newborns[1].

Contaminant	Women of Reproductive Age (ppb)	Newborns (ppb)	Comments
Mercury	≤ 20 'tolerable' > 20 'level of concern' ≥ 40 'level of action'	≤ 10 'tolerable'[a] > 10 'level of concern' ≥ 20 'level of action'	• Newborns are 2-3 times more sensitive than adults to neuro-developmental effects. • Bioconcentration factor is 1.5. • Blood/hair conversion factor is 250 (WHO EHC 101 MeHg).
Cadmium	≤ 5 'tolerable' > 5 'level of concern/ action'	≤2.5 'tolerable' >2.5 'level of conern/ action'	• Cd contamination from consumption of organ meats is negligible compared with contamination from smoking (Benedetti *et al.* 1994). • Cd does not cross placental barrier.
Lead	≤ 10 'tolerable' > 10 'level of concern' ≥ 15 'level of action'	≤ 10 'tolerable' > 10 'level of concern' ≥ 15 'level of action'	• Paired maternal/cord blood analysis shows slightly lower cord blood levels than maternal.
PCBs	≤ 5 'tolerable' > 5 'level of concern/ action'	≤ 2.5 'tolerable' > 2.5 'level of concern/ action'	• Blood lipid assumed to be 50% lower in cord vs. maternal blood. • There is evidence of a selective placental barrier for some PCB congeners.

[a] [Hg] Women of reproductive age x 1.5/3 = [Hg] Newborn

[1] For further details regarding discussion that took place to establish these levels, please refer to the NWT Human Contaminant Blood Guidelines Report.

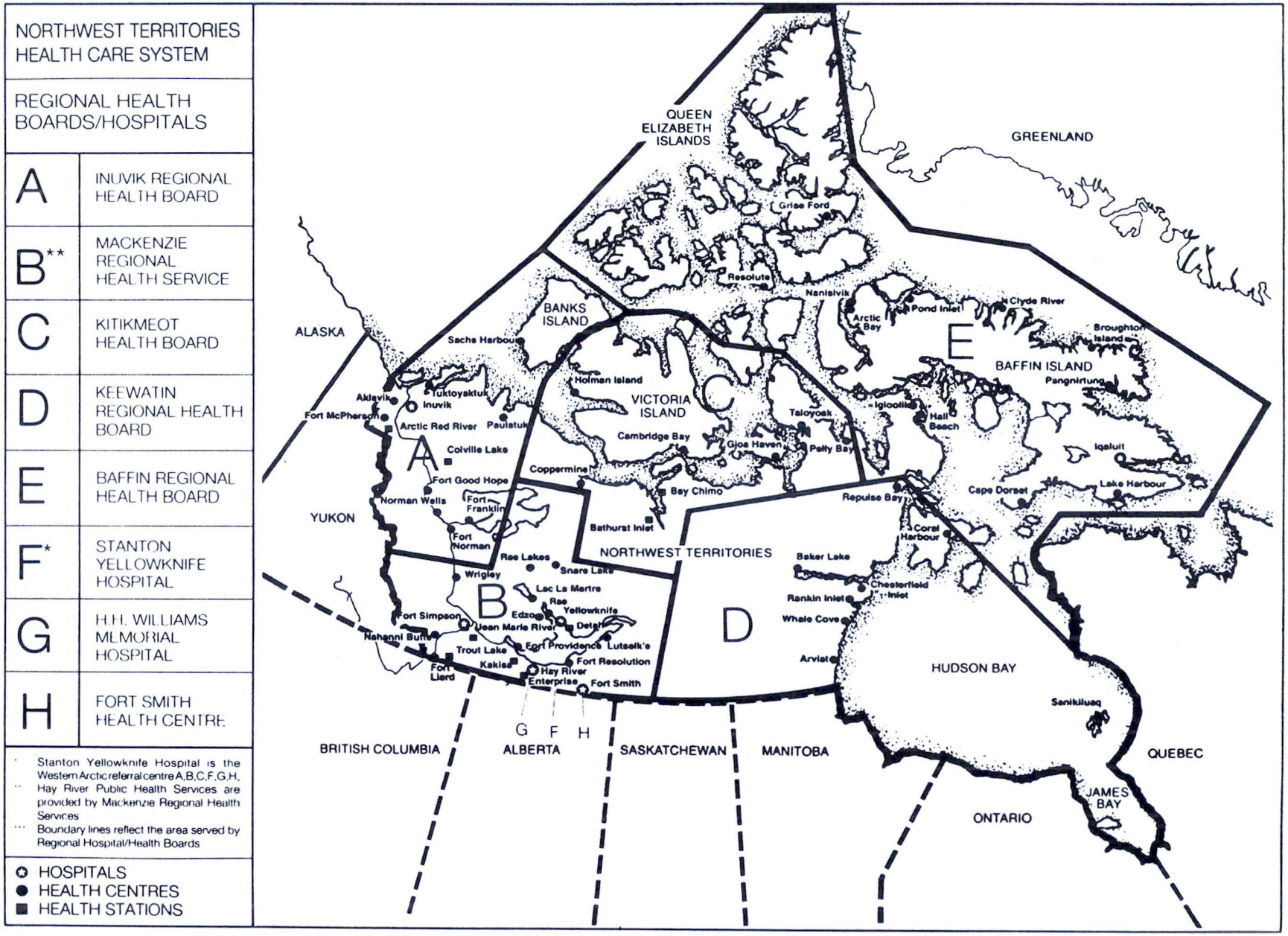

Figure 1. Northwest Territories Health Care System

CORD BLOOD STUDY-NUNAVIK

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OBJECTIVES

Because lead, mercury and organochlorines are transferred to the fetus through the placental barrier, prenatal exposure can be properly assessed by measuring the concentration of contaminants in the cord blood at birth. The general objective of this project is to monitor prenatal exposure to food chain contaminants in Nunavik during 1994/95 in order to assess spatial and temporal trends.

The specific objectives are:

1. To measure lead, mercury and organochlorines in the cord blood of all Inuit newborns from Nunavik between April 1994 and March 1995;

2. To link levels of exposure with personal (age of the mother, weight before and after birth, parity, use of medication and smoking habits), environmental (community of residence) and dietary (omega-3 fatty acid content in plasma phospholipids) variables;

3. To study the relationship between plasma levels of omega-3 fatty acids and birth weight;

4. To compare the levels of exposure found in Nunavik with data from other regions in Québec, Labrador, the Northwest Territories and other circumpolar countries (Alaska, Finland, Greenland, Iceland, Russia and Sweden) in order to contribute to the Human Health Subprogramme of the Arctic Monitoring and Assessment Programme (AMAP);

5. To establish, in collaboration with the Public Health Department of the Nunavik Regional Board of Health and Social Services, the background of a risk management procedure.

DESCRIPTION

Early work conducted on Baffin Island has demonstrated that because of their traditional dietary habits, Inuit people are exposed to unusually high quantities of contaminants, mainly heavy metals and organochlorines (Kinloch *et al.* 1992).

Most epidemiological and experimental studies on health effects related to lead, mercury and PCB exposure suggest that prenatal life is the most susceptible period for induction of adverse neurodevelopmental effects. In the Great Lakes area results reported in 1983 indicated that newborns of women who had eaten large quantities of contaminated fish were smaller at birth (Fein *et al.* 1984). Furthermore, there was a delay in the maturation of their motor abilities and cognitive functions; they also had poorer visual recognition memory at one year of age (Jacobson *et al.*1985). Researchers reported recently that, at four years old, 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.*1990a, 1990b). In addition to PCBs, lead and especially methylmercury are recognized as major neurotoxic compounds, particularly for the fetus.

In contrast, high exposure to omega-3 fatty acids during the prenatal period improves birth weight and visual acuity of newborns (Granjean 1992). Inuit people have very high blood levels of omega-3 fatty acids. The Santé Québec health survey, conducted during 1992 in Nunavik (Dewailly *et al.* 1994), has shown that a diet rich in fishes and marine mammals results in high levels

of omega-3 fatty acids in the plasma of adults. These substances are transmitted to the fetus during pregnancy and have a direct effect on the weight of the newborn and on prolonging the gestation period. Selenium is another essential nutrient found in sea products. This element is an anticarcinogen and can antagonize mercury-induced toxicity.

To properly assess the risks and benefits from the Inuit diet, the prenatal exposure to contaminants and nutrients must be determined and therefore a cord blood study was initiated in Nunavik as well as in other Arctic regions.

ACTIVITIES IN 1994/95

Every mother delivering at the Tulattavik Health Centre of Ungava and at the Inuulitsivik Health Centre in Puvurnituq was asked to participate in the program after receiving proper information. After signing the consent form, blood was collected at birth from the umbilical cord. Since 1993, a total of 238 samples were received at the QuébecToxicological Centre. To date, 238 analyses of metals and 219 of organochlorines have been performed. Furthermore, 135 analyses of phospholipids have been conducted.

Heavy metals (lead and mercury) and selenium were measured in whole blood. For blood samples containing more than 100 nmol/L of total mercury, inorganic mercury was also measured. Organochlorines included 14 PCB congeners (IUAPAC no 28, 52, 99, 101, 105, 118, 128, 138, 153, 156, 170, 180, 183, 187) and pesticides (aldrin dieldrin, heptachlor epoxide, β–BHC, α– and δ–chlordane, *cis*-nonachlor, *p,p'*–DDE, *p,p'*–DDT, hexachlorobenzene, mirex, oxychlordane and *trans*-nonachlor). Detection limits were 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. Total blood lipids were also measured in order to express organochlorine concentrations on a lipid basis.

Recently, data was extracted from the medical files of participating mothers and their babies. The following information was obtained: newborn weight, height, cranial circumference and APGAR (newborn health examination) at five minutes following birth; maternal weight before and after delivery, length of gestation and date of last menses, ultrasound performed, total number of live births, use of medication or vitamins during pregnancy, smoking habits and all blood pressure measurements during labour. These data have been analysed and a detailed report will be available in fall 1995.

Finally, in collaboration with the Health Department of the Northwest Territories, a proposal was elaborated for biological guidelines concerning the concentrations of lead, mercury and PCBs in cord blood of newborns living in Arctic Canada.

RESULTS AND DISCUSSION

Figures 1 to 4 display the mean concentrations for mercury, lead, PCBs, selenium and fatty acids in cord blood samples from Nunavik, and in Southern Québec samples collected during 1993-1994 (Rhainds *et al.* 1994). Tables 1 and 2 show arithmetic and geometric means as well as comparative data between Hudson and Ungava Bay regions. In calculating mean concentrations, non-detected results were given a value of equal to half the detection limit.

Heavy Metals

Mercury: The mean concentration of total mercury measured in 238 samples was 68.8 nmol/L (95%-confidence interval (95 %-CI): 62.1-76.1). This concentration is approximately twice the level of 40 nmol/L found during the Québec Inuit Health survey among women aged 18 to 25 years. In cord blood samples recently collected from Southern Québec newborns (N= 954), the mean concentration was 6.4 nmol/L (95%-CI: 3.6-4.3).

Even though the levels measured in Nunavik newborns were ten times greater that those measured in Southern Québec, newborns, the mean level found in Inuit newborns is still below the intervention level set at 150 nmol/L. However, 18% of Inuit newborns had concentrations above this safe biological level. Furthermore, since there is uncertainty regarding the possibility of neurodevelopmental effects occurring under this intervention level, a study was initiated to investigate the impacts of this prenatal exposure on the neurobehavioural and psychomotor development in Inuit infants (this study will be realized this coming fall under supervision of Dr. Gina Muckle).

Lead: The mean concentration of lead in Nunavik samples was 0.20 µmol/L (95%-CI: 0.18-0.21). By comparison, the average concentration found in 955 Southern Québec samples was 0.09 µmol/L (95%-CI: 0.08-0.10). In Nunavik, 7% of newborns had a blood concentration above the intervention level of 0.48 µmol/L. Since we have little information about lead exposure sources in adults and infants from Nunavik, we plan to investigate the sources of lead exposure in this population in collaboration with the Nunavik Public Health Direction.

Organochlorines

PCBs and Pesticides: On a lipid basis, the mean (geometric) PCB concentration, expressed as Aroclor 1260, was 774 µg/kg (95%-CI: 703-852). The arithmetic mean, 995 µg/kg, was three times greater than that found in Southern Québec (200 µg/kg) and less than half the mean concentration measured in milk fat of Inuit mothers during 1990/91 (2900 µg/kg). This suggests that the transport of these substances from the mother to the fetus is partially hindered by the placental barrier. However analysis of paired samples are required before concluding with regard to maternal-fetal PCB transport.

The PCB congener profile observed in Inuit samples was similar to that observed in Southern Québec samples (Figure 2). Major congeners were PCB IUPAC no. 153, 138, 180, 99 and 187. Congener nos. 28, 52, 105, 128 and 156 were detected in less than half of Inuit samples. Pesticide concentrations in Nunavik samples were generally higher than those observed in Southern Québec (Figure 3).

Nutrients

Omega-3 fatty acids: Plasma analysis performed on 135 Inuit cord blood samples indicated a mean concentration of eicosapentanoic acid (EPA 20:5n3) of 0.36% (percentage of total phospholipid), compared to 0.20% in the 30 cord plasma samples from Southern Québec controls ($P < 0.001$). The ratio EPA/AA (AA: arachidonic acid) was 0.035 for Nunavik and 0.012 for Southern Québec controls (Figure 4).

Selenium: The mean (geometric) concentration of selenium in 231 whole blood samples was 3.7 µmol/L (95%-CI: 3.5-3.9). In Southern Québec, the mean concentration measured in 144 samples was 2.4 µmol/L (95%-CI: 2.3-2.4). Selenium and mercury concentrations were strongly correlated. In Faroe Island, the median concentration determined in 1020 cord blood samples was 1.4 µmol/L, whereas in West and East Greenland, median concentrations were 3.1 and 1.86 µmol/L, respectively (Hansen 1988). However, in the latter studies, selenium was measured in plasma and, consequently, comparisons with our data should be made with caution.

CONCLUSIONS

Prenatal exposure to organochlorines and heavy metals in the Arctic largely exceeds that encountered in meridional regions of the province of Québec. However, cord blood concentrations of important nutrients such as selenium in omega-3 fatty acids are greater in Nunavik than in Southern Québec newborns and may afford protection against contaminants in the Inuit population. This cord blood study will continue in 1995/96 and trends of human contamination throughout the Canadian Arctic will be analysed when results from the Northwest Territories and Labrador will be made available. Part of the funding for these activities will be provided by Health and Welfare Canada-Food Directorate.

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Table 1. Concentration of PCBs, chlorinated pesticides, selenium, heavy metals and fatty acids in cord blood of Nunavik newborns.

Contaminant	n	Mean Arithmetic	Mean Geometric	(95 % CI)	(Range)	% detected
PCB-Total (µg/L)	219	2.497	1.944	(1.767–2.139)	(0.190–15.600)	100
Lipid basis (µg/kg)	216	994.608	773.849	(703.050–851.778)	(73.021–5429.864)	
PCB congeners (µg/L)						
28	219	0.011	0.010	(0.010–0.011)	(0.010–0.130)	2
52	219	0.020	0.017	(0.015–0.018)	(0.010–0.089)	49
99	219	0.069	0.055	(0.050–0.060)	(0.010–0.460)	96
101	219	0.021	0.018	(0.016–0.019)	(0.010–0.080)	56
105	219	0.016	0.014	(0.013–0.015)	(0.010–0.070)	34
118	219	0.056	0.045	(0.042–0.050)	(0.010–0.290)	96
128	219	0.010	0.010	(0.010–0.010)	(0.010–0.020)	2
138	219	0.198	0.156	(0.142–0.171)	(0.020–1.250)	100
153	219	0.282	0.218	(0.198–0.240)	(0.020–1.670)	100
156	219	0.019	0.016	(0.014–0.017)	(0.010–0.130)	42
170	219	0.043	0.030	(0.027–0.034)	(0.010–0.240)	78
180	219	0.127	0.094	(0.085–0.104)	(0.010–0.750)	99
183	219	0.018	0.015	(0.014–0.016)	(0.010–0.080)	45
187	219	0.061	0.048	(0.044–0.053)	(0.010–0.330)	97
Pesticides (µg/L)						
Aldrin	219	0.010	0.010	(0.010–0.010)	(0.010–0.032)	1
ß–BHC	219	0.026	0.023	(0.021–0.024)	(0.015–0.120)	43
α–chlordane	219	0.011	0.010	(0.010–0.010)	(0.010–0.200)	1
γ–chlordane	217	0.010	0.010	(0.010–0.010)	(0.010–0.030)	0
Cis-nonaclor	219	0.035	0.026	(0.023–0.028)	(0.010–0.180)	68
pp'–DDE	219	1.318	0.989	(0.897–1.090)	(0.125–14.000)	100
pp'–DDT	219	0.062	0.044	(0.039–0.048)	(0.015–0.550)	77
Hexachlorobenzene	219	0.185	0.146	(0.133–0.161)	(0.020–1.200)	100
Mirex	218	0.017	0.013	(0.012–0.014)	(0.010–0.125)	26
Oxychlordane	219	0.105	0.073	(0.065–0.082)	(0.010–0.670)	95
Trans-nonachlor	219	0.172	0.128	(0.115–0.143)	(0.010–1.130)	99
Selenium (µmol/L)	228	4.022	3.665	(3.473–3.867)	(1.420–14.100)	
Heavy metals						
Mercury (nmol/L)	238	93.508	68.757	(62.096–76.133)	(6.000–495.000)	
Lead (µmol/L)	238	0.236	0.198	(0.184–0.213)	(0.040–1.280)	

Table 1. (continued)

Contaminant	n	Mean Arithmetic	Mean Geometric	(95 % CI)	(Range)	% detected
Phospholipids (%)						
14:0	135	0.825	0.716	(0.649–0.789)	(0.024–2.813)	
14:1	135	0.205	0.183	(0.164–0.204)	(0.000–0.598)	
15:0	135	0.200	0.164	(0.144–0.188)	(0.000–2.485)	
16:0	135	31.526	31.425	(30.991–31.865)	(20.916–37.773)	
16:1	135	1.589	1.283	(1.146–1.437)	(0.168–11.211)	
18:0	135	12.947	12.772	(12.433–13.120)	(8.773–28.706)	
18:1	135	14.399	14.114	(13.631–14.614)	(4.275–23.987)	
18:2N6	135	9.976	9.779	(9.458–10.110)	(5.433–20.199)	
18:3N6	135	0.161	0.144	(0.125–0.166)	(0.000–0.629)	
18:3N3	135	0.023	0.061	(0.046–0.080)	(0.000–0.747)	
18:4N3	135	0.001	0.023	(0.016–0.034)	(0.000–0.044)	
20:0	135	0.727	0.724	(0.705–0.743)	(0.000–1.005)	
20:1	135	0.026	0.067	(0.055–0.083)	(0.000–0.496)	
20:2N6	135	1.311	1.161	(1.056–1.276)	(0.000–3.541)	
20:3N6	135	5.142	5.045	(4.875–5.221)	(2.343–7.343)	
20:4N6	135	10.477	10.191	(9.795–10.603)	(5.748–18.589)	
20:3N3	135	0.057	0.116	(0.104–0.128)	(0.000–0.228)	
20:4N3	135	0.016	0.109	(0.093–0.128)	(0.000–0.221)	
20:5N3	135	0.418	0.362	(0.324–0.405)	(0.000–1.845)	
22:0	135	1.050	1.039	(1.005–1.074)	(0.000–1.439)	
22:1	135	0.570	0.522	(0.482–0.564)	(0.000–2.045)	
22:2N6	135	0.007	0.060	(0.049–0.073)	(0.000–0.105)	
22:4N6	135	0.459	0.455	(0.438–0.472)	(0.000–0.764)	
22:5N6	135	0.609	0.612	(0.529–0.708)	(0.000–1.551)	
22:5N3	135	0.250	0.248	(0.229–0.267)	(0.000–0.922)	
22:6N3	135	3.918	3.753	(3.569–3.948)	(1.429–7.262)	
24:0	135	0.905	0.890	(0.857–0.925)	(0.000–1.495)	
24:1	135	2.204	2.169	(2.102–2.238)	(1.121–3.046)	
EPA/AA	135	0.042	0.035	(0.031–0.040)	(0.000–0.197)	
DHA/AA	135	0.383	0.368	(0.351–0.386)	(0.166–0.760)	
EPA + DHA	135	4.337	4.125	(3.907–4.355)	(1.429–8.046)	
Total phospholipids	135	98.210	95.996	(92.768–99.337)	(59.480–299.000)	
Σ Omega 3	135	4.684	4.449	(4.211–4.701)	(1.551–8.883)	

Table 2. Concentration of PCBs, chlorinated pesticides, selenium, heavy metals and fatty acids in cord blood of Nunavik newborns, according to region of residence.

Contaminant	Region	n	Mean Arithmetic	Mean Geometric	(95 % CI)	(Range)
PCB-Total (µg/L)	Hudson	97	2.986	2.217	(1.887–2.605)	(0.190–15.600)
	Ungava	122	2.109	1.751	(1.566–1.957)	(0.270–8.400)
Lipid basis (µg/kg)	Hudson	94	1209.332	876.997	(740.179–1039.106)	(73.021–5429.864)
	Ungava	122	829.165	702.727	(632.016–781.349)	(138.748–2757.432)
PCB congeners (µg/L)						
28	Hudson	97	0.010	0.010	(0.010–0.010)	(0.010–0.030)
	Ungava	122	0.011	0.010	(0.010–0.011)	(0.010–0.130)
52	Hudson	97	0.022	0.018	(0.016–0.020)	(0.010–0.089)
	Ungava	122	0.019	0.016	(0.014–0.017)	(0.010–0.070)
99	Hudson	97	0.077	0.058	(0.050–0.068)	(0.010–0.460)
	Ungava	122	0.063	0.053	(0.047–0.059)	(0.010–0.210)
101	Hudson	97	0.017	0.014	(0.013–0.016)	(0.010–0.080)
	Ungava	122	0.024	0.021	(0.019–0.023)	(0.010–0.060)
105	Hudson	97	0.016	0.014	(0.012–0.015)	(0.010–0.070)
	Ungava	122	0.016	0.014	(0.013–0.015)	(0.010–0.060)
118	Hudson	97	0.058	0.045	(0.039–0.052)	(0.010–0.290)
	Ungava	122	0.055	0.046	(0.041–0.051)	(0.010–0.200)
128	Hudson	97	0.010	0.010	(0.010–0.010)	(0.010–0.020)
	Ungava	122	0.010	0.010	(0.010–0.010)	(0.010–0.020)
138	Hudson	97	0.232	0.174	(0.148–0.204)	(0.020–1.250)
	Ungava	122	0.171	0.142	(0.127–0.159)	(0.021–0.660)
153	Hudson	97	0.341	0.252	(0.214–0.296)	(0.020–1.670)
	Ungava	122	0.235	0.195	(0.174–0.218)	(0.030–0.960)
156	Hudson	97	0.023	0.017	(0.015–0.020)	(0.010–0.130)
	Ungava	122	0.017	0.014	(0.013–0.016)	(0.010–0.072)
170	Hudson	97	0.054	0.036	(0.030–0.044)	(0.010–0.240)
	Ungava	122	0.034	0.026	(0.023–0.030)	(0.010–0.160)
180	Hudson	97	0.162	0.114	(0.096–0.135)	(0.010–0.750)
	Ungava	122	0.100	0.081	(0.072–0.090)	(0.010–0.460)
183	Hudson	97	0.019	0.016	(0.014–0.018)	(0.010–0.080)
	Ungava	122	0.016	0.014	(0.013–0.015)	(0.010–0.080)
187	Hudson	97	0.070	0.053	(0.045–0.061)	(0.010–0.330)
	Ungava	122	0.053	0.045	(0.041–0.050)	(0.010–0.230)
Pesticides (µg/L)						
Aldrin	Hudson	97	0.010	0.010	(0.010–0.010)	(0.010–0.020)
	Ungava	122	0.010	0.010	(0.010–0.010)	(0.010–0.032)
ß–BHC	Hudson	97	0.028	0.022	(0.020–0.025)	(0.015–0.120)
	Ungava	122	0.026	0.023	(0.021–0.025)	(0.015–0.066)
α–chlordane	Hudson	97	0.012	0.010	(0.010–0.011)	(0.010–0.200)
	Ungava	122	0.010	0.010	(0.010–0.010)	(0.010–0.010)
γ–chlordane	Hudson	97	0.010	0.010	(0.010–0.010)	(0.010–0.030)
	Ungava	120	0.010	0.010	(0.010–0.010)	(0.010–0.010)
Cis-nonaclor	Hudson	97	0.039	0.028	(0.024–0.033)	(0.010–0.180)
	Ungava	122	0.032	0.024	(0.021–0.027)	(0.010–0.170)
pp'-DDE	Hudson	97	1.621	1.129	(0.956–1.332)	(0.170–14.000)
	Ungava	122	1.077	0.890	(0.796–0.996)	(0.125–4.600)
pp'-DDT	Hudson	97	0.075	0.047	(0.040–0.057)	(0.015–0.550)
	Ungava	122	0.051	0.041	(0.036–0.046)	(0.015–0.220)
Hexachlorobenzene	Hudson	97	0.185	0.140	(0.121–0.163)	(0.029–1.200)
	Ungava	122	0.185	0.151	(0.134–0.170)	(0.020–0.690)
Mirex	Hudson	96	0.021	0.016	(0.014–0.018)	(0.010–0.125)
	Ungava	122	0.013	0.012	(0.011–0.012)	(0.010–0.080)
Oxychlordane	Hudson	97	0.118	0.081	(0.067–0.097)	(0.010–0.670)
	Ungava	122	0.095	0.068	(0.058–0.079)	(0.010–0.630)
Trans-nonachlor	Hudson	97	0.195	0.143	(0.122–0.168)	(0.020–1.130)
	Ungava	122	0.153	0.117	(0.102–0.135)	(0.010–0.650)

Table 2 . (continued)

Contaminant	Region	n	Mean Arithmetic	Mean Geometric	(95 % CI)	(Range)
Selenium (µmol/L)	Ungava	112	3.881	3.555	(3.301–3.829)	(1.800–11.050)
	Hudson	116	4.159	3.774	(3.493–4.076)	(1.420–14.100)
Heavy metals						
Mercury (nmol/L)	Hudson	118	114.686	88.562	(77.202–101.593)	(6.000–495.000)
	Ungava	120	72.683	53.607	(46.744–61.478)	(9.000–443.000)
Lead (µmol/L)	Hudson	118	0.256	0.213	(0.191–0.237)	(0.040–1.210)
	Ungava	120	0.216	0.184	(0.167–0.203)	(0.050–1.280)
Phospholipids (%)						
14:0	Hudson	63	0.789	0.724	(0.653–0.802)	(0.325–1.635)
	Ungava	72	0.856	0.709	(0.604–0.832)	(0.024–2.813)
14:1	Hudson	63	0.202	0.193	(0.175–0.212)	(0.000–0.348)
	Ungava	72	0.208	0.174	(0.143–0.212)	(0.000–0.598)
15:0	Hudson	63	0.220	0.184	(0.165–0.204)	(0.087–2.485)
	Ungava	72	0.182	0.148	(0.116–0.188)	(0.000–0.566)
16:0	Hudson	63	31.696	31.575	(30.868–32.297)	(20.916–37.773)
	Ungava	72	31.376	31.295	(30.764–31.834)	(23.534–36.923)
16:1	Hudson	63	2.017	1.712	(1.501–1.953)	(0.406–11.211)
	Ungava	72	1.215	0.997	(0.852–1.167)	(0.168–2.881)
18:0	Hudson	63	12.364	12.125	(11.581–12.694)	(8.773–28.706)
	Ungava	72	13.457	13.366	(13.014–13.727)	(10.157–21.044)
18:1	Hudson	63	14.444	14.211	(13.611–14.837)	(10.880–23.987)
	Ungava	72	14.360	14.030	(13.299–14.800)	(4.275–20.156)
18:2N6	Hudson	63	10.323	10.185	(9.777–10.610)	(5.957–17.375)
	Ungava	72	9.673	9.436	(8.976–9.920)	(5.433–20.199)
18:3N6	Hudson	63	0.207	0.170	(0.142–0.203)	(0.007–0.629)
	Ungava	72	0.121	0.121	(0.098–0.150)	(0.000–0.308)
18:3N3	Hudson	63	0.023	0.080	(0.048–0.134)	(0.000–0.747)
	Ungava	72	0.023	0.054	(0.038–0.075)	(0.000–0.189)
18:4N3	Hudson	63	0.000			(0.000–0.000)
	Ungava	72	0.002	0.023	(0.016–0.034)	(0.000–0.044)
20:0	Hudson	63	0.719	0.712	(0.687–0.737)	(0.449–0.928)
	Ungava	72	0.733	0.734	(0.706–0.764)	(0.000–1.005)
20:1	Hudson	63	0.030	0.077	(0.057–0.103)	(0.000–0.496)
	Ungava	72	0.023	0.060	(0.045–0.080)	(0.000–0.235)
20:2N6	Hudson	63	1.374	1.271	(1.154–1.401)	(0.530–3.541)
	Ungava	72	1.257	1.070	(0.917–1.249)	(0.000–3.236)
20:3N6	Hudson	63	5.185	5.111	(4.894–5.337)	(2.929–6.703)
	Ungava	72	5.105	4.988	(4.736–5.254)	(2.343–7.343)
20:4N6	Hudson	63	9.792	9.622	(9.175–10.092)	(5.748–13.420)
	Ungava	72	11.076	10.716	(10.099–11.372)	(6.288–18.589)
20:3N3	Hudson	63	0.073	0.128	(0.113–0.146)	(0.000–0.228)
	Ungava	72	0.043	0.102	(0.086–0.120)	(0.000–0.185)
20:4N3	Hudson	63	0.020	0.118	(0.091–0.152)	(0.000–0.221)
	Ungava	72	0.013	0.100	(0.082–0.121)	(0.000–0.164)
20:5N3	Hudson	63	0.482	0.425	(0.364–0.496)	(0.000–1.845)
	Ungava	72	0.363	0.314	(0.269–0.367)	(0.000–1.310)
22:0	Hudson	63	1.018	0.999	(0.952–1.049)	(0.572–1.433)
	Ungava	72	1.079	1.075	(1.028–1.125)	(0.000–1.439)
22:1	Hudson	63	0.537	0.513	(0.474–0.556)	(0.097–1.203)
	Ungava	72	0.598	0.529	(0.464–0.603)	(0.000–2.045)
22:2N6	Hudson	63	0.005	0.085	(0.072–0.100)	(0.000–0.105)
	Ungava	72	0.008	0.052	(0.042–0.065)	(0.000–0.089)
22:4N6	Hudson	63	0.445	0.438	(0.419–0.458)	(0.282–0.763)
	Ungava	72	0.470	0.470	(0.444–0.498)	(0.000–0.764)
22:5N6	Hudson	63	0.733	0.696	(0.604–0.802)	(0.000–1.313)
	Ungava	72	0.501	0.526	(0.403–0.686)	(0.000–1.551)
22:5N3	Hudson	63	0.239	0.254	(0.228–0.282)	(0.000–0.522)
	Ungava	72	0.260	0.243	(0.218–0.271)	(0.000–0.922)

Table 2 . (continued)

Contaminant	Region	n	Mean Arithmetic	Mean Geometric	(95 % CI)	(Range)
22:6N3	Hudson	63	3.952	3.788	(3.517–4.080)	(1.429–7.262)
	Ungava	72	3.889	3.724	(3.475–3.990)	(1.991–6.623)
24:0	Hudson	63	0.891	0.875	(0.834–0.918)	(0.528–1.238)
	Ungava	72	0.918	0.904	(0.854–0.958)	(0.000–1.495)
24:1	Hudson	63	2.220	2.187	(2.092–2.287)	(1.121–3.023)
	Ungava	72	2.191	2.153	(2.059–2.251)	(1.264–3.046)
EPA/AA	Hudson	63	0.050	0.044	(0.038–0.052)	(0.000–0.197)
	Ungava	72	0.035	0.029	(0.025–0.035)	(0.000–0.143)
DHA/AA	Hudson	63	0.411	0.394	(0.365–0.424)	(0.166–0.760)
	Ungava	72	0.359	0.347	(0.328–0.368)	(0.178–0.649)
EPA + DHA	Hudson	63	4.434	4.209	(3.877–4.570)	(1.429–8.046)
	Ungava	72	4.251	4.053	(3.770–4.357)	(2.094–7.281)
Total phospholipids	Hudson	63	93.867	92.466	(88.628–96.471)	(59.480–175.530)
	Ungava	72	102.011	99.195	(94.224–104.428)	(63.000–299.000)
Σ Omega 3	Hudson	63	4.790	4.546	(4.187–4.935)	(1.551–8.883)
	Ungava	72	4.591	4.366	(4.053–4.702)	(2.292–7.894)

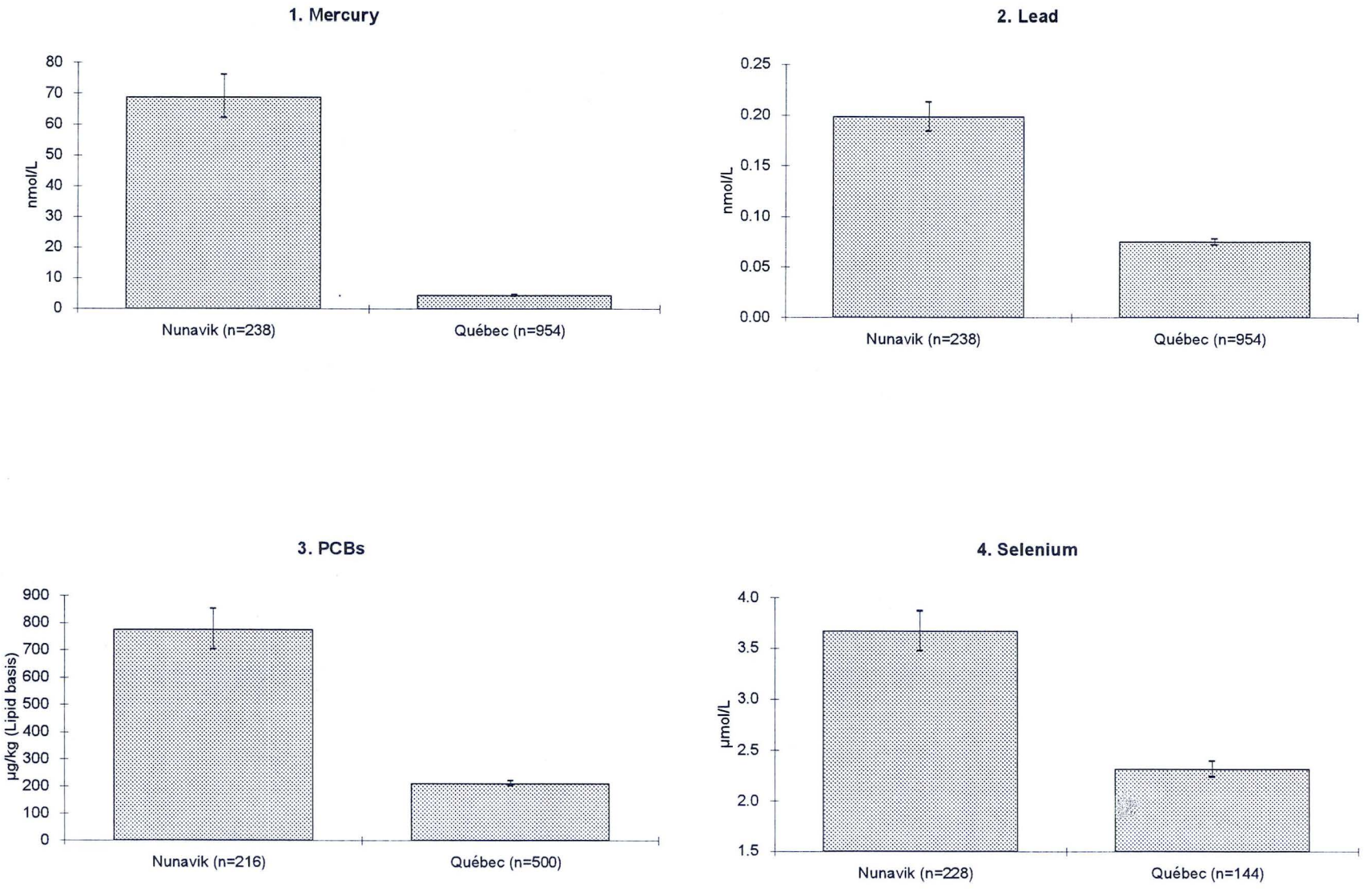


Figure 1. Mean concentration (geometric) of heavy metals and PCBs in cord blood samples from Nunavik and Southern Québec newborns

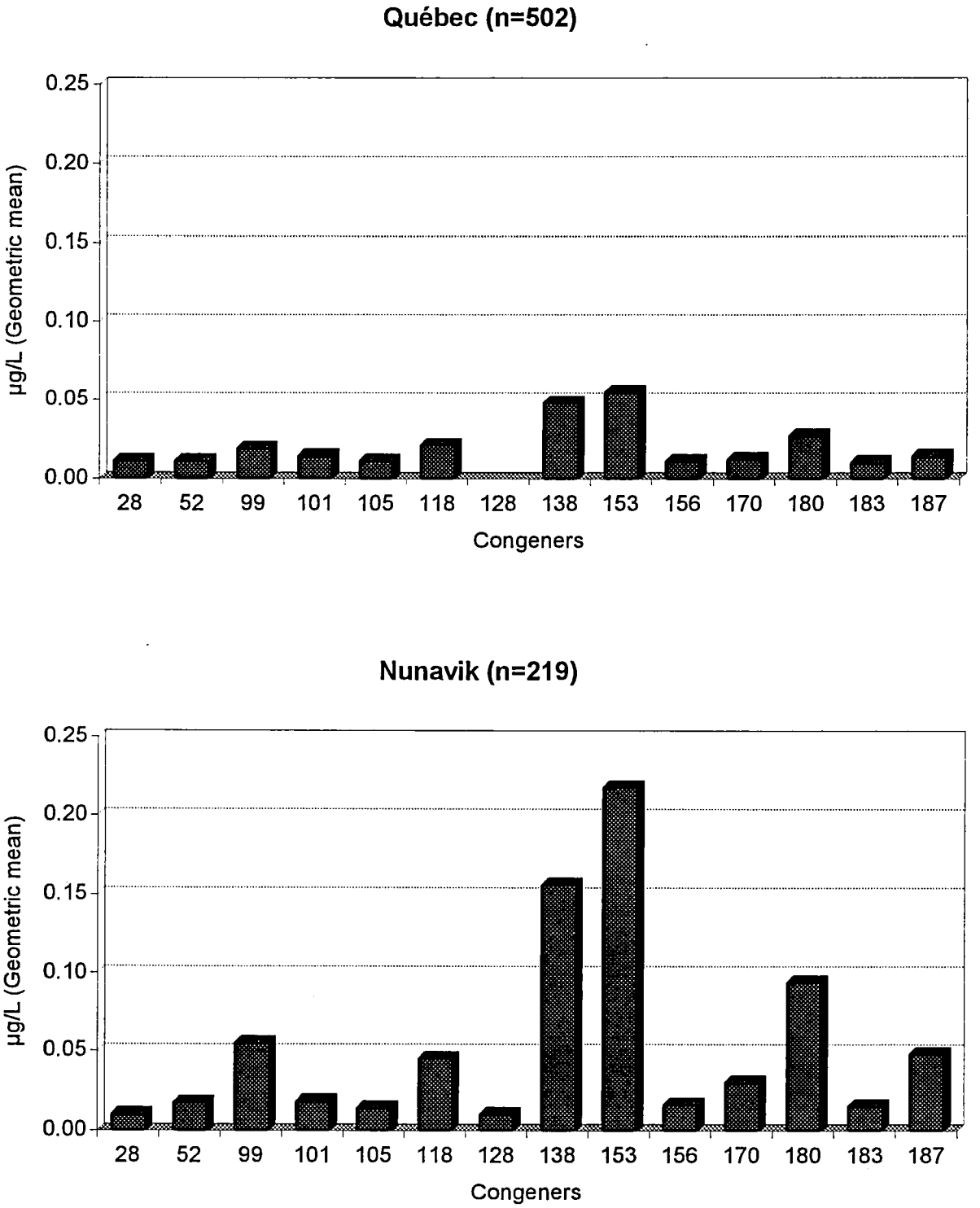
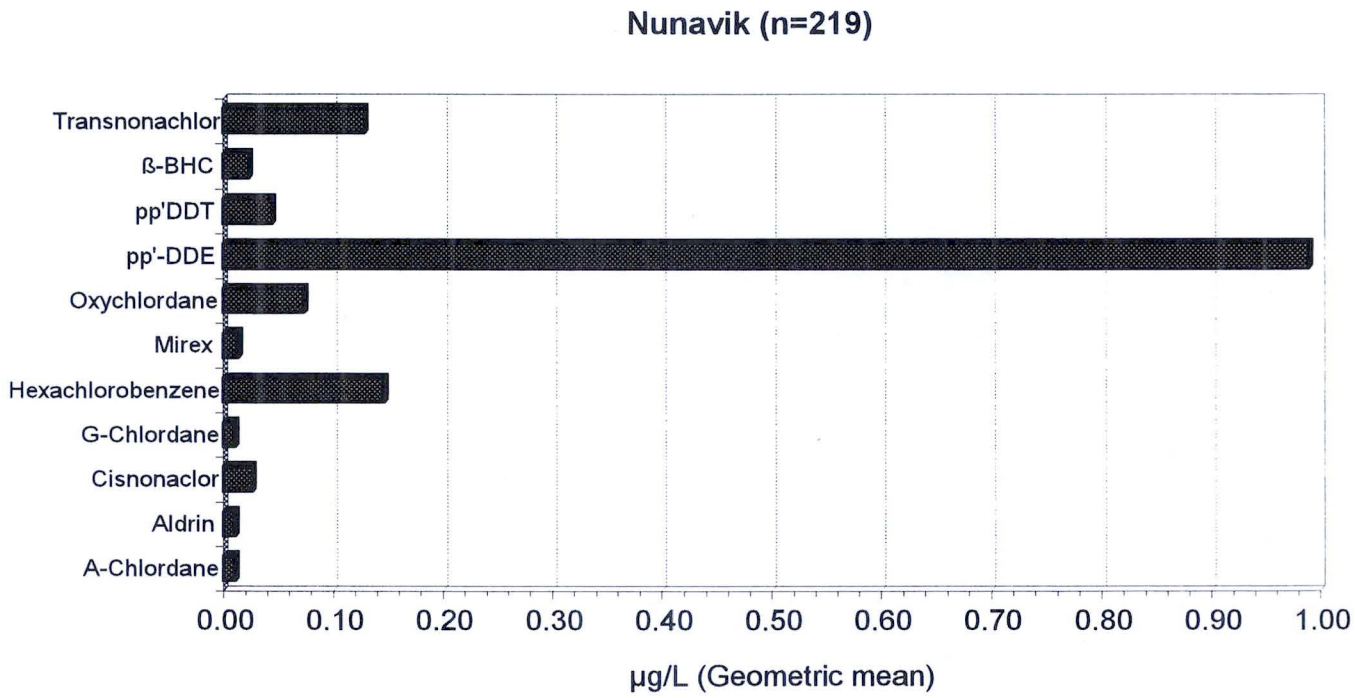


Figure 2. Concentrations of PCB congeners in cord plasma from Nunavik and Southern Québec newborns



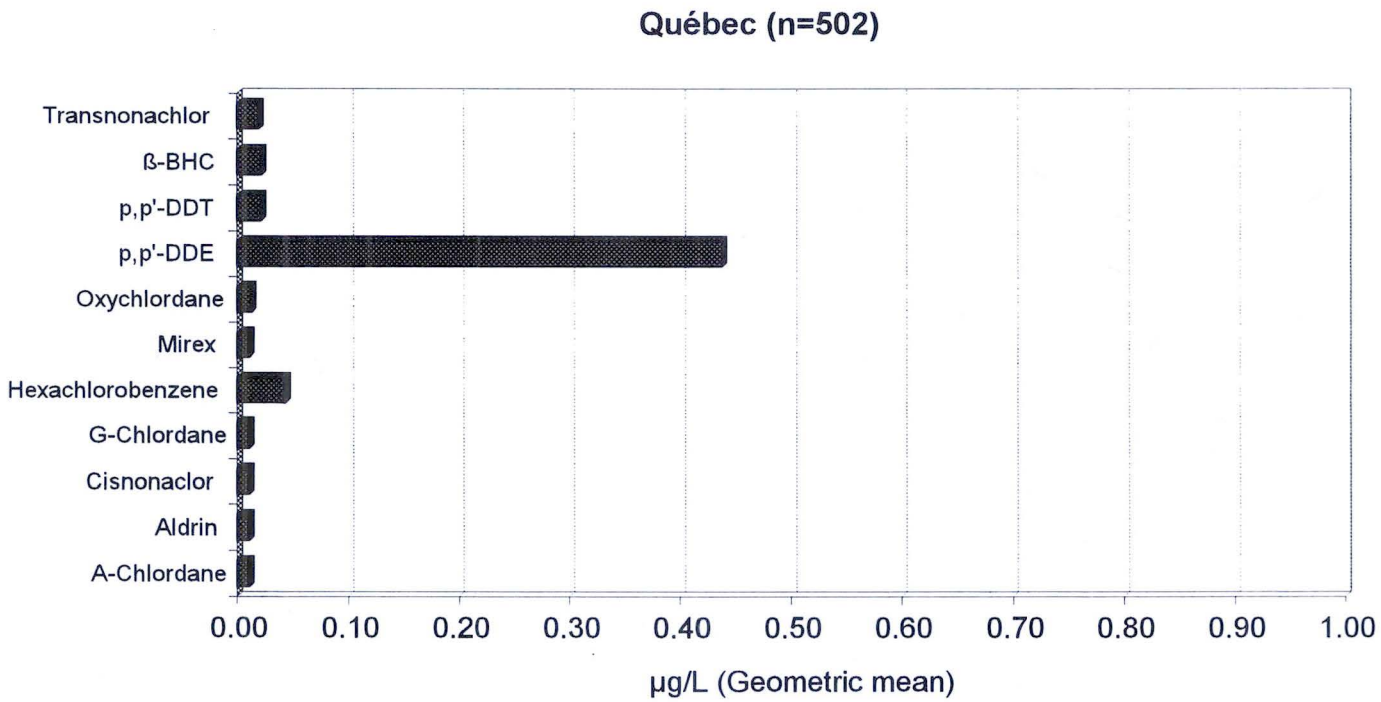
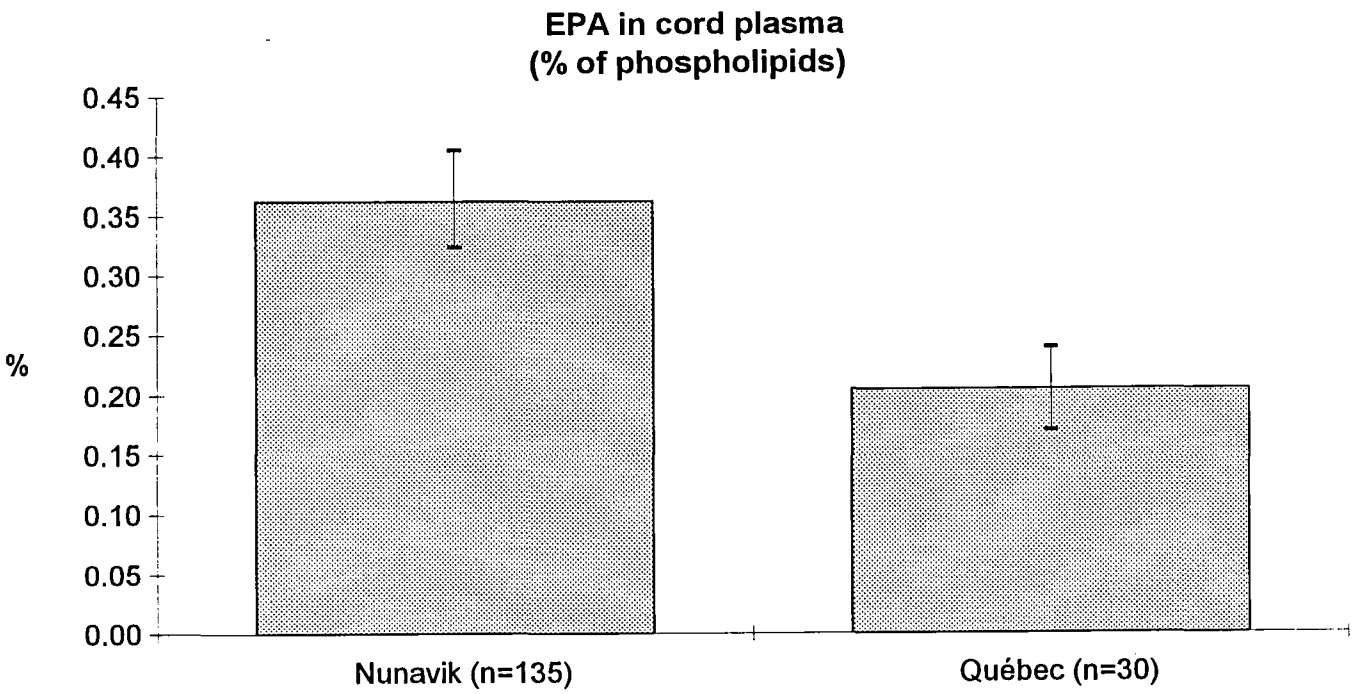
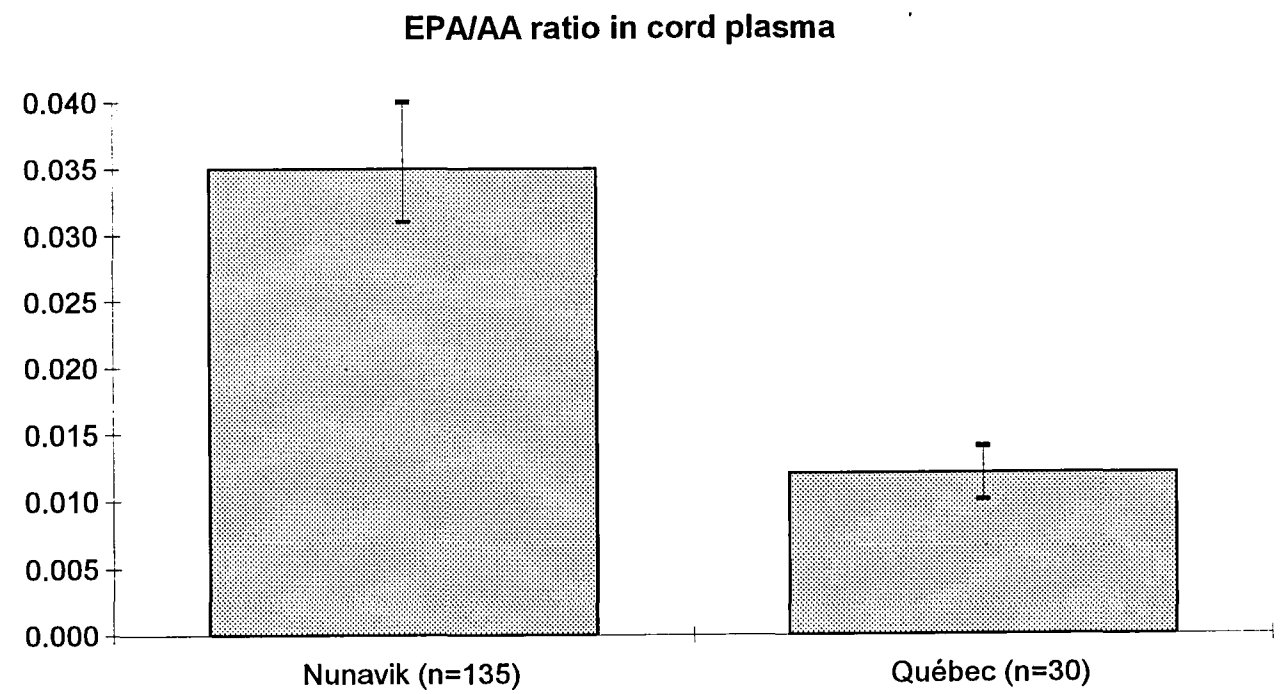


Figure 3. Concentration of chlorinated pesticides in cord plasma from Nunavik and Southern Québec newborns



EPA : Eicosapentanoic acid



AA : Arachidonic acid

Figure 4. Concentration of fatty acids in cord plasma from Nunavik and Southern Québec newborns

ESTIMATION OF CADMIUM EXPOSURE FROM THE CONSUMPTION OF TRADITIONAL FOOD IN FORT RESOLUTION

Program Leader: Centre for Nutrition and the Environment of Indigenous Peoples (CINE), McGill University

Project Team: L.H.M. Chan, O. Receveur, B. Masazumi

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, 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 Cd in the environment (WHO, 1991). Results of a study undertaken by the Canadian Wildlife Service showed that elevated levels of Cd were found in caribou and muskoxen caught between 1985-1990 in locations across the Yukon and the Northwest Territories (Gamberg and Scheuhammer 1994). The highest Cd concentration observed was 166 µg/g dry tissue weight in the kidney of a caribou. Regular consumption of food items with such high concentrations of cadmium may cause chronic kidney diseases. Due to the predominance of traditional food in the diet of Indigenous People of Fort Resolution, and the proximity of this community to the Pine Point Mine, the possibility of chronic Cd toxicity is a concern. Since Cd bound to metallothionein is more toxic than free Cd (Chan *et al.* 1992) and chronic Cd toxicity is dependent on both the total oral dose of Cd and its biological form, it is important to assess the Cd concentrations and the proportion of cadmium-binding to metallothionein in food as consumed.

ACTIVITIES IN 1994/95

Two dietary surveys and two food sample collection periods were conducted in spring (May) and fall (November) of 1994 by a trained local research assistant, Mr. Frank Mckay. Fifty-one dietary interviews (26 males and 25 females) and forty-six dietary interviews (26 males and 20 females) were conducted in Spring and Fall respectively. A total of 104 food samples (both raw or cooked) were collected and shipped to CINE. Laboratory analyses were undertaken by Ms. Christine Kim.

Food samples were digested with nitric acid at 100°C and metal contents (cadmium, copper, and zinc) 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).

The proportion of Cd bound to metallothionein (MT) in caribou kidney and effects of cooking were studied. Ten caribou kidneys were divided into two portions. One portion was baked at 350°C for 40 min. Moisture contents of raw and cooked samples were measured after drying in a vacuum oven (20 mm Hg) at 60°C until constant weight. About 0.5 g of both raw and cooked samples were homogenized in 2 mL of Tris-HCl (30 mM, pH 8.6), and centrifuged at 10,000 g for 20 min. at 4°C. Levels of Cd and MT levels in the supernatant were measured. MT was measured by the silver saturation method (Scheuhammer and Cherian 1986). An aliquot (100 µL) of the supernatant was fractionated on a calibrated Superose-12 HR 10/30 column (Pharmacia, Baie-d'Urfe, PQ) connected to a Beckman Gold HPLC system (Beckman Instruments Inc. Mississauga, ON) with a flow rate at 1 mL/min. A 10mM Tris-HCl (pH 7.0) solution was used as running buffer. One mL fractions were collected every minute. Cd concentrations of the collected fractions were measured.

Statistical Analysis of Dietary Data

Differences in contaminant intakes across age-groups were tested by ANOVA followed by Bonferroni t-tests. Differences in food intake according to exposure categories were tested by Student's t-tests. Because food and contaminant intake distributions are positively skewed in these data sets, all data were transformed [log (value + 1)] before performing statistical tests (SAS/STAT, Version 6, SAS Institute Inc., Cary, NC, USA). A P value of <0.05 was considered significant in all statistical tests.

Laboratory Quality Assurance

Two sample blanks were analysed together with each batch of samples. Concentrations of Cd were below the detection limits in all analyses. A spiked blank was analysed during each analysis to ensure day to day reproducibility. Each standard and sample was measured in duplicate and the sample was re-analysed if the relative standard deviation of the two measurements was higher than 5%. Coefficients of variations of the three replicates of the samples were generally less than 10% and the mean was used as the representative value for the sample. Standard reference materials from the National Institute of Standards and Technology (Oyster tissue SRM 1566a, Apple leaves SRM 1515 and Bovine liver SRM 1577b) were digested and analysed with each batch of samples. Results of Cd always fell within 1 SD of the certified values. Our laboratory also participated in the interlaboratory comparison organized by the Northern Contaminants Program.

RESULTS AND DISCUSSIONS

Cadmium was detected in 102 out of 104 food samples; concentrations are presented in Table 1. Mean, median and range of Cd in all food samples were 136, 2.0, and 0-5056 µg/100g, respectively. The corresponding figures for food composites found in Canada are 1.37, 0.54 and 0.007-29.7, respectively (Dabeka and McKennzie 1992). Concentrations of Cd in most food items were below the "action level" of 100 µg/100g or 1.0 ppm established by Agriculture Canada. Only liver and kidney samples of caribou and moose exceeded the "action level." Food items are classified into four major categories and their Cd concentrations are compared to the values of Canadian food composites (Table 2). Similar to Canadian food, higher concentrations of Cd were found in organ meats of traditional food. Average levels of Cd in the traditional food items measured in this study were similar to those of the Canadian market food. The low Cd levels found in local fruits and vegetables suggest the soil in Fort Resolution is not contaminated with Cd.

The seasonal average daily Cd intakes during days of traditional food consumption for both men and women were compared and no significant differences were found (data not shown). Therefore, the results from both genders were pooled and the results of average daily intake were calculated. A log transformation was performed as the data are not normally distributed. The geometric mean of daily Cd intake was 7.2 µg per day and the 95% confidence levels were 1.4 µg. This level is much lower than the average Canadian intake level of 14.5 - 52 µg per day (Conacher and Mes 1993). Assuming the average body weights of women and men are 50 and 65 kilograms respectively, and that the probability of consuming traditional food on any given day is 0.65 and 0.61 for females and males respectively (based on the proportion of food recalls with traditional food mentioned), the average weekly intake was calculated (geometric mean of daily intake x probability of consuming traditional food x 7 /body weight) and compared with the Provisional Tolerable Weekly Intake (PTWI) levels established by the Joint Food and Agriculture Organization/ World Health Organization Expert Committee on Food Additives and Contaminants (WHO, 1989)(Table 3). The weekly Cd intake levels for both genders were 10 times below the safe intake guidelines.

The frequency of consumption of liver and kidney of caribou and moose, which had the highest Cd concentrations, are shown in Table 4. Woodland caribou liver and kidney were not consumed in the spring and 2% of the people consumed them less than once per week in the fall. About 20% of the people consumed barrenland caribou liver and kidney less than once per week in both seasons. Less than 20% of the people consumed moose liver and kidney and those consuming them had less than one meal per week. These results suggest that the organs are not frequently consumed by the community. Thus, even though higher levels of Cd were found in the organs, they should not pose any health hazard to the people in terms of Cd intake.

Baking had no effect on the Cd concentrations of caribou kidney (Table 5). Metallothionein (MT) concentrations, however, were lowered, probably caused by oxidation of the protein. Chromatograms of the kidney cytosol are presented in Figure 1. Cd was found mainly associated with the high-molecular-weight-proteins (MW 100-450 KD, elution time 6-10 min) and metallothionein (MW 6-8 KD, elution time 13-14 min). The rest of the Cd was associated with some small peptides or existed as free ions. The distributions of Cd in different fractions of kidney cytosol are summarized in Table 6. About 35% of Cd was bound to the high-molecular-weight-proteins, 25% was bound to MT and 40% existed as free Cd ions.

After baking, there was no significant changes of the proportion of Cd bound to MT. However, the high-molecular-weight-proteins were denatured and the bound Cd was released as free Cd. These results suggest that the effect of cooking on Cd toxicity is minimal in terms of the amount of metallothionein bound Cd.

CONCLUSIONS

Average cadmium intake of inhabitants of Fort Resolution from traditional food is low and should cause no health concern. Liver and kidney of caribou and moose had the highest cadmium concentrations but they were not consumed frequently enough to cause concerns. Cooking did not alter the proportion of cadmium bound to metallothionein. A more detailed risk assessment which will include data on smoking habits will be conducted. Final results will be communicated to the community in August, 1995.

Expected project completion date: August, 1995

Partners: Deninu Kue First Nation, Métis Local #53, Dene Nation, Métis Nation.

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Table 1. Cadmium Concentrations in Traditional Food from Fort Resolution : Preliminary Data.

Food			Preparation	N[a]	Cd (μg/100g wet weight)
Meat					
Moose	*Alces alces*		dried & smoked	2	4.4 ± 0.1
			raw	4	2.5 ± 1.5
			fried	1	1.4
			boiled	2	1.9 ± 2.3
			smoked	2	4.5 ± 5.0
			smoked & fried	1	15.8
Caribou	*Rangifer tarandus*		raw	5	1.7 ± 1.5
Rabbit	*Lepus americanus*		raw	1	1.9
Bear	*Ursus americanus*		raw	3	1.1 ± 0.6
			smoked	1	1.0
Muskrat	*Ondatra zibethious*		raw	1	3.9
Buffalo	*Bison bison*		raw	1	1.0
Beaver	*Castor canadensis*		raw	2	9.1 ± 9.9
			smoked & boiled	1	2.1
Ptarmigan	*Lagopus mutus*		raw	2	1.4 ± 0.7
			fried	1	1.9
			boiled	1	0.6
Mallard duck	*Anas platyrhynchos*		boiled	1	4.6
Fruits and Vegetables					
Cranberry	*Oxycoccus spp.*		raw	4	0.2 ± 0.2
			jam	1	0
Mooseberry	*Viburnum edule*		raw	1	0
Rhubarb	*Rheum rhaponticum*		raw	2	0.2 ± 0.1
Berry			raw	2	1.3 ± 0.4
Garden potato			raw	3	1.7 ± 0.8
Organ					
Moose	*Alces alces*	liver	raw	2	703 ± 379
			boiled	1	121
		kidney	raw	3	1869 ± 276
			boiled	1	787
		heart	raw	4	6.2 ± 4.6
			boiled	3	4.6 ± 5.6
		entrails	raw	2	16.9 ± 3.3
			boiled	2	17.3 ± 11.0
		tongue	raw	1	14.3
		internal fat	raw	1	0.3
Caribou	Rangifer tarandus	marrow	raw	3	1.9 ± 0.4
		heart	raw	3	1.2 ± 0.5
		kidney	raw	3	126 ± 74.9
		liver	raw	2	161 ± 146
		intestine	raw	3	2.6 ± 2.1
Fish					
Whitefish	*Prosopium cylindraceum*	flesh	raw	5	1.4 ± 0.9
Jackfish	*Esox lucius*	flesh	raw	5	9.3 ± 18.0
			fried	1	10.9
		intestine	raw	4	13.7 ± 10.9
		egg	raw	1	0.6
Sucker	*Catostomus catostomus*	flesh	raw	5	1.9 ± 2.3
			smoked	1	16
Trout	*Savelinus namaycush*	flesh	raw	1	1.6
Loche	*Lota lota*	flesh	raw	2	0.2 ± 0.1

[a] Number of independently harvested samples

Table 2. Mean Cadmium Concentrations (µg/100 wet weight) in Traditional and Canadian Market Food: Preliminary Data.

Food	Traditional Food from Fort Resolution				Canadian Market Food[a]			
	N	mean	median	range	N	mean	median	range
Meat	32	42	2	0.6~16	18	0.9	0.4	0.1~7
Organ	34	255	17	0.3~1869	12	271	17	1~18 500
Fish	25	6	2	0.216	5	11	0.5	0.1~8
Fruits and Vegetables	13	0.6	0.2	0~2	37	2	1	0.1~12

[a] Dabeka and McKenzie 1992.

Table 3. Comparison of Average Weekly Cadmium Intake from Traditional Food with the Provisional Tolerable Weekly Intake (PTWI) (µg/kg body weight/week).

Group	N	Calculated Cd intake[a]
Women > 20 years	43	0.7
Men > 20 years	54	0.4
PTWI[b]		7.0

[a] Geometric mean of daily intake x 7 x probability of consuming traditional food on any given day/ body weight (50 kg for women, 65 kg for men). The probability of consuming traditional food was calculated as the proportion of 24hr recalls that mentioned traditional food to all 24hr recalls in each gender group (28/43, and 33/54 for women and men, respectively).

[b] From World Health Organization, 1989.

Table 4. Frequency of Consumption of Traditional Food with Highest Cadmium Concentrations: Preliminary Data.

Food and Frequency	Season				Cd concentration[b] (mg/100g wet weight)
	Winter		Summer		
	N[a]	%	N[a]	%	
Caribou W. liver					161[c]
None	51	100	45	97.8	
<1/week	0	0	1	2.2	
Caribou B. liver					
None	42	82.4	36	78.3	
<1/week	9	1706	10	21.7	
Caribou W. kidney					126[c]
None	51	100	45	97.8	
<1/week	0	0	1	2.2	
Caribou B. kidney					
None	44	86.3	35	76.1	
<1/week	7	13.7	11	23.9	
Moose liver					703
None	41	80.4	40	87.0	
<1/week	10	19.6	6	13.0	
Moose kidney					1869
None	49	96.1	40	87.0	
<1/week	2	3.9	6	13.0	

[a] number of food frequency record collected in each season

[b] cadmium levels measured in raw samples

[c] average of Cd levels measured in both species

W—woodland

B—barren land

Table 5. Preliminary Concentrations of Cadmium (Cd) and Metallothionein (MT) in Raw and Cooked Caribou Kidneys: Preliminary Data.

	n	Raw	Cooked	p
Total CD (µg/g dry wt.)	10	15.6 ± 11.0	15.3 ± 7.8	n.s.
MT (µg/g wet wt.)	10	16.7 ± 16.9	16.4 ± 16.4	n.s.
MT (µg/g dry wt.)	10	56.4 ± 22.0	30.8 ± 31.0	<0.05

Table 6. Speciation of Cadmium (Cd) in Raw and Cooked Caribou Kidneys: Preliminary Data.*

	n	Raw	Cooked	p
Cd bound to high molecular weight protein	10	35.4 ± 20.2	10.1 ± 8.4	< 0.01
Cd bound to metallothionein	10	23.9 ± 14.5	14.8 ± 15.4	n.s.
Free Cd	10	40.8 ± 28.1	75.1 ± 17.6	< 0.01

* Data are presented in percentage of the total Cd in kidney cytosol.

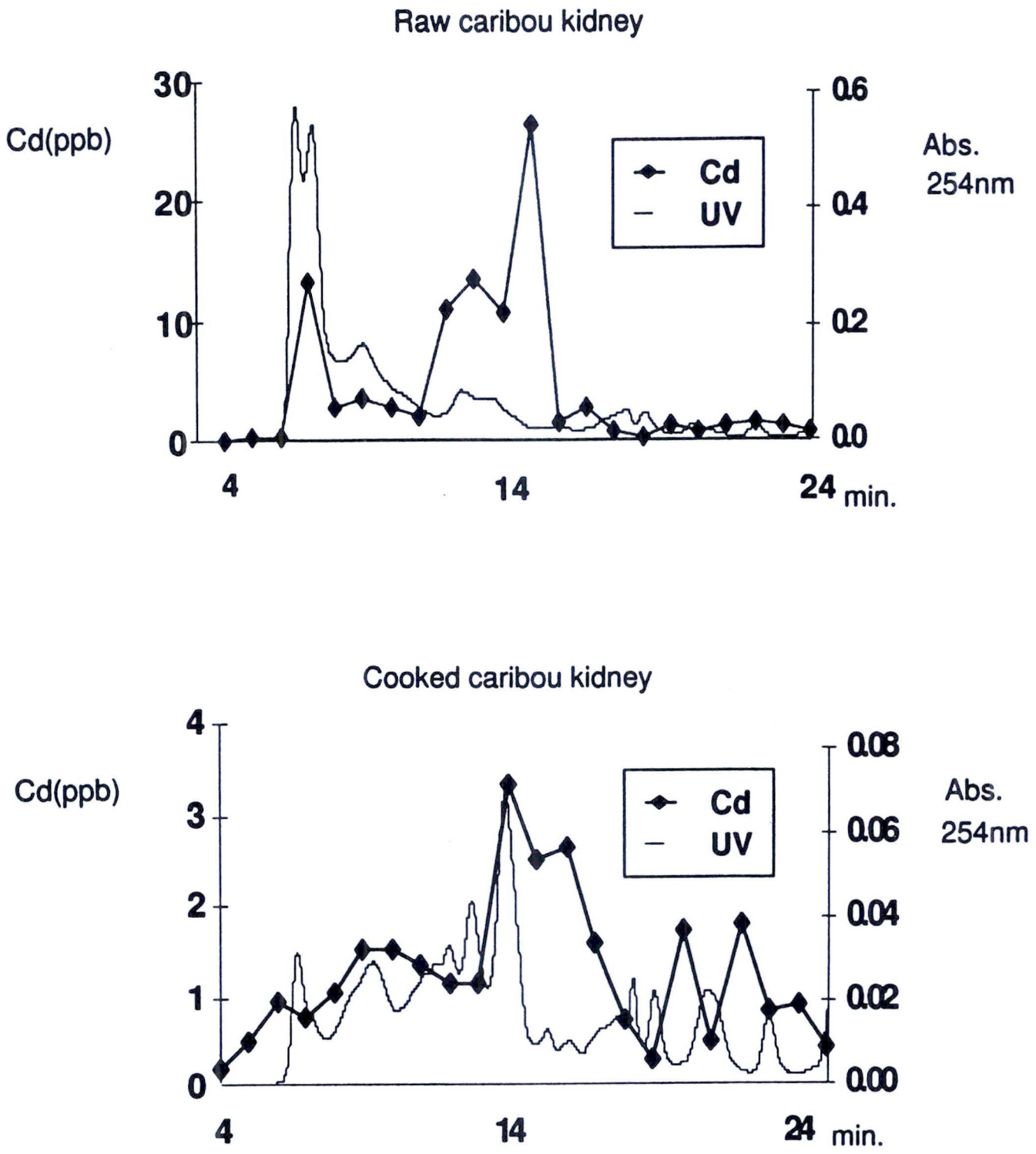

Figure 1. Cadmium distribution in raw and cooked kidney cytosol

PRELIMINARY DIETARY STUDY IN OLD CROW AND ROSS RIVER (YUKON)

Program Leader: Centre for Nutrition and the Environment of Indigenous Peoples (CINE), McGill University (Contact: H.V. Kuhnlein)

Project Team: CINE, Council for Yukon Indians, Yukon Contaminants Committee

OBJECTIVES

1. To establish a baseline qualitative list of traditional foods and their attributes in at least two communities of the Yukon;

2. To assess the extent of existing data and the need for additional dietary information.

DESCRIPTION

In the Yukon, caribou kidney and various species of fish have been shown to contain significant amounts of contaminants (Mychasiw 1993, Palmer 1992), but present levels of dietary intake are unknown except for the communities of Haynes Junction, Teslin and Old Crow (Wein 1994). Members of Yukon First Nations have expressed concerns as to the consequences of a shift toward increased consumption of market food, a shift that may be accelerated by the reported presence of contaminants in traditional food.

ACTIVITIES IN 1994/95

In October 1994, the Methodology Development Workshop attended by representatives of all Yukon First Nations, identified particular research questions and the methods to be used, that will be addressed in 1995. A list of traditional food consumed in each community was completed. In the following months a research agreement was negotiated with all Yukon First Nations not previously included in dietary surveys.

The new project entitled "Yukon First Nations Assessment of Dietary Benefit/Risk" was initiated as a direct outcome of this preliminary dietary study. Data collection proceeded between February and April, 1995, in 10 communities: Dawson, Mayo, Carmacks, Ross River, Watson Lake, Lower Post, Beaver Creek, Burwash Landing, Carcross and Atlin. A total of 409 individual interviews were completed and transferred to electronic form. In addition, 38 food samples were collected and analysed for nutrient contents.

RESULTS

The direct objectives of this preliminary study were met in October, 1994. In consequence, a complete dietary assessment of benefit/risks was initiated in 10 Yukon communities.

DISCUSSION/CONCLUSION

Close collaboration between CINE and the Yukon Contaminants Committee made the development of this project possible. Thanks to the guidance of the Council for Yukon Indians, negotiation of the research agreements and the actual administration of this project were successfully completed.

This preliminary study led to the development of the more extensive survey which consisted of a set of interviews (24-hour diet recall, traditional food frequency and socioeconomic questionnaires) administered to a representative sample of adults in participating communities during late winter and fall, 1995. In addition, food samples are being collected for nutrient analyses to complete the traditional food composition database, and for contaminant analyses, if requested. Data collected in this study will be merged with existing contaminant databases to estimate benefits and risks of diets as consumed by Yukon First Nations. This project will provide Yukon First Nations with valid estimates of dietary intake among adults; it also will document benefits of traditional food and integrate nutritional and contaminant information relevant to the consumption of various types and amounts of traditional and market food.

Project completion date: March, 1995

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THE EFFECTS OF *IN UTERO* ORGANOCHLORINE AND HEAVY METAL EXPOSURE ON THE NEUROBEHAVIORAL AND PSYCHOMOTOR DEVELOPMENT OF INUIT INFANTS: A PILOT STUDY

Project Leaders: G. Muckle, Public Health Centre, Québec region; É. Dewailly, Wayne State University; J.L. Jacobson, Wayne State University; S.W. Jacobson, Wayne State University; P. Ayotte, Public Health Centre, Québec region; S. Bruneau, Public Health Centre

OBJECTIVES

1. To evaluate the feasibility of a prospective longitudinal study on infant development;

2. If the project meets feasibility criteria, to elaborate the research protocol for a prospective study of newborns.

DESCRIPTION

Available data on Inuit exposure have confirmed that newborns from this population are exposed to higher organochlorine levels than newborns from Southern Québec. For example, the mean level of polychlorinated biphenyls in human milk is 111 µg/L (Aroclor 1260) for Inuit women compared to 28 µg/L for women from southern Québec. Aroclor 1260 concentrations in milk fat are 2.9 and 0.52 mg/kg respectively, for Inuit and women from southern Québec (Dewailly *et al.* 1992). This level among Inuit is 5 times that of southern women and is higher than the 50 µg/L minimal acceptable concentration established by NIOSH (1977). Results from the Santé Québec Inuit Health Survey (Dewailly *et al.* 1994) show that Aroclor 1260 concentration in adult plasma is 27 µg/L (n=491) in Nunavik. This level is 7 times that of North American adult levels (from 4 to 7 µg/L) (NIOSH 1977) and 9 times that of Montreal adults (3 µg/L). The plasma concentration of Aroclor 1260 in 68 Inuit women aged 20 to 45 years is 15 µg/L (Dewailly *et al.* 1993). This concentration is higher than that measured in the Michigan cohort study which reported neurobehavioural and foetotoxic effects (Jacobson *et al.* 1985). However, despite these levels of organochlorine compounds, until now there have been no effects studies conducted in the Inuit population.

ACTIVITIES IN 1994/95

The specific activities to be carried out in 1994/95 revolved around the execution of a pilot study. The pilot study was conducted by G. Muckle, S.W. Jacobson and S. Bruneau in October 1994 at the Inuulitsivik Health Center in Povungnituk. This pilot study was supported by the Kativik Regional Health and Social Services Council, the Board of the Nunalituqait Ikajuqatigiitut Inuit Association, and the Pauktuutit Inuit Women's Association.

METHOD

The sample is made up of 3 pregnant women and 9 mother-infant dyads among which 5 infants were aged between 19 to 27 weeks; the other 4 infants of the dyads were aged between 41 to 62 weeks. The subjects were all from Povungnituk. The birth register of the health center was used to identify the subjects. The goals of the research and its procedures were explained to the participants before obtaining their written consent. The pregnant women were called for an interview lasting approximately two and one-half hours. The subjects were met at the hospital where the women were interviewed and where the infant's development was assessed. All women were initially supposed to be interviewed in Inuktitut by a midwife from the hospital who had been trained to conduct the interviews beforehand. However, most mothers were fluent in English and required only little translation, many of the concepts were easier to understand in English, and most mothers were more comfortable providing personal information to a Caucasian interviewer from outside their community. Consequently, after the fifth interview, the interviewee could choose the language. Hence, three interviews were done in Inuktitut, two were done in both languages, and seven in English only.

The selection of measures that would be indicative of adverse effects rests on five criteria as follows; they: 1) must allow a comparison with previous cohort studies; 2) should have been validated; 3) must be able to discriminate the infants from a non-clinical sample; 4) should assess several aspects of child development; and 5) can be used with various economic and cultural

groups. Many of the instruments chosen to assess control variables were not included in all maternal interviews. As this study was a pilot study, one of its purposes was to identify the appropriate measures that could control for confounding variables. Consequently, different measures were used for the same construct when the first measure was not completely understood by the respondents. The difficulties in understanding were attributable to the formulation of the questions, or the choice of answers.

MAIN RESULTS

In the first place, data analysis was used to identify the instruments that pose a problem relative to cultural and social differences, or problems related to the translation of abstract constructs in Inuktitut. In the second place, the mean and the variance of the scores were compared to the norms. The data analysis was performed by G. Muckle and J.L. Jacobson.

Infant Variables

The Bayley Scales-II (Bayley 1993) were administered to 9 infants. The scores were in the range expected (Mental Development Index: min=71, max=108; Psychomotor Development Index: min=58, max=106) and the only unexpected finding was that the range of the Mental Development Index scores for younger infants was unusually narrow (min=92, max=98). On the Behavioural Rating Scale (Bayley 1993), 5 infants received questionable or nonoptimal scores on orientation/engagement, one scored nonoptimal on motor quality, and all received normal scores on emotional regulation. Five of the children were administered the Visual Acuity Test (Teller *et al.* 1986) which they all passed. Seven children were administered the Fagan Test of Infant Intelligence (Fagan and Singer 1983). The Fagan scores were in the range expected at these ages and the novelty preference scores ranged from 52% to 60%. The group mean of 56.4% was slightly lower than the mean of 57.3% found in the Michigan cohort (Jacobson *et al.* 1985).

Confounding Variables

Occupational status was determined by the Hollingshead Index (Hollingshead 1976). It ranged from 1 to 6, and the rank-order correlation between occupational status and year of education was high (r=.70, n=6). We administered the NCAT and NCAF scales (Barnard 1980) to assess the quality of intellectual stimulation provided by the mother. This measure was difficult to administer because many Inuit mothers do not engage their infants in playing with toys. Based on preliminary pilot testing, we have concluded that a modified version of the Home Observation for Measurement of the Environment (Caldwell & Bradley 1979) can be administered instead. Additional pilot testing of the modified version is planned. The Colored Raven Matrices (Raven *et al.* 1992), a non-verbal intelligence test recommended for non-English speakers, was administered to obtain information regarding maternal intellectual competence. The mothers' raw scores (n=10) were ranging from 20 to 34 (maximum score is 36) and the mothers had no difficulties following the test instructions. There was a high correlation between the maternal Ravens scores and the infants' BRS orientation/engagement scores (r=.83, n=6). This suggests that the infants of the intellectually more competent mothers responded more actively to the Bayley test procedures, and confirms that the Ravens raw scores rank ordered the women appropriately.

The Beck Depression Inventory (Beck *et al.* 1961) was administered, but the mothers had difficulty understanding the questions and concepts, even when translated into Inuktitut. Therefore, the IDPESQ-14 (Préville *et al.* 1992), which had been used successfully in the recent Inuit Health Survey, and the Brief Symptom Inventory (BSI) (Derogatis 1993) were administered. The depression score of the IDPESQ-14 and the BSI were highly correlated (r=.83, n=5). Two questions about suicide were included (Tousignant *et al.* 1984). Of 11 mothers, 4 reported having seriously thought about committing suicide at one time in their lives.

The Conflict Tactics Scales (Strauss 1979) were administered to assess marital conflict and violence. Mothers had difficulty responding to the first 3 items but had no problem with the remaining items. Verbal and physical aggression scores were high: 77th and 96th percentile, respectively. These results indicate that marital violence is a significant risk factor for the development of Inuit infants and that the Inuit women are comfortable enough with the interview procedure to report violence. The MAST (Selzer 1971) and the CAGE (Ewing 1984) are screening instruments developed to identify risk drinkers. The MAST had to be discarded because women had difficulties understanding its questions, which was not the case for the CAGE. We administered the two-week, daily drinking history interview used in the Detroit prenatal alcohol exposure study (Jacobson *et al.* 1991) and all women denied any drinking during pregnancy. Dr. S.W. Jacobson and G. Muckle, therefore, modified and simplified the interview. Several prompts for use with reticent respondents were also developed. With the new version, 5 of the 7 mothers interviewed admitted that they drank during their pregnancy. A similar interview procedure was used for

drugs: 7 of 10 mothers reported using marijuana during pregnancy or within the past 6 months, 2 and 6 women admitted that they had used cocaine and sniff solvents, respectively in their lifetime. Eleven women were interviewed about smoking habits during pregnancy and their actual smoking status. They all smoked during pregnancy and are current smokers. The number of cigarettes smoked every day ranges from 3 to 12.

Statistical Power Analysis

Dr J.L. Jacobson reanalysed the Michigan data using a new composite prenatal exposure measure. This new analysis showed that the effect size for most of the correlations of prenatal PCB exposure with developmental outcome was at least $r = .16$. With an alpha $< .05$ and a beta $< .20$, the sample size needed to detect an effect of $r = .16$ is 306 (Cohen 1988).

DISCUSSION/CONCLUSIONS

The pilot study showed that the Inuit infants responded positively to the testing procedures, and they obtained scores in the same range as American infants. The pilot study confirmed that the types of tests currently used in studies with North American infants are suitable for research with the Inuit. Inuit mothers volunteered to participate with their infants. Some standard assessment procedures had to be discarded or modified. Nevertheless, the pilot study demonstrated that these mothers do confide personal information to Caucasian interviewers and that it is feasible to assess the control variables needed in this type of study. Such variables include: maternal intellectual competence, quality of parental stimulation, alcohol, drug and tobacco use during pregnancy, and emotional problems such as depression or marital conflicts. Despite cultural differences and logistic difficulties related to data collection in remote and isolate areas, we are confident about the feasibility of a prospective study of newborns from Nunavik. The research protocol developed following this pilot study was submitted to the National Institute of Health in June 1995; the research was proposed by J.L. Jacobson with S.W. Jacobson, É. Dewailly, G. Muckle and P. Ayotte as co-investigators. The financial support received from Indian and Northern Affairs Canada (Northern Contaminants Program) in 1993/94 and 1994/95, and from Health Canada in 1993/94 was essential in carrying out the pilot study, as well as all the scientific activities that allowed us to develop a network of collaborators in Inuit and scientific communities.

Expected project completion date: July 1995.

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BIOMARKERS OF EARLY BIOLOGICAL RESPONSES INDUCED BY ORGANOCHLORINE EXPOSURE IN WOMEN GIVING BIRTH IN ARCTIC QUÉBEC

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Project Team: 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 with 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 nursing their babies were asked to submit a milk sample for organochlorine compound (OC) analysis. Results for 105 mothers' 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 lipids, was six times greater than that measured in 550 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. The 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).

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 that could be induced by OCs, biological markers discussed below were proposed in order to improve health risk assessments.

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 and 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).

DNA Adduct Formation

Polycyclic aromatic hydrocarbons (PAHs) such as benzo(a)pyrene and dibenzo(a,h) anthracene are ubiquitous contaminants that undergo biotransformation to reactive intermediates. Binding to DNA and other macromolecules occurs and chemically-modified nucleotides can be detected by the ^{32}P-postlabelling method. There is some evidence to suggest that some PCB congeners (lower-chlorinated) can form reactive intermediates leading to DNA adduct formation (Oakley *et al.* 1995). PCB exposure can also induce the activity of biotransformation enzymes, which catalyze PAH-DNA adduct formation.

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, or 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.

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; c) natural killer cell assay. These responses are well understood in humans and represent validated biomarkers of immune system function.

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 organochlorine or heavy metals: workers occupationally exposed to PCBs, Inuit from Greenland consuming large amounts of seal, and subsistence fishermen from the Lower-North-Shore (Québec), who consume contaminated sea-bird eggs.

OC Analysis

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.

Cotinine Determination

Meconium and cord blood samples will be analysed for cotinine, since maternal smoking is known to influence several biomarkers measured in the present study. Whereas cord blood levels reflect exposure during the past few days, meconium content indicates longer-term exposure to cigarette smoke during pregnancy.

ACTIVITIES IN 1994/95

During spring 1995, 20 women delivering in Kuujjuaq, Arctic Québec, and 20 women giving birth in Sept-Îles, Southern Québec (control group) were recruited for this project. Women on continuous medication were excluded. Participants were asked for permission to use their placenta, a cord blood sample and meconium samples for biomarker analysis. Placenta samples were frozen on site at –80°C and sent in dry ice to the laboratories involved in the measurement of cytochrome P450 induction, DNA adducts and stress proteins. Cord blood samples for the measurement of immunotoxicity biomarkers and sister chromatid exchange assay were to be kept at 20°C and sent within 48 hours to the laboratories. Although tissue collection and shipping was handled easily for the control group from Sept-Îles, several blood samples sent from Nunavik arrived late to the laboratory and consequently some biomarker results will not be available for all Nunavik women. All analyses have been completed to date, except DNA adduct measurements and OC analysis in placental tissue and cord blood samples. Statistical analysis of the data is underway and only limited results are available for presentation in this synopsis. Here we will focus on results from the determination of cytochrome P-450 associated enzyme activities.

RESULTS AND DISCUSSION

Table 1 presents results for the determination of EROD activity in placental tissue samples obtained from Inuit women and the control women from Sept-Îles. Mean EROD activity in the Inuit group was marginally (22%) higher than that of the control group; this difference was

not statistically significant. Since EROD activity is strongly influenced by tobacco smoking during pregnancy (Manchester and Jacoby 1981), results were broken down according to the declared smoking status of the mothers. The percentage of smokers in the Inuit group was 85%, compared with only 40% in the control group. Mean activities measured in samples obtained from smoking mothers were similar in both groups. Comparison between nonsmokers could not be effected because the number of nonsmokers in the Inuit group was too small (N=3).

The relationship between EROD activity and maternal smoking was further studied by conducting a linear regression analysis (Figure 1). When data from both groups were included in the analysis, a moderately strong, statistically significant correlation coefficient was obtained ($R = 0.59$; $P < 0.0001$; $N = 40$). In further analysis of this relationship, cotinine concentration in cord blood and in meconium will be used as an objective measure of maternal tobacco consumption.

While results suggest that maternal smoking is a major determinant of placental EROD activity, PCB body burden does not appear to modulate EROD activity. Indeed, no statistically significant difference was observed between both groups of women as to placental EROD activity, despite the fact that the mean PCB (Aroclor 1260) concentration in cord plasma lipids in the Inuit group was four times greater ($p < 0.0001$) than that of the control group [695 ± 84 (SEM) µg/kg vs 176 ± 13 (SEM) µg/kg]. The importance of organochlorine body burden on EROD activity will be further examined when results from OC analyses in placenta become available.

PROD activity was not frequently detected in placental tissue samples from both groups (27% of Inuit samples and 20% of control samples). Mean values ± SEM for the Inuit and the control group were 4.3 ± 1.3 and 4.5 ± 1.4 picomoles resorufin/mg protein/min, respectively (only positive results were considered).

CONCLUSIONS AND UTILIZATION OF THE RESULTS

A preliminary assessment of results obtained to date, indicate that the PCB body burden of Inuit women may not be high enough to induce EROD activity in placental tissue above those level found in subjects of the control group. Maternal smoking was associated with EROD activity in both groups of women. The results from this pilot study will be used to prepare a report to the Northern Contaminants Program on the feasibility/usefulness of measuring biomarkers in the health risk assessment process in the Arctic. Biomarkers showing the highest correlations with the health status of the newborn at birth will be selected for inclusion in a larger study to be initiated next fall, investigating possible adverse neurodevelopmental effects induced by organochlorine exposure and drug consumption in this population (funded by an Eco-research grant from the Tri-Council Green Plan Program).

Expected project completion date: September 31, 1995.

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Table 1: EROD activities in placental samples from Inuit women and women from Sept-Îles (control group).

	Control group (Sept-Îles)			Nunavik		
	Mean*	SEM**	N	Mean	SEM	N
Non-smokers	8.3	2.5	12	4.2	0.1	3
Smokers	28.5	11.0	8	22.8	6.5	19
1-20 cig./day	14.1	6.8	5	14.6	2.4	13
> 20 cig./day	52.4	22.6	3	40.7	19.1	6
All	16.4	5.0	20	20.0	6.1	22

* Arithmetic mean
** SEM: Standard error of the mean

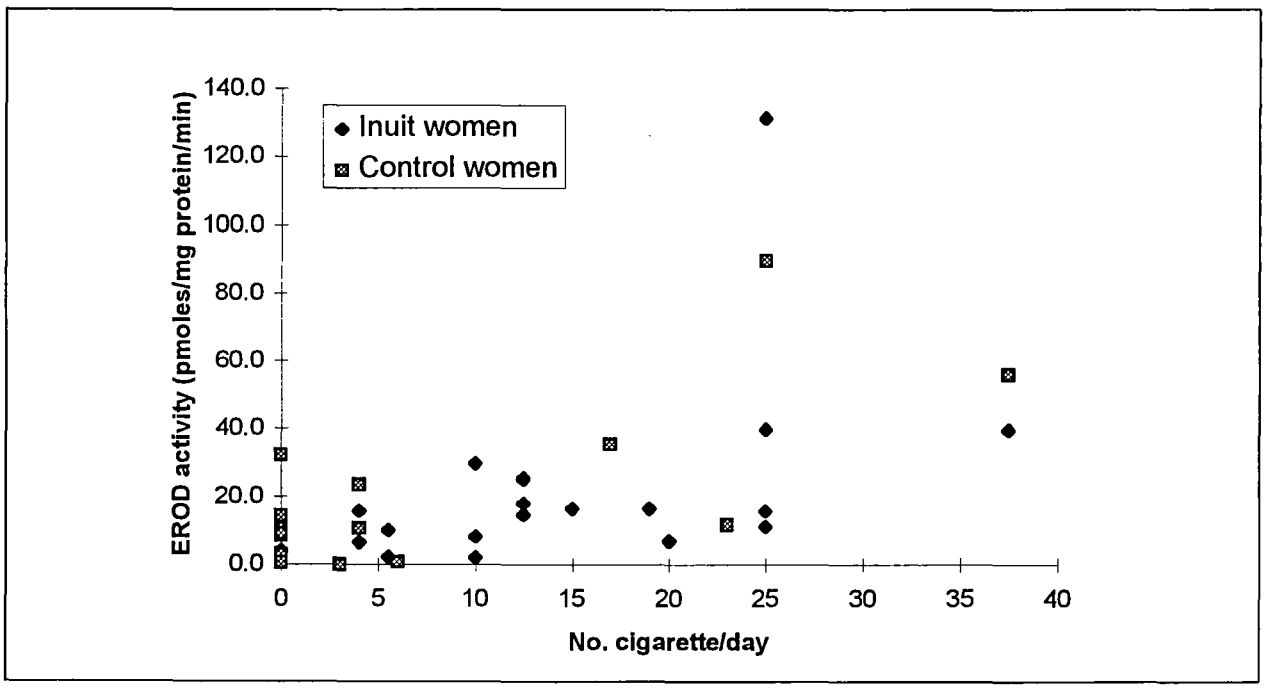

Figure 1. Relationship between maternal smoking and EROD activity in placental samples from Sept-Îsles women (control group) and Inuit women

VARIANCE IN FOOD USE IN DENE/MÉTIS COMMUNITIES

Project Leader: Centre for Nutrition and the Environment of Indigenous Peoples (CINE), McGill University

Project Team: H.V. Kuhnlein, B. Erasmus, B. Masuzumi, C. Mills, W. Carpenter, O. Receveur

OBJECTIVES

1. To define 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, initiated by Dene Nation and Métis Nation (NWT), builds on the experiences and food use data completed in K'ásho Got'ine/K'áhbami Túé (Kuhnlein 1991) and aims at providing information necessary to evaluate benefits/risks of consuming various types and quantities of traditional and market foods in Dene/Métis communities.

After an exploratory phase during which the study protocol was designed to incorporate community concerns and suggestions (1993-94), individual interviews were administered in 16 Dene/Métis communities. Each interview included: 1) a frequency of traditional food use questionnaire; 2) a 24-hour diet recall; and 3) a sociocultural questionnaire. In addition, a price list for market food and a traditional food harvest calendar were completed in each community.

ACTIVITIES IN 1994/95

A total of 1012 individual interviews were collected in random samples of adult males and females during two seasons: Winter and Fall, 1994. Participating communities included: Aklavik, Tssigehtchic (Arctic Red River), Teetl'it Zheh (Fort McPherson), K'áhbami Túé (Colville Lake), Kásho Got'ine (Fort Good Hope), Déline, Thedzeh Koé (Wrigley), Liidli Koé (Fort Simpson), Thehzehk'édli Koé (Jean Marie River), Yahti Dewé Ko (Fort Providence), Bècho Ko (Rae), Edzo, Lutzel K'e (Snowdrift), Deninu Koe (Fort Resolution), Hay River Dene Reserve, Thebacha (Fort Smith).

The data were converted to electronic form and one person in each community was instructed on the use of Epi-Info to access files. Data analyses proceeded at CINE.

RESULTS

Interpretation of the results includes visits to the communities and discussion of preliminary results before finalizing the final report by Fall, 1995.

Preliminary results of community interest relate to overall diet adequacy and the particular role of traditional food in the food system. Data are being analysed with both regions and communities as units of analyses.

Table 1 shows that calcium and vitamin A may be nutrients at risk of inadequate intake. In the Gwichin and South Slave regions, vitamin A intakes were higher because of caribou liver, and caribou and moose liver, respectively. No traditional food contributed significantly to calcium intake. At the regional level, traditional food contributed a range of 10-27 % of total energy intake, 35-61% for protein, 4-17% for fat, 34-64% for iron, 34-65% for zinc, 5-82% for vitamin A and 3-9% for calcium. Particular food species and absolute amounts consumed vary by community. Current work focuses on quantifying and understanding the patterns of variation.

Table 2 presents traditional foods that are the most consistently consumed, as measured by the average weekly frequency of consumption (days/week/person) over two seasons, summer (June-September) and winter (December-March). Caribou and whitefish are the principal foods in all regions, with moose and trout being often, but less uniformly consumed.

Table 3 presents a list of all traditional food consumed in Dene/Métis communities. Certain foods are consumed in some but not all communities and great geographical variation is present as to the particular foods and the quantities consumed across communities.

When compared with market food, study participants identified the following main advantages of traditional

food: low cost, healthiness, absence of additives/ preservatives, taste, and ease of preparation. The relative cost of traditional food was perceived as its main advantage with 28% of respondents reporting they could not afford to buy all their food if they had to; this proportion varied from 12 to 86% among communities.

When respondents were asked whether they agreed, disagreed or had no opinion on a list of statements, over 90% of respondents agreed on the following attributes of traditional food:

Harvesting and using traditional food by the family:
- contributes to physical fitness and good health
- is a favourite outdoor activity
- provides people with healthy food
- keeps people "in tune" with nature
- favours sharing in the community
- saves money
- is an essential part of the culture
- is an occasion for adults to display responsibility for their children
- provides education on the natural environment
- contributes to children's education and in particular it:
  - provides skills in survival
  - provides skills in food preparation at home
  - is an opportunity to learn patience and other personal qualities

In addition, successful harvest:
- brings respect from others
- builds one's pride and confidence

DISCUSSION/CONCLUSION

This 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 a preliminary report will be discussed this summer with community members before being finalized in the fall.

In parallel, additional food samples are being collected for nutrient analyses in order to complete the traditional food composition database for complete analysis of dietary recalls.

Expected project completion date: September, 1995

REFERENCES

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Table 1. Average daily nutrient intake (mean ± SE) of adults over 20 years of age in Dene/Metis communities (fall/early winter and late winter seasons combined).

	REGION				
NUTRIENT	GWICHÍN (n=195)	SAHTÚ (n=180)	DOGRIB (n=109)	DEH-CHO (n=217)	SOUTH SLAVE (n=311)
Energy (Kcal)	2051 ± 63	2194 ± 68	1989 ± 68	1985 ± 52	2542 ± 61
Carbohydrate (g)	208 ± 8	166 ± 7	187 ± 9	206 ± 6	256 ± 7
Protein (g)	134 ± 6	171 ± 7	140 ± 6	113 ± 4	142 ± 4
Fat (g)	75 ± 4	91 ± 4	74 ± 4	79 ± 3	105 ± 4
Vitamin A (RE)	2930 ± 1814	**521 ± 49**	**397 ± 50**	**561 ± 35**	1005 ± 244
Iron (mg)	22 ± 2	27 ± 2	21 ± 1	17 ± 1	23 ± 1
Calcium (mg)	**514 ± 23**	**443 ± 26**	**368 ± 20**	**486 ± 20**	**679 ± 28**
Zinc (mg)	16 ± 1	24 ± 1	18 ± 1	17 ± 2	22 ± 1

Note: Bold values are below recommended nutrient intake (RNI) for Canadian adults over 18 years of age. (RNI per day: energy 1700-3000 kcal, protein 50-64 g, vitamin A 800-1000 RE, iron 8-13 mg, calcium 700-800 mg, zinc 9-12 mg)

Table 2. Traditional food consumed by adults **more than once/week** during both summer and winter in Dene/ Métis communities.

Region	Species	Parts	Days consumed (per week)
Gwichín (n=195)	Caribou-B	meat cooked	3.1
		bone in soup	1.4
		flesh smoked/dried	1.3
	Whitefish	flesh cooked	1.4
		flesh smoked/dried	1.0
Sahtú (n=180)	Caribou-B	meat cooked	1.8
		meat smoked/dried	1.1
		ribs	1.0
	Caribou-W	meat cooked	1.8
		meat smoked/dried	1.0
	Moose	meat cooked	1.2
	Trout	flesh cooked	1.1
	Whitefish	flesh cooked	1.0
Deh-Cho (n=217)	Moose	meat cooked	2.8
		meat smoked/dried	1.6
		bone in soup	1.4
		ribs	1.4
		bone marrow	1.1
		fat	1.1
	Caribou-W	meat cooked	1.3
	Whitefish	flesh cooked	1.2
Dogrib (n=109)	Caribou-B	meat cooked	3.8
		meat smoked/dried	2.3
		ribs	2.2
	Whitefish	flesh cooked	1.2
South Slave (n=311)	Caribou-B	meat cooked	2.0
		meat smoked/dried	2.0
	Whitefish	flesh cooked	1.0

Table 3. List of traditional food consumed by adults in Dene/Métis communities during both summer and winter (all regions combined).

Species	Parts
Fish	
Whitefish	flesh cooked, flesh smoked/dried, head, eggs, fish-pipe, boiled skin, fins, gills, gut, liver, tail
Connie	flesh cooked, flesh smoked/dried, head, eggs, fish-pipe, fins, gut, liver
Cisco	flesh cooked, flesh smoked/dried, head, eggs, fish-pipe, liver, tail
Trout	flesh cooked, flesh smoked/dried, head, eggs, fish-pipe, fins, gut, liver, tail
Loche	flesh cooked, flesh smoked/dried, head, eggs, fish-pipe, liver, skin
Northern Pike (Jackfish)	flesh cooked, flesh smoked/dried, head, eggs, fish-pipe, liver, tail
Grayling	flesh cooked, flesh smoked/dried, head, eggs, fish-pipe, liver
Walleye	flesh cooked, flesh smoked/dried, head, eggs, fish-pipe, liver
Longnose sucker	flesh cooked, flesh smoked/dried, head, eggs,fish-pipe, tail
Arctic char	flesh cooked, flesh smoked/dried, head, eggs, fish-pipe
Beluga whale	flesh, muktuk, blubber, oil
Other Fish	ocean cod
Land Animals	
Caribou-W	meat cooked, meat smoked/dried, ribs, head, heart, tongue, liver, blood, stomach, kidney, bone marrow, soup with bone, fat, backbone, feet, hooves, tendons, bone fat, gut
Caribou-B	meat cooked, meat smoked/dried, ribs, head, heart, tongue, liver, blood, stomach, kidney, bone marrow, soup with bone, fat, backbone, feet, hooves, tendons, bone fat, gut, neck, fetus
Moose	meat cooked, meat smoked/dried, ribs, head, heart, tongue, liver, blood, stomach, kidney, bone marrow, soup with bone, fat, backbone, feet, hooves, tendons, gut, neck, nose, eyes
Rabbit	meat cooked, meat smoked/dried, head, liver, blood, brain, heart, kidney, ribs, tongue, backbone, eyes, lungs
Beaver	meat cooked, meat smoked/dried, tail & feet, liver, blood, brain, kidney, ribs
Muskrat	meat cooked, meat smoked/dried, tail, liver, blood, brain, kidney, ribs
Lynx	meat cooked
Porcupine	meat cooked, meat smoked/dried, liver, blood, fat, feet
Dall Sheep	meat cooked, meat smoked/dried, liver, blood, brain, ribs, feet, heart
Bear	meat cooked, meat smoked/dried, fat, blood, kidney
Buffalo	meat cooked, meat smoked/dried, ribs, tongue, heart
Other Animals	deer, elk, muskox, polar bear

Table 3. (continued)

Species	Parts
Birds	
Spruce Hen	meat cooked, meat smoked/dried, gizzard, kidney, heart, liver, eggs, head, eyes, backbone, legs
Prairie chicken	meat cooked, meat smoked/dried, gizzard, kidney, heart, liver, eggs, backbone, legs
Ptarmigan	meat cooked, meat smoked/dried, gizzard, kidney, heart, liver, eggs, backbone, legs
Black ducks/Scoter	meat cooked, meat smoked/dried, gizzard, kidney, heart, liver, eggs, backbone, legs, head, gut, neck
Mallard	meat cooked, meat smoked/dried, gizzard, kidney, heart, liver, eggs, backbone, legs
Fish ducks	meat cooked, gizzard, kidney, heart, liver, eggs, gut
Oldsquaw (Squaw duck)	meat cooked, meat smoked/dried, gizzard, kidney, heart, liver, eggs, bone
Wigeon (Whistling duck)	meat cooked, meat smoked/dried, gizzard, kidney, heart, liver, eggs
Canvasback	meat cooked, meat smoked/dried, gizzard, kidney, heart, liver, eggs
Canada goose	meat cooked, meat smoked/dried, gizzard, kidney, heart, liver, fat, eggs, backbone, bones in soup, head, gut, legs
Snow goose (wavies)	meat cooked, meat smoked/dried, gizzard, kidney, heart, liver, eggs, legs
Pintail	meat cooked, meat smoked/dried, gizzard, kidney, heart, liver, eggs, fat, head, legs
Swan	meat cooked, meat smoked/dried, gizzard, kidney, heart, liver, eggs
Plants	labrador tea, low (grey) blueberries, high (black) blueberries, cranberries, green gooseberries, purple gooseberries, blackberries, wild raspberries, wild strawberries, cloud berries/knuckleberries, red currants, black currants, saskatoon berries, rosehips, wild peppermint, mushrooms, wild greens, wild onions, wild rhubarb, birch bark, crowberries, dandelion, fireweed, muskeg tea, ratroot, red willow bark, sage, spruce bark, spruce gum, wild parsnips, yarrow tea, wild rose leaves

SANIKILUAQ TRADITIONAL FOOD STUDY

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Project Team: M.M.R. Freeman, Canadian Circumpolar Institute, University of Alberta; M. Inuktaluk, Environmental Committee, Municipality of Sanikiluaq; M. Meeko, Environmental Committee, Municipality of Sanikiluaq

OBJECTIVES

The purpose of this study is to assess the importance of traditional Inuit foods in contemporary diets of the Inuit of the Belcher Islands. Specific objectives are as follows:

1. To document the annual frequency of consumption of traditional Inuit food species among Inuit households in Sanikiluaq;
2. To demonstrate the variety of traditional food products prepared and consumed from these species;
3. To examine the frequency and average amounts of Inuit foods in daily diets among a sample of adults;
4. To assess daily nutrient intakes in relation to health recommendations among a sample of young and old men and women;
5. To examine the degree of preference for selected traditional and market foods, among adults and young people;
6. To provide insight into the continuing cultural and social importance of traditional foods to Inuit living on the Belcher Islands.

DESCRIPTION

To achieve the study objectives, 102 Inuit households (98%) in Sanikiluaq participated in a food frequency interview; 48 randomly selected adults further provided two 24-hour recalls of daily food consumption in two different seasons; and 100 adults (from 96% of the households) plus 64 young people (84% of those in Grades 6-11) provided food preference data. All the data were obtained by two residents who were trained to conduct the interviews and enter the data for analysis.

ACTIVITIES IN 1994/95

During this year data collection was completed, entered and analysed, and the project report was written. Upon completing the draft report, the project team presented the results of the study to several groups and organizations in Sanikiluaq. In addition to members of the community and representatives of community groups and organizations, the Regional Nutritionist from the Keewatin Regional Health Board, nurses and teachers met to review the report as well. Several comments and suggestions were received from these meetings, and incorporated into the final report.

RESULTS

The results indicated that traditional foods are widely used in the community. Households used traditional foods, on average, 1171 ± 852 times annually, or more than three times daily (Table 1). Fish and other seafood, birds, and sea mammals were most frequently used, along with berries and land mammals. Among the 48 adults who provided recall data, on average 799 grams of Inuit food, mostly meat, were consumed per person per day (Table 2). Inuit foods provided on average 47% of daily energy (calories) and over 80% of daily protein, iron, zinc and niacin. These results show the importance of traditional meat sources in contemporary Inuit diets. Intakes of vitamins A and C and of calcium, however, were low, and over 50% of adults were at risk of

inadequate intake of these nutrients. Preference ratings of 32 Inuit and 8 market foods showed that most Inuit foods were well-liked by adults and young people, although adults rated 25 Inuit foods higher ($p<0.05$) and 2 market foods lower ($p<0.05$) than young people did.

DISCUSSION/CONCLUSIONS

Traditional foods remain a large and important part of everyday diets in Sanikiluaq as shown by their widespread use among households and their thrice daily consumption (as estimated on average by households). Seafood, birds and sea mammals are most often used, followed by berries and land mammals.

Traditional Inuit foods, particularly meats, provide a large part of daily food and nutrient intakes of adults, especially older adults, as shown by the large amounts in daily diets, and the 47% of daily energy (calories) which comes from Inuit foods. Inuit foods also contribute substantially to the high protein, iron and zinc intakes. Total daily fat intakes are relatively low, and approach the health recommendation to limit total fat to 30% of dietary energy. For many adults, however, Vitamins A and C and calcium intakes, fall below the amount recommended for health.

Both adults and young people indicated a high preference for most Inuit foods; mean preference ratings were generally in the "like" (rating of 4) and "like very much" (rating of 5) categories. Adults, however, rated most Inuit foods higher (closer to "like very much") than young people did (closer to "like"). Favourites among both groups included seal, muktuk, char, goose, eider duck, reindeer, and mussels.

Respondents expressed a very strong belief in the health and satiety value of Inuit foods, and explicitly described the cultural, social and economic importance of Inuit foods to them:

> *We can't live without wild animals to eat. They are our foods. The elders from the past survived from wildlife. That's why we are here today. We want our country food to continue, for our children's children.*
>
> *Whales are shared with everyone...people are not cheap with whales. When hunters arrive from whale hunting they cut the whale into pieces near the shore. The news is announced through the radio and people come and get some. The whole community shares the whale.* (Wendy Takatak, Grade 11 Student)

Overall, Inuit foods remain an essential part, nutritionally, economically and culturally, of contemporary diets in Sanikiluaq.

Expected project completion date: the project and final report (listed below) were completed in June 1995.

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Table 1. Number of user households and mean annual household frequency of consumption of Inuit foods (mean ± S.D., N=102).

Food species	Number of user households[1]	Mean annual household frequency of consumption[2]
Ringed seal	99	122 ± 109
Beluga whale	100	26 ± 26
Bearded seal	81	25 ± 61
Walrus	75	11 ± 23
All sea mammals		**184 ± 161**
Reindeer	101	34 ± 61
Arctic hare	25	3 ± 18
Polar bear	53	3 ± 9
Caribou	25	3 ± 13
Arctic fox	26	1 ± 3
All land mammals		**45 ± 70**
Blue mussels	101	95 ± 90
Arctic char	101	90 ± 99
Sea urchin	93	87 ± 91
Sea cucumber	93	83 ± 92
Lake herring (Whitefish)	88	58 ± 98
Seaweed	60	46 ± 78
Tom cod	94	34 ± 40
Sculpin	91	29 ± 36
All seafood		**523 ± 490**
Eider duck	99	92 ± 105
Canada goose	99	66 ± 56
Snow goose	100	53 ± 50
Merganser	85	21 ± 28
Wild bird eggs	95	18 ± 17
Ptarmigan	52	3 ± 8
All birds and eggs		**254 ± 204**
Blueberries	101	43 ± 28
Crowberries	98	43 ± 31
Bog cranberries	94	40 ± 43
Cloudberries	100	33 ± 30
Red bearberries	39	7 ± 19
All wild berries		**166 ± 115**
All Inuit food species		**1171 ± 852**

[1] Number of households who reported use of this species during the year, December 1992 to November 1993.

[2] Number of eating occasions (i.e. meals or snacks).

Table 2. Frequencies and mean (± S.D.) weights (grams) of Inuit foods in daily food recalls by season (N=48 persons).

Food	February-March		October-November		Both*
	Frequency	Grams	Frequency	Grams	Grams
Land Mammals					660
Reindeer meat					
cooked	31	608 ± 458			
raw or frozen	3	670 ± 488	1	252	
dried	2	80 ± 0			
dried stomach	1	210			
Arctic fox	1	350			
Sea Mammals					749
Ringed seal meat					
raw or frozen	23	691 ± 668	2	506 ± 25	
boiled	3	415 ± 430	4	455 ± 265	
dried	1	200			
Bearded seal meat					
boiled	1	1400	11	550 ± 25	
raw			2	472 ± 74	
Walrus meat					
boiled			4	630 ± 352	
raw			2	770 ± 99	
Walrus skin	1	175			
Beluga muktuk			1	210	
Fish and Seafood					257
Arctic char	6	325 ± 280	11	302 ± 189	
Tom cod	1	840	4	370 ± 262	
Blue mussels	4	46 ± 22	1	75	
Sea cucumber	2	202 ± 104	1	128	
Sculpin			2	140 ± 159	
Sea urchin	1	30	1	50	
Birds					148
Eider duck					
raw			2	735 ± 544	
boiled			2	116 ± 44	
Goose			1	89	
Scoter duck			1	420	
Berries					105
Red bearberries			2	105 ± 49	
Total frequency	**81**		**55**		

* Mean weight of all items in the category over both seasons

ASSESSMENT OF EFFECTS OF PREPARATION ON LEVELS OF ORGANIC CONTAMINANTS IN INUIT TRADITIONAL FOOD

Project Leader: Centre for Nutrition and the Environment of Indigenous Peoples (CINE), McGill University.

Project Team: L.H.M Chan, O. Receveur, H.V. Kuhnlein

OBJECTIVES

1. To assess the effects of food preparation methods on levels of organic contaminants that are of concern in Inuit diets; chlorinated pesticides and PCBs will be determined;

2. To suggest alternative food preparation methods to reduce the intake of contaminants, while maintaining acceptable intake of essential fatty acids;

3. To study the effects of food preparation on fatty acid composition, to address benefits as well as risks.

DESCRIPTION

Preliminary food composition data collected from Broughton Island, Fort Good Hope and Colville Lake showed considerable variations/differences in levels of PCBs and toxaphene in raw versus prepared (e.g. boiling or aging) samples (Kinloch *et al.* 1992) (Appendix 1). Further sampling is needed because of the small number of replicates in these studies. Even though high levels of organic contaminants have been reported in various species consumed as traditional food (Northern Affairs Program 1993), certain food processing methods have been shown to reduce PCB levels in fish (Trotter and Corneliussen 1989) and pesticide levels in fruits and vegetables (Elkins 1989). Therefore, calculated total daily intake (TDI) based on results of analysis of raw food samples may over-estimate actual intake. Thus, it is important to study the effects of food preparation, particularly the traditional methods used in indigenous communities where high contaminant levels have been reported. If certain food preparation methods decrease the levels of contaminants significantly, it may be possible to lower the intake of organic contaminants through consumption of traditional food by recommending adaptations to cooking methods.

Fatty acid composition varies by species and following food preparation. The benefits of consuming the types of fatty acids found in Inuit traditional foods are documented (Kuhnlein *et al.* 1991). Changes in fatty acid composition by food preparation require investigation.

ACTIVITIES IN 1994/95

A meeting was held with the Council members of the Hamlet of Broughton Island. Various aspects of the traditional food system were discussed and a briefing of this study was presented. The Hamlet of Broughton Island agreed to participate in the project. It was decided to study walrus blubber, seal meat and blubber, narwhal mattak and blubber. They were chosen because of their high fat content and relative importance in the traditional diet. A local research assistant, Ms. Mary Killiktee, was trained to collect and prepare the samples. Five replicates of each of the five food items were portioned and prepared as they are usually served. Samples were frozen at –20°C and shipped to CINE for analysis.

METHODS

Total fat contents for the samples were determined using an automatic soxhlet system (Soxtec HT-6, Tacater AB, Hoganas, Sweden) with petroleum-ether (40-60)°C as an extracting solvent.

For measurement of organochlorines, samples were spiked with aliquots of a surrogate internal standard solution containing ^{13}C-labeled PCB IUPAC No 3, 77, 202 and 209, $^{13}C_{12}$-*p,p'*-DDT and $^{13}C_6$-γ–lindane and ground with 20 g of anhydrous sodium sulfate in a mortar until a free flowing powder was obtained. The ground samples were packed into a glass column (2.5 cm i.d. x 30 cm) and immersed with 75 ml of solvent (1:1 methylene chloride/hexane) for 45 min. The solvent was eluted from the column at a flow rate of 3-5 ml/min and further extracted with 200 ml of solvent. The extracts were concentrated, filtered and defatted with a SX-3 Biobeads

gel permeation column (3 cm i.d. x 70 cm; solvent: 1:1 methylene chloride/hexane; flow rate: 5 ml/min) connected to a Beckman gold HPLC system (Beckman Instrument Inc., Fullerton CA). The first 175 ml containing higher molecular weight lipids were discarded. The next 115 ml containing the PCB and chlorinated pesticides were collected. The collected fractions were concentrated and applied onto a florisil (Supelco, Ont.) column (1 cm. i.d. x 30 cm) for further purification and fractionation. Three fractions were collected: the first fraction (36 ml hexane) contained PCB congeners, hexachlorobenzene, *p,p'*–DDE, heptachlor, mirex and photomirex; the second fraction (36 ml of 15% methylene chloride/hexane) contained hexachlorocyclohexanes, chlordanes and *p,p'*-DDT; and the third fraction (55 ml 1:1 methylene chloride/hexane) contained heptachlor epoxide and dieldrin. The three fractions were reduced to 50 µl , spiked with the volumetric internal standard d_{12}-chrysene and made up to 100 µl with isooctane for GC analysis.

Characterization of the three fractions was conducted using a Varian Saturn III GC-Ion trap mass spectrometer. A DB-5MS (J&W Scientific) (30 m x 0.25 mm i.d. and 0.25 µm film thickness) capillary column was used. Samples were loaded onto a Varian 8200cx autosampler and 1 µl injections were made using the sandwich injection technique. A total of 51 PCBs and 17 chlorinated pesticides was screened in the samples. Levels were measured using the internal standard method in conjunction with the corresponding external standards. ^{13}C-PCBs, $^{13}C_{12}$-*p,p'*-DDT and $^{13}C_6$-γ–lindane surrogates were only used to evaluate the extraction and purification efficiency of the analytical method. Linearity of the ion-trap-ms was verified by injecting levels of standards ranging from 10 pg/µl - 1000 pg/µl . Any compound measured below this minimum quantitation limit and that had a matching spectra was given the minimum detected limit of 1 pg/µl which corresponded to 0.05 ng/g of wet sample weight.

For fatty acid analysis, approximately 1 g of the sample was weighed into 50 ml centrifuge tubes and extracted with 18 ml of chloroform:methanol mixture (2:1) by sonication for 30 min. Five ml of saturated aqueous NaCl were then added. The final mixture was vortexed and centrifuged at 2000 rpm for 5 min. Aliquots (2 ml) of the lower chloroform layer were evaporated to dryness and derivatised to their methyl esters (FAME). The derivatisation was done according to a modification of the boron fluoride-methanol (BF_3.MeOH) method of Morrison and Smith (1961). The derivatisation reagent (4:3:4 BF_3.MeOH:benzene:methanol) was added to the dry lipid residue and incubated at 100°C for 45 min. The FAME were extracted into 2 ml of hexane. Aliquotes (250 µl) of the hexane extract were spiked with an internal standard (C17:0 methyl ester) and analyzed by gas chromatography (GC). GC analysis was performed using a 30 m supelcowax–10 fused capillary column (0.32 ID, 0.25 mm film thickness), fitted on a Varian Star 3400 CX chromatograph (Varian Inc. Walnut Creek, CA). Quantification was performed with the Varian Chromatographic Work Station Software-(Ver-4), using a 5 point calibration curve.

Quality Assurance/Control

Standard reference materials (CLB-1 PCB solutions from the National Research Council of Canada and SRM 1588 organics in cod liver oil from National Institute of Standards and Technology) were measured with each batch of samples. The results were always within 1 SD of the certified values. Our laboratory also participates in the Northern Contaminants QA/QC Program.

Statistical methods

Differences in lipid, contaminant and fatty acid levels were tested by paired t-test (SYSTAT, Version 5.02, SYSTAT Inc., Evanston, IL, USA). A P value of <0.05 was considered significant in all statistical tests.

RESULTS

Effects of food preparation on organochlorine and fatty acid levels in walrus blubber are presented. Total lipid content did not change after frying but decreased significantly after boiling ($T=4.04$, $D.F.=4$, $P<0.05$) (Figure 1). There were variations in the total PCB (the sum of 51 congeners) and the total pesticide concentrations (the sum of pentachlorobenzene, α–HCH, β–HCH, γ–HCH, hexachlorobenzene, heptachlor, heptachlor epoxide, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor, *p,p'*-DDE, *p,p'*-DDD, *p,p'*–DDT, photomirex, mirex) among the five walrus blubber samples. Both pesticide and PCB levels seem to be lower in the boiled and fried samples but the results are not significant (Figures 2 and 3). When the individual pesticide group and PCB homologue were considered, the fried samples had significantly less total chlorobenzene (the sum of penta- and hexa-chlorobenzenes) (Figure 4). Both the boiled and fried samples were significantly lowered in total nona-chlorinated biphenyls ($T=16.9$ for boiled sample and $T=2.9$ for fried samples, $d.f.=4$)(Figure 5). One of the reasons for the decrease may be the decrease of lipid content. However, the decrease may also be caused by the evaporation of the relatively more volatile chlorobenzenes and the loss of the chlorine ions from the more heavily chlorinated biphenyls.

Results of the fatty acid composition of the walrus blubber samples are summarized in Table 1. Data of the oil residue after frying are also included. The boiled sample had significantly less lipid and lower W-6 levels (T=3.7, d.f.=4) than the raw samples.

CONCLUSIONS

From the preliminary results, there seem to be less organochlorines in the prepared food samples. The total polyunsaturated fatty acids, however, remained unchanged. A more detailed analysis and diet suggestions will be communicated to the community when all results are available.

Expected project completion date: December, 1995.

Partners: Inuit Tapirisat of Canada, Inuit Circumpolar Conference, the Hamlet of Broughton Island, Baffin Regional Health Board, CRSS-Katavik/Nunavik.

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Table 1. Fatty Acid Composition of Walrus Blubber.

Preparation	N	Lipid (%)	Total Saturated[a]	Total Unsaturated[a]	Mono-unsaturated[a]	Total PUFA[a]	Ω-3[a]	Ω-6[a]
Raw	5	85.99 (0.79)[b]	10.08 (0.74)	55.11 (4.70)	38.46 (3.86)	12.87 (1.53)	12.22 (1.59)	2.75 (0.19)
Boiled	5	83.01 (1.26)[c]	8.70 (1.51)	4.8.41 (4.90)	34.12 (3.73)	9.74 (1.54)	10.20 (1.85)	1.53 (0.25)[c]
Fried	5	85.89 (1.22)	10.48 (0.78)	57.84 (3.98)	41.15 (2.85)	12.68 (1.00)	11.92 (0.92)	2.84 (0.25)
Oil	4	93.67 (0.37)	11.38 (1.22)	63.30 (7.66)	43.16 (5.08)	14.77 (1.87)	13.64 (1.68)	2.13 (0.32)

[a] g/100 g wet weight
[b] mean (standard deviation)
[c] significantly difference from raw sample ($P < 0.05$)

Table 2. Examples of differences in levels of PCBs and toxaphene in raw and prepared parts from the same animal.[a]

Species	Parts	Preparation	PCB (ng/g)	Toxaphene (ng/g)
Narwhal	blubber	raw	1675	11690
		boiled	1487	4312
Walrus	meat	raw	108	46
		boiled	90	17
	blubber	raw	5974	3039
		boiled	5013	39
Bearded Seal	meat	raw	25	4
		boiled	4	1
Ringed Seal	meat	raw	47	6
		boiled	57	4
		aged	64	9
	blubber	raw	435	123
		boiled	352	109
		aged	438	183

[a] From Kinloch *et al.*, 1992.

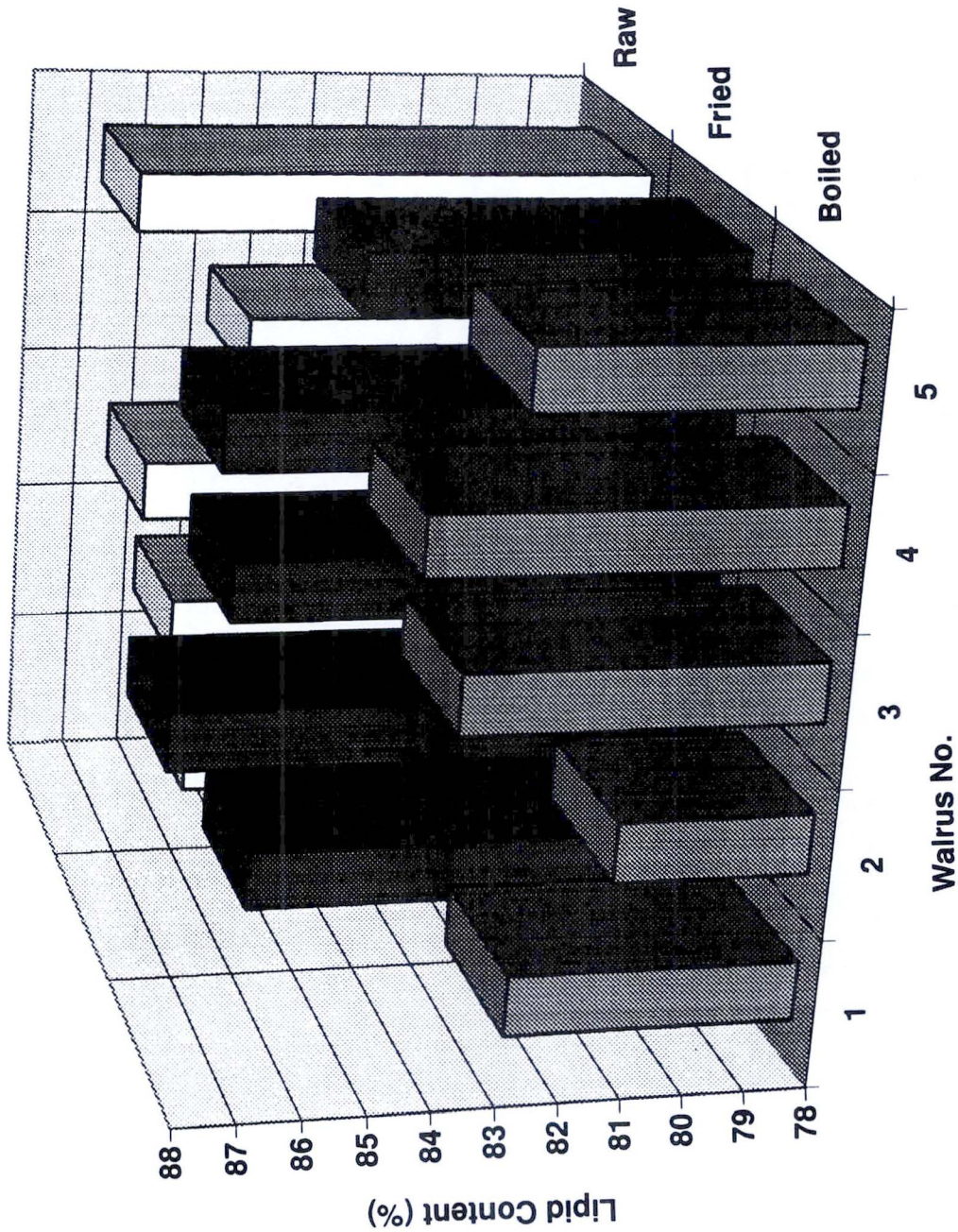

Figure 1. Lipid content in walrus blubber (%)

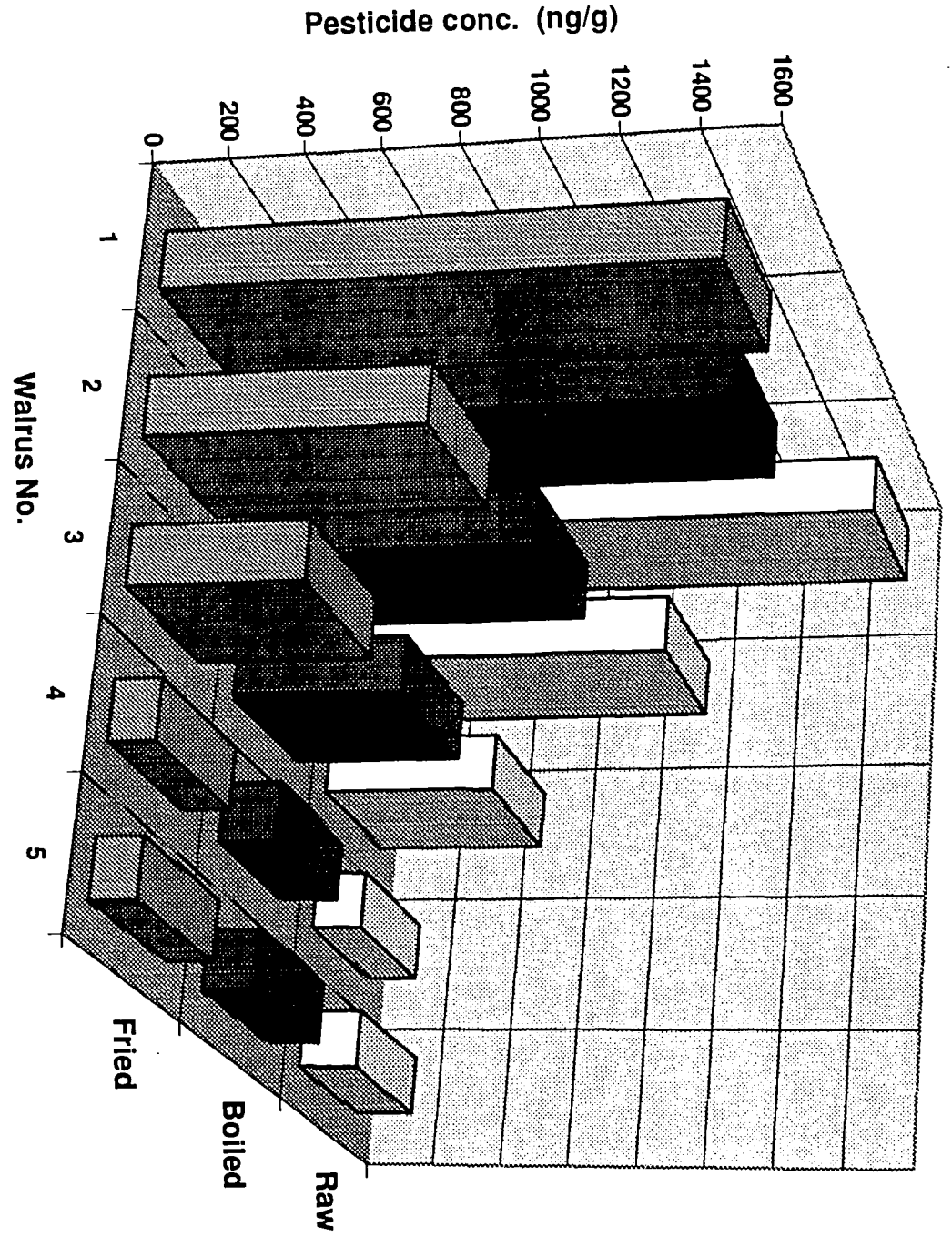

Figure 2. Total pesticide concentrations in walrus blubber (ng/g wet weight)

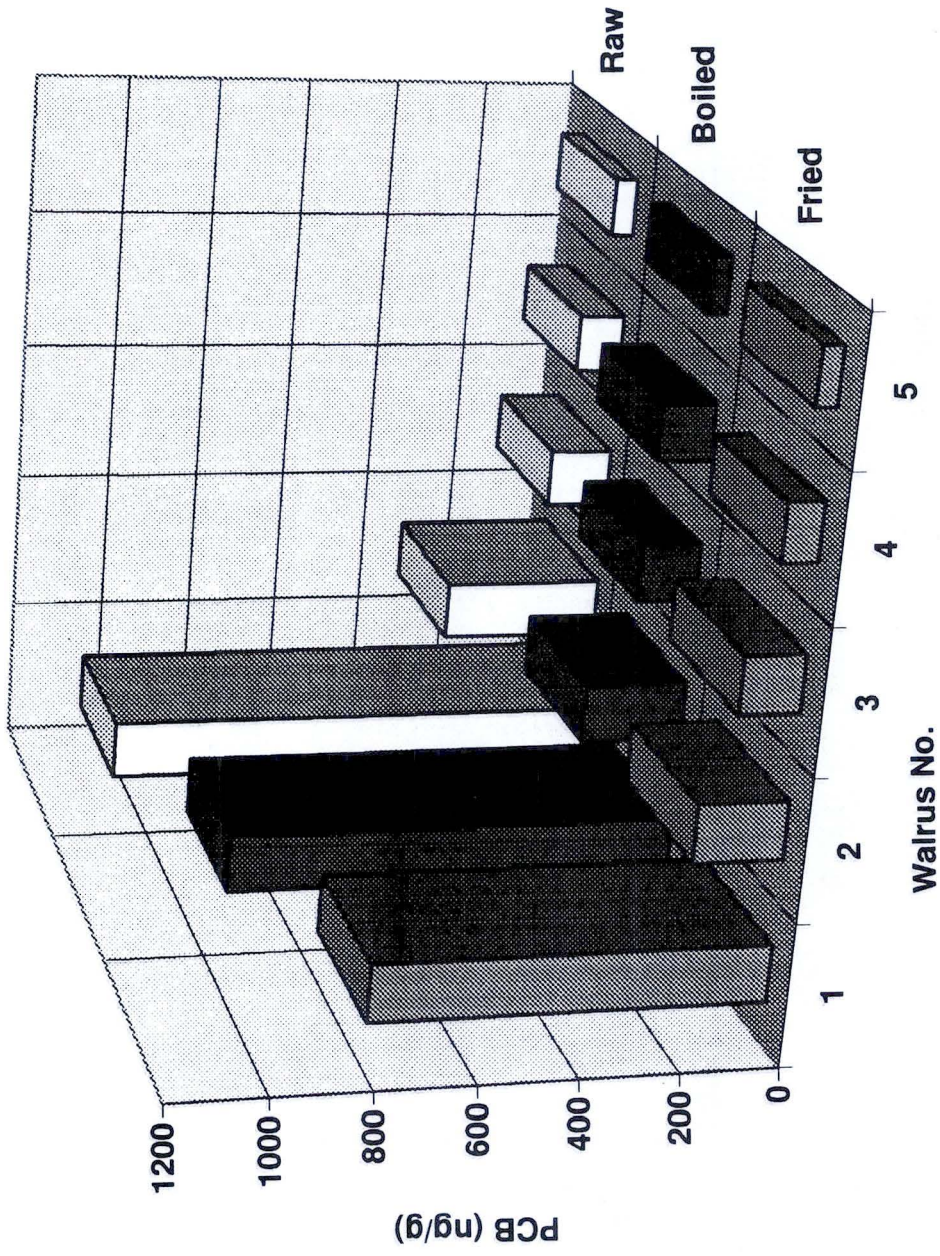

Figure 3. Total PCB concentrations in walrus blubber (ng/g wet weight)

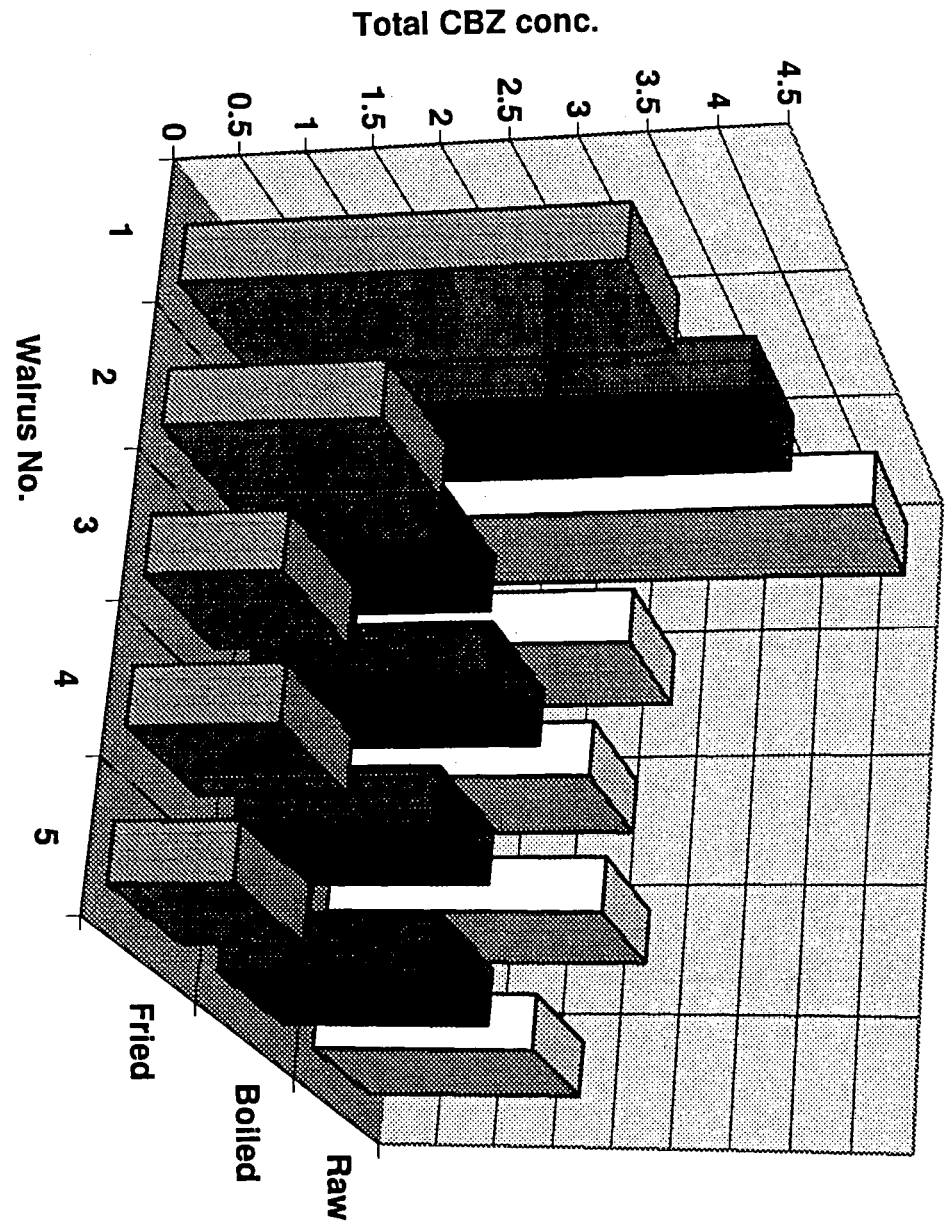

Figure 4. Total chlorobenzenes in walrus blubber (ng/g wet weight)

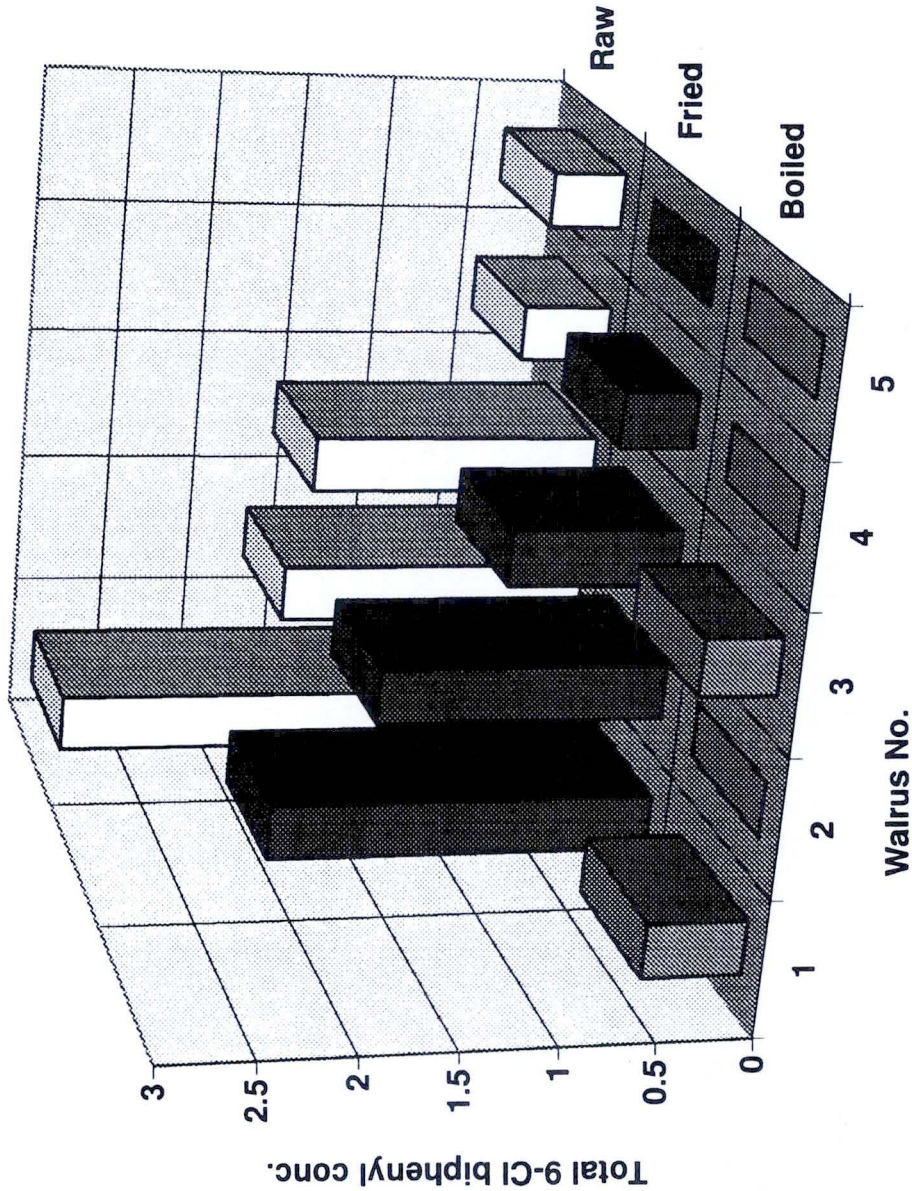

Figure 5. Total nona-chlorinated biphenyls in walrus blubber (ng/g wet weight)

HEALTH RISK ASSESSMENT AND ELABORATION OF PUBLIC HEALTH ADVICE CONCERNING FOOD CONTAMINANTS IN NUNAVIK

Project Leader: É. Dewailly, Public Health Centre, Québec region

Project Team: P. Ayotte, Public Health Centre (Québec region); G. Carrier, University of Sherbrooke; C. Blanchet, Public Health Centre (Québec region); S. Bruneau, Public Health Centre (Québec region); L. Sauvé, Public Health Centre (Québec region); M. Grey, Food, Contaminants and Health Committee, Kuujjuaq, Québec; B. Holub, Department of Nutrition Sciences, University of Guelph; H. Kuhnlein, Department of Nutrition, McGill University

OBJECTIVES

The general objective of this study is to assess the health risks associated with the presence of contaminants in country foods (organochlorines and heavy metals) and propose, if necessary, public health recommendations aimed at reducing exposure to these chemicals, while ensuring that major nutritional benefits are maintained. The specific objectives are:

1. To assess the human exposure to these contaminants using biological measurements and data on food consumption and contamination obtained during previous surveys;

2. For each subgroup (pregnant and breast-feeding women, infants, hunters) and each contaminant, determine the percentage of the population exposed over critical levels that could induce a public health risk;

3. To establish the objectives for exposure reduction, when required, using toxicokinetic models to translate target blood concentration into dietary intake reduction;

4. To select the optimal scenarios resulting in the desired risk reduction while maximizing the dietary benefits using a matrix containing data on food contamination, nutrient content and food consumption for each subgroup of the population;

5. To propose these scenarios to the local public health authorities and Native groups so that they can undergo a social, economic and cultural acceptability and feasibility evaluation.

DESCRIPTION

Contaminants such as heavy metals and organochlorines reach the Arctic and are biomagnified in terrestrial and aquatic food chains. As the Inuit diet relies heavily upon sea products, the Inuit are more exposed to these food chain contaminants than populations living in meridional regions (Dewailly *et al.* 1994). Since 1986, we have conducted various studies and programs in Nunavik in order to assess which contaminants are potentially harmful to health, to what levels are Inuit people (nursing babies, fetus and adults) exposed, and which effects could be linked to this exposure (nursing infants and, forthcoming, fetus) (Dewailly *et al.* 1989a, 1989b, 1992a, 1992b, 1993a, 1993b). More recently, pilot studies were conducted regarding early effects of prenatal exposure to food chain contaminants at the biological levels (cf. in this publication, pilot study on biomarkers in placenta and cord blood lymphocytes, Ayotte 1995) and at the clinical level (cf. in this publication, pilot study on neurobehavioural deficits, Muckle 1995). Risk characterization by comparing the exposure with known safety levels recommended by various health organizations was also initiated (Ayotte *et al.* 1995).

In order to balance potential health risks related to contaminants exposure, we evaluated benefits of country foods particularly in protecting against ischaemic diseases such as heart attacks among adults (Dewailly *et al.* 1994). Of special interest are nutrients found in food items from the marine food chain. Omega-3 fatty acids are derived essentially from the consumption of marine products and a high intake of these polyunsaturated fatty acids has been linked to a lower incidence of thrombotic disease and other chronic illnesses (Dierberg *et al.* 1975, 1978, Yamori *et al.* 1985, Olsen 1992, Nettleton 1993). Indeed, for Inuit living along the shore of Hudson Bay, death owing to ischaemic illnesses is rare, if not non-existent (Corriveau 1993). Selenium is an essential human nutrient and it is the consumption of fish

and seafood that constitutes the primary source of this element. Selenium and other antioxidants such as retinol (vitamin A) are known anticarcinogens (Health and Welfare Canada 1990). Furthermore, selenium may actually reduce the potential risk of mercury poisoning (Kershaw *et al.* 1980, Turner *et al.* 1980). Proteins provide dietary energy and are necessary for tissue synthesis and in the regulation of body functions. Zinc plays a key role in genetic expression, cell division and growth, promotes wound-healing, and prevents infection, as well as neuropsychologic impairments (Sanstead 1994). Finally, several minerals such as iron, calcium, magnesium and phosphorus have several essential roles in maintaining a healthy status.

The first step in this health risk assessment involves assessing exposure using biological measurements, food contamination and consumption data from the Hudson Bay area. Biological measurements include concentrations of organochlorine in human milk samples and lead, cadmium, mercury and organochlorine concentrations in blood samples from Inuit adults (Dewailly *et al.* 1992a, Dewailly *et al.* 1994) . Food contamination data were produced by Hydro-Québec's extensive surveys in Great Whale and Nottaway-Broadback-Rupert areas, covering species of both fresh water and marine fishes, marine mammals, and edible waterfowl (Somer inc. 1993, 1994). The following contaminants were measured in these species: arsenic, cadmium, chromium, lead, manganese, nickel, mercury, HCB, α– and γ–BHC, heptachlor, heptachlor epoxide, aldrin, endrin, dieldrin, α– and γ–chlordane, α– and β–endosulfan, *pp'*-DDE, *op'- and pp'*-DDT, *pp'*-DDD, mirex, methoxychlor, 43 PCB congeners (including non-ortho coplanar congeners).

The nutrients considered in this project are proteins, lipids, omega-3 fatty acids, vitamin A, iron, calcium, selenium, zinc, magnesium, and phosphorus. Food consumption data were obtained by two dietary questionnaires administered during the Santé Québec Inuit Health Survey (24-hour dietary recall and food frequency) (Santé Québec 1994). Recommended nutrient intakes (RNI) were based on nutrition recommendations made by the Scientific Review Committee (Health and Welfare Canada 1990). Dietary allowances for all nutrients were established for healthy individuals by age-sex-weight category.

Secondly, in order to determine the percentage of the population at risk, one needs to compare contaminant exposure with critical doses or biological indices of public health concern. These will be based on data available from epidemiological and experimental studies and from guidelines published by various public health authorities (WHO, EPA, HWC, NIOSH, FDA, ATSDR). A statistical analysis of biological data and dose calculation data will be made in order to estimate the percentage of the general population or subgroups that is exposed above critical levels.

Thirdly, if exposure exceeds the level of action defined for a given contaminant, in a significant proportion of individuals from specific subgroups, scenarios of risk abatement will be generated, considering the contribution of each food item to the total dose and their nutritional value. Scenarios will be generated in which the intakes of the most contaminated food items are reduced one at a time in order to achieve the required reduction in exposure. Toxicokinetic models will allow for the estimation of the proper dietary dose reduction to achieve the required diminution in contaminant blood levels. Optimal scenarios will be those that result in the desired reduction of exposure to contaminants while maintaining the proper intake of nutrients.

Several scenarios will be supplied in order to allow for selection by local authorities of the most viable options for risk reduction. The main priority is to make available for the Nunavik population, the results of this study. This will be effected with the help of the Food, Contaminants and Health Committee in Kuujjuaq, Québec. This committee, following consultation with northern organizations and residents of some communities (public meeting), is also planning to produce a nutrition guide adapted to the needs of different subgroups of the population (pregnant women, young adults, elders).

ACTIVITIES IN 1994/95

In 1994/95, nutritive values of archived samples (11 species of fishes, 3 species of marine mammals and 8 species of edible waterfowl) collected by Hydro-Québec were determined in two laboratories. Animals and tissues that are most often eaten by Inuit population were selected. Analysis of 103 samples for total lipids and fatty acids (saturated and polyunsaturated fatty acids including omega-3) were conducted at the laboratory of the Department of Nutritional Sciences at the University of Guelph. Analysis of 118 samples for proteins, vitamin A, iron, calcium, selenium, zinc, magnesium and phosphorus were completed in June by the laboratory of the Ministère de l'Agriculture, des Pêcheries et de l'Alimentation du Québec, Québec City.

Data on country food contamination were extracted from an existing database elaborated by Hydro-Québec. Additional data on fishes and marine mammals were obtained from the Northern Contaminant Database

developed at our centre (cf. in this publication, Careau 1995). Statistical analysis of contaminant and nutrient content data is underway.

Preliminary data analysis has been effected to evaluate frequency and quantity of country food consumption by the Inuit population and the contribution of these foods as sources of nutrients.

Finally, a critical evaluation of the literature pertaining to neurodevelopmental effects induced by prenatal exposure to contaminants is being completed.

RESULTS

For this report, only limited descriptive data (arithmetic means and percentages) are presented; further statistical analyses are in progress.

Food Contamination

Samples analysed for contaminant levels were collected in 1990 and 1991 and therefore, actual levels could differ somewhat (Table 1). Among fishes, the Northern Pike, the Lake Trout and the Walleye were the most contaminated species, in terms of to mercury levels (greater than 0.7 mg/kg). OC levels were generally low (not detected to a few µg/kg) in all species. Among fish-eating bird species, the Herring Gull and the Common Loon showed the highest mercury and OC concentrations. The mean PCB concentration in Herring Gull was close to 4 mg/kg. The Northern Pintail, the Green-winged Teal and the American Black Duck contained relatively elevated concentrations of lead (~0.3 mg/kg).

Fatty tissues from white whale (beluga) showed the greatest OC concentration of all country foods (5.3 mg/kg; Aroclor 1254: 1260, 1:1). The mean mercury level in white whale meat (2.6 mg/kg) was also greater than that of all other food items consumed by the Inuit.

Nutritive Values of Food Items

Mean nutritive values of animal tissues are presented in Table 2. Inuit country foods are important sources of protein, iron, selenium, zinc and phosphorus as well as the greatest source of omega-3 fatty acids (eicosapentaenoic and docosahexaenoic acids). As expected, marine mammal fat possesses a high content in omega-3 fatty acids and vitamin A, a fat-soluble vitamin. For the meat, fish shows the largest omega-3 fatty acid concentrations, followed by marine mammals and waterfowl. Marine mammal meat and waterfowl are also important sources of iron and zinc. However, these food items contain small amounts of vitamin A (retinol), calcium and magnesium. A more extensive analysis of total lipid and fatty acid contents will be presented in the final report.

Country Food Consumption

Food consumption data are presented by sex and age in Table 3. Average portion size in grams of country foods consumed by Inuit adults varied according to sex and age. For fish, wildfowl and white whale, average amounts are higher among men, particularly in the older age group. Frequency analysis of country food consumption is underway. Preliminary results about marine mammals indicate that men and women have similar patterns of consumption: seal meat and seal fat are consumed most often on a monthly basis, followed by white whale skin, blubber and white whale meat (Table 4). On a yearly basis, fish consumption is also very high while wildfowl consumption occurs primarily during the hunting season.

CONCLUSION

All data on nutrient and contaminant content in traditional food items have been obtained, as well as food consumption data. However, in order to elaborate sound public health advice regarding food contaminants in Nunavik, the contaminant load and nutritional value of imported foods will be evaluated in 1995/96. In addition, we plan to include in our evaluation results obtained by the Centre for Nutrition and the Environment of Indigenous Peoples (CINE) of the impact on contaminant and nutrient intakes of various food preparations. During the same year, scenarios developed during this research program will be submitted to local health authorities.

Expected project completion date: March 31, 1996.

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Table 1. Mean concentrations of heavy metals and organochlorines in animal tissues (per kg, wet weight).

Species name/ Contaminants		Mercury (mg)	Lead (mg)	Cadmium (mg)	HCB (µg)	*pp'*-DDE (µg)	Mirex (µg)	Dieldrin (µg)	PCB[1] (µg)
FISH:	**muscle**								
Longnose Sucker *(Catostomus catostomus)*		0.161	0.004	nd[2]	nd	0.941	nd	nd	5.729
White Sucker *(Catostomus commersoni)*		0.134	nd	nd	nd	0.678	nd	nd	1.575
Lake Whitefish *(Coregonus clupeaformis)*		0.151	0.006	0.002	nd	0.845	nd	nd	2.461
Northern Pike *(Esox lucius)*		0.716	0.009	0.002	nd	1.027	nd	nd	4.682
Arctic Cod *(Gadus ogac)*		0.058	nd	0.02		0.8	nd		
Fourhorn Sculpin *(Myoxocephalus quadricornis)*		0.205	nd	0.003	nd	0.46	nd	nd	2.7
Brook Trout *(Salvelinus fontinalis)*		0.122	nd	0.002	nd	1.05	nd	nd	3.017
Lake Trout *(Salvelinus namaycush)*		0.739	nd	0.001	nd		nd	nd	
Ouananiche *(Salmo salar ouananiche)*		0.151	nd	nd	nd		nd	nd	
Walleye *(Stizostedion vitreum)*		0.858	0.008	0.017	nd	1.213	nd	nd	3.81
Red Charr[3] *(Salvelinus salvelinus)*		0.038			6.49	2.168	0.02	2.27	14.5
Atlantic Salmon[3] *(Salmo Salar)*		0.68							
WILDFOWL:	**muscle**								
Northern Pintail *(Anas acuta)*		0.176	0.372	0.016	nd	4.5	1.167	0.33	6.334
Green-winged Teal *(Anas crecca)*		0.139	0.26	0.01	nd	0.001	nd	nd	0.005
American Black Duck *(Anas rubripes)*		0.194	0.334	0.06	nd	27.51	6.25	3.000	113.0
Canada Goose *(Branta canadensis)*		0.046	0.061	0.048	nd	5.334	nd	1.67	1.667
Common Loon *(Gavia immer)*		0.704	0.03	0.105	4.003	199.1	11.33	19.01	840.5
Herring Gull *(Larus argentatus)*		0.998	nd	0.048	18.1	492.5	16.42	17.09	3854

Table 1. (continued)

Species name/ Contaminants		Mercury (mg)	Lead (mg)	Cadmium (mg)	HCB (µg)	*pp'*-DDE (µg)	Mirex (µg)	Dieldrin (µg)	PCB[1] (µg)
Willow Ptarmigan *(Lagopus lagopus)*		0.03	0.064	0.228	0.012	nd	nd	nd	2.702
Black Scoter *(Melanitta nigra)*		0.245	0.065	0.03	0.5	3.516	0.001	1.000	16.58
MARINE MAMMALS:									
White Whale[3]	**meat**	2.603	0.05	9.224	13.8	53.14	0.6	3.11	46.7
(Delphinapterus leucas)	**fat**	0.073			570.1	8440	38.00	580.6	5260
	skin	0.56				2.8	41.00		
Ringed Seal: *(Phoca hispida)*	**meat**	0.319	nd	0.07	0.885	22.05	0.33	2.175	31.6
Freshwater Seal[3]	**meat**	1.095	nd	0.01	0.517	13.22			
(Phoca vitulina)	**fat**	0.075			19.83	870.3			

[1] PCB concentrations are expressed as Aroclor 1254:1260 (1:1), except for fishes (Aroclor 1260).
[2] nd = not detected.
[3] Only partial results are available.

Table 2. Mean nutritive values of animal tissues (per 100 grams, wet weight).

Species name/Nutrient	Proteins (g)	Vitamin A (I.U.)	Iron (mg)	Calcium (mg)	Magnesium (mg)	Phosphorus (mg)	Selenium (mg)	Zinc (mg)	EPA[1] (mg)	DHA[2] (mg)
FISH: muscle										
Longnose Sucker *(Catostomus catostomus)*	18.4	2.59	0.238	19.6	17.4	185	0.04	0.52	82.9	179
White Sucker *(Catostomus commersoni)*	17.7	4.35	0.263	63.1	21.8	203	0.05	0.3	75.2	212
Lake Whitefish *(Coregonus clupeaformis)*	23.3	4.88	0.321	25.7	17.2	237	0.05	0.38	59.1	251
Northern Pike *(Esox lucius)*	21.8	6.7	0.208	32.6	17.3	209	0.04	0.41	44.4	165
Arctic Cod *(Gadus ogac)*	24.8	2.49	0.585	20.2	18.1	194	0.07	0.47	165	329
Fourhorn Sculpin *(Myoxocephalus quadricornis)*	20.6	15.3	2.5	96.5	18.5	460	0.05	0.79	198	324
Brook Trout *(Salvelinus fontinalis)*	23.5	2.4	0.3	9.3	21.0	230	0.04	0.46	112	322
Lake Trout *(Salvelinus namaycush)*	20.9	3.94	0.246	6.11	20.8	209	0.08	0.38	72.7	232
Ouananiche *(Salmo salar ouananiche)*	24.3	2.1	0.378	11.6	22.9	240	0.05	0.57	269	612
Walleye *(Stizostedion vitreum)*	20.1	7.7	0.203	31.0	21.2	216	0.04	0.32	52.2	156
Red Charr[3] *(Salvelinus salvelinus)*	20.2		0.23	7.2		257				
Atlantic Salmon *(Salmo Salar)*	19.8	40.0	0.8	12.0	29.0	200		0.64	321	111
WILDFOWL: muscle										
Northern Pintail *(Anas acuta)*	26.4	14.3	7.1	2.1	13.5	275	0.04	1.14	58.7	54.0
Green-winged Teal *(Anas crecca)*	26.0	13.2	5.37	9.93	15.3	260	0.04	0.84	79.1	51.4
American Black Duck *(Anas rubripes)*	25.7	21.5	6.18	6.24	17.3	215	0.05	0.96	71.9	40.1
Canada Goose *(Branta canadensis)*	23.9	36.5	5.63	8.07	13.3	250	0.02	1.33	12.9	27.9
Common Loon *(Gravia immer)*	24.1	8.7	7.35	5.45	19.0	245	0.06	2.4	76.8	32.0
Herring Gull *(Larus argentatus)*	26.3	154.0	7.38	14.2	17.3	233	0.07	1.6	126	119.0

Table 2. (continued).

Species name/Nutrient		Proteins (g)	Vitamin A (I.U.)	Iron (mg)	Calcium (mg)	Magnesium (mg)	Phosphorus (mg)	Selenium (mg)	Zinc (mg)	EPA[1] (mg)	DHA[2] (mg)
Willow Ptarmigan *(Lagopus lagopus)*		25.6	14.8	5.03	8.04	18.2	252	0.01	0.67	17.8	28.8
Black Scoter *(Melanitta nigra)*		25.1	29.4	7.05	27.1	15.5	311	0.06	1.2	116	103
MARINE MAMMALS:											
White Whale	**meat**	24.2		16.1	4.3	13.0	180	0.17	3.00	80.1	79.4
(Delphinateus Leucas)	**skin**	24.2		0.18	10.0	14.0	140			326	340
	fat		1556	0.28	3.3	0.1	14.0			4303	4974
Freshwater Seal *(Phoca vitulina)*	**meat**	25	19.1	0.16	12.0	22.5	215	0.04	2.2	191	448
Ringed Seal	**meat**	25.7	3.2	21.1	3.87	21.7	191.7	0.05	2.54	88.3	118
(Phoca hispida)	**fat**		2221	1.2	2.5	1.00	21.0			6277	12285

[1] EPA=Eicosapentanoic acid: C20:5n3.
[2] DHA=Docosahexanoic acid: C22:6n3.
[3] Only partial results are available.

Table 3. Mean portion size (grams) of country foods consumed by the Inuit population (Santé Québec, 1994).

Country food	Men		Women	
	18-49 years	50-74 years	18-49 years	50-74 years
Fish	176.9	300.0	121.5	192.0
Wildfowl	73.3	225.4	57.0	70.0
White whale	99.8	100.5	93.4	48.1
Seal	61.3	112.6	129.9	107.5

Table 4. Proportion of Inuit adults who declared having consumed marine mammals at least once during the previous month (Santé Québec, 1994).

Marine Mammal	Men		Women	
	18-49 years	50-74 years	18-49 years	50-74 years
Seal meat	59%	74%	61%	69%
Seal fat	56%	79%	61%	66%
White whale skin	60%	42%	62%	56%
White whale blubber	37%	45%	42%	51%
White whale meat	35%	24%	37%	31%

IV EDUCATION AND COMMUNICATIONS

IV. EDUCATION AND COMMUNICATIONS
NEW INITIATIVES

1) A liaison coordinator has been added to the staff of the Yukon Contaminants Committee (YCC) to answer questions raised within communities on environmental issues as well as bring feedback to the YCC.

2) The five aboriginal organizations and territorial contaminants committees have produced a variety of fact sheets on various contaminants, nutrients in country foods, and important traditionally harvested species. A number of regional workshops were held to inform northerners about contaminants issues, to answer questions about contaminants, to gather input on northerners' concerns and in some cases to assess their level of familiarity with the issues and their information needs. Work led by GNWT Health includes development of information packages for health workers, contaminants videos, establishment of regional consultative working groups. Several NCP participants also issue regular newsletters (e.g. Dene Nation, CINE, GNWT Health) which provide updates on research activities or specific projects, and give general information on environmental topics of interest with regard to the environment, nutrition and/or health.

3) The Métis Nation is in the final stages of developing an environmental contaminants program to be integrated with the existing NWT school curriculum for grades 7 to 9, and with adult education courses offered through Arctic and Aurora Colleges. Published lessons for grades 7 to 9 will be distributed in the 1995/96 academic year to schools and Regional Resource Centres in the NWT. Draft lesson plans for adult education will be distributed via curriculum specialists for Arctic and Aurora Colleges. The educational materials have been pilot-tested and are adaptable to regional needs and able to reflect Dene and Inuit perspectives. The materials also cross-reference NCP research projects. To complement this work, the Métis Nation has developed a database system that provides descriptions of AES-NCP projects, information on health risk assessments conducted in the NWT, and NWT community profiles.

4) In cooperation with Northern Contaminants Program participants, the Métis Nation collaborated with Indian and Northern Affairs and produced an overview booklet that provides non-technical background information on contaminants in northern Canada. The booklet is entitled "Contaminants in Northern Canada" and is available from the Métis Nation.

CONTAMINANT MONITORING AND COOPERATIVE RISK MANAGEMENT IN THE NORTHWEST TERRITORIES

Project Leaders: J.E.B. Walker and J. MacKinnon, Department of Health and Social Services, Government of the Northwest Territories (GNWT).

Project Team: M. Rohlmann, GNWT Health and Social Services, Regional Environmental Health Officers (R. Kielly, Keewatin; F. Hamilton, Mackenzie; R. Phillips, Kitikmeot; D. Paradis, Baffin; B. Wrathall, Inuvik), Regional Contaminants Coordinator (L. Seddon), Dept. Renewable Resources (B. Elkin, S. Matthews), Dene Nation (C. Mills), Métis Nation-NWT (B. Carpenter), Regional Contaminants Consultation Working Groups, Keewatin, Baffin, Inuvik and Kitikmeot Regional Health Boards, Mackenzie Regional Health Service, NWT Technical Committee on Arctic Contaminants.

Collaborators: Technical Committee on Contaminants in Northern Ecosystems and Native Diets; Health Canada (A. Gilman, B. Wheatley).

OBJECTIVES

1. To continue to develop regional capacity for cooperative risk management through the development of appropriate communications 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;

3. To enhance regional and Territorial wide information exchange about contaminants by expanding existing communication networks and developing information and educational tools.

DESCRIPTION

Communication and education about contaminants with Northerners has been fundamental to the overall objective and result of the Arctic Environmental Strategy's Northern Contaminants Program: to reduce, and wherever possible, eliminate contaminants in tradtionally harvested foods resulting in "renewed confidence in 'country foods' as a safe diet." (AES-An Action Plan, 1993).

Since answers to questions that haven't been asked will usually fall short of their mark, the challenge in undertaking communication and education activities is to first establish a common ground for such information exchanges. Several workshops have been held in the Northwest Territories (NWT) for this reason, and also to serve as a departure for more detailed consultations about human contaminants baseline monitoring.

Additionally, there needs to be the capacity for people in the regions and in the communities to respond to local questions and concerns about environmental contaminants, particularly regional health agencies, local health workers, Renewable Resource Officers, and Bands, Métis Locals and Hamlet councils. To this end, these groups are being targeted to receive, and exchange information about, contaminants. This is being done through GNWT Health and Social Services, and the NWT Technical Committee on Arctic Contaminants.

ACTIVITIES/RESULTS 1994/95

Reports from workshops held in Iqaluit (1991), Hay River (1992), Fort Simpson (1993), Taloyoak (1993), Lac La Martre (1994), Rankin Inlet (1994), and Iqaluit (1994) have indicated the following needs:

For Education

NWT Northerners want more information on local contaminants and more discussion of research projects and their results.

For Communications

NWT Northerners want more translation and interpretation of scientific information about contaminants (plain language), and more audio/visual materials (radio, video, TV).

For Community Action
NWT residents want community control over research, community involvement in human health baseline monitoring, and information on local initiatives.

For Follow-up Workshops
NWT residents want more opportunities for community networking on contaminants issues, and more involvement of various community groups/individuals in contaminants discussions.

Some of these recommendations have been incorporated into NWT contaminants-related activities, such as the formation of Regional Contaminants Consultation Working Groups to guide the development and implementation of baseline contaminants monitoring in the NWT, and the translation of the video "Environmental Contaminants in the North" into Inuktitut. Other recommendations, such as the development of a plain language glossary for contaminants terminology, have yet to be addressed.

In 1994/95, the following communication tools were developed and distributed:

- Inuktitut version of the video "Environmental Contaminants in the North" produced and distributed to all Health Centres in the Kitikmeot, Keewatin, Inuvik and Baffin Health Regions, and to Renewable Resource Officers in these Regions. The English version of this video had previously been distributed to all Health Centres and Renewable Resource Officers in the NWT.

- Contaminants workshops summary and map: highlights of issues raised at regional workshops and briefly summarized above.

- Health Risk Assessment summary and map: a regional summary of health risk assessments based on contaminant group.

- Arctic Environmental Strategy (AES) research map: a preliminary mapping of some of the AES contaminants research underway in the NWT, which was done in collaboration with the Métis Nation-NWT.

- Draft Information package for Health Workers: distributed and reviewed by selected Northern Contaminants Program Technical Committee members, and then distributed to Health Regions.

Additionally, the GNWT Department of Health and Social Services hosted a workshop entitled "Mercury—A Health Concern in the NWT?" with funds provided by Medical Services Branch of Health Canada. This workshop was attended by Regional Contaminants consultation Working Groups (Mackenzie and Kitikmeot Regions), Regional Environmental Health Officers, as well as representatives from the GNWT (Renewable Resources, Science Institute), Aboriginal organizations (Dene Nation, Métis Nation-NWT, Dogrib Tribal Council, Inuvialuit Joint Secretariat, Kitikmeot Inuit Association), and the federal government (Indian and Northern Affairs Canada, Fisheries and Oceans Canada, Environment Canada and Health Canada). The Workshop Proceedings provide a summary of the workshop, as well as a regional summary of existing mercury data for each health region in the NWT.

The NWT Technical Committee on Arctic Contaminants produced a Discussion Paper for NWT Environmental Contaminants Research Priorities to assist with the ongoing development of activities in this area. This paper was distributed in February 1995, and will be reviewed and revised periodically.

DISCUSSION

Activities in 1994/95 continued to develop information exchange networks and produce and distribute communication tools. In 1995/96, it is anticipated that this work will focus more specifically on the expansion of cooperative risk management strategies to provide balanced, timely information about benefits and potential risks associated with contaminants in traditional foods to NWT Northerners.

Expected project completion date: this phase will continue until 31 March 1997; communications about research results, and health hazard assessments will likely continue well beyond that time.

CONTAMINANTS CURRICULUM PHASE III - A PROGRAM OF INTEGRATED CURRICULUM DEVELOPMENT FOR NORTHERN EDUCATION/COMMUNICATION

Project Leader: W. Carpenter, Environmental Director, Métis Nation–NWT

Project Team: J. Farrow, Project Coordinator Contaminant Education, Métis Nation - NWT; P. Harmathy, Program Developer Contaminant Education, Métis Nation - NWT; J. Heron, Program Developer Trainee Contaminant Education, Métis Nation - NWT; A. Najduch, Science Coordinator, Curriculum Division, GNWT Education; M. Tolley, Curriculum Specialist, Arctic College

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 from industrial contaminants that are present in the Northern food chain.

DESCRIPTION

The Métis Nation Contaminant Education Program develops and integrates contaminant related program materials with existing NWT school curricula, and with adult education programs. The program materials are cross-referenced to the relevant curricula, and wherever possible to Dene Kede and Inuuqatigiit documents that explore the school curriculae from the Dene and Inuit perspectives, making sure wherever possible to reflect or validate the traditional point of view.

This education program will be distributed to more than 70 schools across the NWT, to Arctic College, Aurora College and to approximately 42 Community Learning Centres. It will also be made available to the Yukon and other Northern jurisdictions.

ACTIVITIES IN 1994/95

Steering Committee

The Métis Nation continues to maintain a client partnership arrangement for this project. Policy is formulated by a Steering Committee made up of, but not restricted to, the following agencies: Science Institute of the NWT, Canadian Polar Commission, Conservation Education Renewable Resources (GNWT), Environment and Renewable Resources (DIAND), Yellowknife Education District No. 1, Department of Education (GNWT), Arctic College, and the Department of Health (GNWT).

Database

The project database that was established during phase two was updated to include data from the Synopsis of Research Conducted under the 1993/94 Northern Contaminants Program (NCP). The search parameters were also expanded to include details of all NCP projects, community profile data and health risk assessments.

Table 1. Database Search Parameters

Author	Animal species
Title	Plant group
Journal	Plant species
Contaminant group	School Board
Contaminants	Community
Funding	Location (other than community)
NCP category	Ocean region
Ecosystem	Health Risk Assessment
Animal group	

The database capability allows cross-referencing of NCP information with: community profile data, school boards, schools, Arctic/Aurora College, Community Learning Centres and wildlife distribution information. This capability allows a better understanding of the target audience whether it is at a regional or community level. It also helps to see relationships between government administrative areas, land claim areas, linguistic groups, school boards, schools, colleges and community learning centres. The database is a powerful tool in the ongoing program development process. It is hoped that it can be made available to educators, online, via the "North of 60 Bulletin Board."

Lesson Plans

Lesson plans have been produced for the NWT school science curriculum for grades 7-9. These lesson plans have been cross referenced to NCP research. Lesson plan booklets are designed to fit a particular unit within the curriculum. In the booklet, teachers are introduced to the Arctic Environmental Strategy and the Northern Contaminants Program, then they are guided to the appropriate curriculum unit. An overall view of lesson plans and sequence are provided to aid teachers in scheduling and preparation.

Inservice Training for Teachers

In the NWT, responsibility for program development or implementation of curriculum requirements, is the responsibility of the regional school boards. With ten divisional school boards operating in the NWT, it is necessary to plan inservice training using a number of different strategies such as; regional workshops, contacts with individual schools, and contacts with individual teachers.

These regional contacts have been established with the full support and help of the Government of the Northwest Territories Department of Education. Inservice training with NWT teachers has taken place in: Rankin Inlet, with teachers from the Keewatin and Kitikmeot School Boards; Inuvik, with teachers from the Beaufort Delta School Board and Yellowknife, with teachers from Yellowknife Districts #1 and #2, Baffin Board and Sahtu Board.

Pilot Testing

Pilot testing of the lesson plans took place during the 1994/95 academic year in selected schools. In the NWT, teachers are allowed considerable flexibility with regard to the order in which units are taught. Because pilot testing had to coincide with the school teaching schedule, the timing varied from school to school.

Publication of Lesson Plans

Feedback from pilot testing was compiled before proceeding with editing and layout for the lesson plan booklets. Distribution will take place during the 1995/96 academic year.

Adult Education

A similar methodology to that employed for the school program was used to develop lesson plans for the Adult Basic Education science curriculum. Pilot testing will take place in the 1995/96 academic year.

NCP Overview Booklet, 'Contaminants in Northern Canada'

In cooperation with AES NCP partnership agencies, the Métis Nation took a lead role in the production of an overview booklet that provides background information on contaminants in Northern Canada.

RESULTS

To date the project has produced a database of NCP contaminant research, school reference materials, community profiles and Health Risk Assessments. Published lessons for grades 7–9 will be distributed in the 1995/96 academic year to schools and Regional Resource Centres in the Northwest Territories. Draft lesson plans for adult education will be distributed via curriculum specialists for Arctic and Aurora Colleges. The overview booklet entitled "Contaminants in Northern Canada," written in non technical language is available to AES partners, government agencies and the general public.

DISCUSSION/CONCLUSIONS

Positive response from the pilot testing and inservice training for the school program resulted in a request from GNWT education to continue the programming at the high school level. Generally reaction to the program has been very positive. As more results become available a way should be found to bring this updated information to the schools.

Expected Project Completion Date: The project is continuing into Phase IV which will see the development of Lesson plans for high school science grades 10 and 11. Pilot testing will be carried out on the adult education program.

Expected project completion date: March 1996.

Table 2. Lesson Plans Produced for Grades 7-9 And Links to the Northern Contaminants Program Categories And Contaminants.

NWT Curriculum Strand and Unit Group	#	Lesson Plan	NCP Category*	Contaminant
GRADE 7 STRAND: MATTER AND ENERGY				
Energy in Our Lives: Nuclear Energy	1	Introduction	EU	Radionuclides
	2	Radiation	EU, SPF	Radionuclides
	3	Radiation in Everyday Things	SPF	Radionuclides
	4	Contaminants	SPF	Radionuclides
	5	Caribou and Radionuclides	EU	Radionuclides
	6	The Nuclear Game	SPF, EU	Radionuclides
GRADE 7 STRAND: LIFE AND THE ENVIRONMENT				
Characteristics of Living Things:	1	Introduction - the Environment		
Environmental Concerns.	2	Local Environmental Problems	SPF, EU	Organochlorines Metals Hydrocarbons
	3	Contaminants	SPF	Organochlorines Radionuclides Metals Hydrocarbons
	4	The Food Chain	EU	Organochlorines
	5	Health Effects	HH	Organochlorines Radionuclides Metals Hydrocarbons
	6	What Can I Do?	EC, SPF	
GRADE 8: LIFE AND THE ENVIRONMENT				
Interactions in our Environment:	1	Introduction - Terrestrial Food Chain	EU	
Northern Food Chains and Webs	2	Marine Food Chain	EU	
	3	Freshwater Food Chain	EU	Organochlorines
	4	Contaminants	SPF	
	5	Bioaccumulation, Biomagnification	EU	Radionuclides
Interactions in our Environment:	1	Introduction		
Harvesting Renewable Resources,	2	Pulp Mills and Drainage Basins	EU, SPF	Organochlorines
Pulp and Paper	3	Contaminants	SPF	Organochlorines
	4	Organochlorines	EU	Organochlorines
	5	Are We Affected?	SPF	Organochlorines
	6	What can we do?	EC	
GRADE 8: EARTH, SPACE AND TIME				
Movements in the Earth's Crust:	1	Introduction	SPF	
Environmental Concerns, Mining	2	Ancient History		
	3	Recent History		
	4	Introduction to Mining	SPF, EU	Metals
	5	The Gold Game		
	6	Contaminants	SPF, EU	Metals
	7	Mercury	SPF, EU, HH	Metals
	8	Lead, Cadmium and Arsenic	SPF, EU, HH	Metals
Movements in the Earth's Crust:	1	Introduction	SPF	Hydrocarbons
Environmental Concerns, Fossil Fuels	2	Where in the NWT?		
	3	History of Oil and Gas in NWT		
	4	Contaminants	SPF, EU, HH	Hydrocarbons
	5	How are we affected?	SPF	Hydrocarbons
	6	Contaminant Sources, Pathways and Fate	SPF	Hydrocarbons
	7	Mini Oil Spill	EU	Hydrocarbons

NWT Curriculum Strand and Unit Group	#	Lesson Plan	NCP Category*	Contaminant
GRADE 9 STRAND: LIFE AND THE ENVIRONMENT				
Diversity of Living Things: Careers	1	Introduction to scientists working in the North	EU, HH	Organochlorines
	2	Science Career Biographies	EU, HH	Organochlorines Metals Radionuclides
Diversity of Living Things: Information, Knowledge, Processes	1	How scientists record information	SPF, EU	Organochlorines Metals
	2	Marine Mammals	EU	Organochlorines Metals
	3	Freshwater Biota	EU	Organochlorines Metals
	4	Birds	EU	Organochlorines
Diversity of Living things: Dissections	1	Respect for Living Things		
	2	Traditional Use	HH	
	3	Body Systems and Organs		Depends on animal being studied.
GRADE 9 STRAND: MATTER AND ENERGY				
Chemical Nature of our Environment: Science and Technology related to Daily Lives	1	Person made industrial compounds	EU	Organochlorines
Solutions and Substances	2	Water soluble, Fat soluble		
Chemical Changes	3	DDT and Toxaphene	EU	Organochlorines

* NCP categories
SPF Sources, Pathways and Fate
EU Ecosystem Contaminant Uptake and Effects
HH Human Health

INFORMATION AND EDUCATION ON CONTAMINANTS IN THE YUKON

Project Leader: Yukon Technical Committee on Contaminants in Northern Ecosystems and Native Diets (Contact: Mark Palmer, Chair)

Project Team: Yukon College, Environment Canada, Council for Yukon Indians, Health Canada, Indian and Northern Affairs Canada, Yukon Territorial Government Renewable Resources

OBJECTIVES

Short-term

1. 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 Northern Contaminants Program. It is critical that decision-makers, those involved in communications, and the general public become better informed about contaminants and issues surrounding contaminants.

Currently, it is 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 informed choices, two initiatives were started. The first, which was completed in 1993, introduced information on contaminants into Yukon College. The 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 1994/95

The Contaminants library which was established at Yukon College in 1992 was expanded in 1993/94 on a opportunistic basis. No additional funds from the AES are being used for this purpose.

A local contractor was hired to complete fact sheets on dioxins/furans and long-range transport of airborne pollutants. Dioxins/furans are of concern due to the use of Tordon 101, a defoliant used on the Haines/Fairbanks pipeline, which includes these two chemicals as active ingredients.

RESULTS/DISCUSSION/CONCLUSIONS

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 in January 1995.

An example of a typical fact sheet appears on the following pages.

Expected Completion Date: March 31, 1997

FACT SHEET

CONTAMINANTS IN THE YUKON

DDT

Dichlorodiphenyltrichlorethane

WHAT IS DDT?

DDT is a pesticide made up of carbon and chlorine. It was developed in the late 1930s, and used world-wide as a pesticide from the 1940s to the 1970s. DDT was proven to be very effective against many insects, with the notable exceptions of grasshoppers and aphids. Unfortunately, the low cost and the effectiveness of DDT as a pesticide, contributed to its overuse and its subsequent reputation as a global contaminant.

HOW AND WHEN WAS DDT USED?

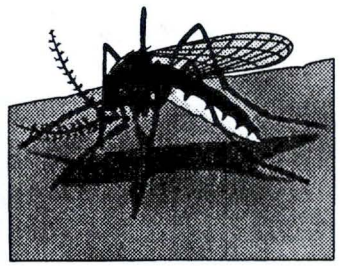
DDT became widely used during World War II to suppress mosquitoes, blackflies, lice and fleas. It quickly became the most popular chemical control for agricultural, forestry, and domestic insect pests. DDT was most commonly used as a liquid spray. Large tracts of forest land, particularly along the Atlantic coast of North America, were sprayed from the air to destroy insect pests during the 1950s and 1960s. Aerial spraying of agricultural crops, especially cotton, was also carried out. DDT was the most widely used pesticide in mosquito and blackfly control programs during this same period. This was accomplished by the systematic aerial and ground spraying of populated areas.

The use of DDT reached its peak in North America during the early 1960s. Increasing concerns over the damaging effects of DDT on the environment led to its banning or restriction as a pesticide in Canada, the United States and most European countries in the early 1970s. The manufacture of DDT continues, however, and is still widely used as a pesticide in developing countries, especially for the control of Malaria.

The primary use of DDT in the Yukon was to suppress mosquitoes in and around the more populated communities. In 1949, the Royal Canadian Air Force (RCAF) began aerial spraying of DDT at their stations near Watson Lake and Whitehorse areas until 1963. Two aerial applications were usually carried out each year. Only the land areas around these communities were sprayed by the RCAF, although wind drift and surface runoff carried DDT into rivers and lakes. Some ground fogging with DDT was also carried out during these years.

In 1964 the Department of Public Works (DPW) assumed responsibility for mosquito control in the Yukon. The DPW, along with the Yukon Forest Service and the City of Whitehorse, continued with the aerial and ground spraying of DDT in the Whitehorse area until 1969. Other Yukon communities that were sprayed with DDT during these years were Watson Lake, Teslin, Carcross, Haines Junction, Beaver Creek, Carmacks, Mayo, Dawson City, Elsa, Keno City, Calumet, Faro and Clinton Creek. Highway maintenance, construction and exploration camps also used DDT to control mosquitoes. As well as aerial spraying and ground fogging, gelatin covered capsules containing DDT were used to control mosquito larvae in stagnant ponds and ditches. DDT was available in drug and hardware stores for household and garden use.

As elsewhere in North America during the late 1960s, growing concern in the Yukon over the harmful effects of DDT on both wildlife and human health led to its gradual replacement as a pesticide. As less toxic and less persistent pesticides were developed, the use of DDT was phased out and was discontinued in 1969. The sale and use of DDT as an insecticide is no longer permitted in Canada.



WHY IS DDT SO HAZARDOUS TO THE ENVIRONMENT?

Because of its extensive use, DDT is the pesticide most frequently found in soils in agricultural areas. Due to its low solubility in water, DDT leaches slowly and may persist in the soils for many years. Most pesticides used today are broken down quickly by digestion in animals, or by bacteria, heat and/or ultraviolet light. DDT, unlike new pesticides, is very stable and may persist in the environment for a long time. This stability made it attractive as an insecticide as fewer applications were needed. DDT is easily dissolved in fat and is stored in the fatty tissues of animals. Since DDT is broken down only slowly by digestion, it accumulates much faster than it is eliminated in the fatty tissues of animals. As a result the level of DDT in the animal's fat would increase over the period of time it is exposed to it. This process is known as bioaccumulation.

Another process, known as biomagnification, results in the highest levels of DDT being found in animals at the top of the food web. This occurs when predators eat prey containing DDT. The concentration of DDT becomes greater in the predator than in the prey. If this predator is in turn eaten by another predator higher in the food web, the higher predator will accumulate even greater DDT concentrations in its fatty tissues.

Predators such as owls, hawks, gulls, polar bears, and seals have been found to have high levels of DDT in their fat tissues. Humans may also be affected by the processes of bioaccumulation and biomagnification of DDT. People most vulnerable are those whose diets are rich in the fats of animals exposed to DDT. Humans have also accumulated high DDT levels in their body tissues by drinking milk from dairy cows raised on DDT-treated hay.

WHAT ARE THE HEALTH EFFECTS OF DDT?

There is still much to be learned about the effects of DDT on the health of wildlife and humans. Experiments with laboratory animals have shown that the chemical may cause liver enlargement, and may have adverse effects on the immune system, the nervous system and the reproductive system. The link between DDT and cancer even in lab animals is still inconclusive.

Although DDT is relatively stable, it does break down to form metabolites. DDE is a break-down product and is produced in most animals when the body attempts to rid itself of DDT. DDE is the most fat-soluble of the DDT metabolites and consequently is routinely measured when determining DDT contamination in the fat of animals or eggs. Although DDE is less toxic than DDT, it is more persistent.

The decline in some populations of predatory birds, such as hawks and falcons, is believed to be the direct result of DDT exposure and its metabolites. The reproductive rate of these birds may be greatly reduced because DDT interferes with the calcification or hardening of eggshells. The thin-shelled eggs are easily broken during incubation and few birds hatch. Also deformities in birds (crossed bills, jaw defects and malformed feet and joints) are thought to be linked to DDT and its metabolites.

The effect of DDT on human health is less understood than that of the much studied predatory birds. DDE is the residue normally stored in human fat tissues. High levels of DDE have also been found in mother's milk.

IS DDT A PROBLEM IN THE YUKON TODAY?

Although the use of DDT was discontinued in the Yukon in 1969, it is still found, especially in fish samples from lakes throughout the Yukon. The northern climate is believed to contribute to the persistence of DDT.

DDT can be transported thousands of kilometres by air currents and deposited with dust, rain, or snow. This is known as long range atmospheric transport. DDT is a global contaminant.

Because DDT has been an environmental concern since the 1960's, there is reasonably good information on DDT levels in the global environment. DDT levels in water and animals on a world-wide basis is declining. DDT levels in the Great Lakes has dramatically declined since the pesticide was banned.

Low levels of DDT in fish in the Yukon are from long range transport. However, fish in two lakes have higher DDT from historic local use. No levels of DDT found in Yukon fish pose a health hazard to consumers.

Research into the way DDT behaves in the Yukon's environment is currently being carried out through the Arctic Environmental Strategy. Lake sediment, water, snow, and air, as well as samples of fish, algae and microorganisms are all being analyzed for DDT and other organochlorines.

Prepared by the Yukon Contaminants Committee and funded through the Arctic Environmental Strategy.
For more information on this and other fact sheets, contact the Chairperson of the Yukon Contaminants Committee, Mr. Mark Palmer at (403) 667-3272.

A STUDY INTO THE SOCIAL, CULTURAL, AND DISCIPLINARY UNDERSTANDING OF RISK PERCEPTIONS AND RISK ACCEPTABILITY OF CONTAMINANTS IN THE CANADIAN ARCTIC

Project Leaders: J. O'Neil, Northern Health Research Unit, Department of Community Health Sciences, University of Manitoba

Project Team: B. Elias, Research Associate, Northern Health Research Unit, Department of Community Health Sciences, University of Manitoba

OBJECTIVES

1. To investigate the various disciplinary paradigms through which environmental risk is defined in the context of the AES.

2. To investigate the relationship between disciplinary approaches to the definition of risk, and communication styles in disseminating risk information to Northern Communities.

3. To provide general guidelines for integrating discipline based approaches to defining and communicating risk assessments with the cultural frameworks of Aboriginal people in Northern Canada.

DESCRIPTION

The report is a sociological examination of environmental discourse in the Canadian Arctic. Documents, interviews, observational notes, and video transcripts of environmental discourse provide the research material for this study. Our analysis is guided by the conceptual framework introduced into social science by Michel Foucault in the last few decades (1960s to 1985).

Foucault asked us to consider the "sciences" as little more than conversations among practitioners where a common story or narrative is constructed over time to define the subject of study. He asked us to consider the "effects" of this discourse on the subjects themselves, and inquire instead into how scientific discourses either illuminate or conceal the "reality" of the subject through the conventions of scientific practice. He asked us to examine scientific discourse in relation to the institutions and social environments through which it operates, and to reflect critically on the "apparatus" of science, that is, the technologies, methodologies, communication strategies, etc. through which science is practised.

Foucault further asked us to consider these scientific discourses as one of the mediums through which power operates in society (1980). Foucault argued that in the global society, power does not operate through brute force or political repression, but rather through the systems of "knowledge" about how the world works. He coined the phrase "power/knowledge" to characterize his appreciation of how knowledge acts to control members of a society by defining what is normal and expected (1979). He further noted that science operates as a system of surveillance, through its practical operations of collecting information about aspects of the world, to ensure that social systems are regulated according to the dominant values of prevailing scientific understandings (1979). Foucault, in addition, contended that scientific discourse is generally rooted in the dominant value systems of ruling interests in a society, since science and state interests are generally interdependent.

We have found these ideas to be particularly useful in examining the problem of risk communication related to contaminants in the Canadian Arctic. Too often, risk communication is viewed as a social-psychological problem, due simply to the "personality" differences, education, language differences, etc. of the scientist and members of the public. The common assumption for scientists is that "if only we could learn to explain ourselves clearly and simply, the problem would be solved." We regard this approach as not only severely limited in providing insight into the issue, but as in fact yet another attempt by science and government to extend their discursive influence over power/knowledge systems in the North.

ACTIVITIES IN 1994/95

We first initiated a review of the literature to help establish the context of the Arctic Environmental Strategy (AES) in terms of the various claims of environmental sovereignty perpetuated by various bodies over the Arctic. Various domains of risk assessments, management and communications were explored to understand the boundary work that occurs in science and which is also

reflected in communications made by scientists. Four workshops were then observed to understand this further. The first, attended by both investigators, was the Arctic Environmental Strategy Scientific Results Workshop (January '95) at the Institute of Ocean Sciences in Sidney, British Columbia, where scientists active in the Northern Contaminants Program presented results of their research to their peers. Observational notes were taken in order to understand communications between scientific disciplines. The second workshop, attended by Brenda Elias, was the Yukon Contaminants Committee Workshop held in Whitehorse in late January 1995. The workshop provided a forum for AES scientists to present contaminant results to community members. Observational notes and verbatim comments were recorded on the interaction between scientists and community members. Also observed were the scoping workshops of the multi-disciplinary Eco-research team that has been funded to study contaminants in the eastern Arctic. These workshops, video taped by John O'Neil, were held in Kuujjuak, Quebec and Nain, Labrador in February 1995 to negotiate research access for the Eco-research team of which we are a part. Another relevant meeting, attended by Brenda Elias, was the International Circumpolar Health Workshop on Research Ethics in Inuvik, Northwest Territories (June '95). In addition to these observational activities, four AES scientists were interviewed by phone using a semi-structured interview.

DISCUSSION/CONCLUSION

Scientific Discourse on Risk

Scientists, regardless of their discipline, produce divergent "risk" narratives which are a specific way of understanding and a form of writing (such as publications produced for journals) about risk. The incoherence generated by diverging interpretations is further illustrated in the following comment made by a scientist in response to a question concerning the inevitability of conflicting messages in science and with research into contaminants:

> *There doesn't seem to be much consistency on spatial and temporal trends. In other words, are they increasing or are they decreasing? As of yet, we don't understand these trends. The various research areas of the AES are so broad...It's hard to say. There is agreement that the levels of contaminants are there and are a concern. But there is a lack of agreement on whether they are increasing or decreasing. There is general agreement that more work is needed. But to date "contaminant movement" research has been successful.*

This presupposition of a social grounding of risk in a shared past, however, identifies a major problem for our analysis. Scientists, government officials, and community members all belong to a multitude of communities or cultures, and their actions are situated in a variety of risk-narrative contexts, which partly overlap. The difficulty in achieving social grounding of risk, with a resultant blurring of boundaries, was reflected upon by one scientist:

> *It depends on the level of complexity. The transfer of knowledge is easy regarding animals. But when it comes of chemistry issues, it is difficult. What we are seeing in the AES is the blending of Chemistry and Biology...the blending of chemists and biologists. At our scientific meetings, there is an interesting discussion going on between the chemists and the biologists, and you can see this blending actually occurring.*

Indeed, attempts to construct a common risk narrative are enhanced in a contested field of competing risk narratives and where more global claims to environmental sovereignty, security and surveillance are at stake. At the Yukon Contaminant Committee Workshop in January, 1995, we had the opportunity to observe this boundary work during a presentation explaining why certain chemical signatures appeared in sediment at specific periods of time. An indigenous participant of this workshop responded to the presentation and to the dialogue that followed. She stated:

> *Looking at all this information...it is wide ranging and it is from a Western science perspective and if our own knowledge was included, there would be less of a mystery and more understanding to your findings.*

It is therefore important to recognize that there is an ongoing struggle to check contrary scientific interpretations with a community's story of risk. But can this struggle form a "shared concern to construct, enforce, and conform to a common narrative which gives a common sense to everyone's endeavours" (Rouse 1989). One scientist responded with this observation regarding a common narrative:

> *The Arctic Environmental Strategy Program is now moving into the social aspect. To make it whole, we have to look at the whole picture. For example, the World Health Organization's definition of health. But something is disturbing me. The physical, biological, and the social sciences as one picture can be constructed. But the pieces are missing.*

All communities or cultural spheres participating in understanding and communicating risks must not only reflect on their own positions. They need to reflect on the positions presented by others, attempt to understand them within the localized context, and relate them to the ongoing reflective activity within their own disciplinary domains. This has been a struggle for many scientists as indicated in the following comment of an AES scientist concerning whether any amount of contaminant would

be a significant human health risk from a Northerner's perspective:

> *The first hurdle is to define things. Their language does not describe what we are looking at. There aren't words for the chemicals and the biological processes. There isn't a word for contaminants. I have heard so many different definitions...like it's a disease in Inuktitut. We are also faced with perception problems. For example, caribou kidney or...burbot livers. We know there are contaminants in the livers but not in the flesh. We understand the biological process and we know these contaminants are not in the flesh. To scientists, this makes sense. But to the average person, it doesn't. It's not just avoiding the liver but it's avoiding the animal but not just the animal but the lake as well. It's both a communication and a perception problem.*

But can the cultural rationality of risk be brought into the risk analysis project?

Traditional Ecological Knowledge

Even the idea of knowledge is understood differently by Indigenous people, and can have many levels or layers. The following summation distinguishing the meaning of knowledge by a Dene woman of the Mackenzie Valley (Denedeh) illustrates the distinctiveness of her knowledge and how it is understood through the Dene language (Nahanni 1992):

> *The term "knowledge" cannot be directly translated in my Dene language, which is slavey, one of the five Athapaskan languages spoken in Denedeh. One can have a general knowledge of this or that..."mo tse dih zho". But, "knowledge" that goes deeper than general knowledge translates into "knowing yourself" or "self-knowing" or "eh tse deh zháh". If you are aware, "ká gu zhon", then it is possible for you to know yourself.*

This reflection on how knowledge is understood demonstrates that even the term "traditional ecological knowledge" can have several different meanings.

Management boards or contaminant workshops provide forums where both collaboration and resistance must occur to check relations of power/knowledge. The following observations substantiate this claim. At the Yukon Contaminant Committee Workshop, an Elder who attentively observed several presentations throughout the morning session later commented that something was missing:

> *They minimized the effect of headwaters. Atlin flows up to Lake Laberge. We have to look at everything. We have to work together. Boundaries, whether they are between the province of British Columbia and the Yukon or between scientists and us, get in the way!*

By equating the development of a unified theory through collaborative knowledge transfer, this Elder had indicated that he was willing to forge a closer relationship with another way of knowing. Although expressing the desire to work collaboratively with scientists, this Elder continued to resist the domination of science by expressing what Foucault has called "subjugated knowledge" or "blocs of historical knowledge of struggles" (Foucault 1980). Also at issue in this comment was how science transforms the environment to suit research objectives.

But from a traditional ecological knowledge perspective, this micro-world approach to risk is troublesome, as explained by one Elder at this Workshop:

> *You people go to school. You should know as a result. But when you come up here, we find that you don't. But you went to school. But what of us? We know things. But no one asks us! We know how the rivers work. We know where the dumps are. But scientists come up here and they look at what they want to look at. But they look at [gestures with his fingers] just a little bit of the fish. What about the other fish. No one talks about all of the environment.*

Rather than have knowledge decontextualized in such a way, it was suggested that it needs to be contextualized into a framework that collaboratively includes traditional ecological knowledge. This observation is consistent with comments made by indigenous people at an Eco-research workshop held in Kuujjuaq in the Eastern Arctic.

At one point of the workshop, an Inuit hunter inquired in Inuktitut on whether scientists would be looking into parasites, bacteria or disease in animals. It was determined that the word "contaminant" was not distinguished from these other "problems" when translated into Inuktitut, which complicated this dialogue on risk research. In response to this problem, one scientist attempted to explain what is a contaminant:

> *The contaminants we are speaking about today are [the following]. You can't see them. You can't smell them. You can't detect them by your own ways...Contaminants like mercury [and] PCBs are detected by a very sophisticated machine. Chemicals are very hard to detect.*

This explanation, though not intended to be condescending, minimized the value that traditional ecological knowledge can play in understanding changes in the environment. But the Inuit hunters were not satisfied with this type of investigation and expressed concern as to whether scientists would study issues that were important to them such as the impacts of mining. They also expressed a great concern with the state of the health of the caribou in terms of both parasites and contaminants.

The researcher studying fish parasites responded to this inquiry by closely identifying with the observations of the Inuit hunters. She expressed a willingness to support a proposal for a further project that would study caribou physiology. This support implied an expansion of her own expertise beyond her disciplinary speciality of fish physiology. Other researchers, however, indicated that there has been much research done on caribou and the information generated by those studies could be made available to the hunters. An Inuit coordinator of the Eco-research project intervened because she thought that the question of the Inuit hunter had not been fully addressed. She asked:

> *Does this mean that your research on fish will be a good indicator of the state of the health of other animals or will you set up further research on other animals?*

This question was an attempt to determine whether results of the fish parasite study could be used to extrapolate risk to other animals. By implication, the advocate was also asking whether the research would extend the very possibility of disciplinarity by generating new stories on other animals. The researcher clarified by stating that:

> *...we will not be able with the research of our team to speak on the health of other animals. But I think that the physiology will be applicable to other animals.*

Another scientist intervened to determine what the concern was or whether there was a communication problem. The Inuit hunter responded in English:

> *We are not getting enough feedback from the researchers on the fish or the caribou other than [feedback] on the caribou liver and the kidney.*

The Inuit advocate intervened to clarify this observation and to maintain the position of the hunter by contesting the boundaries of science. She adamantly explained:

> *Why this keeps coming up is that they are being told not to eat the liver and the kidney...They say they can tell from visual observations of these organs. They ask "why is the liver blue?" They want an answer for that. I know that the Chernobyl fall out and all the radioactivity...you answered all this...that it effects these organs of the caribou. But they want to know why its blue and why they can't eat it? What's the contaminants in it? This is very much needed! I know the scientists and those who are well educated know about all of this. But we don't. We don't know why the liver is blue.*

She further added:

> *One of our major diets other than fish is caribou. What you get on your microscope slide...at the University...of the kidney or liver of caribou is not blue. But every caribou that you open up has a blue liver. That's not normal. It's not!*

A scientist responded by stating that he was sure information could be provided by the hunters on the state of the liver from which the sample had been taken. The Inuit advocate responded by stating that:

> *That's what [he] is saying; that instead of taking a little sliver and taking it to...[the] City they want the researchers to see that blue liver.*

The scientists, in response to this initially expressed resistance, finally conceded and agreed that through both Inuit knowledge and Western science a collaborative project could be initiated through some additional funding arrangements. But what are the prospects for effective risk assessments employing Western and traditional ecological knowledge?

Prospects for Effective Risk Assessments

Habermas has suggested that interaction between two or more participants who seek to reach an understanding about their situation and their plans of action can occur in an ideal speech act or "medium of unhindered understanding" that gives them unequivocal freedom to coordinate their actions by way of agreement (White 1988). He referred to this type of action as "communicative action" (Outhwaite 1994). According to Webler and his colleagues (1992), this is extremely important in that:

> *lay people must become engaged in the substantive parts of the discourse as equals with the risk professionals. This will bring the cultural rationality into the risk analysis project, expanding the knowledge base—though at a cost to risk professionals, who must surrender their claim that only scientific knowledge is valid knowledge. This does not mean that scientific knowledge should be subjugated to the emotions of the lay public. Rather, what is needed is a discourse structure that draws out the strengths of both forms of rationality while attenuating their weaknesses.*

However, it has been suggested that a "communicative synthesis" is not all that viable. In the words of Throgmorton (1991):

> *I can see more clearly how the tensions and ambiguities associated with the various analytical roles are deeply intertwined with the tensions and ambiguities of modernism and the Enlightenment. 'Communicative synthesis' now strikes me as a modernist solution to the quandaries of modern life, for to 'synthesize' is to seek a 'central plateau' (a place from which one can look but not be seen) from which an analytical team can perfectly and legitimately represent the voices of three quite diverse communities.*

So what is possible? Throgmorton (1991) suggests that, as scientists or policy analysts, we should open ourselves up to the possibility of being "persuaded by

people speaking in their 'native tongues' rather than the dominant discourse of politics and science." Similarily, Rappaport (1988) supports a post-modern form of risk analysis that takes into account various local perceptions of risk as well as disciplinary perceptions. We agree that this position can be more rewarding and even realistic since it's something we do everyday. On a more cautionary note, this approach involves being open to other perspectives, even if those perceptions contest the boundary of science to which you lay claim. The following experience of one AES scientist at the Yukon Contaminant Committee workshop illustrates the problem of being open to local knowledge:

> *Comparing last year to this year, we have a holistic approach. But they have more local concerns. That is, some people want to know about the water. Can they drink the water? Is it any good? Well, I don't know anything about those kind of things. I study birds. They expect us to know these things. They don't discriminate between the scientific and the government hierarchies. It just gets too focused and localized. You know...a) I don't know anything about it, and b) there isn't anything I can do about it. It's not my area.*

Overall, it is evident that there is much work that still needs to be done. Scientists still hold out the possibility of a unified scientific view of the world. Some feel they have already achieved it while others think it is a continuous possibility. Scientists also have different perspectives on the universality and the localization of knowledge: Most scientists consider community knowledge as narrowly focused. Other scientists regard local knowledge as important to providing a global or holistic context for integrating the particular site knowledge of different scientific disciplines. These differences are evident in comments made by two AES scientists:

> ***Scientist A:*** *Ecological information is important. They have a lot to contribute in terms of changes in organisms...that is...the perception of change over time. They would have invaluable information. A lot of scientists have not brought this ecological side together with the contaminant side and that's what's needed.*

> ***Scientist B:*** *We need to ask them what is important to them. What is harvestable? What do they use for medicinal purposes? Local people know where the herds are. They know the habits of the animals. They are better at that than we will ever become. They are closer to the environment. We should focus in on what impacts them.*

From these comments, it is evident that new forms of environmental understanding can be achieved through innovative approaches to collaboration in knowledge construction. But there are several issues that must be considered.

Scientific communication in the North is rooted in the traditions and expectations of sovereignty, security and surveillance. Local resistance to scientific communication reveals that colonialism and decolonization are still evident in the discourse of risk in the Arctic. Whether scientific communication proceeds as an act of collaboration or is confronted with resistance will depend largely on how issues of sovereignty, as they pertain to local autonomy, scientific hegemony, or geopolitical interests, are engaged by the various parties to the discourse. Scientists should understand that their work occurs in the context of resistance to colonization. They should also be aware that resistance also structures the possibilities for collaboration. Seemingly external issues, such as self-government and land claims, may threaten the domain of science. But these issues must be respected and accommodated through boundary work.

The question, still remains: Is transcultural transmission of contaminant knowledge possible? Can these distinct knowledge domains overlap and form a discourse (power/knowledge) where contaminant information can be exchanged among various spheres of environmental sovereignty. Our conclusion is that this communication will occur at the margins, or the boundaries between systems of knowledge. It is in these margins where the discourse lacks consistency, is more fractured, and open to transformation. For scientists willing to explore these boundary regions and for northern communities similarly inclined, the possibility exists for real collaboration in risk assessment, management and communication.

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TECHNICAL SUPPORT FOR THE YUKON CONTAMINANTS PROGRAM TOWARDS EFFECTIVE COMMUNICATION OF THE ARCTIC ENVIRONMENTAL STRATEGY PROGRAM AND RESULTS

Project Leader: Yukon Technical Committee on Contaminants in Northern Ecosystems and Native Diets (Contact: Mark Palmer, Chair)

Project Team: Yukon College, Environment Canada, Council for Yukon Indians, Health Canada, Indian and Northern Affairs Canada, Yukon Territorial Government Renewable Resources, Yukon Territorial Government Health

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 publics, 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 retain technical experts on an as-required basis to assist the Yukon Contaminants Committee (YCC) in presenting the contaminants program to the public.

DESCRIPTION

The first years of the program have produced a significant amount of scientific information. It is necessary to address the issue of effective communication as well as to ensure that northern communities are active participants in developing action plans. This need for greater attention to effective communication was raised both during the program audit and the priorities workshop.

The YCC was established to facilitate regional and local involvement in the contaminant 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 obtain 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, a response to the desire of local communities to participate in communications with their members is critical.

ACTIVITIES 1994/95

In January 1995, the YCC held its second annual Contaminants Workshop. Representatives from all Yukon First Nations, as well as approximately 80 individuals from the general public attended the two-day workshop. The goals of the workshop were to provide an overview of the work carried out in the Yukon, and to provide basic information on the chemical and physical properties of contaminants (primarily organochlorines and metals) and the potential impacts they have on the environment, including human health. The workshop also provided the opportunity for scientists to mingle with the participants, and for Yukoners to assist in the design of future monitoring programs.

The YCC (as recommended at the 1993 contaminants workshop) hired a First Nations Liaison Coordinator to correspond with the communities. Gerald Isaac, a member of the Dawson First Nation was selected as the Liaison Coordinator for both his communication skills and environmental expertise. Mr. Isaac spent a large portion of his time speaking directly with concerned groups and individuals in the communities. It was the role of the coordinator to answer questions on environmental issues as well as bring feedback to the YCC. This feedback was used when planning future monitoring activities.

RESULTS/DISCUSSION/CONCLUSION

Proceedings from the contaminants workshop will be available in winter 1995. Once again the information gained during the working groups assisted the YCC in developing the 1995/96 workplans. Future plans include regional workshops in the seven linguistic First Nation regions of the Yukon. The workshops took place between October, 1995 and January, 1996.

Although the Liaison Coordinator was a valuable tool for communicating information and receiving feedback from the public, a lack of resources forced the cancellation of the initiative.
The information gathered by the Liaison Coordinator will be valuable for years to come.

Expected project completion date: March 31, 1997.

NORTHERN AQUATIC FOOD CHAIN CONTAMINATION DATABASE (NAFCC DATABASE)

Project Leader: H. Careau, Groupe Conseil Genivar Inc., Division Environnement Shooner

Project Team: H. Careau, É. Dewailly, Public Health Centre, Québec region

OBJECTIVES

1. To update a computerized database on contamination levels in northern aquatic food chains (including humans).

2. To make this research tool available to all the participants of the Northern Contaminants Program and other interested parties.

DESCRIPTION

Since the beginning of the last decade, research activities on levels and trends of contamination of ecosystems of the northern regions of Canada have considerably increased. This is mostly due to the Arctic Environmental Strategy Program (AES) initiated by the Canadian Government, and also because of the interest in supporting the way of life of northern native communities. All this interest has and continues to generate 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 attributes. In fact, it is meant to allow rapid access to contamination summary data covering the Canadian Arctic, Northern Québec and Greenland, through searching by restrictive parameters when needed. Since it covers published and unpublished summary data, it is expected to be as complete as possible. Summary data included in this database are associated with both freshwater and marine environments, including humans as part of the aquatic food chain.

ACTIVITIES IN 1994/95

The main activity for this period consisted of gathering additional information and updating the database. From 18 361 records at the end of March 1994, the count as of April 1995 was 30 106. Each record corresponds to one mean value of contaminant concentration. This includes about 200 new human data from a survey from the Nunavik region.

The Northern Aquatic Food Chain Contamination (NAFCC) database was distributed on request. This allowed researchers from Canada, the US and Europe access to arctic contaminant data. A copy of the latest version of the NAFCC database was installed within the Indian and Northern Affairs office in Ottawa. Currently the database is only accessible with MacIntosh computers; however, with new developments in computer technologies, the accessibility of this database in a PC environment could be possible within the next year.

DISCUSSION/CONCLUSIONS

Since the NAFCC database is a collection of the data generated by the Northern Contaminants Program, it can assist in the upcoming Canadian Arctic Contaminants Assessment Report of the program. This project has helped demonstrate that there is a need for a centralized contaminant data storage facility in order to better assess the health status of the environment.

Expected project completion date: On-going update if funding is available.

Partners: Hydro-Québec, Health Department of Government of Northwest Territories, Health Canada

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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, CWS/NWRC

OBJECTIVES

1994/95:

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. Technical assistants are required to efficiently resolve the space usage needs;

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 principle contact of the network and develop mechanisms to steer overall policies.

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 a specimen bank which consists of a network of facilities which house important collections of arctic biota;

3. To develop policies and procedures which will allow legitimate research access to arctic tissues within the network of facilities.

DESCRIPTION

Rationale

In April 1991, there was agreement among members of the Science Management 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 CWS, Fisheries and Oceans Canada, Health Canada, Parks Canada and the Government of the Northwest Territories in October 1991. NWRC of CWS has been recognized as a world leader in environmental specimen banking. It hosted an international workshop on specimen banking in 1989 and actively participated in the steering committee of the Great Lakes Regional Specimen Bank feasibility study (funded by the Great Lakes Protection Fund) in 1992/93. The Centre also participates on the international Science Committee, which is organizing the Second Biological Environmental Specimen Banking Symposium, to be held in Stockholm in 1996.

The NWRC collection of wildlife specimens, especially of avian species, has been built up at CWS since the 1960s. The facilities were expanded in 1982 with the building of walk-in freezers, enabling specimens to be stored indefinitely at –25°C and –40°C. The locations and pertinent information on these specimens are indexed in a computer database.

Progress to date

In 1992/93, at the request of the Indian and Northern Affairs Canada (INAC), the CWS agreed to manage a contract which involved surveying existing facilities that were known to house arctic specimens. The contract was let to UMA Engineering of Ottawa and required funding of $25K for information from approximately 100 sources to be compiled into a database. The contract was completed on time by March 31, 1993 and within budget.

In 1993/94, the survey material was published in CWS Technical Report 184 and titled "Arctic Specimen Bank Catalogue: Holdings of Flora and Fauna in Canada and the United States." It was distributed to all survey participants and to contacts on a mailing list supplied by INAC.

During the period from January to December 1994, the Specimen Bank facilities were expanded at the NWRC in Hull, Québec. The project comprised the construction of two new walk-in freezer rooms, which are kept at –40°C, the relocation of chest freezers (–85°C), and liquid nitrogen freezers to renovated rooms adjacent to the walk-in freezers. The entire project cost was $192K of which $25K was funded from the Northern Contaminants Program in 1993/94.

In 1994/95, the work of completing and commissioning the new Specimen Bank facilities was the primary focus of the project. The facility is now complete and will be sufficient for the CWS needs for at least five years.

DISCUSSION

The groundwork has been prepared for the project as a whole. A facility at CWS is now large enough to accommodate tissues that are deemed to be important and whose preservation may be at risk in their present location. A series of procedures/protocols are being developed by CWS for its internal specimen bank, which will be used as a model for the Arctic Specimen Bank network. It is expected that there will be a number of approaches to policies regarding access to existing and future specimen holdings and discussions to reach consensus in this matter will be the primary focus of the project over the next year.

Expected project completion date: March 31, 1997

ARCTIC MARINE MAMMAL AND FRESHWATER FISH SPECIMEN BANK

Project Leaders: D. Muir and W.L. Lockhart, Freshwater Institute (FWI), Fisheries and Oceans Canada (DFO), Winnipeg, Manitoba

Project Team: J. Gibson, D. Tretiak, B. Thompsen, R. Stewart, DFO, Winnipeg, Manitoba

OBJECTIVES

1. 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, biomarkers or pathologies associated with contaminants or other potential causes;

2. To provide data from which the health of the marine ecosystem can be assessed and from which retrospective analyses of contaminants can be made. This objective will be pursued over the long term.

DESCRIPTION

The Northern Contaminants Program has stimulated the collection of large numbers of fishes and marine mammal tissues, as well as sediment cores that are currently at the Freshwater Institute (FWI) in Winnipeg or in commercial storage. Combined with existing collections of fish and marine mammal tissues also at the FWI, the Institute 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. The 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 the FWI in order to provide a long-term archive for contaminant measurements and other future studies.

ACTIVITIES IN 1994/95

The funds received in 1994/95 went toward completion of the renovation of a suite of Controlled Environment Rooms into freezers that was begun with funding received in 1993/94. The work is now complete and the freezers have been tested and approved for operation at 35°C to –40°C. The units have about 35m^2 total floor space and about 70 m^3 storage capacity. Sample homogenates as well as whole fish and marine mammal tissues are being transfered to the freezers. Costs were greater than anticipated, but the Regional Director of Science contributed $20K to the project to enable its completion by March 31, 1995.

Clients/Partners

The work will be coordinated with CWS and, if necessary, Health Canada.

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INTERLABORATORY QUALITY ASSURANCE PROGRAM FOR ANALYTICAL DATA PRODUCED BY NORTHERN CONTAMINANTS RESEARCH PROJECTS OF THE ARCTIC ENVIRONMENTAL STRATEGY (AES)

Project Leader: J. Zhu, JP Ztech Company, Gloucester, Ontario

Project Team: Members of Quality Assurance Sub-committee, AES; All laboratories in Northern Contaminants Program

OBJECTIVES

Short-term:

1. To conduct interlaboratory comparison exercises on various contaminants in different matrices including chlorinated pesticides, planar PCBs, dioxin/furans, PAHs and heavy metals;
2. To identify the current status of sampling procedures and associated uncertainties of the data quality;
3. To review analytical data from contract laboratories.

Long-term:

1. To ensure acceptable levels of accuracy and precision of all analytical results reported by laboratories participating in the AES Northern Contaminants Program;
2. To provide AES management with a scientifically sound base on which to evaluate the data quality of the Northern Contaminants Program.

DESCRIPTION

This project is an ongoing program aimed at identifying sources of measurement uncertainties and variation of analytical results to provide information on data quality to the management of the Northern Contaminants Program (NCP) for data evaluation. It is also designed to harmonize the performance of laboratories participating in the NCP by issuing guidelines, giving recommendations, and communicating with each participating laboratory to ensure the compatibility of the results from analyses of a wide range of contaminants in various media (from snow/sediments to mammals/human specimens). The interlaboratory comparison exercise is the key component to achieve these goals. Considering the very diversified types of sampling procedures undertaken in the NCP, it is necessary, and realistic, to collect information on the quality of sampling processes and harmonize procedures where possible. The uncertainties from sampling process should be known to the management when analytical data is evaluated. A considerable portion of the analytical work is carried out by contract laboratories. It is important to review these data independently under this project to ensure that the quality of data is acceptable from a QA/QC point of view.

ACTIVITIES IN 1994/95

In 1994/95, the interlaboratory quality assurance program continued focusing on interlaboratory comparison exercises. The following exercises were undertaken: 1) organochlorine pesticides (OCs) in solution, 2) polychlorobiphenyls (PCBs) and OCs in seal blubber extract, 3) co-planar PCBs in solution, 4) polychlorodibenzo-*p*-dioxins (PCDDs) and polychlorodibenzo-furans (PCDFs) in solution, and 5) polyaromatic hydrocarbons (PAHs) in sediments. In addition, results of the toxaphene round robin, which was conducted by Health Canada in 1993, were reviewed and evaluated in relation to the quality of toxaphene data in the NCP. Further activities in 1994/95 included: 1) survey of current QA/QC status of sampling procedures, and 2) coordination of matrix related sample exchange among AES laboratories.

The following laboratories were visited: the Northern Analytical Laboratory of the Indian and Northern Affairs Canada in Yellowknife, the Centre for Nutrition and the Environment of Indigenous Peoples (CINE) at McGill University, the analytical laboratory at Trent University (TU) and the Analytical Services Laboratory Ltd. (ASL) in Vancouver, BC. In addition, we also spent a few days at the sampling sites to observe sampling work on air, snow, rain water and river/lake water.

RESULTS

The interlaboratory comparison of OCs in solution was conducted to determine both the within-laboratory and between-laboratory variability. The results of direct injections from nine participants showed that most mean values were matching well with the targets—within 20% difference (Table 1). In general, the mean values were slightly lower than the targets at ratios of 0.8 to 1, similar to those found in the interlaboratory comparison on PCB congeners in solution (Zhu 1993). The %RSD s (Relative Standard Deviations) were in the range of 15% to 25%, with a few exceptions. This degree of variability is also comparable to other interlaboratory comparisons such as that in the Integrated Atmospheric Deposition Network, which has a typical %RSD of 20% for OCs (Environment Canada, 1992, 1994). Percent RSDs of the data from work-up were similar to that of direct injections for most congeners, except for dieldrin and heptachlor epoxide. Pooled within-laboratory standard deviation ($S_{(p)}$) of both direct injections and triplicate analyses in this study were about 10% or less. It is found that between-laboratory standard deviation ($S_{(b)}$) in this study was almost the same as total standard deviation of the data set ($S_{(t)}$).

Results of PCBs and OCs in seal blubber extract from nine laboratories provided interlaboratory variation on 'real' samples. While the variation for PCBs (%RSD s 15% to 25%) was similar to that of PCB solution, the variation for OC compounds (%RSD s 20% to 40%) was around two times larger than that of OC solution. A comparison of PCB results from both solution and seal blubber extract shows that the data from the seal blubber extract, which is considered a 'real' environmental sample has the same degree of variability as that from PCB solution sample, which is a clean, matrix-free solution having no background interferences (Table 2). The ICES/IOC/OSPARCOM program has a long history of conducting intercomparisons of PCBs for marine chemistry laboratories worldwide. The results of their recent intercomparison of PCBs in seal oil are also given in Table 2 as well (de Boer and van der Meer 1994). The OC compounds in the seal sample were more difficult to analyze. This was demonstrated by a number of outliers in the data set. In general, the %RSD s of OC compounds in seal blubber in this study were considerably larger (1.5 to 2 times) than the results obtained from interlaboratory comparison on OC compounds in solution (Table 3) (Zhu 1994). The variation of some minor components in this study were much larger, up to 70% (after excluding outlier and Not Detectable numbers).

In response to the concerns about the data comparability of highly toxic co-planar PCBs and PCDDs/PCDFs in the AES program, interlaboratory comparisons of co-planar PCBs (congeners #37, #77, # 126 and # 169) in solution, as well as PCDDs/PCDFs (10 congeners) in solution were conducted. Single injection was required for the analyses. The co-planar PCBs results from the six participants agree well with each other. The %RSDs were 4%, 16%, 13% and 6% for #37, #77, #126 and #169 respectively. Three laboratories participated in the interlaboratory comparison of PCDDs/PCDFs. A total of 17 congeners were reported by all three laboratories, though only 10 congeners were requested. %RSD s of 15% to 30% were achieved.

Three laboratories participated in the interlaboratory comparison of PAHs in sediments. One laboratory received three samples to determine within laboratory variation. Although the within-laboratory %RSDs were 10% to 25%, the interlaboratory %RSD s for most compounds were between 30% to 50%. This degree of variation is much larger than that of PCBs and OCs in seal blubber extract.

Interlaboratory %RSD of toxaphene in cod liver oil from 15 participants, conducted by Health Canada, was 50% with a mean value of 3.99 ppm. Three participating AES laboratories reported total toxaphene levels at either the high (6 ppm) or the low (2 ppm) end. The problem of analyzing toxaphene in various matrices is mainly the lack of reliable standards.

A survey on the current status of sampling work and the existence of a quality assurance program for the sampling is the first step towards the evaluation of sampling quality within the NCP. Information regarding sampling procedures was collected from the NCP project leaders. Twenty-four people have responded to the survey. Some major findings in this survey are: 1) sampling protocols were available only in 50 % of the cases; 2) studies on sampling variability were rarely conducted; 3) people are mostly concerned about the potential contamination of samples during collection, preparation, storage and shipping of the samples, resulting, in part, from lack of trained personnel in the field (including hunters). However, the survey at this stage did not provide sufficient information on the degree of variability of the sampling quality in the NCP. Further investigation on this subject is needed.

DISCUSSION/CONCLUSIONS

Although good within-laboratory precision was found for all participating laboratories, the interlaboratory %RSD for OCs in solution was at a range of 20%. Similar to the results of PCB solution, this interlaboratory variation is mainly caused by the quantification standard solutions among participants. The typical interlaboratory %RSDs

of analytical data in seal sample were 15% to 30% for PCBs, and 20% to 40% for OCs. The data comparability of compounds at low concentration, especially minor OC compounds was much poorer.

From the interlaboratory comparison results of PCBs in solution, OCs in solution and PCBs and OCs in seal blubber extract, the %RSDs of PCB and OC concentrations in NCP data sets may be considered to be in the range of 20% to 40% for most of the main components, while data comparison of minor components will be more difficult. In general, PCB data have better comparability than the OC data. Since PCB and OC data count for a large percentage of the total organochlorine data, it is important to continue to monitor the performance of interlaboratory comparability among NCP laboratories through interlaboratory comparison exercises.

Laboratories have demonstrated good interlaboratory comparability for co-planar PCBs in solution (%RSD around 10%) and PCDDs and PCDFs in solution (%RSD 15% to 30%). However, these highly toxic compounds are present in much lower concentrations in various matrices compared to regular PCBs and OCs. The sample preparation and analysis of these compounds in real samples may prove to be much more difficult. Contamination during sample preparation and background interferences, due to a small final injection volume, could be the real challenge for analysts. Further exercises based on real samples, rather than standard solutions, may be necessary to obtain an estimation on data quality of these compounds within the NCP.

Toxaphene data reported to the NCP management should be used with caution. The problem of analyzing toxaphene in various matrices is mainly due to lack of reliable standards. Percent RSD of 50% to 100% for the total toxaphene concentration is probably a realistic estimation of the current status of toxaphene data quality. Laboratories doing toxaphene analysis should be encouraged to participate in future intercomparison on toxaphene in 1995. Before standards of all toxaphene congeners become available, a relative ratio of other toxaphene congeners to T2 and T12 compounds (Area and/or Height) shall be recorded on electron capture detector (ECD) and electron capture negative ionization (ECNI) chromatograms so that a retrospective examination can be conducted once the standards are available. T2 and T12 quantification standards are now commercially available.

Although over 10,000 samples have been collected with direct involvement of project leaders, only about half of the project leaders had sampling protocols when field work was done. This should be improved. Many concerns, such as avoiding contamination in the field and during storage and shipping; sampling techniques; sample quality (preservation, representativeness, size etc.) can be dealt with through the implementation of sample collection and field QA/QC protocols. All field work should have sampling and field QA/QC protocols, which can provide a) standardized sample collection methods, b) documentation of sample quality, and c) communication channels among project management, laboratory workers and field personnel. This survey of sampling methods provides a preliminary analysis of the status of NCP sampling work. It does not, however, give information on the degree of variability of sampling quality. In order to better assess the uncertainties associated with NCP projects, more work is needed to review and analyse the sampling work which provides samples to generate analytical data. Sampling methods shall be included in the data report to NCP management. More desirable would be to document all the sampling methods and publish this information as supplementary data to NCP research program publications.

The practice of sample exchange was not often undertaken in the Northern Contaminants Program. Although it may be difficult to arrange such an exchange for all projects, the individual project leaders should be encouraged to exchange their samples with others. Results of such a sample exchange can reveal the systematic errors the laboratory may have. Given the fact that a common, suitable matrix is almost impossible to accommodate all NCP laboratories, such sample exchange can be valuable in overcoming the disadvantages of interlaboratory comparison based on standard solutions.

The results of the 1994/95 QA program have been reported to the Department of Indian Affairs and Northern Development in a series of progress reports and a final report (see Appendix).

Expected project completion date: March 31, 1997.

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Appendix A: List of reports of the QA program in 1994/95

1. First progress report on interlaboratory quality assurance program (June 2, 1994): a) Analysis of results of interlaboratory comparison on total toxaphene in cod liver oil (NIST SRM 1588); b) Approach for laboratory selection and reference material circulation plan for interlaboratory comparison exercises.

2. Second progress report on interlaboratory quality assurance program (June 28, 1994): a) Initiation of interlaboratory comparisons; b) Protocol for split sample analyses; c) draft of questionnaire for survey of sampling protocols.

3. Third progress report on interlaboratory quality assurance program (Sept. 30, 1995): a) Interlaboratory comparison of organochlorine pesticides in solution; b) interlaboratory comparison of PCBs and OCs in seal blubber extracts; c) progress on sampling methodology survey; d) site visits to sampling field and laboratories.

4. Fourth progress report on interlaboratory quality assurance program (Dec. 30, 1994): a) Interlaboratory comparison of co-planar PCBs in solution; b) interlaboratory comparison of PCDDs and PCDFs in solution; c) progress on sampling methodology survey; d) preparation and distribution of sediments for PAHs; e) site visits to two laboratories; f) progress on coordinating split sample analyses.

5. Fifth progress report on interlaboratory quality assurance program (March 28, 1995): a) Interlaboratory comparison of PAHs in sediments; b) presentation of QA/QC program at AES workshop in Sidney, BC; c) site visit to one laboratory; d) survey of sampling methods used in the Arctic Environmental Strategy program (AES).

6. Final report on interlaboratory quality assurance program (March 30, 1995): Summary of the activities and results of the QA program in 1994/95, and recommendations to the AES management.

Table 1. Interlaboratory comparison results of organochlorine pesticides in solution.

Compound	Target	Direct injection[a]		Work-up[a]	
		Mean	%RSD (n)[b]	Mean	%RSD (n)[b]
1245-tetrachlorobenzene	1.74	1.66	14.7 (7)	1.51	17.2 (7)
pentachlorobenzene	2.58	2.27	16.4 (8)	2.17	16.5 (8)
hexachlorobenzene	5.16	4.60	17.5 (9)	4.17	16.2 (9)
a-HCH	3.16	2.96	25.8 (9)	2.57	19.2 (9)
ß-HCH	3.10	2.87	27.8 (9)	2.51	27.7 (9)
γ-HCH	2.16	2.06	15.6 (9)	1.88	17.5 (9)
p,p'-DDD	2.04	1.82	18.8 (9)	1.74	20.3 (9)
p,p'-DDE	5.22	4.88	25.2 (7)	4.53	12.2 (9)
p,p'-DDT	1.70	1.60	20.7 (9)	1.67	17.2 (9)
heptachlor	1.82	1.79	22.1 (6)	1.60	24.3 (6)
cis-chlordane	2.82	2.31	21.7 (9)	2.24	24.5 (9)
trans-chlordane	3.60	3.08	18.8 (9)	3.05	19.8 (9)
cis-nonachlor	1.60	1.29	19.0 (8)	1.31	18.4 (8)
trans-nonachlor	7.50	6.00	17.2 (9)	5.94	20.4 (9)
mirex	1.46	1.37	24.1 (9)	1.27	24.2 (9)
photomirex	3.68	2.87	29.3 (7)	2.87	29.5 (7)
dieldrin	2.84	2.69	9.4 (6)	2.42	22.4 (7)
heptachlor epoxide	5.72	5.15	18.4 (8)	4.19	29.9 (8)
oxychlordane	5.04	4.13	13.3 (5)	4.44	17.9 (7)

[a] Check sample in six replicates was injected into instruments with proper dilutions (Direct injection), and another portion of the check sample in triplicate was analysed with laboratory work up procedures (Work up). The average values of these six replicates and triplicate, respectively, from each laboratory were used to calculate the interlaboratory mean values in the table.

[b] Number of laboratories reporting the value of these compounds.

Table 2. Comparison of %RSDs of PCB congeners in two check samples.

PCB congener	Solution	Seal blubber[a]	Ref [b](n=30)
PCB 28[d]	37.5	38.2 (8.5)	149
PCB 74	25.8	22.1 (18.9)	
PCB 99	14.7	25.0 (46.8)	
PCB 118	12.1	11.0 (31.3)	21.3
PCB 105	28.4	19.6 (10.3)	32.5
PCB 153	13.1	17.5 (65.6)	20.0
PCB 138	8.9	15.4 (46.1)	14.7
PCB 187	13.5	18.3 (6.8)	
PCB 156	25.7	39.0 (2.8)[c]	65.5
PCB 180	12.8	22.8 (11.3)	11.9
PCB 170	10.8	26.9 (4.8)[c]	
PCB 194	28.3	30.3 (0.8)[c]	

[a] concentrations are indicated in brackets
[b] de Boer, J. and van der Meer, J 1994
[c] minor components in seal blubber
[d] sum of PCB 28 and 31 due to co-elution

Table 3. Comparison of %RSDs of OC compounds in two check samples.

OC Compound	Solution	Seal blubber[a]	
Pentachlorobenzene	17.8	24.5	(13.9)
Hexachlorobenzene	16.3	20.3	(17.6)
α–HCH	19.8	34.3	(60.1)
ß-HCH	29.4	55.6	(0.6)[b]
cis-Chlordane	25.7	30.9	(1.1)[b]
trans-Chlordane	21.2	71.0	(0.9)[b]
cis-Nonachlor	19.8	39.6	(0.9)[b]
trans-Nonachlor	21.1	29.5	(16.4)
p,p'-DDE	13.1	28.2	(286.3)
Mirex	25.6	19.9	(1.5)[b]
Heptachlor epoxide	31.0	25.2	(9.3)
Oxychlordane	18.0	35.2	(30.3)
Dieldrin	24.7	21.5	(10.7)

[a] concentrations are indicated in brackets
[b] minor components in seal blubber

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