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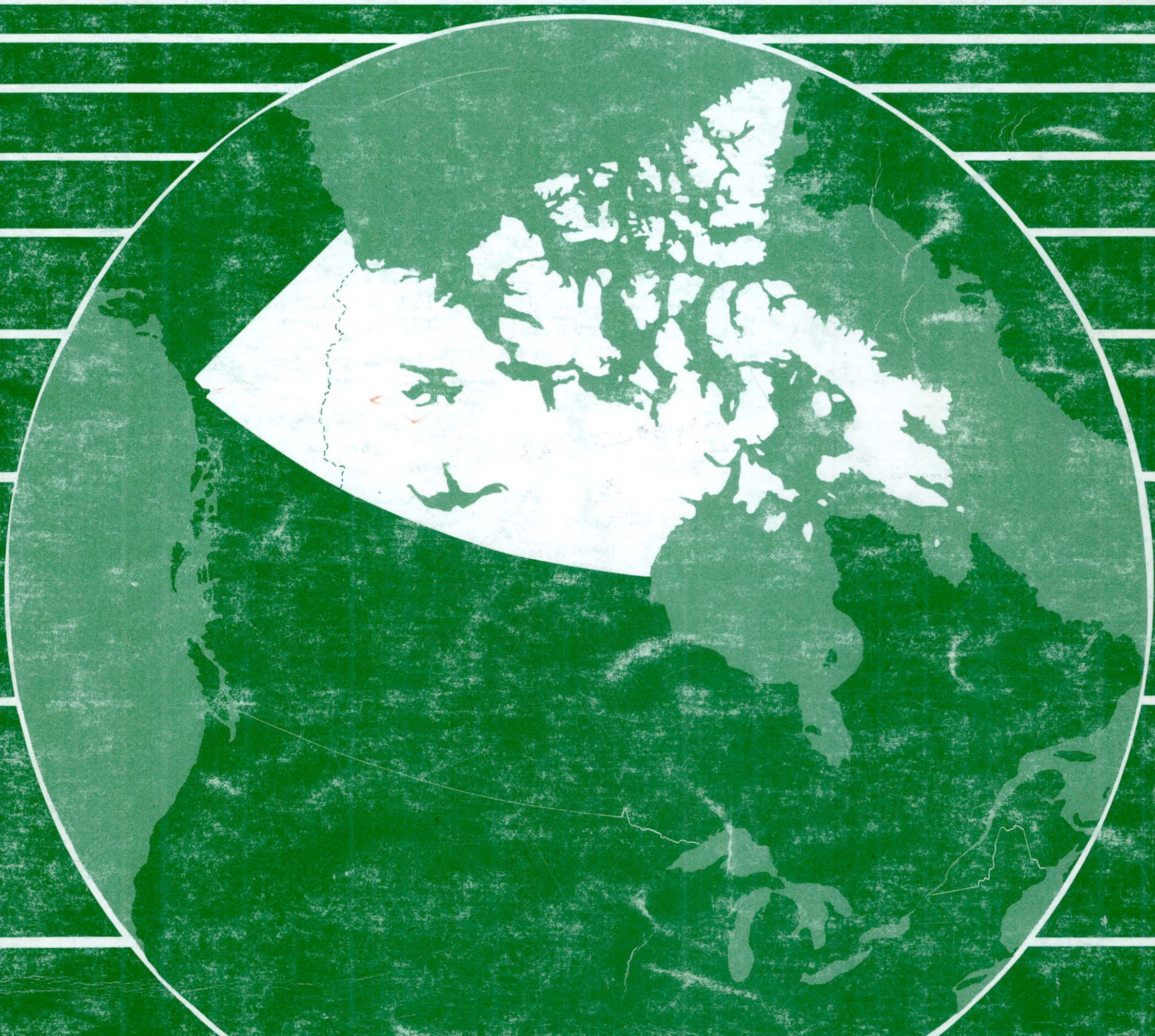
Synopsis of Research Conducted under the 1995-1997 Northern Contaminants Program



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Synopsis of Research Conducted under the 1995-1997 Northern Contaminants Program

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

FOREWORD

This report summarizes the results of research and monitoring studies on contaminants in northern Canada. These studies were conducted under the auspices of the Northern Contaminants Program.

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.

A list of addresses for 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 de lutte contre les contaminants dans le Nord.

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 Northern Contaminants Program (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. The three main contaminant groups of concern are heavy metals, radionuclides, and persistent organic pollutants—particularly organochlorines. These findings were of concern, particularly 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 "to reduce and, wherever possible, eliminate contaminants in traditionally-harvested foods while providing information that assists informed decision-making by individuals and communities in their food use".

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 for the NCP is based on an ecosystem approach, focusing on four main categories: i) Human Health; ii) Ecosystem Uptake and Effects; iii) Sources, Pathways and Fate; iv) Education and Communication. Initiatives to promote international control of contaminants are supported by the scientific research. Since 1991, the NCP has funded approximately $30 million of research, in addition to supporting the McGill Centre for Indigenous Peoples Nutrition and Environment (CINE), and participation of Aboriginal organizations. The NCP Aboriginal partner organizations lead communications activities.

The initial five-year phase of the NCP was focused mainly on assessing where and at what levels contaminants were found in the arctic ecosystem, and confirming the source region. This research has enabled us to 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.

Following the initial assessment phase, the emphasis of the NCP is shifting towards providing advice to communities and reducing source inputs of contaminants. There will be a greater emphasis on human health research, developing effective community dialogue, increasing community participation, and working towards international agreements on emissions controls. The focus of the NCP is directed by a constant feedback loop, where Program research reflects the questions that communities want answered. Some Program projects that reflect the learning process on how to communicate more effectively include: a requirement for researchers to involve communities in their work which was instituted in 1994/95 through the Guidelines for Responsible Research; the Métis Nation's contaminants curriculum project; 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.

Due to the transboundary nature of the issue of contaminants in the arctic food chain, Canada must pursue international initiatives for control of these substances, with the scientific evidence generated by the program providing substantiation for our concerns and calls for action. The 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); 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); and the United Nations Environment Programme's (UNEP) global initiative to negotiate a legally binding instrument on POPs.

This report provides a summary of the research and activities funded by the Northern Contaminants Program in the 1995/96 and 1996/97 fiscal years. Workshops were held in 1997 and 1998 at which researchers presented their results. 1996/97 was the last year of the NCP under the six-year Arctic Environmental Strategy. Additional program funding was procured in January 1998 to continue the program for another five-year period.

I SOURCES, PATHWAYS AND FATE OF CONTAMINANTS

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

Project Leader: M. Alaee, National Water Research Institute, Environment Canada.

Project Team: C. Spencer, R. Wilkinson, NWRI; M. Palmer, DINA, Whitehorse; J. Eamer, DOE, EP, Whitehorse; D. Gregor, Northern Environmental Services

OBJECTIVES

1. To determine the source(s) of high levels of organochlorine (OCs) contamination in lakes Laberge, Atlin, Bennett, Fox, Kusawa, and Marsh as well as the Yukon and Takhini Rivers.

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

DESCRIPTION

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 a separate Northern Contaminants Program (NCP) project; however, rain deposition is measured in this project. Gas exchange can be estimated using the fugacity model developed by D. Mackay (Mackay and Shiu 1981). Using contaminant concentrations in water and air, Henry's Law Constant and mass transfer coefficients, the flux of gaseous contaminants into the water can be estimated. In order to quantify the sources and fate of contaminants in the Yukon River system, a mass balance approach was undertaken. In this model, lakes were compartmentalized within the river system. This is an abiotic model that focuses on the movement of chemicals based on physical processes. Using the conservation of mass and energy principle it is possible to account for the contaminants in the system. This approach has been extensively developed by Mackay and his co-workers (Mackay 1991) and applied to the Great Lakes by Eisenreich *et al.* (1992).
Using the conservation of mass principle:

$$\Sigma F_{j,k} = \Sigma C_{j,k} \ x \ L_j - 0$$

where $C_{j,k}$ is the concentration of chemical "k" in medium "j" and L_j is referred to as the velocity of the transferring compartment. These compartments were divided into two categories-inputs and outputs. The inputs were atmospheric deposition (rain and dry fall), and inflows while outputs were defined as outflow, sedimentation, and volatilization.

HCHs are the predominant organochlorine in most Arctic water systems such as Amituk Lake (Semkin 1995), Mackenzie River (Backus *et al.* 1996), Great Slave Lake (Alaee *et al.* 1996) and the Arctic Ocean (Macdonald *et al.* 1995, Bidleman 1995). HCHs were first registered in 1950 (US-EPA 1988) as an insecticide. Since then, it has been used extensively with worldwide cumulative production in the millions of metric tons (Buser and Müller 1995). The original formulation or technical mixture consisted of 4 major isomers: 60–70% α–HCH, 5–12% β–HCH, 10–15% γ–HCH more commonly known as Lindane, and 6–10% δ–HCH. Only γ–HCH has been identified to have insecticidal properties. Consequently the use of the technical HCH has been banned in Canada, USA, Western Europe and Japan. However, the technical mixture is still in use in many parts of the world including countries in the Far East, Eastern Europe, and South America.

HCHs are among the more volatile organochlorine pesticides, with reasonably high water solubility. They mainly exist in the water column and accumulate to some degree in sediment. These properties result in the evaporation of HCHs from warmer climates. The HCHs then circulate over long distances to be deposited when the air mass cools over the north, condensing and releasing the compound into the Arctic.

In this report, concentration levels for HCHs in water, suspended solids, and precipitation at lakes Laberge, Atlin, Bennett, Marsh and Fox were compared to the less contaminated Kusawa Lake measured over four seasons. A mass balance model for the Lake Laberge System will also be presented.

ACTIVITIES IN 95/96

No sampling was done in 95/96. All work concentrated on the processing and analysis of samples collected in 1994. In 1995/96 127 samples were processed and analysed for OCs and PCBs. Approximately 130 samples from 1993 were also re-injected on the GC and re-analysed for HCHs.

Seventy-one 1994 samples are currently being processed. All processing will be completed by January 1997.

SAMPLING AND ANALYTICAL PROCEDURES

Detailed field sampling and analytical procedures were described in a previous report by Alaee (1995). Modifications and additions to the methods are as follows:

a) After cross comparison of the GC-ECD, non-linearity was observed. In particular the non-linearity affected the components with higher concentrations such as HCHs. To correct this problem a multi-level calibration using a quadratic function was employed. Results from this method were comparable to those obtained using more dilute samples and to the other instruments;

b) Separation of the two optical isomers of α–HCH were accomplished using GC/ECNI/MS. The operation conditions for the modified Finnigan 4500 GC/MS are similar to those described previously (Alaee 1995) with the following exceptions: the injector was operated under isothermal condition and was held constant at 250°C. Analytical separations were performed using a 30m x 0.25mm i.d. 20% permethylated γ-cyclodextran (Supelco) (Falconer *et al.* 1994). Column temperature was at 90°C held for 1 min raised to 140 at 20°C /min, raised to 220°C at 1 °C /min, raised to 240°C at 20 °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. The MS was operated in Selected Ion Monitoring mode (SIM); monitoring m/e 253, 255, 257 corresponding to M–Cl ions produced by HCHs in a single window.

QA/QC

QA/QC procedures were not changed from previous years. We participated in the QA/QC program sponsored by the NCP/AES.

RESULTS AND DISCUSSION

HCHs were the major organochlorine found in the Yukon River system water samples (Alaee 1995, Alaee and Gregor 1994, Gregor and Eamer 1993). Consequently the main focus of this report is on these compounds. A summary of HCH concentration from the four sampling seasons are summarized in Table 1 and presented in Figure 1. It was previously reported that HCH values for summer of 1993 were lower than previous years. After further investigation a non-linearity in the response of the ECD was found to be responsible for this. Subsequently the 1993 samples were re-analysed and the results are presented in Table 1. Over the two-year sampling period the range for α–HCH was 0.43–2.6 ng/L with both mean and median of 1.2 ng/L; and the range for γ–HCH was 0.06–0.76 with a mean of 0.28 ng/L and a median of 0.24 ng/L. These values are comparable to those reported by Semkin (1995) from Amituk Lake, Backus *et al.* (1996) from the major rivers in the Northwest Territories, Alaee *et al.* (1996) from the Great Slave Lake, and Ridal *et al.* (1996) from Lake Ontario.

One of the objectives of this study was to determine the role of the atmosphere in the delivery of contaminants to the Yukon River system. The net direction of the flux across the air water interface was determined using air/water fugacity ratio; which was defined as:

$$\frac{f_a}{f_w} = \frac{C_a R T}{C_w H}$$

where T is temperature in Kelvin (K), R is the universal gas constant in Pa m^3/mol K, H is Henry's Law Constant in Pa m^3/mol, C_a and C_w are the concentrations in air and water respectively. At a steady state equilibrium the fugacity ratio will be equal to one ($f_a/f_w=1$). When the fugacity ratio is greater than one the concentration of the contaminant in the air phase is over saturated with respect to the water concentration of the same contaminant, hence the flux is from air to water. For fugacity ratios less than one the air phase concentration of contaminant is under saturated with respect to the water phase concentration, therefore the contaminants will move from water to the air. Using average air concentrations for summer 1993 reported by Bailey *et al.* (1997) along with H values reported by Kucklick *et al.* 1991 the fugacity ratios for all of the lakes were determined, and presented in Figure 2. As it is shown in Figure 2 both α–and γ–HCH are near equilibrium between air and water and the flux direction changes across the lakes in the Yukon River basin.

Table 1. Concentration of HCHs in the Yukon River Basin during the four sampling seasons.

Sampling Season	**Winter 1992**			**Summer 1993**			**Winter 1993**			**Summer 1994**		
Location	**α–HCH (ng/L)**	**γ-HCH mean (ng/L)**	**α/γ–HCH mean**	**α–HCH (ng/L)**	**γ-HCH mean (ng/L)**	**α/γ–HCH mean**	**α–HCH (ng/L)**	**γ-HCH mean (ng/L)**	**α/γ–HCH mean**	**α–HCH (ng/L)**	**γ-HCH mean (ng/L)**	**α/γ–HCH mean**
Llewellyn Glacier				0.73	0.14	5.2				0.60	0.09	7.2
Atlin Lake	2.6	0.76	3.4	1.6	0.33	5.0	1.64	0.34	4.8	1.7	0.54	3.2
Bennett Lake				0.91	0.11	8.5	0.78	0.11	7.4	0.92	0.15	6.0
Tagish Lake	1.9	.53	3.5	1.1	0.21	5.2	1.2	0.25	4.9	1.1	0.17	7.1
Marsh Lake				1.3	0.48	2.8	1.1	0.23	4.9	1.4	0.40	3.5
Yukon R.[1]	1.2	0.53	3.5	1.3	0.50	2.7	1.2	0.24	5.0	1.3	0.23	5.7
Yukon R.[2]				1.1	0.50	2.2	1.3	0.295	4.5	1.2	0.26	4.5
Kusawa Lake	1.4	0.51	2.7	1.1	0.16	6.7	1.2	0.10	11	1.1	0.11	9.7
Takhini River	0.67	0.25	2.7	0.79	0.13	6.2	0.43	0.06	7.8	0.83	0.13	6.3
Fox Lake				0.93	0.20	4.7	1.1	0.14	7.9	1.4	0.345	4.1
Lake Laberge	1.5	0.52	2.9	1.3	0.24	5.5	0.87	0.17	5.1	1.6	0.29	5.5
Yukon R.[3]				0.94	0.09	10				1.7	0.26	6.5

[1] Before Whitehorse
[2] After Whitehorse
[3] At Lake Laberge

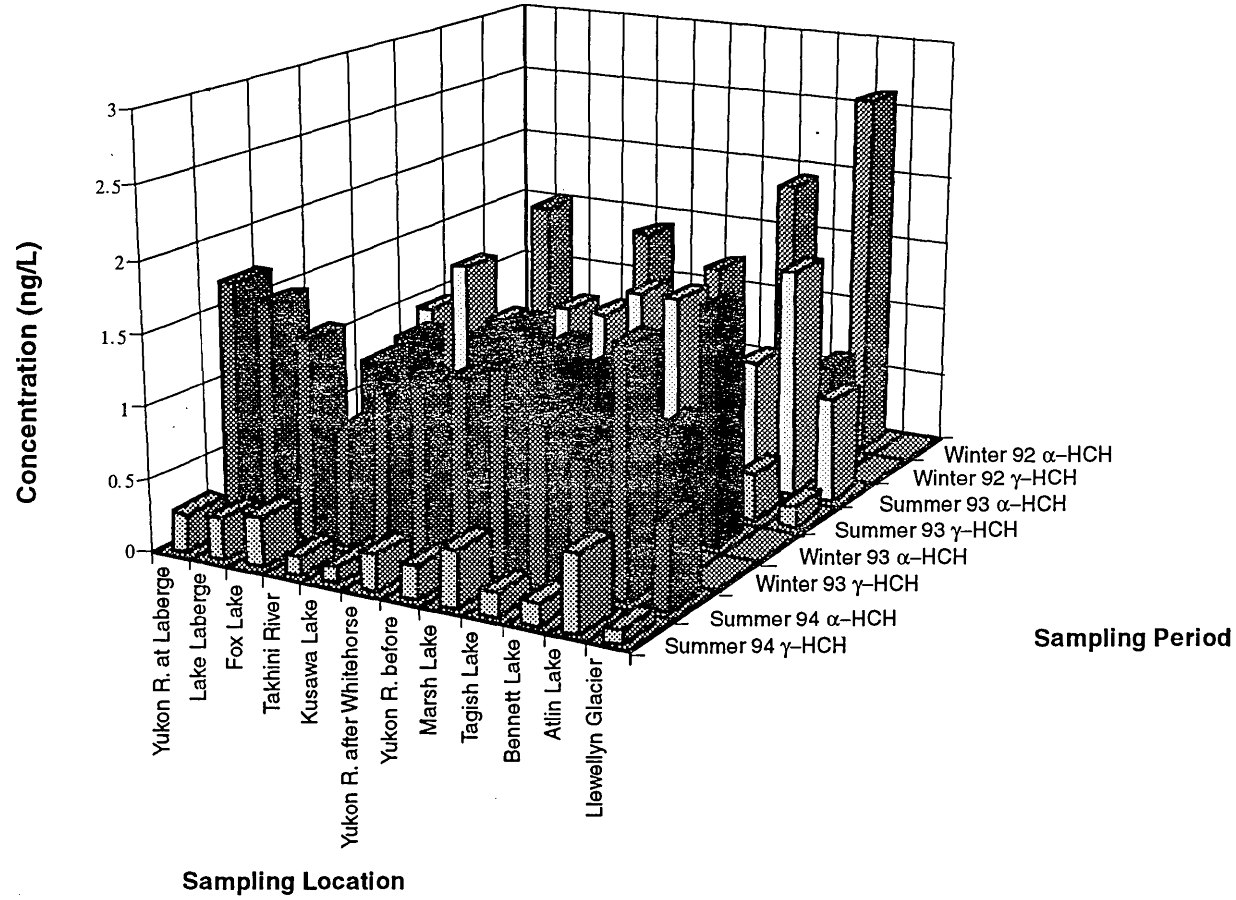

Figure 1. Concentrations of HCHs in the Yukon River basin over the four sampling seasons.

Results from a mass balance model for Lake Laberge using summer 1993 data is presented in Figures 3 and 4. Since the concentration of HCHs in all of the lakes and rivers are similar the flux will be mainly affected by river flow. The Yukon River as the river with the highest flow was responsible for the largest input flux to Lake Laberge (31g/day for α–HCH and 10 g/day for γ–HCH), followed by Takhini River which had an input flux of 12 g/day and 2.9 g/day for α–and γ–HCH respectively. Fox Creek with 0.21 g/day and 0.11 g/day atmospheric deposition made a minor contribution to the γ–HCH flux into the lake and α–HCH was outgasing during this period.

Results from the analysis of chiral components of α–HCH were presented at the Second SETAC World Congress (Alaee *et al.* 1995). Enantiomeric ratios of α–HCH were determined using two different chiral columns β– and γ–cyclodextran) using ECD and ECNI/MS as detectors. A typical ion-chromatogram and the spectra associated with each peak are presented in Figure 5. Identification was based on the chromatographic retention time and the relative ratio of the 3 ions. Bacterial activities are the main source of chiral degradation of α–HCH (Buser and Müller 1995). A summary of enantiomeric rations of α–HCH are reported in Table 2, and presented in Figure 6. All of the sources of α–HCH into the Yukon River system air, rain, snow, and glaciers have an enantiomeric ratio close to 1. The headwater Atlin Lake has an average ratio of 0.3, the lowest value in the system. Atlin Lake receives the majority of its water from Llewellyn Glacier which had a ratio of 1.03, consequently the degradation must take place within the Lake itself. Atlin Lake had a high residence time (18.6 years) and is the deepest lake in the system. Bennett Lake, had a chiral ratio of 0.88. The residence time for Bennett Lake is not known however it is estimated to be lower than Atlin Lake. Tagish Lake receives water from both Atlin and Bennett Lakes. Water samples collected from Tagish Lake at Carcross show a ratio of 0.88 which reflects the values from Bennett Lake, however samples collected at the town of Tagish at the outlet to Marsh Lake, show a ratio of 0.4 which reflects mixing of the

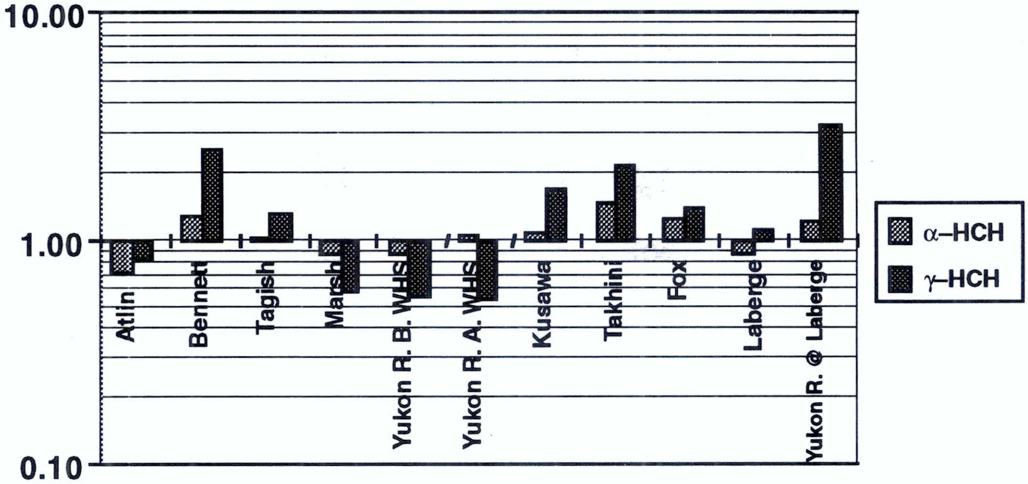

Figure 2. Fugacity ratios for HCHs during summer 1993.

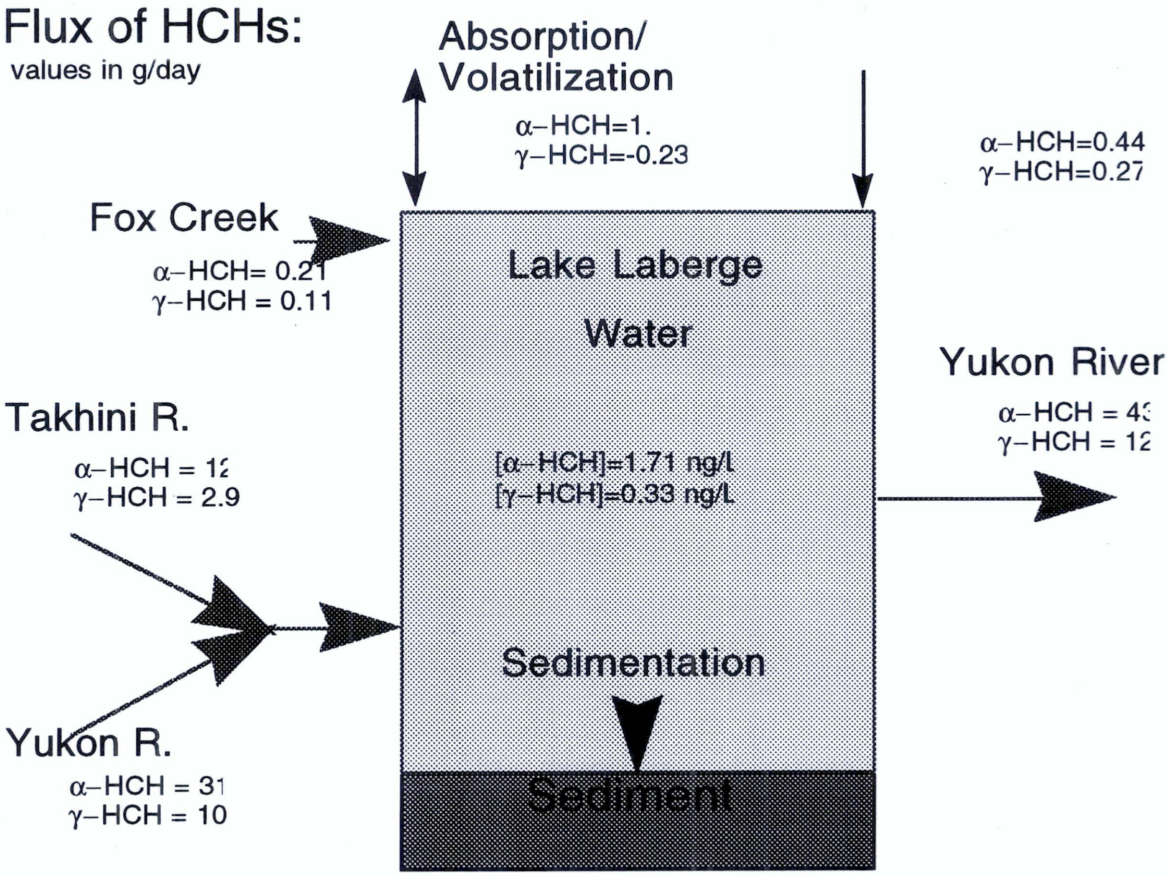

Figure 3. The mass balance of HCH in Lake Laberge

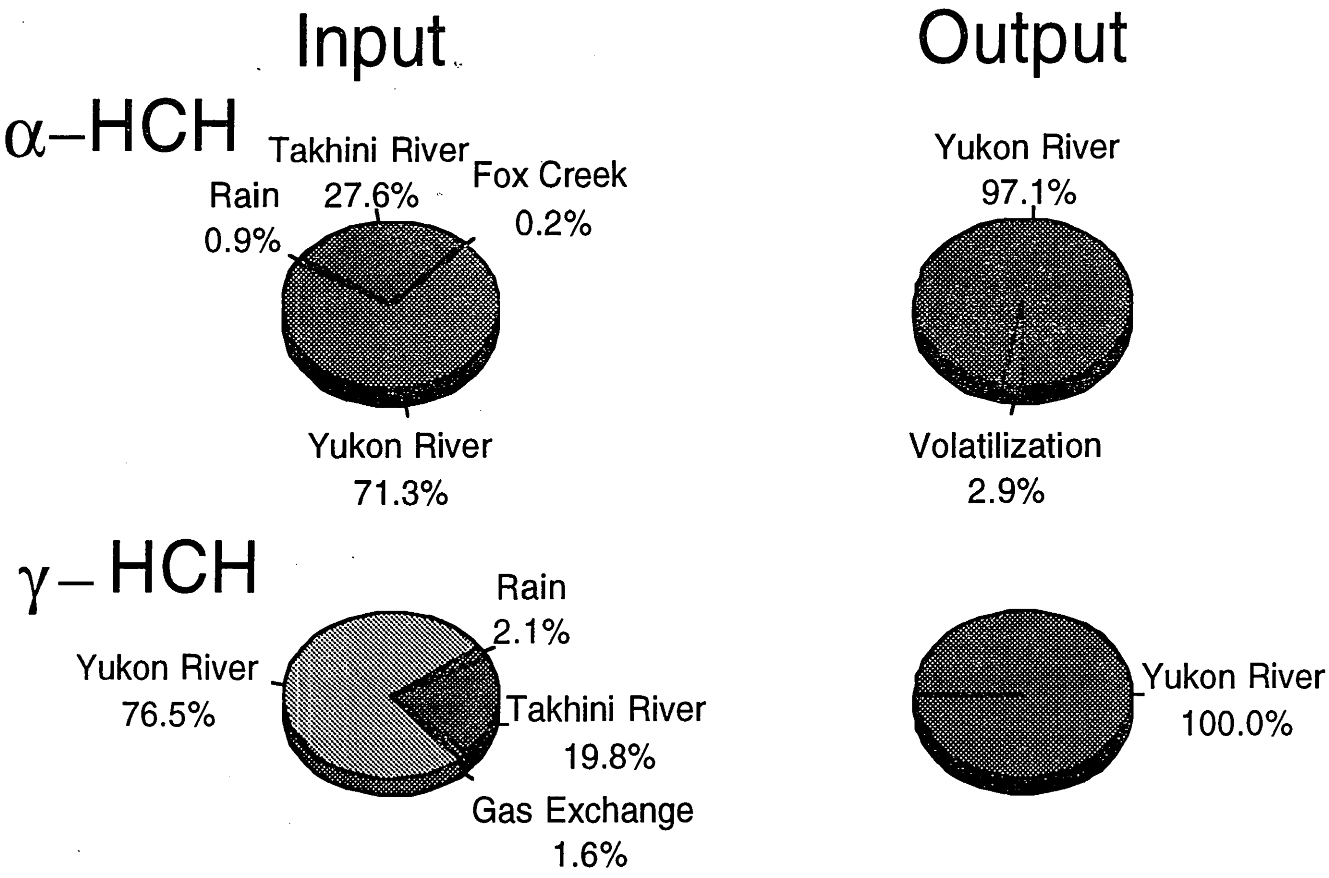

Figure 4. Percent input and output of HCH into and from Lake Laberge.

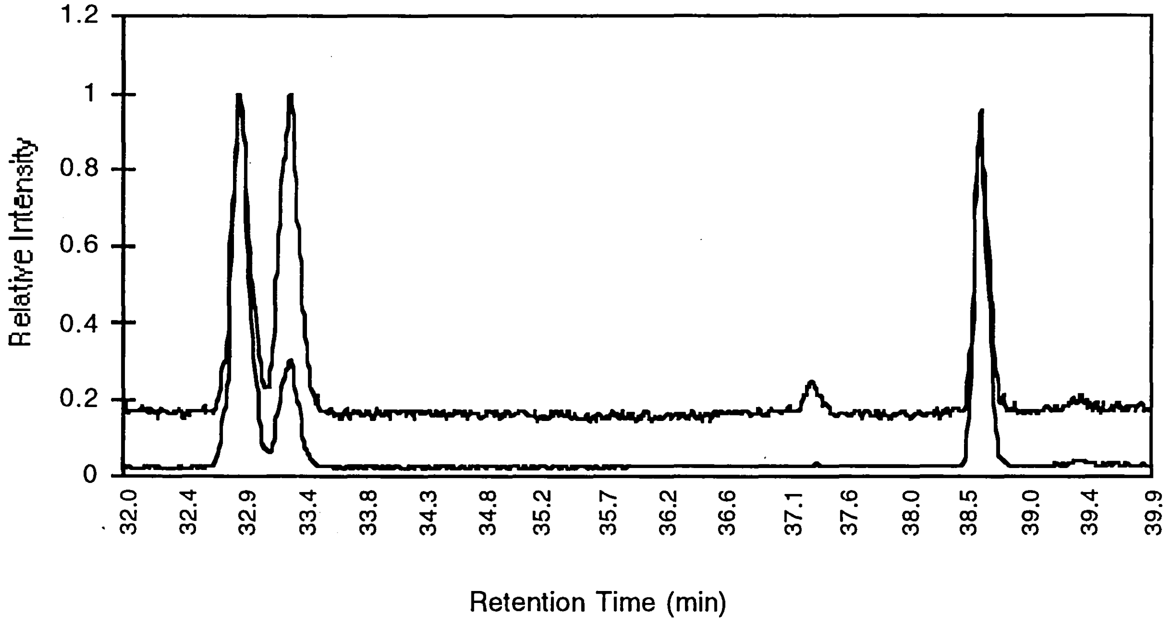

Figure 5. Total ion chromatogram of HCHs from Takhini River and Atlin Lake.

Table 2. Enantiomeric ratios of a-HCHs in the Yukon River Basin.

Sampling Season **Location**	**Winter 1992** **(+/-) α–HCH**[1]	**Summer 1993** **(+/-) α–HCH**[2]	**Winter 1993** **(+/-)α–HCH**[3]	**Summer 1994** **(+/-)α–HCH**[2]
Llewellyn Glacier		0.970		1.090
Atlin Lake	0.367	0.340	0.272	0.237
Bennett Lake		0.895	0.871	0.867
Tagish at Bennett		0.897		0.868
Tagish at Marsh	0.646	0.485	0.387	
Marsh Lake		0.498	0.369	0.387
Yukon R. before Whitehorse	0.525	0.420	0.338	0.397
Yukon R. after Whitehorse	0.499	0.561	0.347	0.404
Kusawa Lake	1.064	0.991	0.981	1.000
Takhini River		0.932	0.926	1.010
Fox Lake		0.894	0.921	0.964
Lake Laberge	0.593	0.473	0.395	0.440
Yukon R. at Laberge		0.431		0.448

[1] Separation achieved on β–Dex Column and analysed using GC/ECD
[2] Separation was achieved using γ–Dex column and analysed by GC/ECNI/MS
[3] Analysed using GC/ECNI/MS with a β-Dex Column

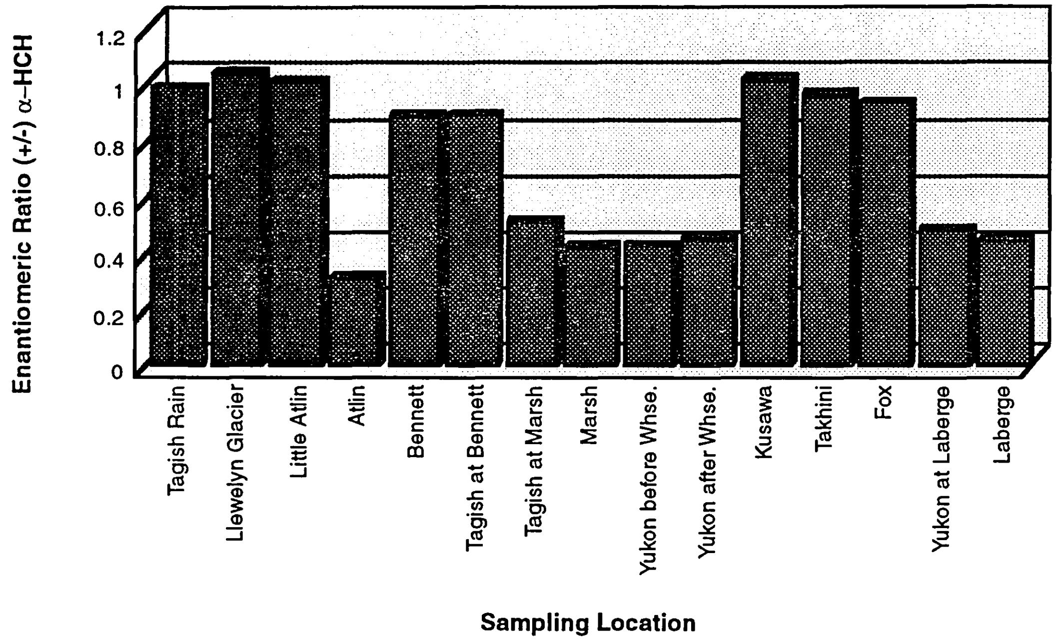

Figure 6. Enantiomeric ratio of α–HCH in Yukon River Basin

water from both Atlin and Bennett Lakes. Kusawa Lake another headwater in this system, has a ratio close to 1. Residence time for this Lake is also not known but it is anticipated to be very low. Takhini river is the outflow from this Lake and has a similar enantiomeric ratio. Fox Lake is a small lake feeding to Lake Laberge. It is mainly glacial fed and has a short residence time. Lake Laberge receives water from all of the above lakes and as such the ratios reflects the contributions of the various components.

CONCLUSION

Riverine inputs account for the majority of the flux of HCH into Lake Laberge. Gas exchange plays a minor role in this system. Chiral ratios of α–HCH indicated that a major portion of HCH input to Lake Laberge is from Atlin Lake.

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NORTHERN CONTAMINANTS AIR MONITORING: BEHAVIOUR OF ORGANOCHLORINE COMPOUNDS IN THE ARCTIC ATMOSPHERE

Project Leader: L.A. Barrie, Atmospheric Environment Service

Project Team: C. Halsall, G. Stern, R. Bailey, P. Fellin, D. Muir, N. Grift, L. Lockhart, and T. Bidleman.

INTRODUCTION

Quality controlled datasets for the northern contaminants air monitoring program now extend into 1995, allowing for a more detailed look at temporal trends occurring in the arctic atmosphere. To examine contaminant behaviour over annual cycles will give greater understanding to the behaviour of the compound(s) in question and also allow the effects of seasonal temperature fluctuations, long-range transport or even periods of pesticide usage to be examined. Following the first phase of data collation in the air program, several key papers highlighting the concentrations of the major compound classes are now in press (Halsall *et al.* 1997, Stern *et al.* 1997, Halsall *et al.* sub.). The second phase is to examine temporal trends with a view to understanding the processes which ultimately control the air concentrations, and thus create a premise for future modelling work and the prediction of contaminant behaviour within the arctic atmosphere.

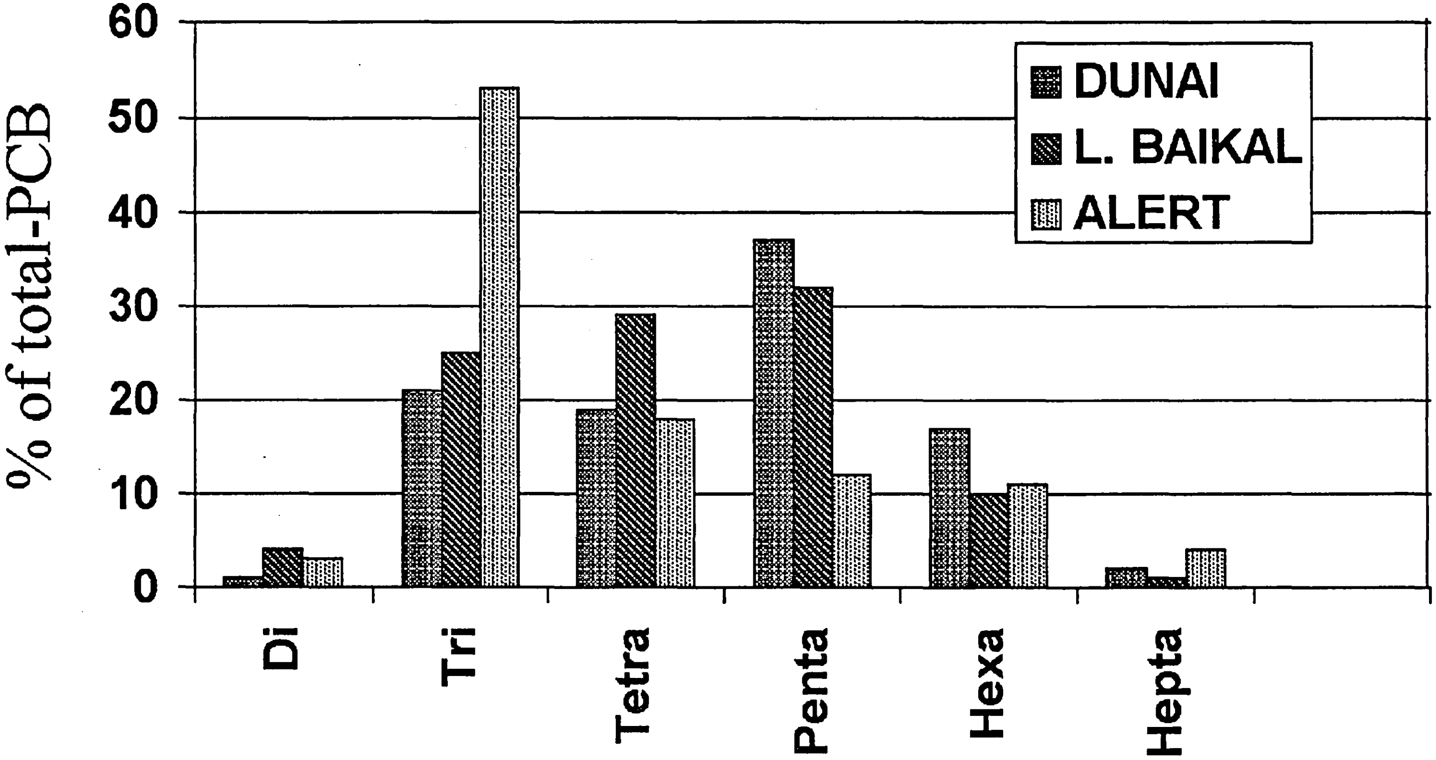
Seasonality in the atmospheric PCB profile

Although a temporal pattern was not observed in the total-PCB concentrations, a change in homologue profile was evident when moving from winter to summer. This was dependent on the location of the sample site and on the particular sample year in question, but in general the heavier penta- and hexachlorinated homologues were enhanced during the summer months. This was most apparent at Dunai in the Russian Arctic, but was also observed to a lesser degree at Alert and Tagish in the Canadian Arctic. This enhancement of the heavier homologues (greater percent contribution to the t-PCB) was found to be strongly correlated with temperature ($r^2 > 0.7$, $p < 0.05$) for all three sites. The percentage contribution by the lighter trichlorinated homologue, however, was negatively correlated with temperature ($r^2 > 0.3$, $p < 0.05$). Reasons for the decline in the tri-homologue during the warmer months are unclear, but could be related to increased photolytic degradation during the 24-hour daylight of the arctic summer. Degradation studies have shown enhanced photolytic breakdown of the lighter di- and trichlorinated congeners in the presence of OH radicals (Anderson and Hites 1996). Aside from this, the enhancement of the heavier homologues in the Russian Arctic may be indicative of a summer PCB profile encountered in Russia. Figure 1 shows the average June profile for air samples taken over Lake Baikal in central Asia. Included for comparison are the June profiles for the arctic sites of Dunai and Alert. Interestingly, the profile for Dunai and L. Baikal are similar, showing a preponderance towards the heavier homologues, whereas Alert is dominated by the tri-homologue. This would suggest that although temperature controls this enhancement of the heavier congeners, the fact that a similar pattern is encountered in the atmospheres of both Dunai and L. Baikal and not at Alert, may be explained by the type of PCB mixtures manufactured and used in Russia. The most abundant of these was 'Sovol', akin to Aroclor 1254, and enriched in the heavier penta- and hexachlorinated congeners (Ivanov and Sandeil 1990). Approximately 100,000 tonnes were manufactured between 1940 and 1990, compared with 25,000 tonnes of the lighter 'Trichlorodiphenyl', the only other major PCB formulation.

Effects of temperature on air concentrations

Seasonal variations in air concentrations have been reported in several temperate studies (Hoff *et al.* 1992, Halsall *et al.* 1995, Hornbuckle and Eisenreich 1996) with OC concentrations being shown to increase in varying degrees with the onset of summer, temperature being invoked as the primary controlling parameter. This results in increased re-volatilization of previously deposited material from surfaces such as aerosol, soil, vegetation and water, leading to higher air concentrations. Conversely during the winter, reduced temperatures result in condensation with a subsequent lowering of the gaseous air concentration. This process is largely dependent on a compound's physical-chemical properties and the ambient temperature.

In the Arctic, this seasonality in air concentrations was apparent for many of the compounds despite the low summer temperatures relative to temperate regions (mean summer temperature at Alert was ~5°C). Table 1 shows the degree of correlation with temperature for a range of OC compounds for the three arctic sites. The strongest correlations tended to be with the transformation/metabolite daughters of the original pesticides, i.e. oxychlordane, heptachlor epoxide and dieldrin, reflecting 1) the widespread distribution of these compounds and their persistence in the environment and



Note: Lake Baikal data from McConnell *et al.*, 1996

Figure 1. Average June PCB-homologue profile.

Table 1. Correlations of arctic atmospheric OC concentrations with temperature.

	ALERT		TAGISH			DUNAI
(n=97)	(n=78)				(n=31)	
	r *	p	r	p	r	p
oxychlor	0.609	$p < 0.01$	0.491	$p < 0.01$	0.71	$p < 0.01$
hept-epox	0.606	$p < 0.01$	0.689	$p < 0.01$	0.686	$p < 0.01$
cis-non	0.715	$p < 0.01$	0.346	$p < 0.01$	0.675	$p < 0.01$
endosulfan	0.414	$p < 0.01$	0.553	$p < 0.01$	0.441	$p < 0.05$
dieldrin	0.507	$p < 0.01$	0.282	$p < 0.05$	0.531	$p < 0.01$
cis-chlor	0.416	$p < 0.01$	0.319	$p < 0.05$	0.447	$p < 0.05$
a-HCH	*-0.071*	*$p > 0.1$*	0.329	$p < 0.01$	*-0.179*	*$p > 0.1$*
g-HCH	*0.032*	*$p > 0.1$*	0.469	$p < 0.01$	*-0.033*	*$p > 0.1$*
p,p-DDE	*-0.482*	*$p < 0.01$*	*-0.381*	*$p < 0.01$*	*0.235*	*$p > 0.1$*

* Pearson product moment correlations

NB: Italics indicate either no significant correlation or negative correlation

2) the likelihood that a large percentage of the parent compounds, many of which are no longer in use, have now been degraded into these secondary compounds which continue to be 'recycled' in the global system. Figures 2a & b present a monthly time series for both Alert and Tagish for several of the organochlorine pesticides that show a notable increase during the warmer months (significantly correlated with temperature). From Table 1, other compounds which also showed a significant correlation include endosulfan, *cis*-chlordane and *cis*-nonachlor. Endosulfan is still currently used in many northern countries as a contact insecticide, with application rates being highest during the warmer months (Hoff *et al.* 1992)

Others factors such as compound stability and current usage must be considered when interpreting arctic atmospheric trend data. For example, *trans*-chlordane actually showed a decline during June, July and August, unlike the more stable isomer *cis*-chlordane. Photodegradation of the *trans*-isomer is believed to account for this decrease during the summer, a similar observation has also been reported from the Norwegian Arctic (Oehme *et al.* 1996). For other compounds such as the HCHs, only the Tagish site showed any correlation with temperature, any pattern at Alert and Dunai being blurred by elevated levels occurring during April and May. Fresh use of these compounds in temperate regions during the spring (either as lindane (γ-HCH) or technical-HCH) followed by long-range transport into the Arctic, are likely to account for these elevated concentrations (Oehme *et al.* 1996, Haugen *et al.* in press). For p,p'-DDT, the active constituent of the DDT group, no discernible seasonal trend was observed, the extremely low levels encountered at each of the arctic sites made the identification of seasonal trends extremely difficult. On the other hand, the metabolite p,p'-DDE, was found to have a negative correlation ($p < 0.05$) with temperature. That is, elevated levels were found during the colder winter months at both Tagish and Alert (1993–1994). Again this observation was supported by a separate Norwegian study (Oehme *et al.* 1996), however, at present no plausible explanation can account for these observations.

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Figure 2a Alert

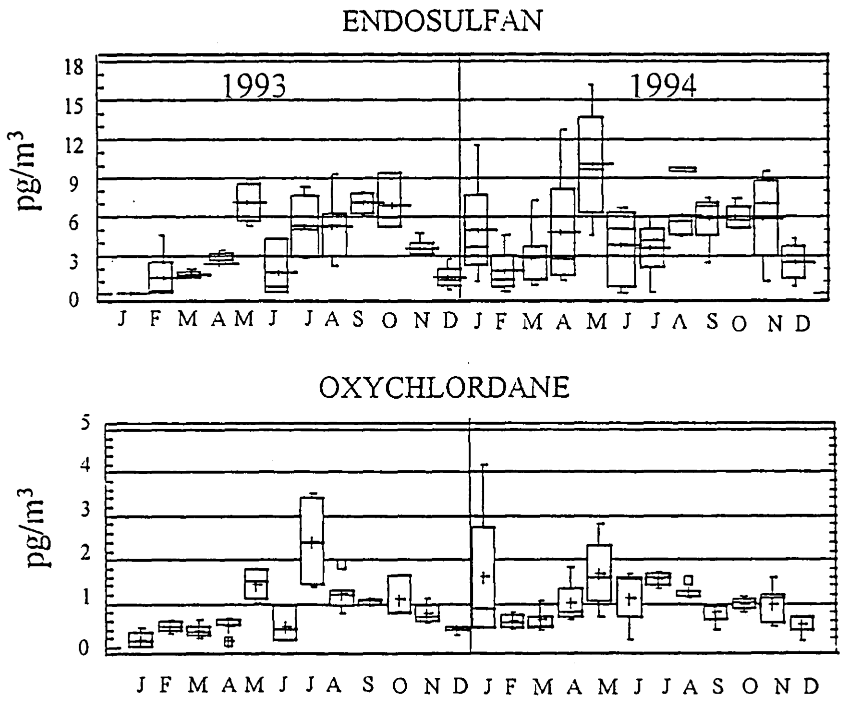

Figure 2b Tagish

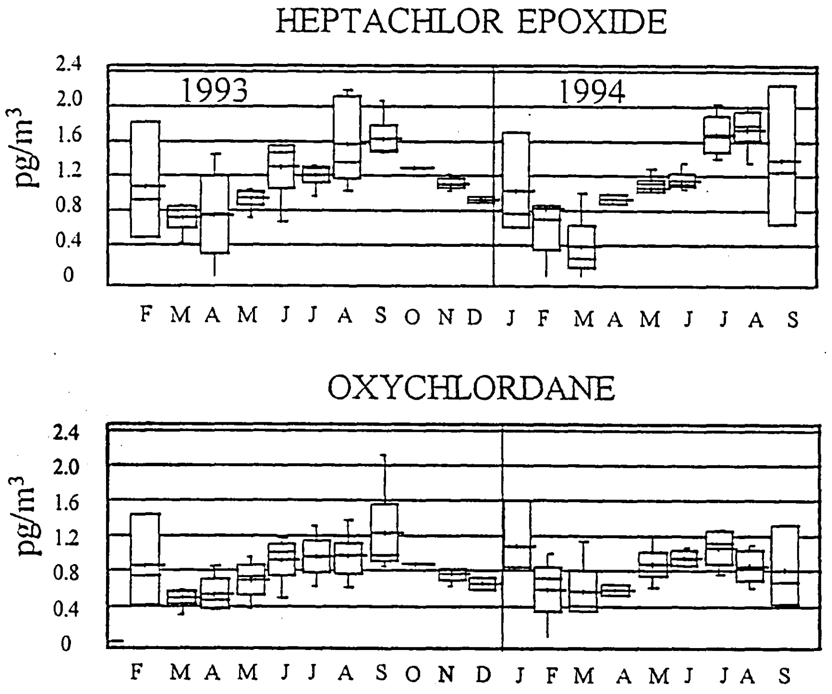

Figure 2. Monthly time series (box & whisker plots) of selected OC pesticides for the sample years of 1993/94. a) Alert b) Tagish

NORTHERN CONTAMINANTS AIR MONITORING: SPATIAL AND TEMPORAL VARIABILITY OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) AND ORGANOHALOGEN COMPOUNDS AT ALERT (NWT), TAGISH (YUKON) AND DUNAI (SIBERIA) (1992–1994)

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OBJECTIVE

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

DESCRIPTION

Weekly atmospheric measurements of selected polycyclic aromatic hydrocarbons (PAHs), organohalogen pesticides and polychlorinated biphenyls (PCBs) have been carried out at several sites in the Canadian Arctic and one site in the Russian Arctic. Sampling commenced in January 1992 at Alert (NWT), followed by Tagish (Yukon) in December 1992 and lastly at Dunai Island (E. Siberia) in March 1993. To date, the dataset is largely complete for the period 1992–1994. As these compounds are semi-volatile the dataset consists of separate filter (particle phase) and polyurethane foam (PUF) (vapour phase) measurements for each compound over the entire sampling program. Added to this, a quality control program consisting of annual minimum detection limits derived from routine field blanks, has been implemented for both filter and PUF concentrations for each sample site. As this is the first large-scale Arctic air monitoring program for toxic organics, attention has focused on total concentrations (particle + vapour), with a view to examining temporal and spatial variations in the Arctic atmosphere and the influence of source regions. In order to make the data more manageable, the dataset has been broken down into the various compound classes. So far a detailed analysis of the PAHs and PCBs has been undertaken for three of the sample sites (Alert, Tagish, and Dunai), with a detailed look at the organohalogen pesticides for the Tagish site.

RESULTS AND DISCUSSION

Spatial and temporal trends of PAHs in the Arctic atmosphere

Overview

Following several studies in the Norwegian Arctic and over the Greenland ice cap PAH contamination in the Arctic environment is now believed to be dominated by atmospheric input (Pacyna and Oehme 1988 Masclet *et al.* 1993). Kawamura *et al.*. (1994) studying ice cores from the Greenland ice cap have shown a dramatic increase in PAH concentrations over the last 100 years in good agreement with the historical record. Similarly, Jaffrezo *et al.* (1994) examining surface snow samples also on the Greenland ice cap, reported that the PAH contamination was essentially due to fossil fuel combustion with some inputs from biomass burning. Therefore, in order to assess the contemporary Arctic atmosphere, PAH air concentrations from the northern contaminants air monitoring program are presented for the 1992–1994 sampling period.

Air concentrations

Summarizing the data, the total(t)-PAH mean (geometric) annual air concentrations for Alert were 465 (1992) 444 (1993) and 330 pg·m^{-3} (1994), while Tagish had concentrations of 194 and 249 pg·m^{-3} for 1993 and 1994 respectively. Dunai in eastern Siberia displayed the highest annual mean concentration of 508 pg·m^{-3} for 1993 (t-PAH=16 compounds: acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]-fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3cd]perylene, dibenz[a,h]-anthracene, benzo-[ghi]perylene). The more southerly Tagish site experienced the lowest mean annual concentrations out of the three sites. For both 1993 and 1994 the mean t–PAH concentrations were lower than Alert by factors of 2.2 and 1.3 respectively. Although naphthalene was found to be the most abundant PAH in the Arctic atmosphere it was excluded from this data set due to its probable underestimation as a result of a sampling artifact.

Seasonal variation

Table 1 displays the individual PAH concentrations for the haze period of 1993/94 along with the corresponding warmer period of May–September 1993 for all three sites. At Alert, however, the warmer period of 1994 has been displayed rather than that of 1993 due to a localized contamination event occurring in July/August of that year. Overall, mean concentrations were greatly reduced during the warmer months, with many of the heavier compounds being below detection limits. The majority of the PAH loading occurs during the colder months, this can be observed in Figure 1 which displays a box-and-whisker plot of monthly t–PAH concentrations for the three sites. At Alert, the mean t–PAH concentration during the cold period was an order of magnitude higher than the warmer season. Indeed, the colder months account for the majority of the annual PAH loading, with concentrations in the high Arctic (Alert and Dunai) typically >1 ng·m^{-3}. These elevated concentrations coincide approximately with the haze period, characterized by an input of anthropogenic-derived aerosol into the Arctic troposphere (Barrie and Bottenheim 1991). From Figure 1 the months with the elevated PAH concentrations occur from November through to March. To display this seasonality, Figure 2 presents the geometric mean concentrations of phenanthrene, benzo[a]pyrene and t–PAH at Alert for the sampling years of 1992/93/94. Both phenanthrene and benzo[a]-pyrene follow the same pattern as the t–PAH with elevated concentrations during the months of November through to March.

Similar to the observed occurrence of PAHs in temperate remote locations (McVeety and Hites 1988, Baker and Eisenreich 1990) the annual PAH profile at the Arctic sites was dominated by the lighter compounds of fluorene and phenanthrene with significant contributions by fluoranthene and pyrene. Figures 3a and 3b display the PAH profiles (vapour plus particulate) at the three sample sites for the haze period of October–April 1993/94 and the corresponding warmer period of May–September 1993. With the exception of retene, the PAH profile during the haze period shows an agreement between the three sites. This would indicate the lack of influence from local sources over any one site during this period. At each site the lighter compounds of phenanthrene and fluorene comprised approximately 50% of the total. The profile for the May–September period shows a marked decrease in the heavier compounds ((five rings) for Tagish and Dunai. However, increases in the relative abundance of retene (a marker for soft wood combustion (Ramdahl 1983)) may indicate the influence of forest fires on the Arctic region at this time of year. Furthermore, the abundance of the less stable benz[a]anthracene over chrysene, at both Tagish and Dunai, would support this scenario of a regional source influence. Alert, however, displays a marked contrast with a greater abundance of the heavier compounds, notably fluoranthene, pyrene, chrysene and benzo[b]fluoranthene. Reasons for this profile difference at Alert during the warmer period of 1993 is essentially due to a contamination event mentioned previously, this occurred from the sample week of July 20th until August 15th and involved the combustion of waste fuel and materials at the Alert military base during a cleanup operation (Alert Laboratory Report 1993). Total-PAH concentrations during this period were comparable to concentrations occurring during the colder haze months (see Figure 1).

Long-range transport

In order to examine PAH contamination during the haze period, air mass back trajectories were computed for February 1994, the month when all three sites were running concurrently and displayed the highest mean concentrations. Five day back trajectories were computed every six hours throughout the whole of this month. The general air flow directions for each site are presented in Figure 4, the two high Arctic sites of Alert and Dunai being clearly influenced by air originating from the Eurasian land mass. Tagish, on the other hand, tends to receive air from the Pacific region, air mass back trajectories being calculated at the 700 mb level due to the elevated location of this site. Interestingly, PAH concentrations for this month are highest in the order of Dunai > Alert > Tagish, indeed for the whole haze period of 1993/94, PAH concentrations at Dunai are significantly higher than the other two sites (Table 1). Figure 5 shows the mean concentrations of phenanthrene (50% particulate bound) and benzo[a]pyrene (100% particulate bound) for February 1994, for both compounds there is a clear decrease from Dunai to Tagish, by a factor of ~10 and ~15 for phenanthrene and benzo[a]-pyrene respectively. Dunai, therefore, is clearly influenced by source regions to the west and south, the higher concentrations reflecting the proximity of this site to source regions. Tagish, however, comes under the influence of air masses largely from the eastern Pacific, but also from North America. Air masses originating from the Pacific region can be considered clean with regards to PAHs and may help to explain why this site displayed the lowest concentrations during the haze period.

Regional influences

Although the haze period consistently displays the highest concentrations for all the sample sites, episodes lasting for a week or longer (where concentrations are comparable to, or higher than, the haze period) occur at other times of the year and require further investigation. The geometric annual means reported in Table 1 (PAHs

Table 1. Seasonal PAH concentrations at Alert, Tagish and Cunai 1993/94 (pg·m-3)

	Alert				Tagish				Dunai			
	Oct.-Apr.		May-Sept.		Oct.-Apr.		May-Sept.		Nov.-Mar.		May-Sept.	
	93/94		94		93/94		93		93/94		93	
Mean Temp. ˚C	-3		-2		-10		11		-30		0	
PAH	**Arith. mean (SD)**	**Geom. mean**	**Arith. mean (SD)**	**Geom. mean**	**Arith. mean (SD)**	**Geom. mean**	**Arith. mean (SD)**	**Geom. mean**	**Arith. mean (SD)**	**Geom. mean**	**Arith. mean (SD)**	**Geom. mean**
ACENAPY	8.73(4.88)	7.57	<0.460	<0.460	4.67(3.08)	3.83	5.94(2.16)	5.74	41.6(69.6)	23.8	14.6(11.9)	11.4
ACENAP	6.97(1.47)	6.84	2.06(0.981)	1.86	15.4(2.66)	15.3	13.6(4.85)	13.1	40.4(69.3)	23.4	9.83(8.81)	7.73
FLUO	311(268)	183	15.1(2.92)	14.8	94.7(80.7)	68.5	20.5(13.5)	17.3	843(757)	555	52.9(54.6)	35.7
PHEN	95.5(61.6)	79.3	30.2(5.79)	29.7	78.6(42.0)	69.6	87.8(38.3)	80.3	499(336)	403	92.5(76.7)	73.1
ANTH	4.44(1.90)	4.05	2.40(0.706)	2.33	4.56(3.06)	3.77	3.21(3.55)	2.44	9.13(7.26)	6.65	8.21(11.2)	4.52
FLA	78.5(60.9)	53.1	11.2(5.41)	10.2	28.5(24.0)	20.3	12.4(5.74)	11.2	369(315)	279	17.7(21.8)	12.4
PYR	51.4(38.4)	36.2	10.2(3.25)	9.71	22.8(21.2)	16.2	14.1(6.60)	12.8	224(196)	166	19.3(24.6)	12.9
RET*	<3.65	<3.65	13.1[1]	-	62.1(137)	20.6	446(1290)	29.8	11.9(7.14)	10.1	83.5(243)	22.1
B[a]A	11.8(6.42)	10.6	4.42[1]	-	3.99(3.44)	2.99	11.6(13.2)	5.82	29.5(26.8)	21.1	5.57(4.68)	3.73
CHRY	29.7(25.9)	16.6	1.72(1.12)	1.46	7.69(9.33)	4.28	2.68(4.94)	1.13	116(108)	77.7	2.92(3.12)	1.76
B[b]F	36.6(35.0)	23.9	2.66(0.73)	2.58	9.62(11.3)	6.16	7.92(14.2)	3.17	127(114)	93	3.05(5.04)	0.440
b[k]F	11.9(9.66)	8.42	<0.560	0.560	3.92(4.56)	2.56	0.62(0.07)	0.61	38.3(32.8)	28.9	0.72(1.74)	0.127
B[e]P	25.7(30.4)	10.3	1.55[1]	-	8.16(9.91)	5.61	28.0(39.9)	5.16	95.1(91.1)	67.6	1.84(2.18)	0.530
B[a]P	7.27(6.15)	3.83	2.32[1]	-	3.81(5.17)	2.21	12.5[1]	-	26.5(25.6)	18.0	0.83(0.86)	0.299
I[123-cd]P	18.9(13.8)	5.26	<0.360	<0.360	3.37(8.15)	3.84	<1.80	<1.80	60.5(41.7)	49.3	<0.801	<0.801
D[ah]A	2.53(3.49)	6.36	<0.140	<0.140	4.37[1]	-	0.413(1.17)	0.037	7.80(5.77)	6.29	<0.02	<0.02
Bghi]P	12.6(11.04)	2.67	<0.140	<0.140	8.93(7.61)	6.52	0.380(1.08)	0.037	48.2(34.3)	38.7	0.73(1.22)	0.090
DBTHPH*	23.5(18.22)	16.8	5.21[1]	-	11.1(5.73)	9.93	12.9(5.31)	12.2	61.2(46.7)	46.3	17.5(14.4)	13.8
PERY*	3.44(1.85)	3.01	3.51[1]	-	1.96(2.55)	0.423	<0.397	<0.397	5.83(5.89)	3.2	<0.02	<0.02
T-PAH (minus*)	720(578)	458	83.9(20.9)	72.7	312(240)	235	149(95.7)	130	2570(1820)	1990	212(197)	160

[1] Concentration occurring for one sample week

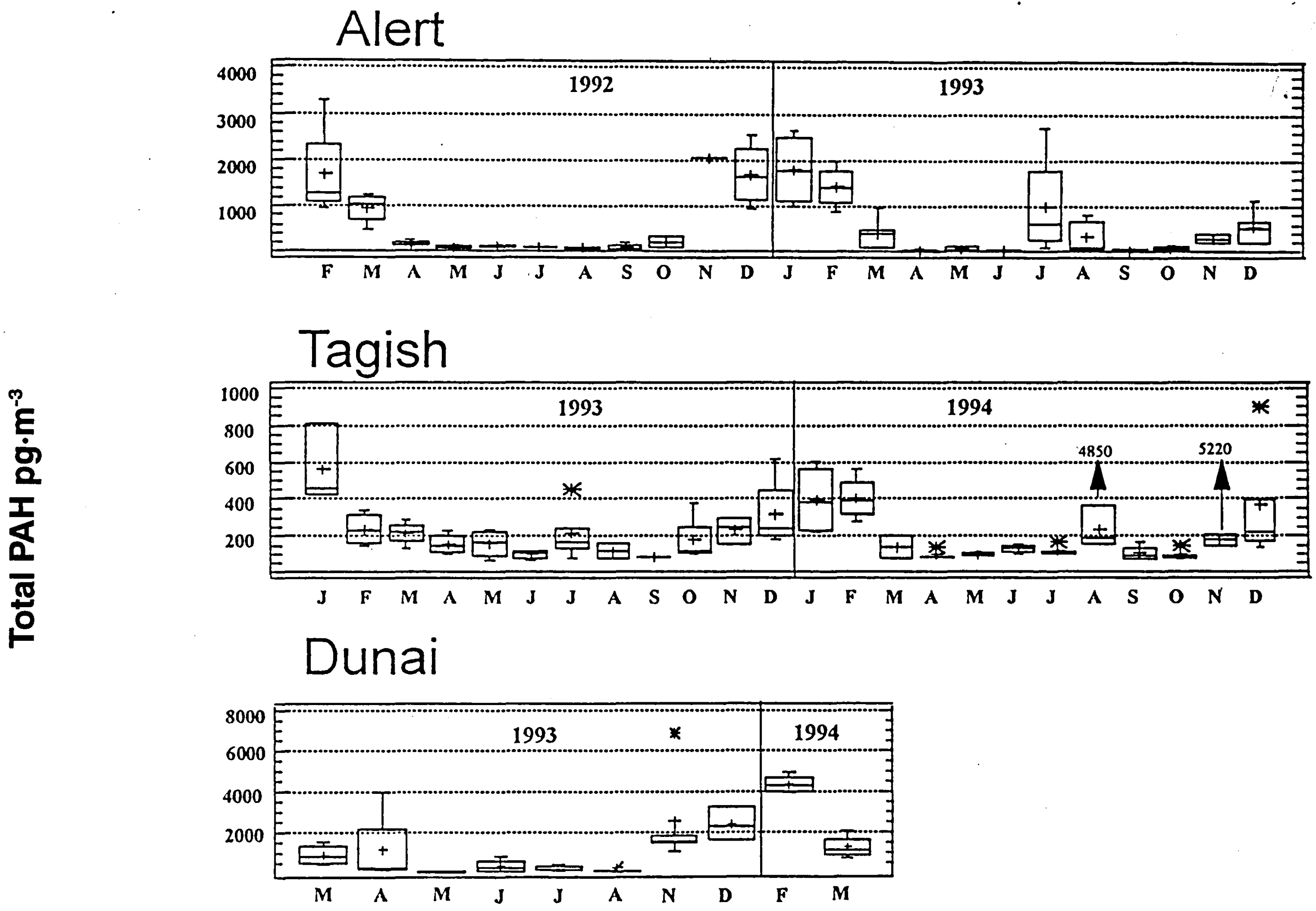


Figure 1. Monthly t-PAH concentrations (pg·m-3) at Alert, Tagish and Dunai. The cross in each box represents the arithmetic mean, the line represents the median. For any one month outlier weeks are represented by an asterisk.

have a log-normal distribution in the atmosphere (Leister and Baker 1994)) have the effect of smoothing elevated concentrations associated with events or episodes. For example, retene, an alkylated three-ringed PAH (1-methyl-7-isopropylphenanthrene) comprised >70% of the t–PAH concentration in the Tagish atmosphere during August and November 1994. Concentrations of retene exceeded 1 ng·m^{-3} on the sample weeks starting the 11th and 18th of August. These Elevated concentrations of PAHs in the Tagish atmosphere during these weeks (t–PAH >4 ng·m^{-3}), marked in particular by retene, are believed to be the result of forest fires. In general, PAH concentrations were higher at Tagish than at Alert during the warmer months (retene, by a factor of 8) which probably indicates the influence of forest fires on the more southerly Arctic regions.

Organohalogen compounds in the Arctic atmosphere

Air concentrations

Table 2 presents a summary of the organohalogen concentrations for 1993 and 1994 at Alert, Tagish and Dunai. Those compound classes comprising of several isomers and/or metabolites are reported as the sum of the individual components, i.e. Σchlordane, ΣDDT. The mean annual concentrations for 1993 are displayed graphically in Figure 6 and show the lack of large spatial variations in air concentrations, indicating a uniform contamination of the polar region over an annual basis. However, elevated mean concentrations of chlordanes, DDTs and endosulfan at Tagish may indicate the relative proximity of this site to North American and Asian source regions. Oehme *et al.* (1996) reporting organochlorine (OC) concentrations in the Norwegian Arctic throughout 1993, found that elevated levels of *trans*-chlordane coincided with air mass movement primarily from North America. Similarly, chlorinated veratroles (metabolites of chlorinated guaiacols and catechols released from bleached kraft mill effluents) have mean concentrations in the order of Tagish > Dunai > Alert, again probably indicating the proximity of these sites to this type of industry. OC concentrations range from 100's pg·m^{-3} for chlorobenzenes and HCHs, to >1 pg·m^{-3} notably for mirex, endrin and trifluralin (a fluorinated herbicide), where maximum concentrations at any of the sites do not exceed 1 pg·m^{-3}.

Long-range transport to the Yukon

Analysis of OC concentrations at Tagish in the Yukon (Bailey *et al.* in prep.), has shown a seasonality in air concentrations with several compounds showing a reasonable correlation with temperature. For example, heptachlor epoxide, oxychlordane and α-HCH displayed significant correlations with inverse temperature. In other words, concentrations were elevated during the warmer months of the year and reduced during the cold periods. Factors blurring this relationship include high concentrations associated with long-range atmospheric transport. For instance, elevated concentrations of *cis*- and *trans*-chlordane, oxychlordane, heptachlor epoxide, dieldrin, α-HCH, γ-HCH and *p,p'*-DDE were observed during the sample week of the 7–14th January 1993. Air mass back trajectories over this period revealed the movement of air from as far away as India, where DDT and HCH are still used for mosquito control in both agricultural and urban areas. Indeed, higher ratios of *p,p'*-DDE/(*p,p'*-DDT + *p,p'*-DDE), than those predicted by temperature for this period, are probably due to the conversion of applied *p,p'*-DDT to *p,p'*-DDE. This photodegradation process occurs post application in agricultural areas and/or during long-range transport.

Interestingly, source regions can be identified by air mass back trajectories and often accompanied by a change in OC profile. For instance, two further episodes occurring during the sample weeks of December 16th 1993 and January 27th 1994, observed elevated concentrations of endosulfan but reduced concentrations of hexachlorobenzene. Air mass back trajectories showed China and Siberia as the source region. Bailey *et al.* (in prep.) summarized that reduced concentrations of hexachlorobenzene (HCB) were probably due to there being no reported use of HCB in China. However, it must be noted that HCB is also released both as a by-product in the synthesis of organochlorine products and from the incomplete combustion of chlorinated wastes from the chemical industry (Muir, pers. comm.). Elevated levels of *p,p'*-DDE along with *o,p'*-DDT were probably from the volatilization of past-use DDT. Furthermore, due to the distance of Tagish from source regions, more stable metabolites of many of the pesticides often prevail. For instance, the ratio of *trans*-chlordane (TC)/*cis*-chlordane (CC) is ~0.8 during the colder months and drops further during the warmer months to ~0.2. As a comparison, technical chlordane has a ratio of TC/CC of 1.26, the lower ratios in Tagish air representing the loss of the less stable TC. Application of chlordane for agricultural uses in Asia would likely occur during the winter months and reflect the fact that ratios of TC/CC at Tagish for this time of year are closer to the technical mixture. The lower ratio of 0.2 during the warmer months may indicate a more aged source, possibly the volatilization of previously deposited chlordane. This is supported by the fact that the ratio of oxychlordane/TC actually increases at Tagish during the warmer months. Suprock *et al.* (1980) have shown that *trans*-chlordane is primarily removed in soils by transformation to oxychlordane.

Table 2. Summary of organohalogen pesticide concentrations (pg·m^{-3}) in the Arctic atmosphere – Alert, Dunai and Tagish (1993/94)

ALERT 1993	ΣCBz	ΣHCH	OCSTYR	ΣCHLOR	DIELD	ΣDDT	MIREX[1]	PCA	ENDOSUL	MEOCL	ΣCL-VER	ENDRIN	TRIFL	ΣTOX
Mean	97.1	71.7	0.60	5.19	1.18	0.82	0.10*	2.53	3.61	0.26	0.97	0.18	0.12	4.43
Min.	13.5	15.2	0.10	0.65	0.06	0.12	0.03	0.01*	0.02*	0.07*	0.10	0.05*	0.03*	0.34
Max.	205	145	1.47	17.2	3.18	2.24	0.26	8.19	9.42	0.72	1.95	0.50	0.32	16.4
1994[2]														
Mean	94.3	76.9	0.98	6.65	1.42	1.40	0.10	3.12	4.89	0.28	1.44	0.20	0.13	5.33
Min.	5.08	7.22	0.20	1.24	0.03*	0.25	0.07	0.17*	0.07*	0.18	0.24	0.13*	0.08	1.09
Max.	526	369	2.96	23.1	4.16	6.79	0.52	20.5	16.2	1.43	10.2	0.99	0.64	12.8
DUNAI 1993	ΣCBz	ΣHCH	OCSTYR	ΣCHLOR	DIELD	ΣDDT	MIREX	PCA	ENDOSUL	MEOCL	ΣCL-VER	ENDRIN	TRIFL	ΣTOX
Mean	85.7	50.9	0.60	4.55	1.11	0.93	0.16	2.92	2.99	0.41	1.93	0.28	0.18	4.70
Min.	21.2	0.71	0.11	0.40	0.02*	0.24	0.08	0.95	0.05*	0.22	0.30	0.15	0.10	1.05
Max.	228	93.2	1.74	10.3	2.04	2.02	0.28	6.92	7.18	0.74	5.85	0.51	0.33	12.4
TAGISH 1993	ΣCBz	ΣHCH	OCSTYR	ΣCHLOR	DIELD	ΣDDT	MIREX	PCA	ENDOSUL	MEOCL	ΣCL-VER	ENDRIN	TRIFL	ΣTOX
Mean	52.7	91.3	0.44	5.63	0.91	1.39	0.11	2.56	5.76	0.31	2.17	0.22	0.13	5.12
Min.	12.6	87.6	0.08*	1.98	0.04*	0.26	0.05*	0.09*	0.08*	0.13*	0.34*	0.09*	0.06	1.42
Max.	196	178	1.31	10.4	2.15	3.21	0.17	5.11	15.3	1.12	6.97	0.44	0.21	14.6
1994[3]														
Mean	44.0	80.4	0.69	5.19	0.81	1.51	0.10	2.25	6.58	0.28	2.05	0.2	0.12	5.35
Min.	13.9	0.52*	0.10	0.71	0.04	0.25	0.06	0.04*	0.08*	0.17	0.23	0.11*	0.07	1.13
Max.	88.3	166	1.65	7.61	2.83	3.23	0.14	5.27	13.9	0.38	6.94	0.47	0.17	10.5

[1] Incuding photo-Mirex

[2] Up to week ending the 26th Sept.

[3] Up to week ending the 25th Aug.

* Below MDL

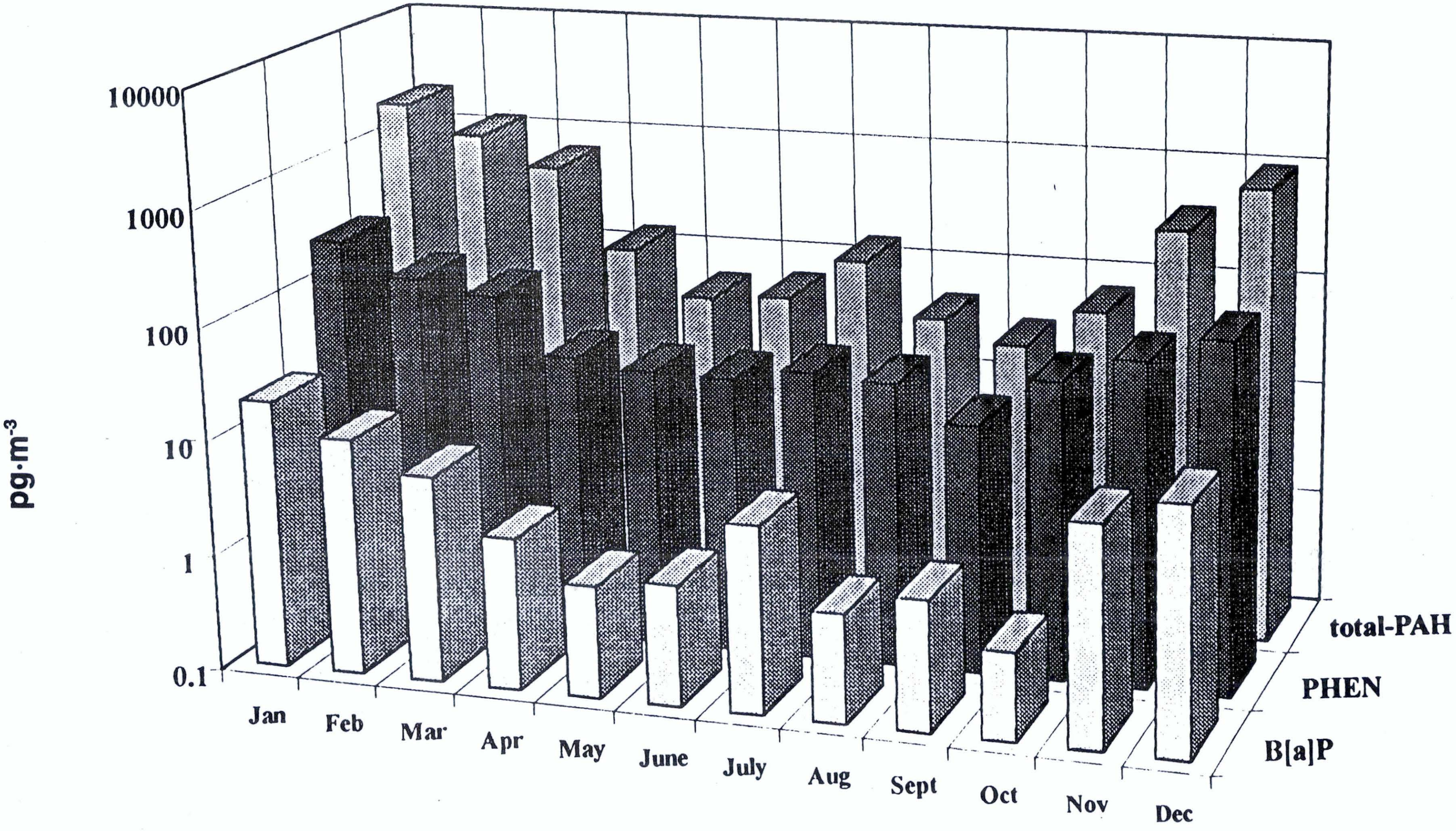


Figure 2. Monthly geometric means at Alert (1992/93/94) for the total-PAH, phenanthrene (PHEN) and benzo[a]pyrene (B[a]P). (Note that July is elevated due to high concentrations occurring during July 1993).

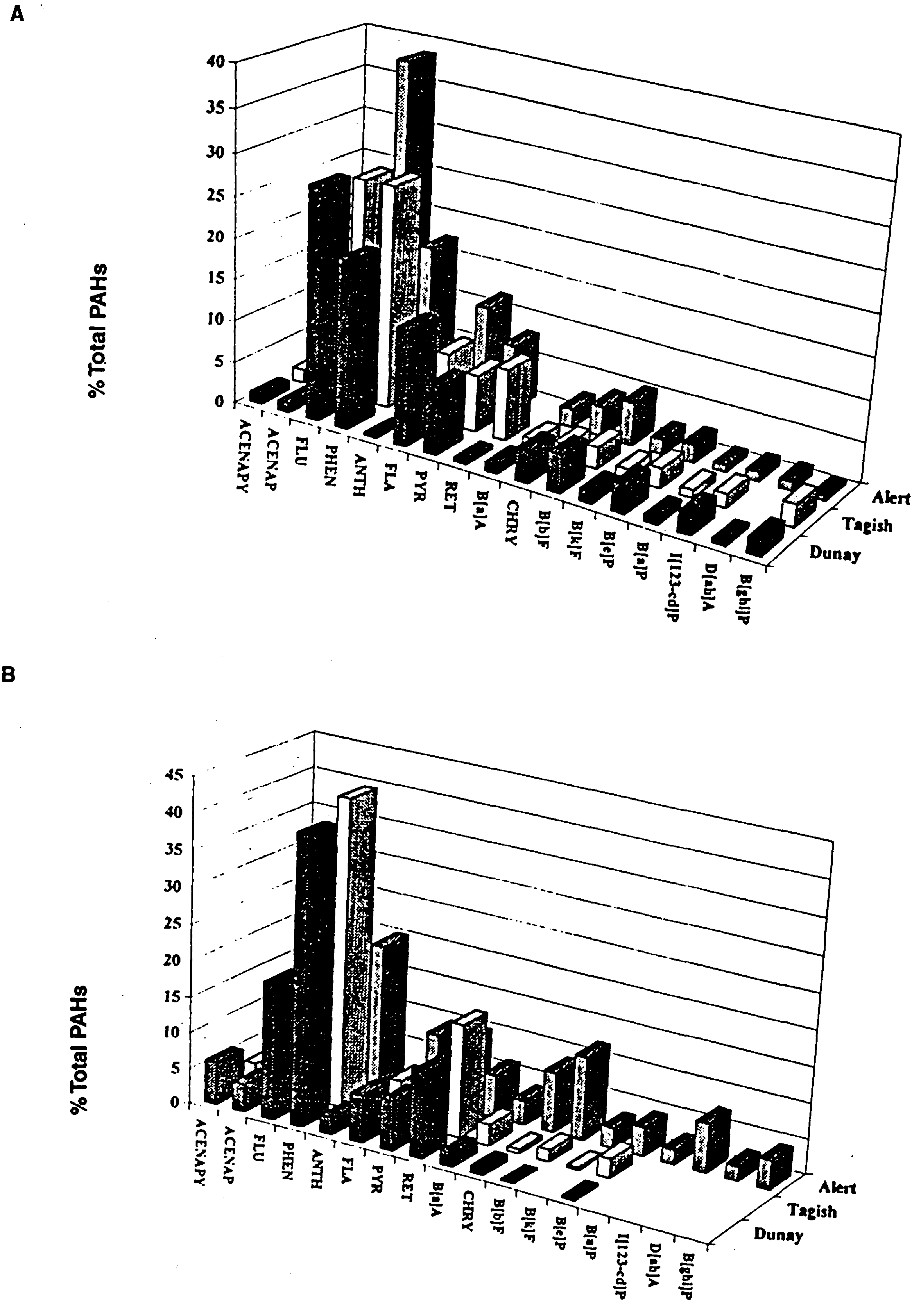
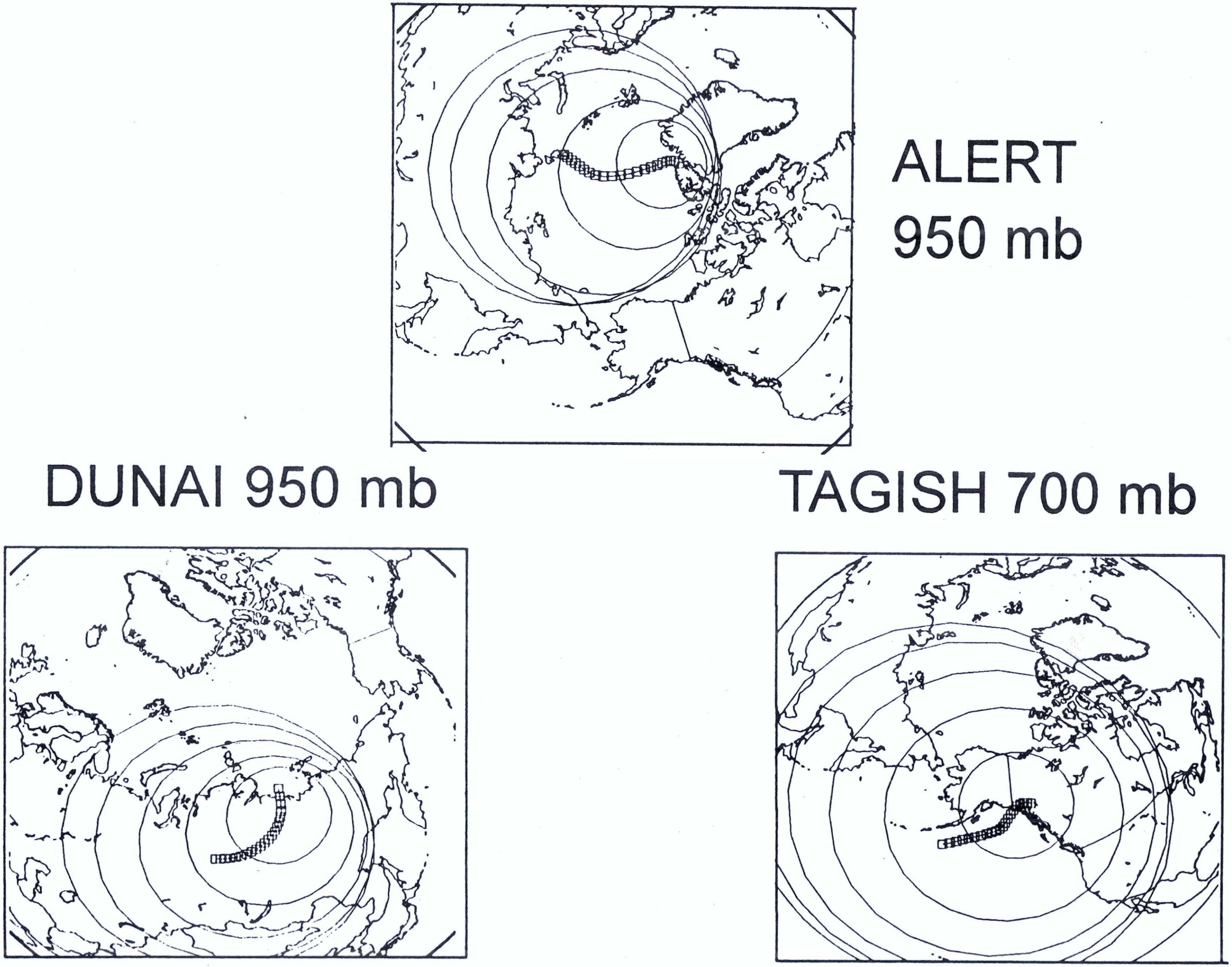


Figure 3. PAH profile in the Arctic atmosphere: A) 'Cold period' (Nov.–Apr. 1993/94); B) 'Warm period' (May-Sept. 1993/94).



ALERT 950 mb

DUNAI 950 mb

TAGISH 700 mb

Figure 4. Mean air flows for the three sites during February 1994. Five day back trajectories carried out at the 925 mb level for Alert and Dunai and 700 mb for Tagish (an elevated site ~1500 m).

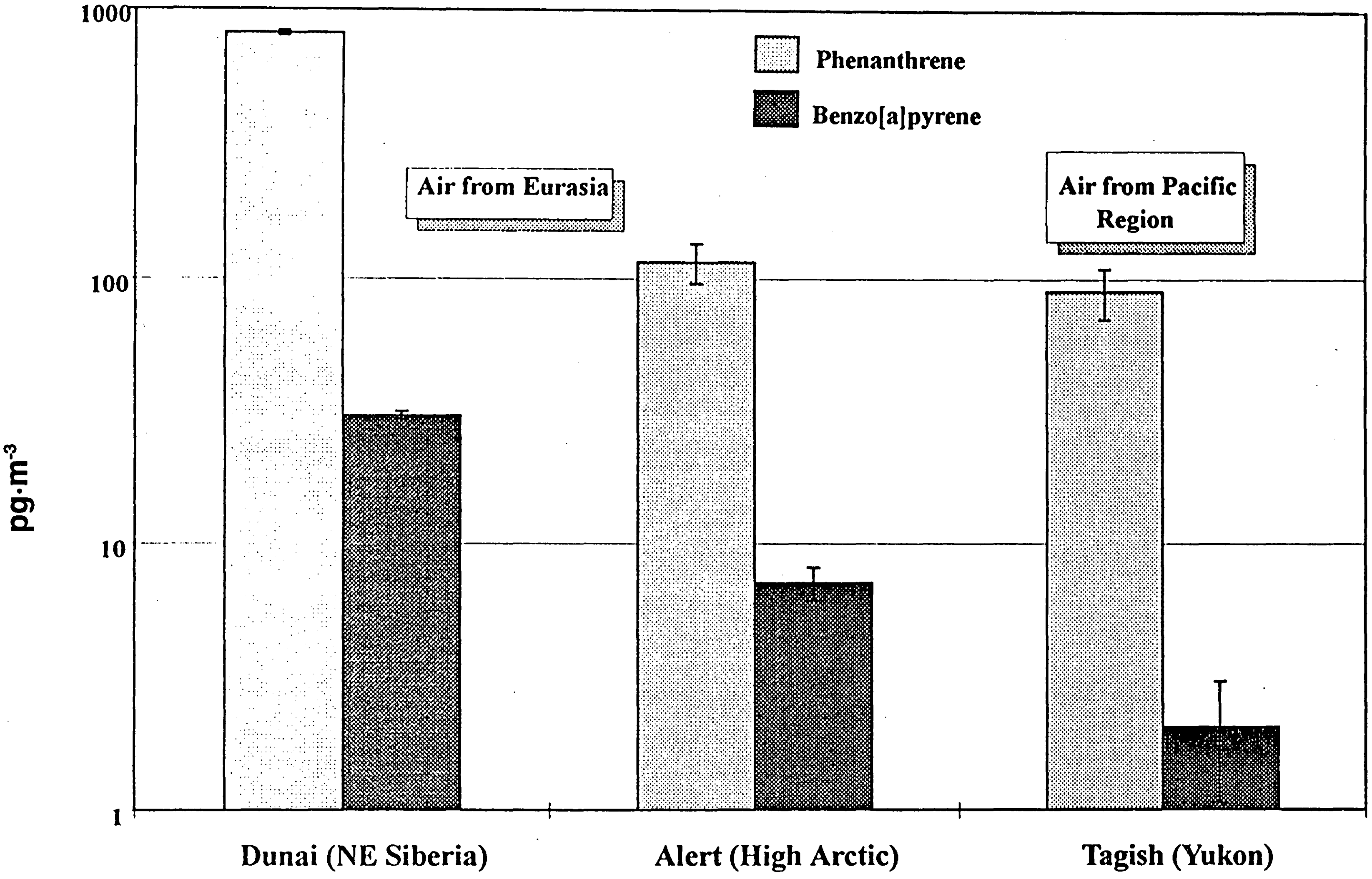


Figure 5. Mean concentrations (pg·m^{-3}) of phenanthrene (PHEN) and benzo[a]pyrene (B[a]P) for February 1994 at the three Arctic sites.

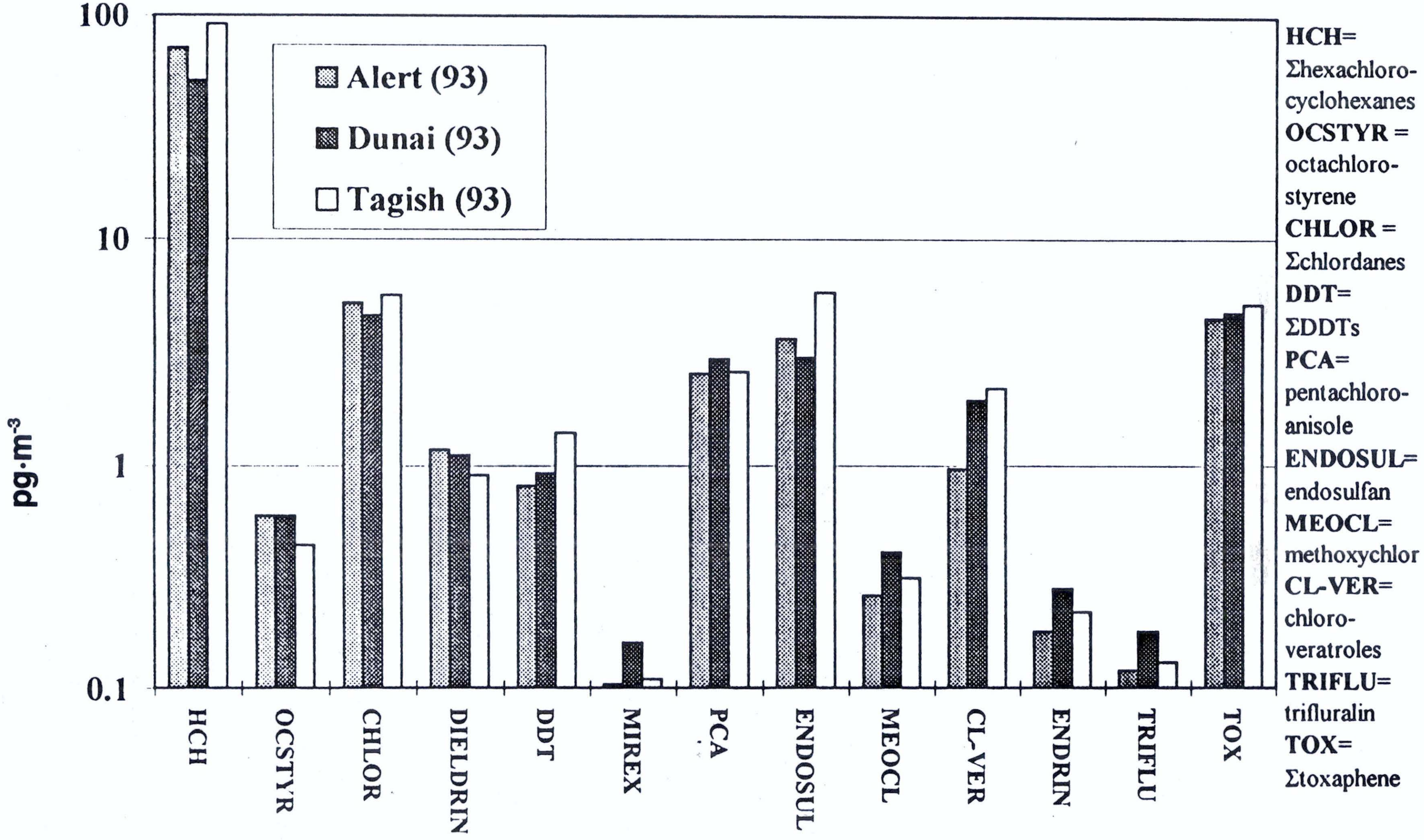


Figure 6. Mean annual organohalogen pesticide concentrations (pg·m^{-3}) for 1993.

Comparison with the Norwegian Arctic

A separate Norwegian study at Ny Ålesund on Spitzbergen Island has allowed for a direct comparison of OC observations from the Northern Contaminants Program. Oehme *et al.* (1996) carried out air sampling for a 48 h period every week for the greater part of 1993, where sampling commenced in April (week number 13) and finished in December. Figures 7a and b compare the sample week concentrations at both Alert and Ny Ålesund for α- and γ-HCH respectively. Mean concentrations (pg·m^{-3}) of both isomers were higher at Ny Ålesund (mean α=78.4(5.3, γ=14.2(1.1) than at Alert (mean α=60.4(3.5, γ =10.6(1.0). Furthermore, summarizing the whole period, Alert displayed a slightly higher α/γ-HCH ratio (6.3(1.7) than Ny Ålesund (5.8(1.9), indicating (along with the lower air concentrations) that Alert is probably less influenced by regional sources over an annual basis than Ny Ålesund. Elevated inputs of γ-HCH at Ny Ålesund can be observed in Figure 7b for weeks 20 and 30, the α/γ-HCH ratio, however, does not change significantly. Oehme *et al.* (1996) suggested that this was due to air moving from a source region such as Russia or Asia, where technical HCH (85% α-HCH, 10-15% γ-HCH) is still in use, rather than Europe where application of pure γ-HCH (Lindane) still occurs. At Alert, the lowest ratios occur in mid May for weeks 19 and 20 (α/γ-HCH=2.9), indicating fresh inputs of γ-HCH into the Canadian high Arctic at this time of year.

Polychlorinated biphenyls

The weekly t–PCB (t=90 congeners) concentrations are displayed in Figure 8 for the Alert, Tagish and Dunai sample sites throughout 1993 and 1994. Mean concentrations for 1993, the year when all three sites were running concurrently, were 27.9, 17.2 and 34.2 pg·m^{-3} at Alert, Tagish and Dunai respectively. Oehme *et al.* (1996) monitoring PCBs at Ny Ålesund, Spitzbergen, reported a mean annual (1993) t–PCB concentration of 13.1 pg·m^{-3}. In this study only a subset of 10 congeners (AMAP congeners) were reported, the equivalent annual mean concentrations for Alert, Tagish and Dunay, using the same ten congeners, were 6.04, 3.70, 8.15 pg·m^{-3} respectively. From Figure 8 seasonal variations in the total concentrations were not evident. This is in contrast to studies carried out in more southerly latitudes, when a summer maximum was observed (Hoff *et al.* 1992, Halsall *et al.* 1995). Reasons for this lack in seasonality are not clear, but may be related to the fact that these Arctic sites are well removed from temperate source areas. Oehme *et al.* (1996) argued that temperatures at Ny Ålesund may not exceed a threshold whereby significant volatilization occurs off surfaces. This scenario may also be applicable to the high Arctic sites of Alert and Dunai of the Canadian Program, but does not explain the lack of seasonality at Tagish, where temperatures often exceed 20°C during the warmer months (Figure 8). Characteristics of the Tagish site, given its location in the Pacific North-West and its higher elevation (~1500 m), relative to the other sites, may be important factors in explaining this anomaly. Nevertheless, taking the Arctic region as a whole, temperatures are considerably lower than those in mid-latitudes, coupled to the fact that contamination of surfaces is considerably less than in temperate regions, may help to explain the lack of seasonality in air concentrations.

Figure 9 presents a summary of the PCB-homologue profiles on a monthly basis. The lighter tri-chlorinated homologue is dominant at each of the sites. Notable exceptions to this occur at Dunai from May to July 1993, were the profile is dominated by the heavier penta-chlorinated homologue. Air mass transport is believed to play an important role in this phenomenon, indeed, at Ny Ålesund the incursion of air masses from southerly regions of Europe/Russia accounted for the majority of sample weeks when PCB concentrations were elevated (Oehme *et al.* 1996). One notable contamination episode occurred at Alert during 10th–17th January 1994 (Figure 8). During this period the profile was dominated by the lighter di-, tri- and tetra-homologues, the air coming directly from central Siberia and the island of Novaya Zemlya.

SUMMARY

1) Mean annual PAH concentrations were in the order of 100's pg·m^{-3} with the majority of the loading occurring during the colder haze period. During February 1994 t-PAH concentrations were highest in the order of Dunay (4.2 ng·m^{-3}) > Alert (1.4) >Tagish (0.5) with air mass back trajectories suggesting PAH contamination from source regions in Eurasia. The more southerly site of Tagish, however, displaying the lowest concentrations, was largely influenced by air from the eastern Pacific during this period.

2) Elevated concentrations or episodes during the warmer season (May–Sept) results in several sample weeks where concentrations are comparable to, or higher than, the haze period. Greater contributions of retene in the atmospheres of Dunai and Tagish, marked by several weeks of high concentrations (>1 ngRET/m^{3}) at the Tagish site, indicate the influence of forest fires on this region. The most northerly site at Alert can be influenced by local anthropogenic activity during this warmer period, as in July and August of 1993.

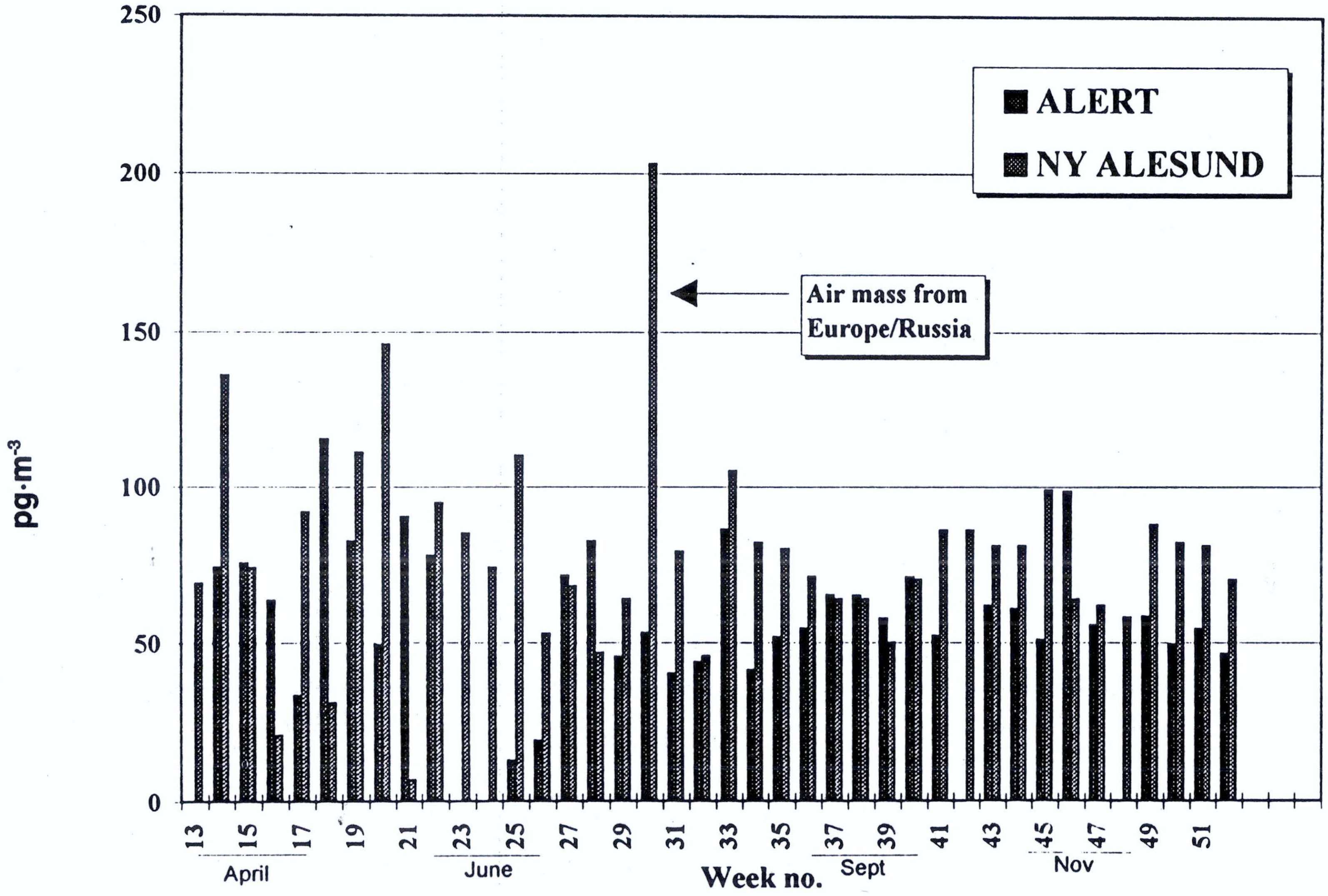


Figure 7a. Weekly α–HCH concentrations (pg·m-3) at Alert and Ny Alesund, Spitzbergen. April–December 1993.

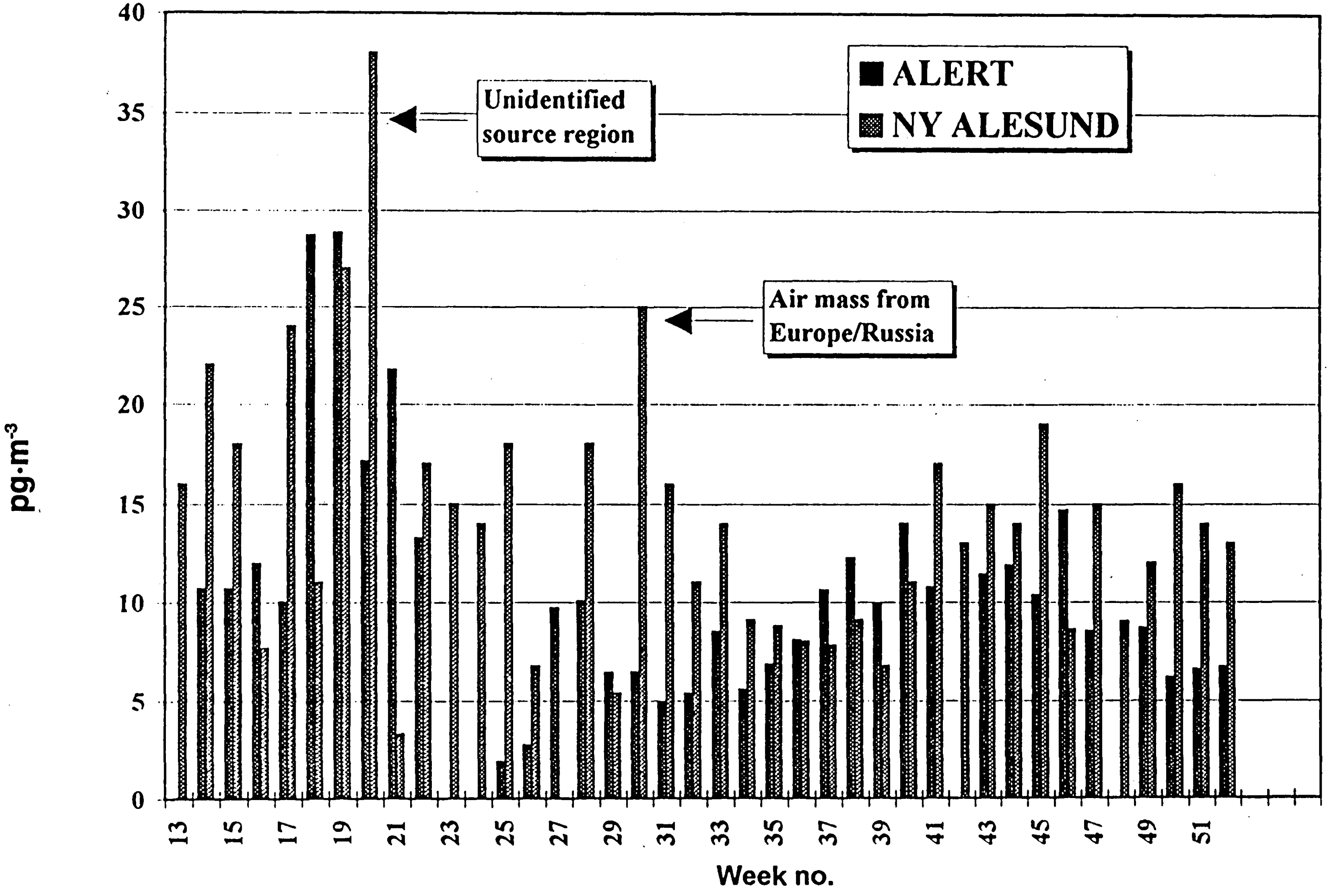


Figure 7b. Weekly γ–HCH concentrations (pg·m^{-3}) at Alert and Ny Alesund, Spitzbergen. April–December 1993.

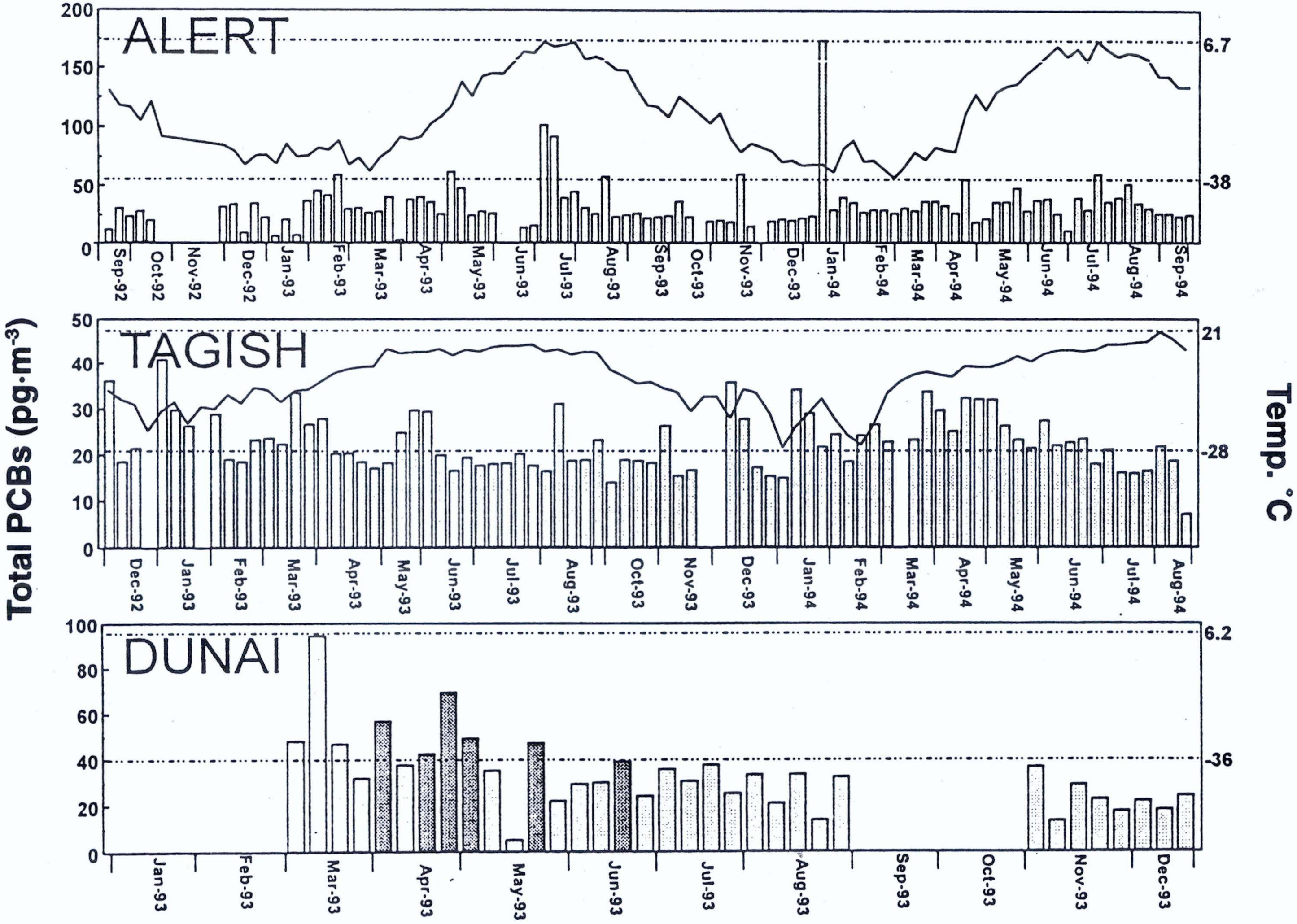


Figure 8. Weekly total-PCB concentrations (pg·m^{-3}) at Alert, Tagish and Dunai. Sampling at Dunai commenced in March 1993. (Missing weeks indicate sample loss through error or mechanical failure).

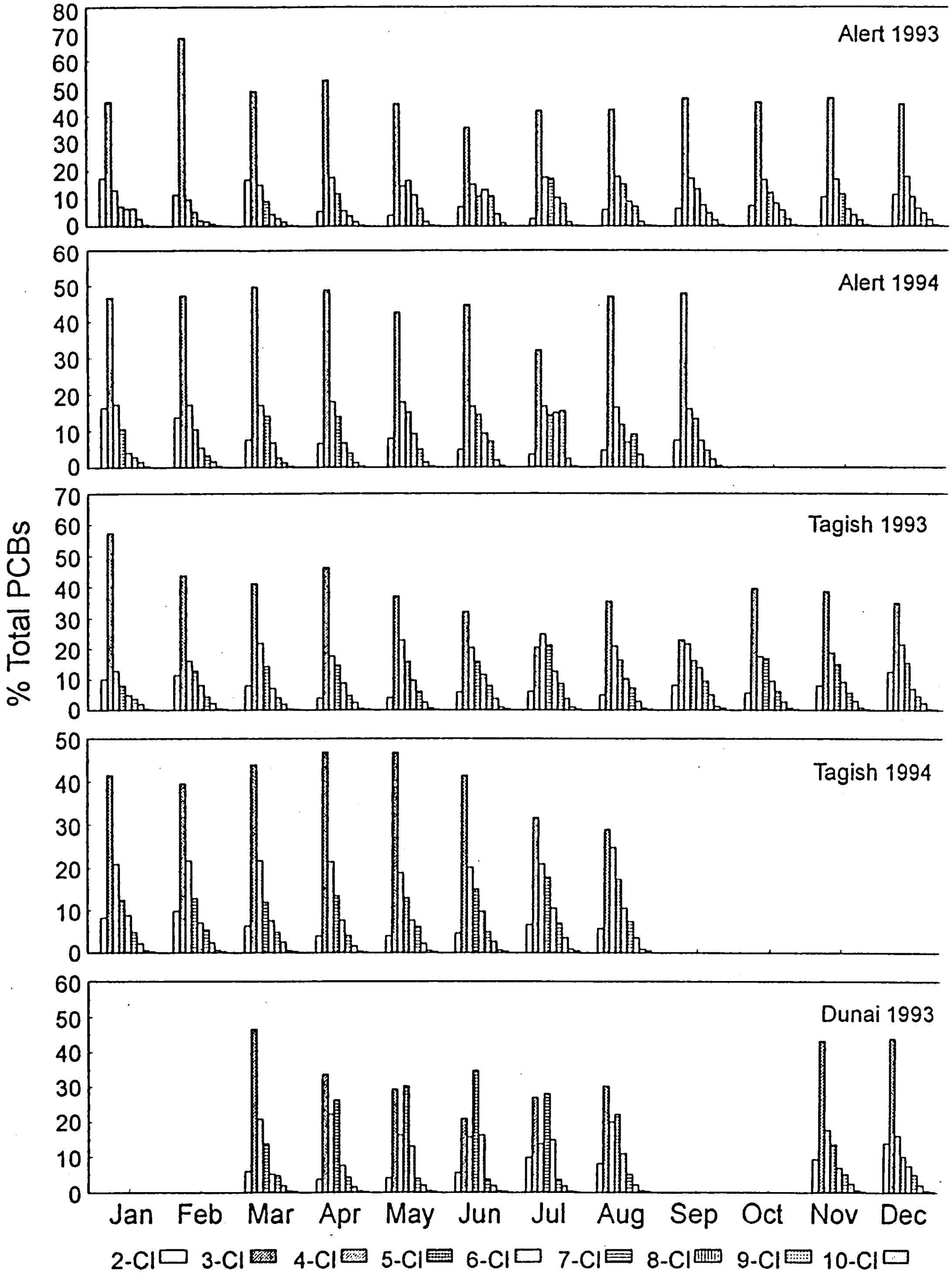


Figure 9. Monthly PCB-homologue profiles in the Arctic atmosphere (% of total PCBs).

4) Large spatial differences in the annual mean (1993) organohalogen concentrations were not evident between the three sites. Mean annual concentrations ranged from 100's pg/m^3 for chlorobenzenes and HCHs, to >1 pg·m^{-3} for mirex, methoxychlor, endrin and trifluralin.

5) Mean annual (1993) t-PCB concentrations were 17.2, 27.9 and 34.2 pg·m^{-3} for Tagish, Alert and Dunai respectively. Mean annual t-PCB concentrations (where t=10 AMAP congeners) for the three sites ranged from 3.70 – 8.15 pg·m^{-3} compared to the 1993 mean of 13.1 pg·m^{-3} at Ny Ålesund in the Norwegian Arctic (Oehme *et al.* 1996). The trichlorinated homologue dominated the PCB profile at each site on a monthly basis, however, increases in the heavier homologues during the warmer months was evident at Alert and Dunai.

Further work for the coming year

1) A detailed examination of the PCB and organohalogen pesticide concentrations at all three NCP sites to establish spatial and temporal information.
2) Use of air mass back trajectories to establish source regions and explain contaminant characteristics peculiar to each site.
3) Further investigation into the partitioning of semi-volatile organic compounds in the Arctic atmosphere. Utilization of partitioning theory to predict the gas-particle distribution at ambient Arctic temperatures.

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ATMOSPHERIC TRANSPORT AND CYCLING OF TOXAPHENE AND OTHER ORGANOCHLORINE PESTICIDES IN THE ARCTIC OCEAN

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OBJECTIVES

1. Determine concentrations and compare the gas exchange rates of chlorobornanes (CHBs, e.g. toxaphene) and hexachlorocyclohexanes (HCHs) in arctic waters.
2. Determine the physicochemical properties of CHBs that affect their atmospheric transport and deposition.
3. Characterize the changes in HCHs and CHBs that accompany transfer from air to water to the lower food chain.

DESCRIPTION

Toxaphene and similar pesticides are complex mixtures consisting largely of chlorinated bornanes (CHBs) with a small proportion of chlorinated camphenes. The theoretical number of components having 6 to 10 chlorines is over 16,000 (Vetter *et al.* 1993), although only a few hundred of these are likely to occur in the environment to a significant extent (Hainzl *et al.* 1995). CHBs are the most abundant organochlorine (OC) pesticide residues in fish and marine mammals in the Canadian Arctic (Muir 1996, Kidd *et al.* 1995, Norstrom and Muir. 1994) and have been found in milk from women in arctic Quebec (Stern *et al.* 1992). Selective metabolism (Bidleman *et al.* 1993, Hargrave *et al.* 1993, Miskimmin *et al.* 1995, Muir *et al.* 1992) and physical "weathering" due to the differential volatility and water solubility of the components (Bidleman *et al.* 1995a) lead to profiles of CHB residues in biota that are substantially altered from their pattern in technical toxaphene. Despite the uniformly high occurrence of CHBs in the arctic food chain, they are the most poorly understood OCs with respect to levels in arctic air and water and physicochemical properties.

More information is available on environmental concentrations and physicochemical properties of hexachlorocyclohexanes (HCHs) than for any other OC pesticide, making them the best candidate substances for investigating transport and exchange processes and for global modelling. Moreover, the air-water exchange properties of HCHs are similar to those of CHBs. The overall goal of this study is to develop a better understanding of how CHBs and other OCs are transferred from air to water to the lower food chain in the Arctic Ocean. To this end we are investigating the air-water gas exchange of CHBs, HCHs and other OC pesticides and using selective chemical markers as indicators of metabolism in the water column as a basis for understanding air-water and water-biota exchange processes. The work described in this report is a continuation of previous studies which have been published in other Northern Contaminants Program documents (Bidleman 1994, 1995).

ACTIVITIES IN 1995/96

In FY 95/96 we completed the analysis of the samples from the 1994 Arctic Ocean Sections cruise (AOS-94) for CHBs, HCHs and other OC pesticides. Concentrations of these were determined in surface water samples from across the Arctic Ocean to establish spatial trends. It is unfortunate that the main target compounds—CHBs—were not able to be measured in the air samples from AOS-94 because of chromatographic interferences (despite the use of negative ion mass spectrometry). Here we present the data for CHBs and HCHs in water and HCHs in air. The analytical results for other OCs (chlordanes, nonachlors, endosulfans) need to be finalized and will be reported in 1996/97.

We also synthesized the results of our investigations for the Canadian Arctic Contaminants Assessment Report (Barrie 1996), and have taken the lead in writing two special topics sections for this report, one on the budget of HCHs in the Arctic Ocean and the other on the atmospheric transport and deposition of toxaphene.

RESULTS AND DISCUSSION

Spatial Trends of HCHs and CHBs in Ocean Water

A continuing emphasis in this work is to obtain measurements of HCHs, CHBs and other chlorinated pesticides in the Arctic Ocean and its regional seas. The surface water data are coupled with atmospheric concentrations to estimate air-sea gas fluxes. Two cruises in the Bering-Chukchi seas (BERPAC-93, August–September 1993) and across the polar cap (AOS-94, July–September 1994) provided good coverage of the western portion for HCHs and CHBs (Figure 1). Over 50 measurements of HCHs were made in the surface and deep water of the Bering-Chukchi seas in 1993 and 1994 (Jantunen and Bidleman 1995, 1996). These results are used in budget calculations which show that the flow through Bering Strait provides 21% of the HCH input to the Arctic Ocean (Barrie 1996).

Concentrations of HCHs (Figure 2a) and CHBs (Figure 3) are two to three times higher in the surface water of the Canada Basin than in the Bering-Chukchi seas. Both OCs peak close to the North Pole and then fall off in the Greenland Sea. The following scenario is suggested to account for the curious peaking of CHBs and HCHs in high-latitude waters: Atmospheric levels of HCHs in the early to mid-1980s were about four to eight times higher than present-day values (Bidleman *et al.* 1995b, Jantunen and Bidleman 1995). Although CHB measurements in arctic air are sparse, a comparison of measurements from 1986–87 and the early 1990s suggests that CHBs were also higher in the last decade, perhaps by a factor of 2–6 (Barrie 1996). Thus it is likely that atmospheric loadings of these pesticides were greater in the past, especially to the marginal seas which surround the central Arctic Ocean. These seas are largely unfrozen during the summer months and are susceptible to gas exchange, whereas exchange at higher latitudes is inhibited by the ice cap. Over time, water which received loadings of CHBs and HCHs by gas exchange has been transported from the regional seas into the central Arctic Ocean. Today the marginal seas have cleared themselves by outgassing and sedimentation and have thereby become adjusted to reduced atmospheric inputs, but these processes do not operate efficiently in the high Arctic. Volatilization is retarded by the ice cap and sedimentation takes place more slowly because of lower productivity. CHBs and HCHs which are trapped under the polar cap are thus "ghosts of the past", and their future decline is pegged to the water residence time of approximately 10 to 20 years (Barrie 1996).

Water is drained from the central Arctic Ocean primarily through the Canadian Archipelago and secondarily via the East Greenland Current (Barrie 1996). As a consequence, outflow of polar water containing high concentrations of CHBs and HCHs will impact biota in the Archipelago and Baffin Bay. Hargrave et al. (1996) monitored OC pesticides in the upper 50 m of the water column at Resolute Bay for the year of 1993. Mean concentrations of HCHs (4100 pg/L) and CHBs (85 pg/L) were similar to levels found under the polar cap on AOS-94 (Figures 2a and 3).

Air-Sea Gas Exchange

Atmospheric concentrations of HCHs and the α-HCH/γ-HCH ratio in air from BERPAC-93 and AOS-94 are summarized in Figures 2b and 2c. An interesting decline in α-HCH with increasing latitude can be seen in Figure 2b, from about 100–120 pg/m^3 over the Bering-Chukchi seas to 50–80 pg/m^3 over the polar cap. The high-latitude values from the cruise agree excellently with those measured at Alert (Fellin *et al.* 1996). The concentration dip may result from: a) reduction in sea-to-air transfer by the ice cap (see below), b) scavenging of HCHs by fog, which is often prevalent over the ice cap, and c) limited transport of HCHs into the high Arctic during summer.

The air-water flux of gaseous HCHs and CHBs is estimated by the two-film model, which considers the resistance to transfer to be limited by diffusive exchange across thin air and water films at the air-sea interface. Discussions of the relevant equations and their application to the exchange of persistent organic pollutants in lakes and oceans are given by Bidleman and McConnell (1995). The potential for net exchange is expressed by the water/air fugacity ratio, f_w/f_a (Bidleman and McConnell 1995, Jantunen and Bidleman 1995):

$$f_w/f_a = C_wH/C_aRT \quad (1)$$

where C_w and C_a are the dissolved and gaseous concentrations in water and air (ng/m), H is Henry's law constant at the water temperature (Pa m^3/mol), T is the air temperature (K) and R is the gas constant (8.31 Pa m^3/mol K). When deposition and volatilization take place at the same rate (equilibrium) the fugacity ratio is 1.00 and the net flux is zero. Values of the fugacity ratio <1.00 and >1.00 imply net deposition and volatilization.

Based on air and water measurements from BERPAC-93 and AOS-94, fugacity ratios of α-HCH are >1.00 in all regions of the Bering-Chukchi seas, the Canada Basin and the Greenland Sea. (Figure 2d). Oversaturation of γ-HCH occurs in the Bering Sea and in the Canada Basin north of 75°. The potential for volatilization is greatest near the North Pole where water concentrations are

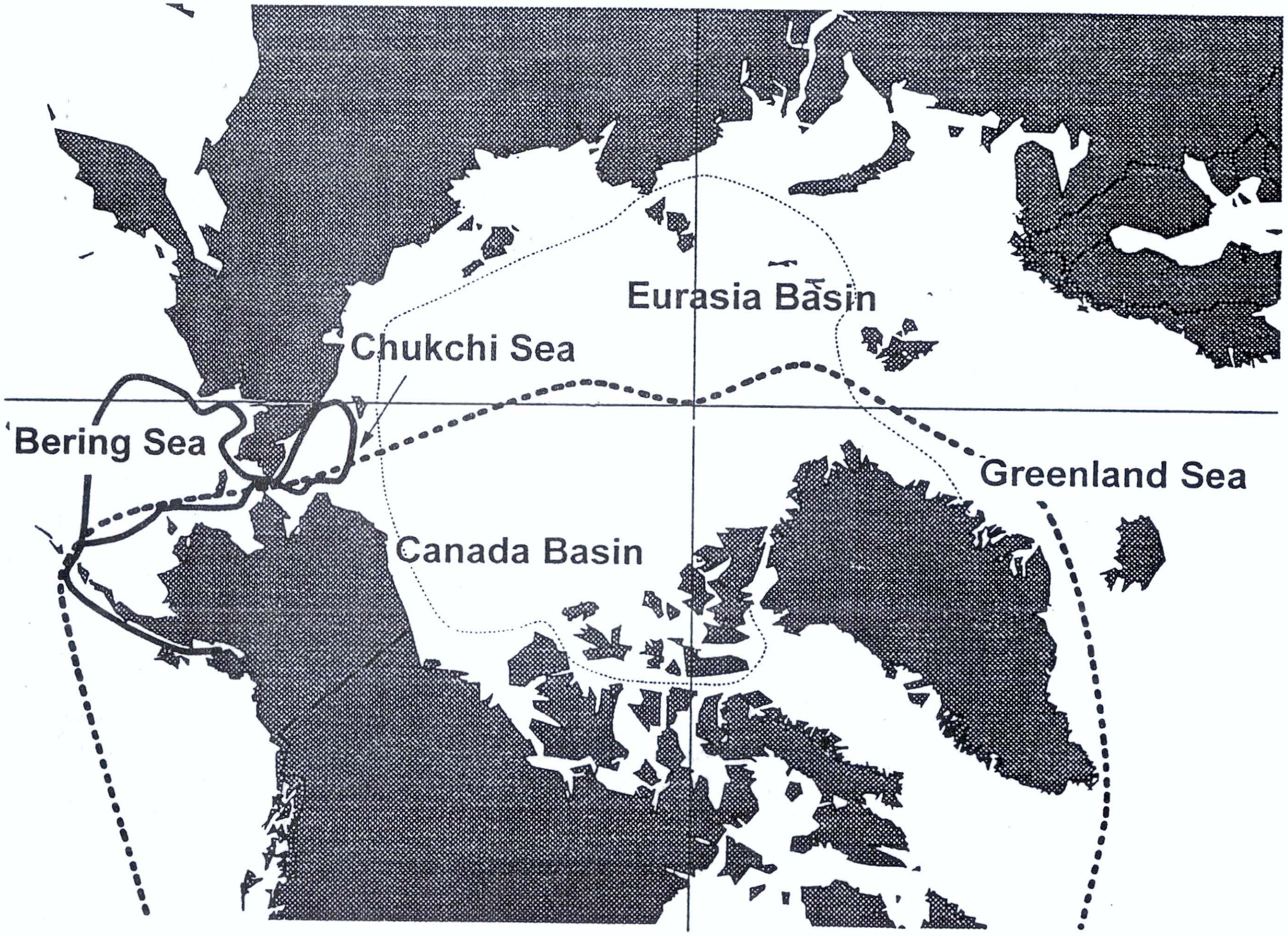

Figure 1. Cruise tracks of 1993 Bering-Chukchi (BERPAC-93, solid line) and 1994 Arctic Ocean Sections (AOS–94, dotted line) expeditions.

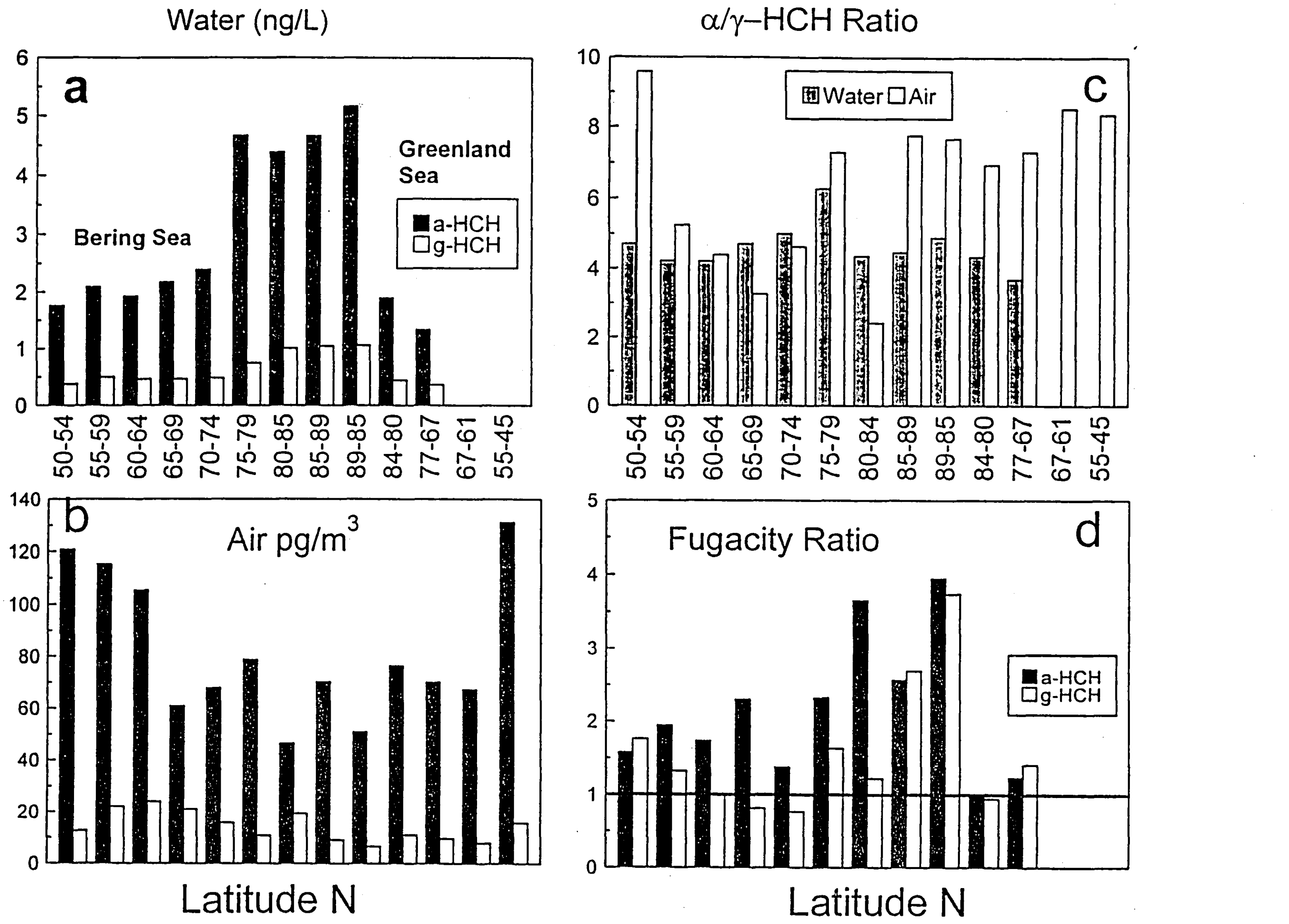

Figure 2. a) Concentrations of HCHs in surface water from samples collected on BERPAC-93 and AOS–94 cruises, grouped in five-degree latitudinal bands; b) Ratios of α–HCH/γ–HCH in water and air; c) Variation in atmospheric concentrations of HCHs with latitude, from the Bering Sea across the polar cap to the Greenland Sea. c) Water/air fugacity ratios of HCHs in different latitudinal regions.

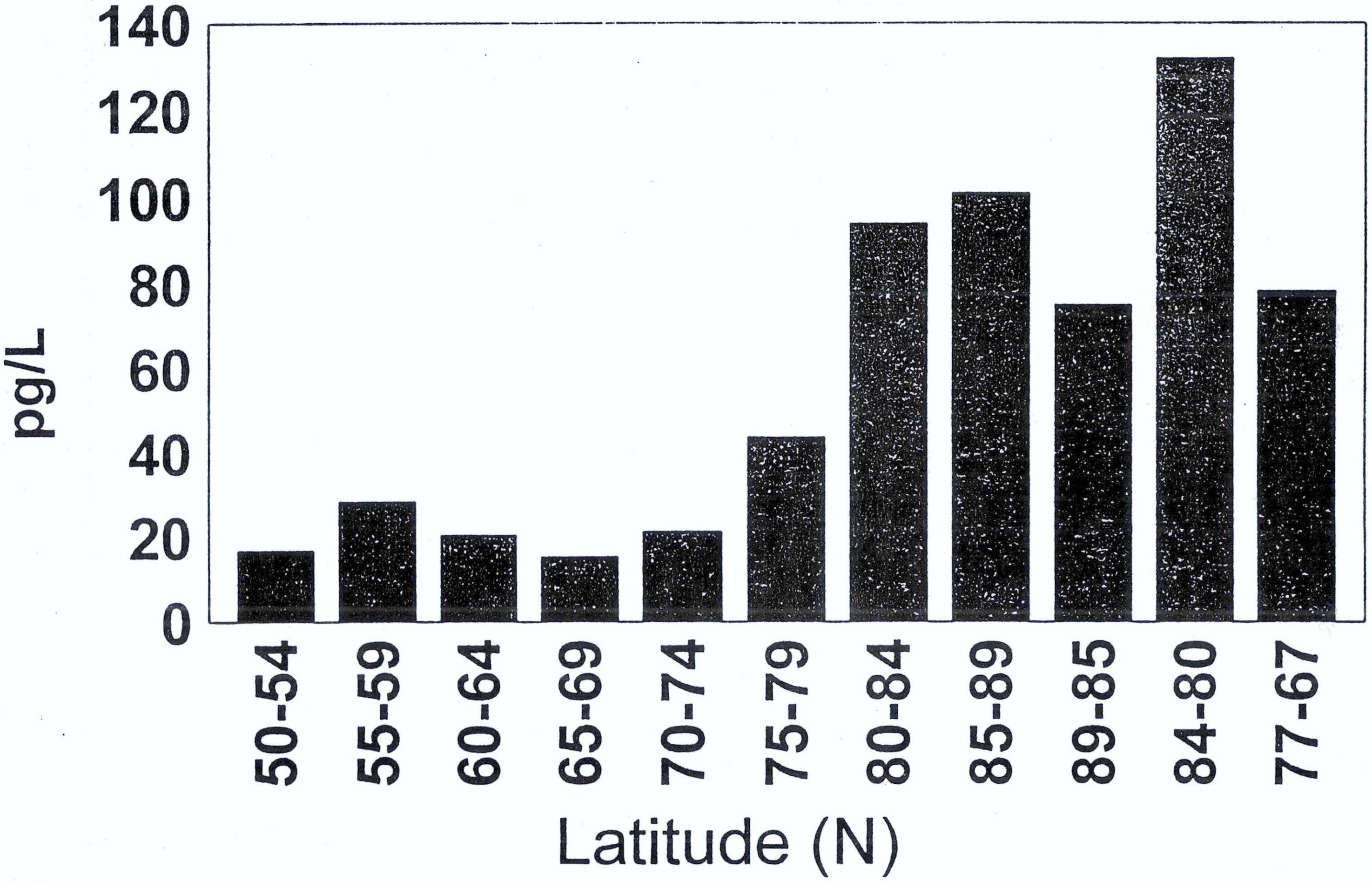

Figure 3. Variation in the concentration of CHBs in surface water with latitude on BERPAC–93 and AOS–94.

highest, but fluxes are limited by the extensive ice cover. Most gas exchange of HCHs and CHBs takes place in the Eurasia Basin and its regional seas, where the fraction of open water is greater on an annual basis (Barrie 1996).

Tracing Gas Exchange with α-HCH Enantiomers

The two enantiomers of α-HCH are broken down at different rates in northern waters, yielding an enantiomeric ratio (ER) which differs from the racemic ER (1.00) of the manufactured product (Falconer *et al.* 1995a,b). Selective degradation of (-)α-HCH occurs in the Bering and Chukchi seas, whereas (+)α-HCH is preferentially lost in the Canada Basin and the Greenland Sea. The opposite selectivity may be related to different microbial populations in these waters (Jantunen and Bidleman 1996). Loss of (+)α-HCH increases with depth in the Greenland Sea, as shown by the enantiomeric profiles of dissolved HCHs in the water column (Figure 4). Regeneration of HCHs into the dissolved phase by biotic re-working of sinking particles may explain this observation.

Selective loss of enantiomers shows that microbial breakdown plays an important role in removing HCHs from the water column. At the present time we are unable to quantify the rate of this process other than to say that it is surely faster than chemical hydrolysis, which degrades HCHs with a half-life of >50 y at the temperature and pH of arctic seawater (Ngabe *et al.* 1993). More work is needed to assess the significance of microbial degradation in clearing HCHs and other OCs from the Arctic Ocean.

The α-HCH in air sampled within 40 m of the ocean surface shows the same enantiomeric profile as the surface water, depleted in (-) α-HCH over the Bering-Chukchi seas and (+) α-HCH over portions of the Canada Basin and the Greenland Sea (Figure 5a). When viewed in five-degree latitudinal bands (Figure 5b), the ER values for air show a clear trend from >1.00 over the Bering-Chukchi seas to near-racemic over the northern Canada Basin and finally <1.00 over the Greenland Sea. The appearance of non-racemic α-HCH in boundary-layer air is a clear indication of volatilization from surface water. The racemic ER values for air at high latitudes may due to dampening of outgassing by ice cover or mixing of air parcels arriving from east and west which are depleted in the opposite enantiomers (Jantunen and Bidleman 1996).

These results demonstrate that enantiomeric signatures in air and water can be used to distinguish "new" α-HCH from the "recycled" pesticide (Jantunen and Bidleman 1996). As evidence of this, we analysed six air samples collected in Bermuda in 1992 and four taken in Columbia, South Carolina in 1994. The ER of these samples was 1.00 ± 0.02. Concentrations of HCHs are low in the subtropical Atlantic Ocean, the net gas exchange direction is depositional (Schreitmüller and Ballschmiter 1995), and the airborne α-HCH is likely to come from long-range transport from source countries rather than from revolatilization.

CONCLUSIONS

1. Concentrations of CHBs and HCHs in the surface water of the Canada Basin are two to three times higher than those in the Bering and Chukchi seas lying to the south. This pool of enriched pesticides may be a remnant of higher atmospheric loadings in the past, coupled with more limited removal by revolatilization and sedimentation. Outflow of polar water containing elevated levels of CHBs and HCHs may impact biota in the Canadian Archipelago for years to come.

2. Declining atmospheric concentrations of a-HCH have led to a reversal of the net gas exchange direction, from deposition in the 1980s to volatilization in the 1990s. The potential for volatilization is greatest in the Canada Basin because of the high concentrations of HCHs in water, but the actual amount of outgassing is limited by ice cover. It appears that the Arctic Ocean "breathes" largely through its marginal seas and portions of the Eurasia Basin, where the ice cover is less extensive.

3. Enantioselective degradation of (-)a-HCH occurs in the Bering and Chukchi seas, whereas (+)a-HCH is preferentially lost in the Canada Basin and the Greenland Sea. The opposite selectivity may be related to different microbial populations in these waters. These results suggest that microbial activity may play a role in clearing OCs from arctic waters, but nothing is known about degradation rates at present.

4. The α–HCH in air sampled within 40 m of the ocean surface shows the same enantiomeric profile as the surface water—depleted in (-)α–HCH over the Bering-Chukchi seas and (+) α–HCH over the open water areas of the Canada Basin and the Greenland Sea. This is direct evidence of revolatilization from surface water, since the α–-HCH that has been recently transported from source regions is racemic.

Expected project completion date: April 30, 1998.

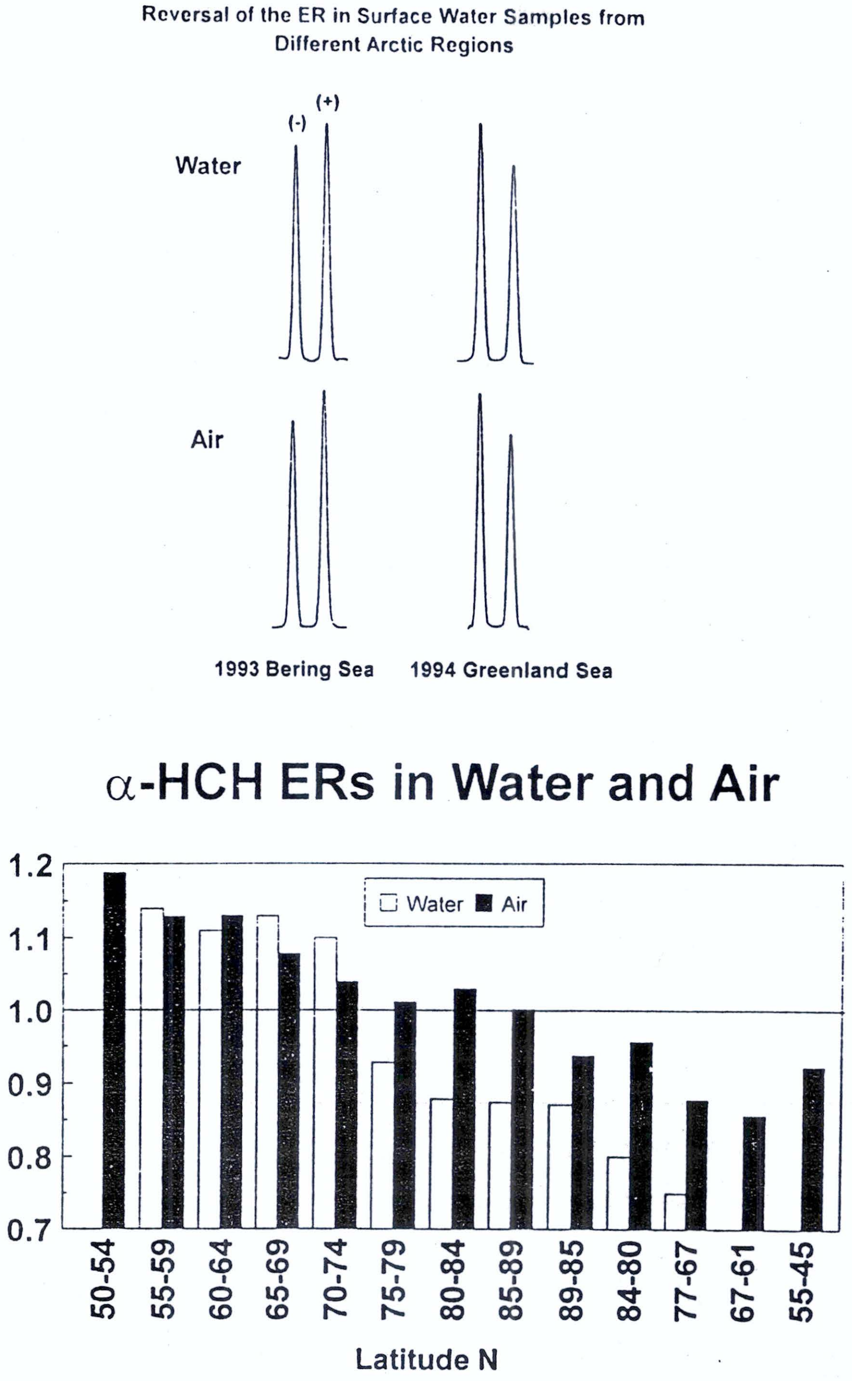

Figure 5. a) Chromatograms of the two α–HCH enantiomers in water and air from the Bering Sea and the Greenland Sea; b) Enantiomer ratios, ER = (+)/(-) α–HCH, measured in water and air on transects from the Bering Sea to the Greenland Sea, across the polar cap.

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TOXAPHENE AND HCHs IN THE ARCTIC: ATMOSPHERIC CYCLING AND TRANSFORMATION IN THE LOWER FOOD CHAIN

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Project Team: L. Jantunen (AES), T. Harner (AES), L. Barrie (AES), W. Strachan (NWRI), B. Hargrave (BIO), R. Macdonald (IOS), Henrik Kylin (Swedish Univ. of Agricultural Sciences)

OBJECTIVES

1. Determine concentrations and compare the gas exchange rates of chlorobornanes (CHBs; e.g., toxaphene) and hexachlorocyclohexanes (HCHs) in arctic waters.
2. Determine the physicochemical properties of CHBs that affect their atmospheric transport and deposition.
3. Characterize the changes in compound profiles that accompany transfer from air to water to the lower food chain.

ACTIVITIES IN 1996/97

Results from the AOS-94 Expedition

Results for HCHs (including enantiomers of α-HCH) in air and water, and CHBs in surface water samples are given in the 1995/96 report. We were unable to determine CHBs in air by GC- negative ion mass spectrometry (GC-NIMS) because of interferences at the ion masses monitored for these compounds (343, 379 and 413). Interferences were not a problem for the cyclodiene compounds (chlordanes, nonachlors, heptachlor *exo*-epoxide and endosulphans), and the levels in air are given in Table 1.

Spatial trends of organochlorines in surface water are shown in Figure 1 as average concentrations within 5° latitudinal bands. HCHs in the upper 40–60 m of the water column increase slightly along the AOS–94 track from the Chukchi Sea to the pole, then drop off in the Eurasian Basin and the Greenland Sea (Jantunen and Bidleman 1996). Peak concentrations of 2.5–2.7 ng/L α-HCH in waters north of 85° are lower than the 4–6 ng/L found in the Canada Basin and Archipelago (Jensen *et al.* 1997). In recent years, water of Atlantic origin has intruded from the Eurasian Basin into the northern portion of the Canada Basin (Macdonald 1996). The AOS–94 expedition traversed the northern Canada Basin where the two water types, containing lower and higher α-HCH concentrations, are mixed.

Chlordanes and nonachlors in surface water show less trend with latitude. Concentrations are slightly higher under the polar cap and lower in the Greenland Sea. The sum of trans- and cis-chlordane averages 2.9 ± 0.9 pg/L. The few other chlordane measurements available for comparison are from the Archipelago in 1992 (11.8 pg/L, Bidleman *et al.* 1995a) and 1993 (1.8 pg/L, Hargrave *et al.* 1997) and the Bering-Chukchi seas in 1990 (3.4 pg/L, Iwata *et al.* 1993). Heptachlor-*exo*-epoxide concentrations are highest in the central Arctic Ocean (mean 16.8 ± 3.9 pg/L) and lower in the Chukchi Sea, Eurasian Basin and Greenland Sea (mean 7.4 ± 1.7 pg/L).

CHBs also increase with latitude, from 18–32 pg/L in the northern Chukchi Sea to an average of 79±29 pg/L in central Arctic. The peak of elevated CHBs appears to be shifted slightly eastward from that of the HCHs and heptachlor *exo*-epoxide (Figure 1). This suggests that Atlantic water may have higher CHB concentrations than the Pacific water which enters through the Bering Strait. These spatial trends are based on only a few samples however, and a more thorough survey of the Arctic Ocean and its regional seas is required to define the "hot spots" and advective transport regions. Concentrations of CHBs in the Arctic Ocean compare well to those found in the Archipelago during 1992–93 (40–140 pg/L, Bidleman *et al.* 1995a, Hargrave *et al.* 1997).

HCHs in the Eastern Arctic Ocean

In July – October 1996 we collected air and water samples from the Swedish icebreaker *Oden* in the Barents Sea and eastern Arctic Ocean. The cruise track is shown in Figure 2. Concentrations of α- and γ-HCH in surface water averaged 0.90–0.34 and 0.27 ± 0.08 ng/L

Table 1. Organochlorine Compounds in AOS-94 Air Samples, pg/m^3

	Mean	Std. Dev.	Samples
α-HCH	84	34	22
γ-HCH	15	10	22
Trans-chlordane	0.59	0.34	16
Cis-chlordane	0.93	0.87	16
Trans-nonachlor	0.58	0.26	16
Cis-nonachlor[1]	0.056	0.052	16[2]
Nonachlor-III[1]	0.063	0.062	16[3]
Endosulphan-I	5.9	4.1	16
Endosulphan-II	0.12	0.18	16[4]

[1] Quantified using the response factor of trans-nonachlor.

[2] Nine samples above the LOD (~0.01 pg/m^3)

[3] Eight samples above the LOD (~0.01 pg/m^3)

[4] Eleven samples above the LOD (~0.01 pg/m^3)

(n=21). These agree excellently with the 1985 measurements of Gaul (1992) in the Barents Sea (α-HCH = 1.03 ± 0.25 ng/L; γ-HCH = 0.22 ± 0.08 ng/L) and suggest that little change has taken place in the HCH content of eastern arctic waters over the last decade. These α-HCH concentrations are about a factor of 2–3 lower than levels in the Bering-Chukchi seas (BERPAC–93) and along the AOS–94 track across the top of the Canada Basin, but similar to those found on AOS–94 when traversing the western Eurasian Basin and northern Greenland Sea. HCHs in the Beaufort Sea and Archipelago are even higher, typically ranging from 4–6 ng/L α-HCH and 0.5–0.8 ng/L γ-HCH (Jensen *et al.* 1997). Thus, the central Canada Basin is a pool of enriched HCHs, surrounded by cleaner waters. The main outflow of this water is through the Canadian Archipelago, and comparably high concentrations of HCHs are found in Resolute Bay (Falconer *et al.* 1995, Hargrave *et al.* 1997).

Concentrations of α- and γ-HCH in air samples from the *Oden* expedition are 35 ± 13 and 17 ± 12 pg/m^3 (n=34). This confirms the downward trend in α-HCH concentrations that has taken place over the last seventeen years (Bidleman *et al.* 1995b, Jantunen and Bidleman 1995, 1996). The ratio of average α-HCH/ γ-HCH concentrations on the Oden cruise is 2.05, compared with 5.53 on AOS–94 and 3.95 on BERPAC–93.

Water/air fugacity ratios were calculated from concentrations of the HCHs in surface water and air, using the Henry's law constant at the water temperature (Jantunen and Bidleman 1995, 1996, Kucklick *et al.* 1991). The percent saturation (100 x fugacity ratio) values in the eastern Arctic are 100 ± 33 for α-HCH and 42 ± 16 for γ-HCH. This indicates that α-HCH in air is in equilibrium with surface water and γ-HCH is undergoing net deposition. A comparison with the situation in the Bering-Chukchi seas and western Arctic Ocean is shown in Figure 3. In these regions α-HCH is undergoing net volatilization (% saturation >100) and γ-HCH is close to air/water equilibrium.

Henry's Law Constant of Technical Toxaphene. The Henry's law constant (Pa m^3/mol) as a function of temperature and salinity is needed to estimate the water/air fugacity ratio of CHBs in arctic waters. Henry's law constant determinations were done over a temperature range of 10–40°C by the bubble stripping method (Jantunen 1997, Kucklick *et al.* 1991) using Milli-Q water and technical toxaphene. Attempts to measure the constant at lower temperatures were not successful because of the long time required to strip measurable amounts of toxaphene from the water.

A plot of log H vs. reciprocal temperature (K) is shown in Figure 4. Regression parameters are:

$$\text{Log } H = 10.42 - 3209/T$$

with standard deviations of 310 and 0.33 for the slope and intercept. The value of H at 20°C is 0.29, compared with 0.67 determined by Murphy *et al.* (1987).

The Henry's law constant expressed by this relationship is for the mixture of CHBs in technical toxaphene, and represents a weighted average for the different components. It was noted that bubbling generally resulted in preferential stripping and higher apparent Henry's law constants of the more volatile components, but a few later-eluting components were also stripped quite rapidly (Jantunen 1997). Thus, Henry's law constants are needed for individual CHB congeners.

Determinations were not done in seawater because our past experience has been that stripping experiments

Figure 1

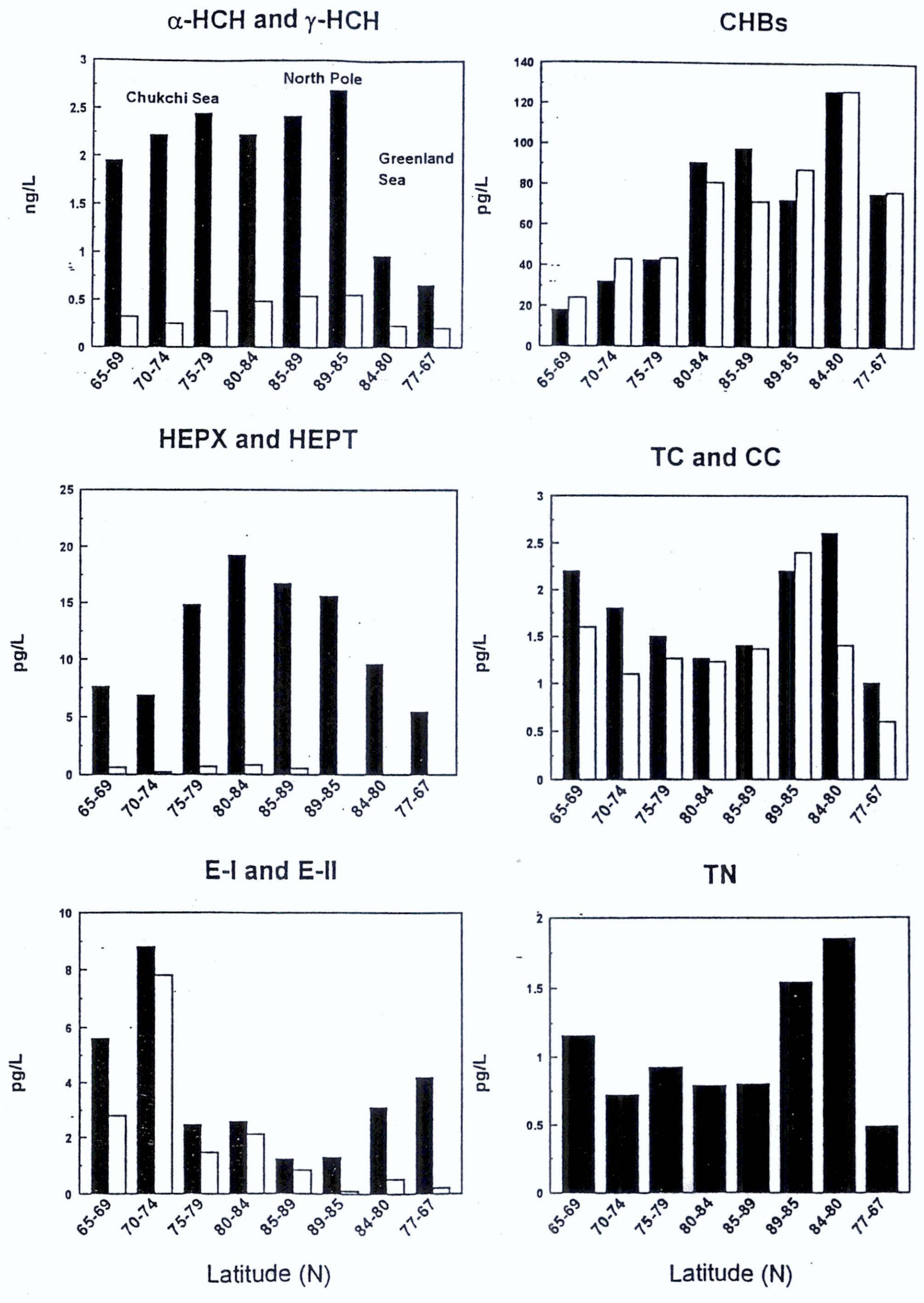

Figure 1. Spatial trends of organochlorines in the mixed layer of the Arctic Ocean, determined on AOS-94. α-HCH (black bars) and γ-HCH (white bars) = α– and γ–isomers of hexachlorocyclohexane, HEPT(white bars) and HEPX (black bars) = heptachlor and its metabolite heptachlor exo-epoxide, TC (black bars) and CC (white bars) = trans- and cis-chlordane, E-I (black bars) and E-II (white bars) = endosulphan I and II, TN (black bars) = trans-nonachlor. In the case of chlorobornanes (CHBs) the black and white bars indicate residues quantified by single- and multiple-response factor methods respectively (Jantunen 1997).

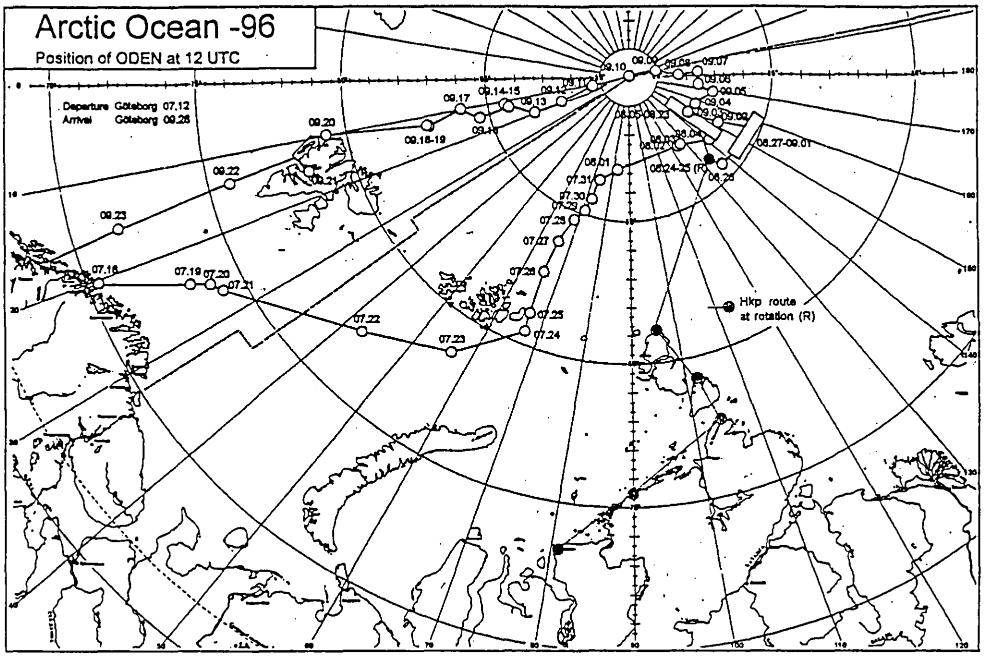

Figure 2. Cruise track of *Oden*-96 (white dots).

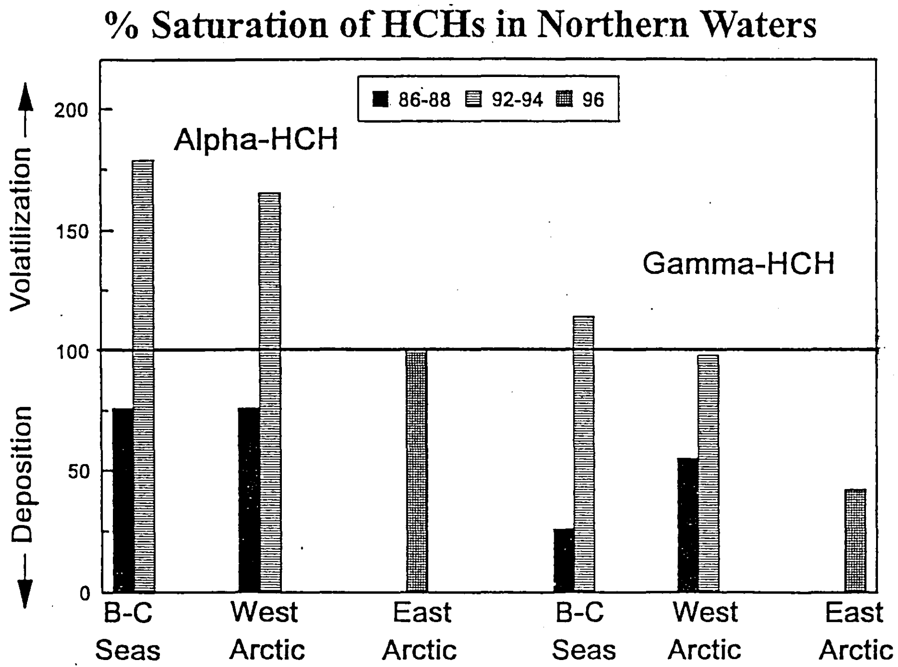

Figure 3. Percent saturation (100 x water/air fugacity ratio) of HCHs in arctic waters.

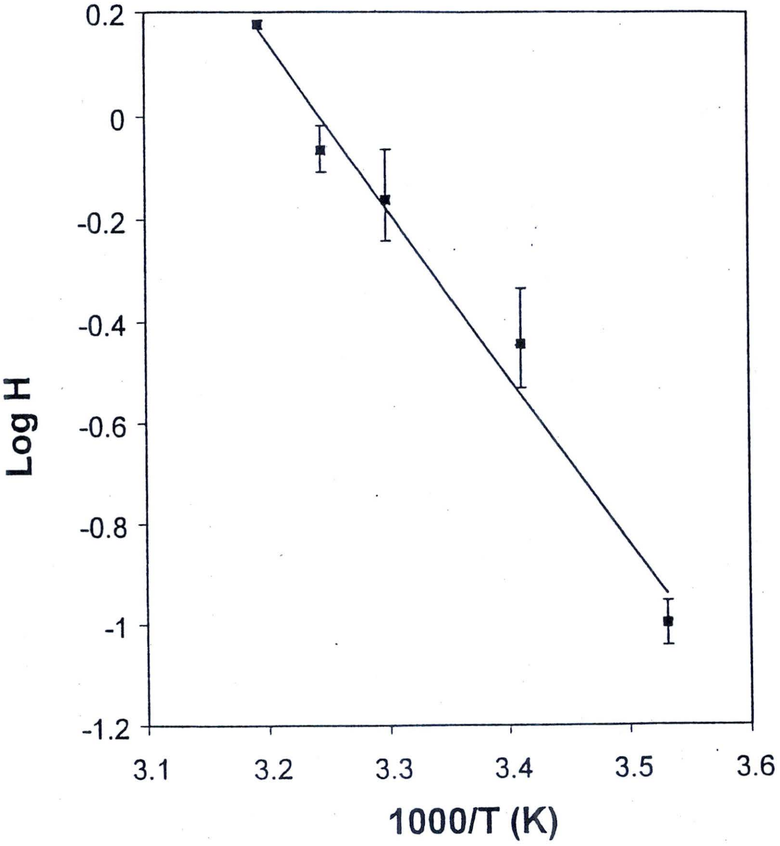

Figure 4. Temperature dependence of the Henry's law constant (Pa m^3/mol) of technical toxaphene.

yield spuriously high Henry's law constants for hydrophobic substances. Adsorption on the bubble surface may be the cause, as the surface-to-volume ratio is higher for the smaller bubbles that are produced in seawater. We estimate that the Henry's law constant in seawater is about 45% higher than the constant in Milli-Q water. This is based on predictions of the Setchenow equation, which indicates that PCBs are about 45% less soluble in seawater due to the "salting-out" effect. We assume the same solubility reduction for toxaphene (Jantunen 1997).

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MODELLING INORGANIC AND ORGANIC CONTAMINANTS IN ARCTIC FRESHWATER LAKES

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OBJECTIVES

Short-term

1. To develop a general fate and transport model for inorganic and organic contaminants in arctic lakes and apply the models to high and subarctic lakes.

2. To investigate key factors controlling contaminant loadings and movement within an arctic lake and exposure to aquatic organisms.

3. To identify long-term and transient skins of inorganic and organic contaminants, and the response time of lakes to loading changes.

4. To investigate the rate and factors controlling the enantioselective degradation of α–HCH in arctic watersheds.

Long-term

1. To quantify the fate and transport of a variety of inorganic and organic contaminants in arctic and subarctic freshwater systems.

2. To evaluate the sensitivity and response of arctic and subarctic lakes to contaminants loadings.

3. To extend our understanding of contaminant dynamics within arctic lakes, to the larger arctic ecosystem.

4. To determine factors leading to variability in contaminant dynamics spatially and temporally in order to identify sensitive geographic areas and, annually, times of maximum contaminant exposure for biota.

5. To understand factors leading to the bioaccumulation of contaminants in arctic freshwater fish.

DESCRIPTION

Lakes are found throughout arctic and subarctic Canada, and are intermediaries between watersheds and the Arctic Ocean. As well, lakes supply habitats for aquatic organisms that are consumed as part of traditional diets. Our research focuses on understanding and quantifying the fate of contaminants in aquatic systems and contaminant exposure to freshwater biota. The overarching objective of all projects is to improve our understanding of processes whereby chemicals move through the arctic environment, and then to translate this understanding to the broader arctic ecosystem.

Since beginning the research we have developed a general model of contaminant fate in northern lakes, and applied these models to several systems in the high arctic and subarctic. We have also developed a general model of contaminant uptake through an aquatic food chain and applied it to the simple trophic structure found in Char and Amituk Lakes on Cornwallis Island in the high Arctic. Much of this work has been through the Amituk Lake Project coordinated by R. Semkin of the National Water Research Institute (NWRI).

The main result of our modelling work has been to show that arctic lakes act primarily as conduits for contaminants, with minimal chemical being retained in the system (Diamond 1996, 1994, Freitas *et al.*, in press). This view is consistent with our knowledge of high arctic lakes (e.g., Bergmann and Welch 1985, Semkin 1996) and has important implications for the role of lakes in contaminant transport, the interpretation of sediment core data and contaminant exposure for aquatic organisms, as discussed below.

Recently we have turned our attention to better understanding the enantioselective degradation of α-HCH, the most abundant organochlorine in arctic air and waters. Faller *et al.* (1991) reported selective degradation of an enantiomer of α-HCH in oceanic waters and hypothesized that it was due to bacterial processes rather than a physical degradative process that is not stereoselective.

The magnitude of degradation can be expressed as the ratio of (+) to (–) α-HCH or enantiomer ratio (ER). Falconer *et al.* (1995a,b) measured ERs in various media in the Resolute Bay area. They found air and snow samples to have ERs of 1.00, indicating a racemic mix, but ERs of stream and lake water of 0.97 to 0.62 and 0.77, respectively. Stream ERs were inversely related to temperature. The mechanism of degradation and factors controlling degradation remain unclear. However, it is surprising that degradation occurs at a rapid rate during the short arctic summer.

The enantioselective degradation of α-HCH is of interest since this is the most abundant organochlorine. Understanding the degradation process can also help us to understand processes controlling the fate of contaminants in general. Two main hypotheses have been proposed to account for non-racemic ERs in arctic waters. First, it is suggested that microbial degradation is responsible, with microbes using the persistent organochlorines as a carbon source in nutrient limited system. This hypothesis would account for lower ERs found in carbon-limited northern waters than in the relatively carbon-rich waters of the Great Lakes (e.g., Ridal *et al.* 1997). The second hypothesis, that is less likely, attributes non-racemic ERs to preferential sorption by stereospecific binding sites on clays (e.g., Bondy and Harrington 1979) however evidence for this process has not been reported under ambient environmental conditions.

ACTIVITIES IN 1996/97

Lake Modelling

1. We examined the effect of annual variations in contaminant air and snow concentrations on lake concentrations using data from the Amituk Lake project for 1993. The results were compared to those obtained by Freitas (1994) for the 1992 data, and will be compared with those obtained for 1994 to investigate annual effects.
2. To improve our confidence in the conclusions drawn from the Amituk Lake research, we are verifying estimates of contaminant concentrations and dynamics in Char Lake by acquiring contaminant data for the lake and using it in the model of Char Lake parameterized by Freitas (1995). During the summer of 1997, P. Helm collected lake water and sediment cores from Char Lake for contaminant analysis. (The core was taken in conjunction with M. Douglas, Dept. of Geology, Univ. of Toronto). Modelling work will proceed after sample analysis at AES (Bidleman) and NWRI (Muir).
3. The preliminary model of contaminant bioaccumulation through an arctic lake food chain will be tested using data from the Amituk Lake project and data forthcoming from sampling conducted during summer 1997 at Char Lake.

Enantioselective Degradation of α-HCH

1. To improve our understanding of factors contributing to enantioselective degradation of α–HCH, extracts of water samples taken from Amituk Lake and creeks during 1994 by R. Semkin (NWRI) were analysed to quantify the enantiomer ratio (ER) of (+) to (-)-HCH. This work was done in conjunction with T. Bidleman (AES).
2. In July 1997, P. Helm resampled the creeks and water column of Amituk Lake, as well as Char and Meretta Lakes. Samples were collected from the Amituk watershed and a wetland north of Char and Meretta Lakes, to investigate factors controlling changes in ER. Meretta and Char Lakes were sampled to assess the influence of nutrient status and biological activity on enantiomer degradation. Meretta Lake is eutrophic whereas nearby Char is oligotrophic (Schindler *et al.* 1974a,b), as is Amituk Lake (Semkin 1996).
3. An *in situ* experiment was conducted to test the influence of nutrient status and the role of sediments on degradation. Six limnocorrals were deployed in the shallow littoral zone of Char Lake during July. Duplicate limnocorrals were (a) open to the sediments, (b) open to the sediments and spiked with carbon, phosphorus and nitrogen, and (c) isolated from the sediments. Water samples for enantiomer analysis were taken at intervals during the one week deployment. Enantiomer analyses are being conducted in conjunction with T. Bidleman.

RESULTS

Lake Modelling

Results obtained by applying 1993 Amituk Lake data to the steady-state Amituk Lake model substantiated our previous observations—from 80 to 99% of contaminant loadings to the lake were exported downstream, with the percentage being inversely related to particle-

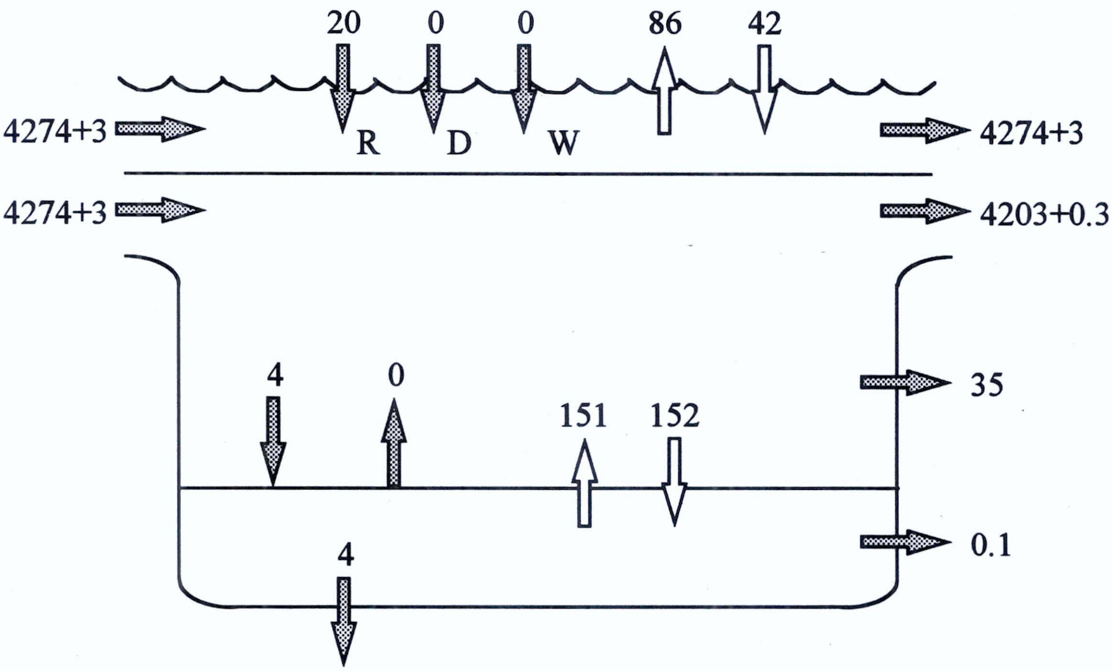


Figure 1. Contaminant fluxes (mg/year) for α–HCH predicted with 1993 loadings.

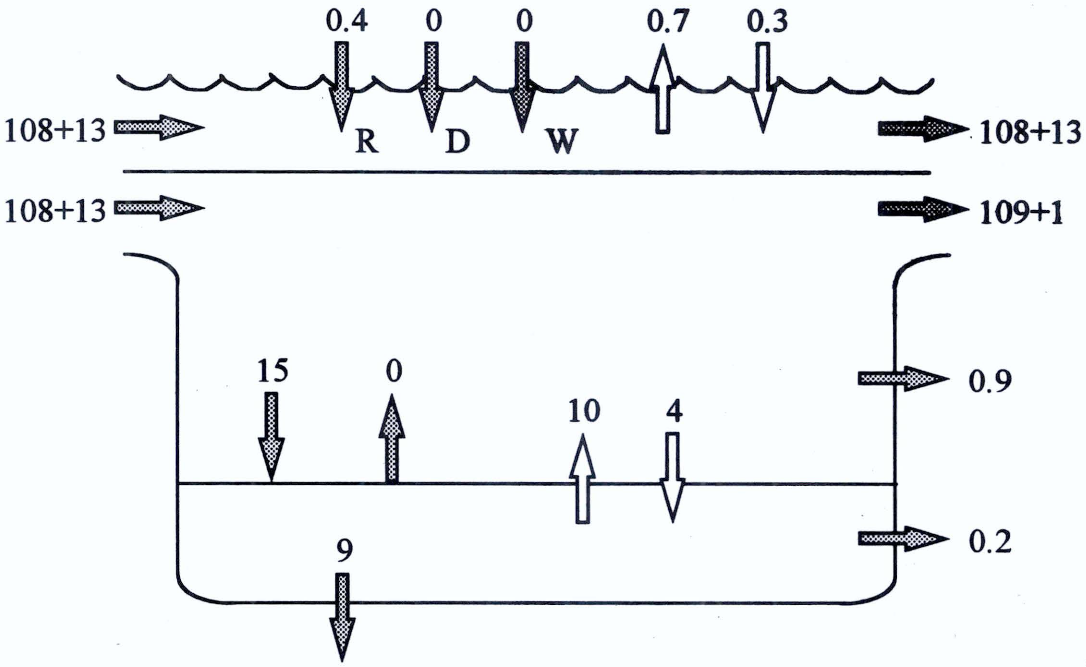


Figure 2. Contaminant fluxes (mg/year) for ΣDDT predicted with 1993 loadings.

sorption (i.e., greater retention of the more particle-bound contaminants such as DDT). Figures 1 and 2 illustrate the estimated mass balances obtained for α–HCH and ΣDDT using measured inflow and air concentrations (air concentrations were from Alert, Barrie, unpubl. data). The 1992 and 1993 results were obtained assuming that 50% of meltwater flowed through the lake without mixing with the water column, i.e., the same throughflow percentage was used for both years. The agreement between measured and observed water concentrations for five organochlorines from 1992 and 1993 lends credibility to results obtained from the model since only inflow concentrations were changed.

The behaviour of arctic lakes as conduits has important implications for contaminant fate. First, contaminants deposited to terrestrial surfaces that lack significant vegetative cover will be largely conveyed to an oceanic sink. The exception is the fraction that volatilizes from the snowpack prior to melt and lake during the brief ice-free period. . Volatilization from the open lake is chemical dependent, but is generally very low whereas loss from the snowpack has yet to be quantified. A second implication lies in the interpretation of lake sediment cores. We suggest that the sedimentary record of lakes provides important information on relative rates of contaminant deposition, but can not be used to reliably estimate absolute rates. Muir *et al.* (1995, 1996) have reported rates of contaminant accumulation (burial) of organochlorines in recent sediments of 11 arctic, subarctic and temperate lakes. These rates (focus corrected) are generally within an order of magnitude of rates of deposition directly to surfaces. However, our work indicates that sediment burdens represent the small fraction of chemical deposited to the catchment that is retained in lake sediments after losses due to revolatilization from the snowpack and retention in catchment soils and vegetation, and export of most chemical through the lake during snowmelt. The relatively close correspondence between rates of direct surface deposition and sediment burial remains puzzling and requires further investigation.

A third implication of these results is that arctic lakes will respond to changes in contaminant loadings according to water renewal time, with minimal influence from the sediments. This is fortunate because the sediments respond to changes much more slowly than the water column. Figures 3 and 4 illustrate the rapid response of water column concentrations of α–HCH and ΣDDT to loading changes in 1992 and 1993. Also illustrated is the estimated response of the sediments that is an artifact of the steady-state simulation, i.e., lake sediments do not respond on an annual basis. Future work will focus on better approximating the slow sediment response through an unsteady-state simulation. We will also be further exploring the response of the lake with the 1994 Amituk Lake data set.

Enantioselective Degradation of α–HCH

Analyses of 1994 Amituk stream samples for their α–HCH enantiomer ratio (ER) support the finding of Falconer *et al.* (1995) that (+) α–HCH is preferentially degraded relative to (-) α–HCH in stream and lake waters. Figure 5 indicates that the ER decreases from 1.0, indicating the racemic mix in air, to as low as 0.35 in Gorge Creek in early August when stream flows are minimal. Degradation is positively related to stream temperature (Figure 6), as Falconer *et al.* reported.

We also analysed Amituk Lake water column samples at 3, 20, and 40 m depths (Figure 7). ERs at 20 and 40 m depth are relatively stable throughout the season at 0.70 to 0.75. ERs at 3 m reflect processes occurring in the lake. The ER increases from 0.80 at the onset of snowmelt, to 0.90, representative of the ER in the incoming meltwater. The ER then declines to 0.75 after most flow has ceased and the water column mixes. The temporal pattern of ERs is similar in the outflow. The difference in ERs at surface and depth in the water column and the outflow indicates that minimal degradation occurs within the lake. Rather, the ER of the lake reflects that of the inflow streams when the lake mixes which, confirms the deduction that a high proportion of meltwater, with its contaminant burden, flows through and exits the lake, rather than mixing with the lake.

DISCUSSION/CONCLUSIONS

Contaminant concentrations are general very low in arctic lakes compared to lakes receiving direct industrial or urban discharges. The results of obtained from assessing contaminant dynamics through mass balance modelling indicate that lakes function as rivers or conduits rather than sinks for contaminants deposited in the watershed. Minimal retention in lakes is attributable to the asynchronous timing of snowmelt and water column mixing: most meltwater flows through lakes while they are ice-covered and stratified which prevents mixing. Secondly, low retention is due to minimal particulates conveying contaminants from the water column to sediments. This result implies that most contaminants that accumulate in the barren terrestrial environment of the high arctic over a year are conveyed to the oceans, water concentrations can respond rapidly to loading changes and the interpretation of the sedimentary record as indicative of relative deposition fluxes.

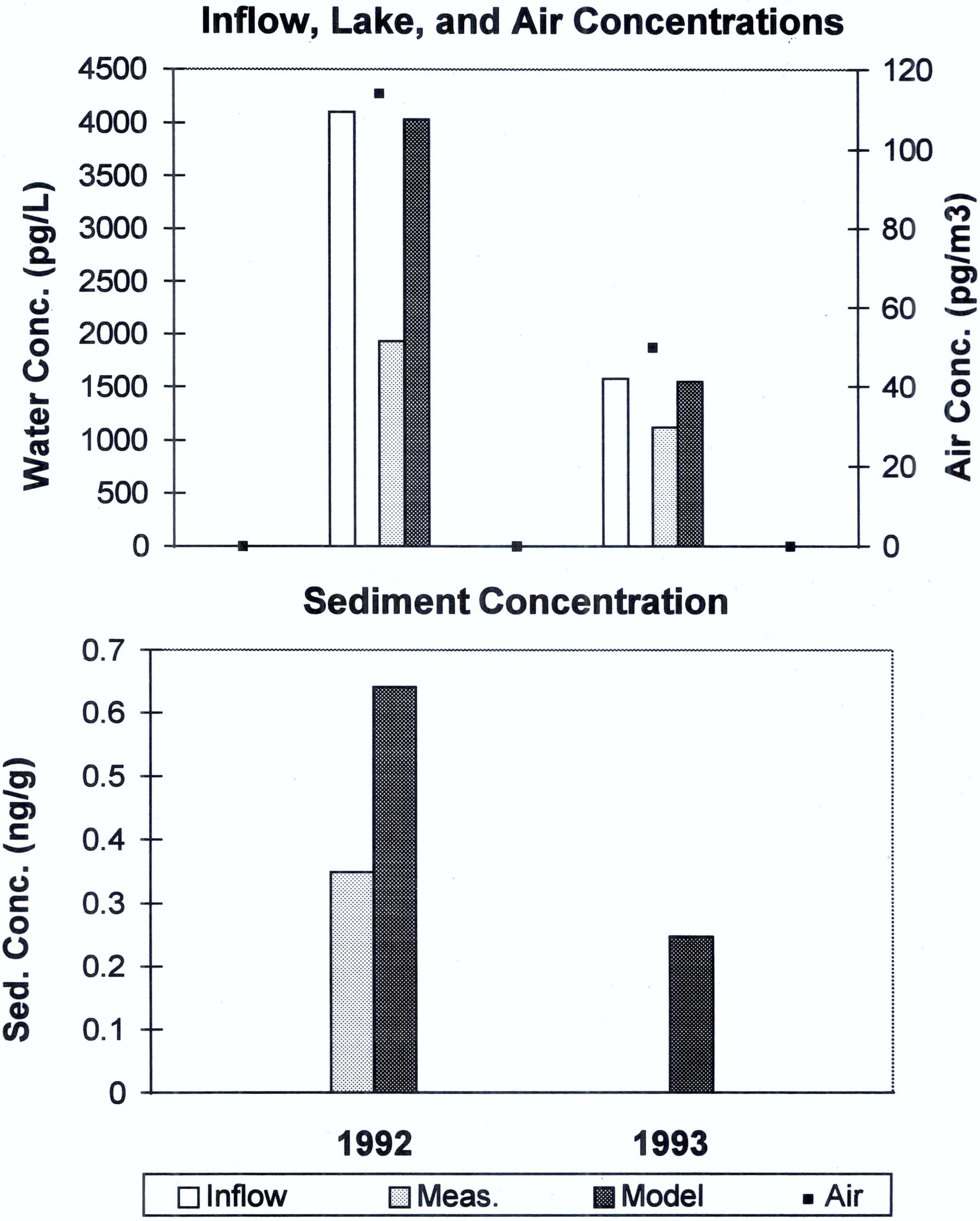
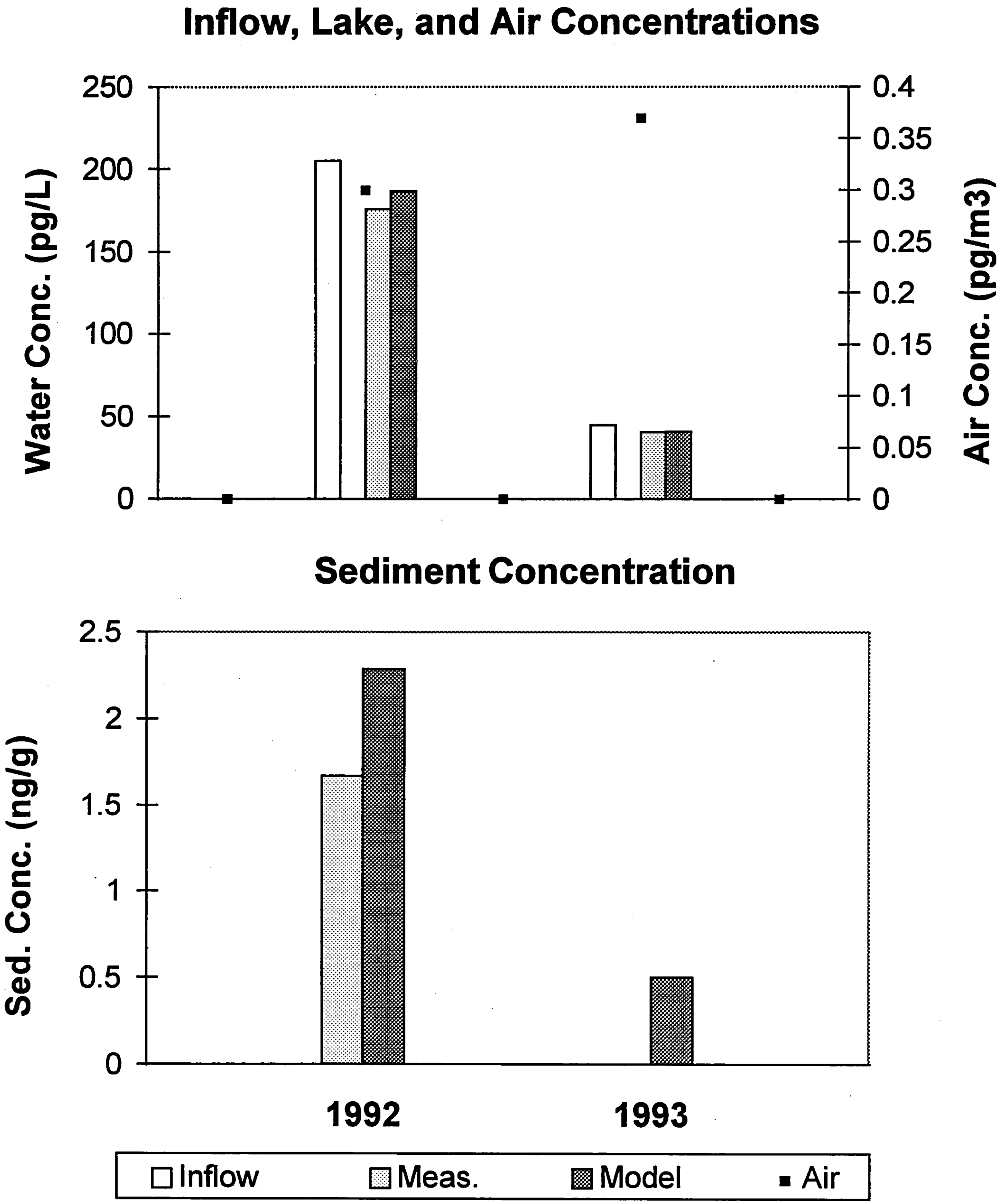


Figure 3. Contaminant loadings and concentrations for α–HCH.



Inflow, Lake, and Air Concentrations

Sediment Concentration

Figure 4. Contaminant loadings and concentrations for ΣDDT.

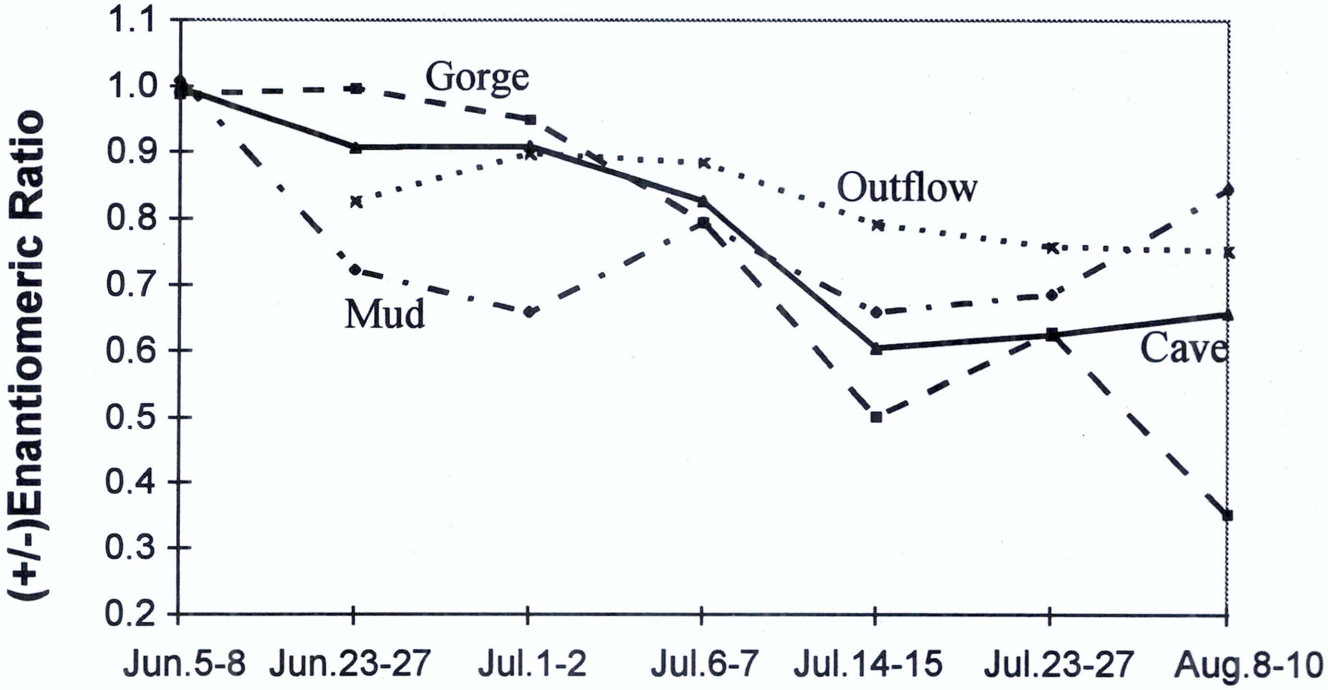


Figure 5. 1994 α–HCH enantiomer ratios.

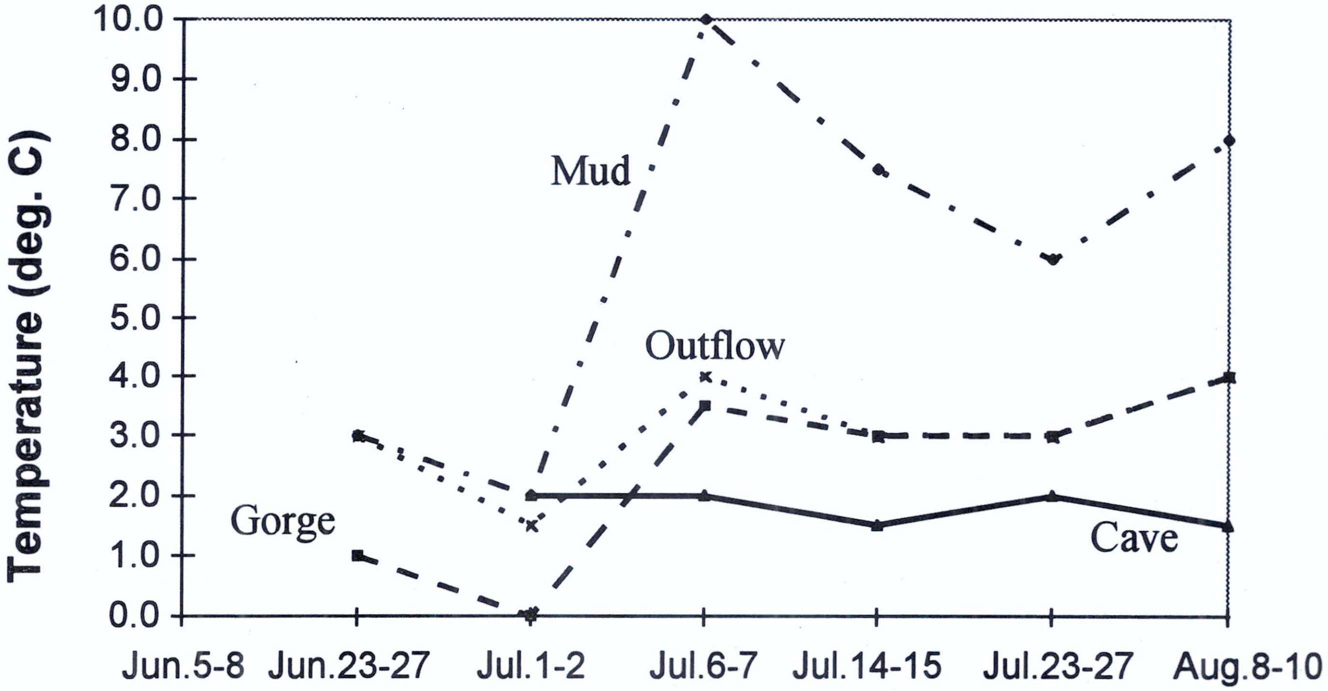


Figure 6. 1994 stream temperatures.

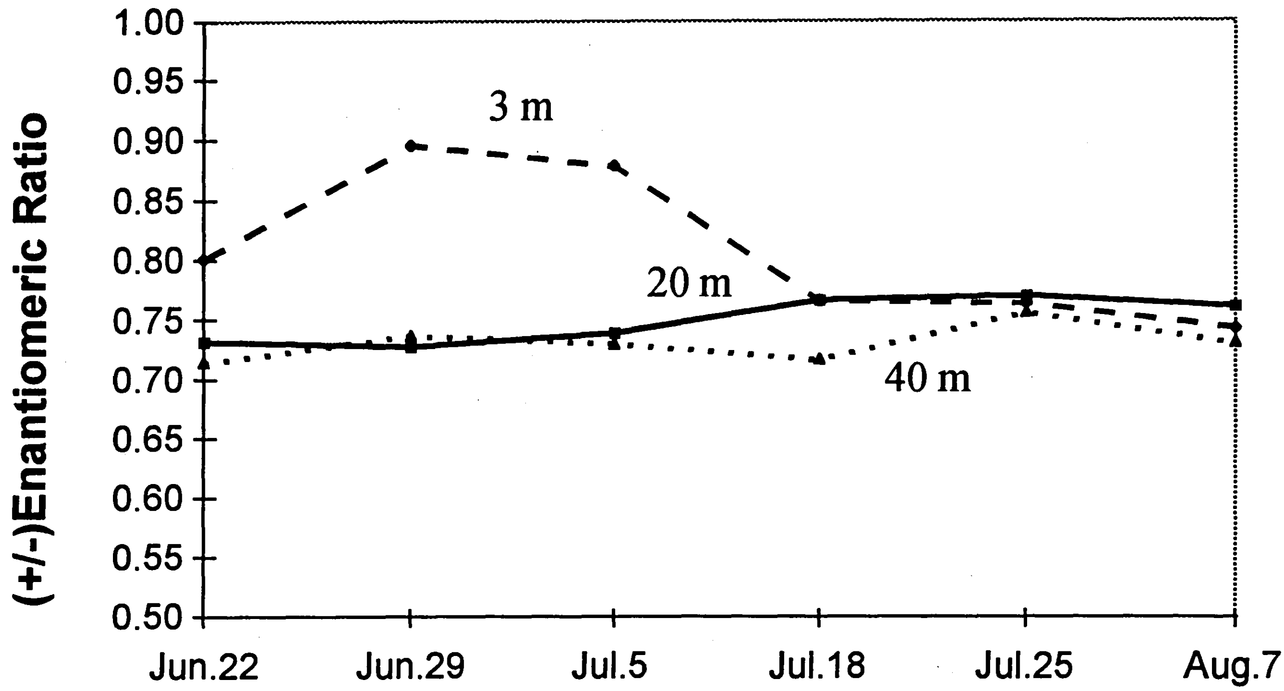


Figure 7. 1994 lake ERs at various depths.

Analysis of α-HCH enantiomers indicates that the selective degradation of (+)α-HCH occurs in streams feeding Amituk Lake, but does not appear to occur at appreciable rates within the lake itself. Reduction in the enantiomer ratio (ER) coincide with temperature increases in the streams and is greatest in Mud Creek which has a south-facing aspect. Determination of ERs in surface lake waters support the conclusions that minimal within lake degradation occurs and minimal contaminants from meltwater mix with the water column.

Expected project completion date: Summer 1998

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RIVERINE INPUTS OF CONTAMINANTS

Project Leaders: D. Jeffries and J. Carey, National Water Research Institute, Environment Canada; M. Swyripa, Water Resources Division, Department of Indian Affairs and Northern Development

Project Team: S. Backus, Backus Consulting, Stoney Creek, ON.; D. Gregor, Burlington, ON.; S. MacDonald, IWD-Northwest Territories; E. Graf Pannatier, Institut Forel, Versoix, Switzerland; J. Parrott, National Water Research Institute, Burlington, ON.; M. Yunker, Brentwood Bay, BC.

OBJECTIVES

Short-term

1. To estimate and characterize the total contaminant load delivered by major river systems to the arctic marine environment
2. To characterize its source and seasonal variability
3. To 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
2. To assess the applicability of existing predictive models and refine as necessary
3. To 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, existing information for North America focused on the Mackenzie River since it is the largest riverine system. However, 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) baseline information on the magnitude, source, and spatial and temporal variability of contaminant delivery by river systems to the Arctic Ocean;
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.

Study progress prior to this report was summarized in Jeffries *et al.* (1994, 1996), which contains basic information on sampling sites and sampling methods, analytical and QA/QC methods, riverine major ion and nutrient chemistry, concentrations of selected organic compounds in sediments from a lake in the Mackenzie River delta, and the concentration range of selected organic compounds observed in water samples from all rivers.

ACTIVITIES IN 1995/96 AND 1996/97

Chemical Analyses

Samples collected from the Mackenzie River in 1995 were processed through the full analytical protocol (i.e. for PCB congeners, organochlorine pesticides, PAHs and n-alkanes) as described in earlier progress reports. Preliminary results of a Principal Components Analyses (PCA) (Yunker 1996a) identified a need to analyse the samples for some additional parent PAHs (e.g. benzo[b/j/k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene and perylene) and this work was completed as well. Processing and interpretation of the analytical data identified outliers or otherwise unexpected values, and these have been re-analysed to confirm or correct the results. Once all of the above was completed, the analytical data were detailed in a summary report (Backus 1996). This report also includes all pertinent detail concerning field and analytical methods and serves as the central, citable source of the data.

The National Water Research Institute (NWRI) also contributed to the DIAND/Yellowknife "Fort Good Hope" project by assessing the presence and distribution of mixed function oxygenase (MFO) inducing compounds in the Mackenzie River using semi-permeable membrane devices (SPMDs). The SPMDs were deployed in the refinery effluent stream at Norman Wells and upstream and downstream in the Mackenzie River. The SPMD extracts were analysed for PAHs using the same protocol as above to ensure compatibility with the remainder of the riverine database. Analyses and data interpretation are complete (Parrott *et al.* submitted).

Data Processing and Interpretation

Understanding hydrocarbon and contaminant transport processes in the Arctic, and characterizing sources is being accomplished by development of one or more models using PCA. PCA allows classification of samples based on their alkane and PAH distributions or profiles and is used to compare contaminant distributions among areas of the Arctic and to interpret their sources and geochemistry. It also permits maximum usage of all the available data, i.e. our water, suspended sediment, and lake sediment data, as well as other data from the Mackenzie River, Mackenzie shelf, and the Beaufort Sea. The final PCA model will build on models already developed for the Mackenzie River and Beaufort Sea (Yunker and Macdonald 1995), but modelling of the Nunavut rivers is entirely new. The integration of our 1994/95 hydrocarbon data for northern rivers and Mackenzie Delta lakes with 1987 "NOGAP" data from the Mackenzie River (Yunker *et al.* 1993) was conducted in 1995/96 (Yunker 1996a). Differences between our 1994/95 and the 1987 data (e.g. in PAH profiles and some variable ratios) prompted some re-analyses to determine whether they were real or an analytical artifact. While substitution of new results for benzo[b/j/k]fluoranthene, benzo[e]pyrene, 1,2/1,7-dimethylnaphthalene and 1,6-dimethylnaphthalene moved the datasets much closer together, some differences in PAH composition remain. This has not hindered interpretation of the hydrocarbon geochemistry of the rivers.

Unsupervised PCA was performed using the nonlinear iterative partial least squares (NIPALS) algorithm (Yunker 1996a,b, Yunker *et al.* in prep.). Alkanes and PAHs that were undetected were replaced by the limit of detection. Samples were normalized using a subset of the variables with mid-range standard deviations and means and then autoscaled before PCA. The lake sediment cores and the suspended particulate samples from the Mackenzie River provided a data set where most alkane and PAH compounds were usable for PCA modelling (Table 1). The Nunavut suspended particulate samples all had too many undetectable values to provide reliable projections. Nevertheless, a few of the Nunavut samples were included in preliminary models, but projections were highly influenced by detection limit artifacts. Similarly, the water (dissolved phase) samples also contained too many undetectable values for the higher PAHs to be included in a PCA model.

Several different PCA models were constructed that contained different subsets of the samples and the variables. Different methods of data preprocessing (normalization, log transformation, mean centering, autoscaling, Varimax rotation) were also investigated. Models included either all of the variables in Table 1, just the PAHs, or the 10 parent PAHs that are major constituents of anthropogenically produced samples (marked with "*" in Table 1). Perylene was excluded from this latter list because it is produced *in situ* in some sediments.

RESULTS

An example of the data produced by this project (Backus 1996) is presented in Table 2. It is these data that were integrated with the 1987 Mackenzie NOGAP data prior to PCA (Yunker 1996a,b).

DISCUSSION

Preliminary interpretation of the data and PCA modelling has focused on suspended particulate matter from the rivers and delta lake sediments (Yunker 1996a,b). The final interpretation will be detailed in Yunker *et al.* (in prep.) and the final report of this project.

General

Concentrations of hydrocarbons associated with riverine suspended particulate matter (SPM) can be expressed either on a ng/g basis (reflecting the hydrocarbon concentration on the particulate matter) or on a ng/L basis (reflecting the quantity of hydrocarbons transported by the river). On either basis, no relationship was identified between Mackenzie River alkane or PAH concentrations and sampling location. However, a relationship did emerge with sampling date. Both alkane and PAH SPM concentrations were low in late winter (March and early April) when the Mackenzie River flow and SPM are still low, and were generally much higher in spring and summer (May to September) when river flow and SPM are higher.

Table 1. Alkane and PAH variables used for Principal Components Analysis

Alkane	Abbr.	PAH	Abbr.
n-Undecane	11	Naphthalene	Na
n-Dodecane	12	Fluorene	F
n-Tridecane	13	Phenanthrene*	Pn
n-Tetradecane	14	Anthracene	An
n-Pentadecane	15	Fluoranthene*	Fl
n-Hexadecane	16	Pyrene*	Py
n-Heptadecane	17	Benz[a]anthracene*	BaA
Pristane	Pr	Chrysene*	Ch
n-Octadecane	18	Benzo[b,k]fluoranthene*	BF
Phytane	Ph	Benzo[e]pyrene*	BeP
n-Nonadecane	19	Benzo[a]pyrene*	BaP
n-Eicosane	20	Perylene	Per
n-Heneicosane	21	Dibenz[a,h]anthracene	DA
n-Docosane	22	Indeno[1,2,3-cd]pyrene*	IP
n-Tricosane	23	Benzo[ghi]perylene*	Bghi
n-Tetracosane	24	2-Methylnaphthalene	2MN
n-Pentacosane	25	1-Methylnaphthalene	1MN
n-Hexacosane	26	2,6 & 2,7-Dimethylnaphthalene	2,6/2,7N
n-Heptacosane	27	1,3 & 1,7-Dimethylnaphthalene	1,3/1,7N
n-Octacosane	28	1,6-Dimethylnaphthalene	1,6N
n-Nonacosane	29	2,3- & 1,4-Dimethylnaphthalene	2,3/1,4N
n-Triacontane	30	1,5-Dimethylnaphthalene	1,5N
n-Untriacontane	31	1,2-Dimethylnaphthalene	1,2N
n-Dotriacontane	32	2,3,6-Trimethylnaphthalene	2,3,6N
n-Tritriacontane	33	3-Methylphenanthrene	3MP
n-Tetratriacontane	34	2-Methylphenanthrene	2MP
		9/4-Methylphenanthrene	9MP
		1-Methylphenanthrene	1MP
		3,6-Dimethylphenanthrene	3,6DP

There were differences between years for both alkanes and PAHs on Mackenzie SPM. Post-freshet concentrations were roughly comparable in 1987 and 1994, but both differ from 1993 when the lowest concentrations were observed.

There was little difference in mean ng/g concentrations of alkanes and PAHs between sediment from lakes in the middle and outer delta and in the near shore Beaufort Sea and post-freshet SPM from the Mackenzie River in 1987 and 1994. Mean concentrations generally decreased from river particulate, to the middle and then the outer delta lake sediments, and then to Beaufort Sea sediment, but the differences were not significant. This equivalence of hydrocarbon concentrations is a reflection of physical processes in the delta:

1) post-freshet Mackenzie River SPM is deposited in the delta lakes when the river floods over its banks each summer, and

2) the Mackenzie River SPM is the principal source of sediment to the Beaufort Sea shelf.

The low concentrations in Mackenzie River SPM observed in 1993 were not representative of the recent history of the river, particularly for the alkanes. The highest total alkane and PAH concentrations found on river particulate in 1993 (8900 and 2900 ng/g, respectively) were higher than the minimum concentrations in the lake cores (7700 and 870 ng/g), but most 1993 samples had much lower concentrations. Alkane and PAH distributions were not markedly different in 1993 suggesting that the concentration differences do not reflect a change in hydrocarbon composition. It may be that the larger river flow that occurred during the 1993 freshet mobilized larger quantities of low organic soils (e.g., glacial till) than usual, and that the lower 1993 concentrations reflected this dilution.

When alkane and PAH data for the three years of sampling were pooled, the ng/L hydrocarbon concentrations in the Mackenzie River exhibited a linear relationship with SPM. A better fit was obtained between concentrations of the higher alkanes and alkyl PAHs and SPM ($r^2 = 0.79$ and 0.72, respectively) than with the lower alkanes and Σ178—278 parent PAHs ($r^2 = 0.57$ and 0.54, respectively) although all of the correlations were significant ($p < 0.001$). These correlations suggest that higher plant debris and petroleum material are more

Table 2. An example of chemical data from Backus (1996). Analyte concentrations (ng/g dry weight) extracted from 30 g of sediment taken from the 9–11 cm section of a core collected at Station 3.1 in the Mackenzie Delta. The organic carbon content of the sediment was 2.14%.

Organochlorine Pesticides		Polycyclic Aromatic Hydrocarbons		n-Alkanes		PCB Congeners			
1,3-DCB	ND	Naphthalene	130	n-Undecane	140	1	ND	110	0.071
1,2-DCB	ND	Acenaphthylene	0.092	n-Dodecane	300	3	ND	82	ND
1,4-DCB	ND	Acenaphthene	—	n-Tridecane	170	4-10	ND	151	0.016
1,3,5-TCB	ND	Fluorene	33	n-Tetradecane	270	7-9	ND	135-144-147	ND
1,2,4-TCB	ND	Phenanthrene	180	n-Pentadecane	350	6	ND	107	ND
1,2,3-TCB	ND	Anthracene	2.0	n-Hexadecane	380	8-5	Tr	149-118	0.093
1,2,3,5 (1,2,4,5)-TTCB	ND	Fluoranthene	28	n-Heptadecane	390	19	ND	114	ND
1,2,3,4-TTCB	0.018	Pyrene	50	n-Octadecane	440	12-13	ND	131-134	ND
PECB	0.032	Benz[a]anthracene	16	n-Nonadecane	420	18-15	0.030	146	ND
HCB	ND	Chrysene	92	n-Eicosane	480	17	Tr	105-132	0.014
Heptachlor	ND	Benzo[b,j,k]fluoranthene	68	n-Heneicosane	500	24-27	ND	153	0.036
Heptachlor Epoxide	ND	Benzo[e]pyrene	100	n-Docosane	500	16-32	ND	141	ND
Aldrin	ND	Benzo[a]pyrene	20	n-Tricosane	700	54	ND	179	ND
Endrin	ND	Perylene	210	n-Tetracosane	670	29	ND	176	ND
Dieldrin	ND	Indeno[1,2,3-cd]pyrene	13	n-Pentacosane	1000	26	0.046	138	0.067
o,p-DDE	ND	Dibenz[a,h]anthracene	7.5	n-Hexacosane	620	25	0.020	158-160	ND
p,p-DDE	ND	Benzo[g,h,i]perylene	72	n-Heptacosane	2000	31	0.20	129	ND
o,p-DDT	ND	2-Methylnaphthalene	260	n-Octacosane	530	28	0.11	178	ND
p,p-DDT	ND	1-Methylnaphthalene	160	n-Nonacosane	1200	33-53-20	0.15	175	ND
o,p-DDD	ND	2,6 & 2,7-Dimethylnaphthalene	120	n-Triacontane	370	22-51	ND	187	ND
p,p-DDD	ND	1,3 & 1,7- Dimethylnaphthalene	71	n-Untriacontane	1000	45	ND	128	ND
Mirex	ND	1,6-Dimethylnaphthalene	63	n-Dotriacontane	270	46	ND	183	ND
_-HCH	0.18	2,3- & 1,4-Dimethylnaphthalene	190	n-Tritriacontane	530	52	0.66	167	ND
_-HCH	ND	1,5-Dimethylnaphthalene	51	n-Tetratriacontane	160	49	0.25	185	ND
_-HCH	ND	1,2-Dimethylnaphthalene	15	n-Pentatriacontane	140	47	0.13	174	ND
_-Chlordane	ND	2,3,6-Trimethylnaphthalene	64	n-Hexatriacontane	86	48	0.041	177	ND
_-Chlordane	ND	2,3,5-Trimethylnaphthalene	97	Squalane	56	44	0.10	171-156	ND
_-Endosulfan	ND	3-Methylphenanthrene	71	Pristane	300	42-59	0.12	157-202	ND
_-Endosulfan	ND	2-Methylphenanthrene	86	Phytane	130	64-41-71	0.10	173	ND
Methoxychlor	ND	2-Methylanthracene	3.0			40	ND	200	ND
		9/4-Methylphenanthrene	97			103-57	ND	172	ND
		1-Methylphenanthrene	67			100-67	ND	180	ND
		9-Methylanthracene	0.95	Total n-alkanes		63	Tr	193	ND
		3,6-Dimethylphenanthrene	26	nC11-C35	14000	74	0.11	191	ND
		9,10-Dimethylanthracene	1.6	nC11-C19	2700	70-76-98	0.17	199	ND
		2-Methylfluoranthene	11	nC20-C29	8200	66	0.14	170	ND
				nC30-C35	2600	95	0.19	190	ND
				nC15-C19	2000	91-55	0.055	198	ND
				nC23-C33	9000	56-60	0.060	201	ND
						92	0.053	203-196	ND
				OEP at C17	0.92	84	ND	189	ND
				OEP at C25	1.42	101	0.24	195	ND
				OEP at C27	2.66	99	0.099	208	ND
				OEP at C29	4.45	119	ND	207	ND
				Pristane/Phytane	1.31	83	ND	194	ND
						97	0.064	205	ND
						87-81	0.050	206	ND
						85	0.036	209	ND
						136-77	Tr	Total PCBs	3.5

strongly associated with SPM in the Mackenzie River than the lower alkanes or parent PAHs.

Mean concentrations of the lower and higher alkanes on SPM from the Nunavut rivers were not much different than in the Mackenzie River during summer; PAH concentrations were about 10 times lower for the parent PAHs and 100 times lower for alkyl PAHs. There was also considerable concentration variation between the individual rivers: total alkane concentrations ranged from below detection in the Andrews River to 51,000 ng/g in the Back River, while total PAH concentrations ranged between 0.7 ng/g in the Andrews River to 250 ng/g in the Kazan River. As in the Mackenzie River, the same alkane and PAH relationships were maintained if particulate concentrations are expressed on a µg/g organic carbon basis. However, the Nunavut rivers were much more homogeneous on a volume basis. Excluding the Andrews River, total alkane concentrations ranged from 3.4 ng/L in the Kazan River to 56 ng/L in the Back River, while total PAH concentrations ranged from 0.03 ng/L in the Quioch River to 0.6 ng/L in the Coppermine River.

n-Alkane and Isoprenoid Distributions

Based on concentration profiles for the discrete alkanes, it appears that the 1993 and 1994 samples of SPM from the Mackenzie River generally have a lower odd-even predominance (OEP) for the higher plant n-alkanes than the 1987 samples. The OEP essentially measures the predominance of the higher plant n-alkanes above a background of other, less specific alkanes. Part of this difference may be due to differences in water flow through the centrifuge: a flow of 4 L/min. was used for the 1993/1994 samples, while 1 L/min. was used for the 1987 samples. From the operational characteristics of the centrifuge, more efficient trapping of low density plant debris is to be expected at the lower flow rate, and a higher OEP would result.

A few samples (Inuvik, July 27 and Sept. 7, 1993, Mar. 19, 1994; Arctic Red River, Mar. 20, 1994) have a distinct predominance of n-C_{33} alkane suggesting a large contribution of peat to the sample. The predominance of peat in winter samples from the river was noted by Yunker *et al.* (1993).

Alkane profiles of a few samples (Aklavik, March 19, 1994; Arctic Red River, June 23 and July 22, 1994) suggest that recent inputs of oil have occurred. The presence of anthracene in high concentration in the Aklavik sample is also a strong indication of petroleum.

Alkane profiles for all of the Nunavut rivers except the Back River have an alkane maximum at n-C_{17}. This indicates that algal productivity makes a major contribution to the alkane profiles in these rivers.

The lake cores generally have a low OEP. This low OEP could indicate either a low flux of terrestrial higher plant debris or high bacterial activity, or both. The third possibility—chronic inputs of petroleum hydrocarbons—is less likely since the lower alkanes lack an unresolved complex mixture typical of such occurrences. Alkanes with an algal origin (n-C_{17} or pristane) are not elevated in near-surface core sections, indicating that algal productivity is low in the lakes.

PAH Distributions

Work published to date has described the dominant influence of the Mackenzie River on the hydrocarbon geochemistry of the Mackenzie shelf (Yunker *et al.* 1993, 1994, 1995). Results based on 1987 data indicated that the river transports a mixture of petrogenic (2- and 3-ring) and multi-ring (4- to 6-ring) PAHs that is relatively constant in composition. The two components vary independently of one another, and the major parent PAH molecular mass constituent alternates between 178 and 252 in individual river and shelf samples. Profiles for the mono- and dimethylnaphthalenes and monomethylphenanthrenes are also relatively constant from sample to sample.

Our 1993 and 1994 suspended particulate samples from the Mackenzie River generally have 178 and 252 as the major molecular mass constituents, but the composition of the parent PAHs is much more variable than in the 1987 samples, and molecular mass 178 (phenanthrene plus anthracene) is a more dominant constituent. Distributions of the monomethylnaphthalenes and phenanathrenes are similar to the 1987 samples. Parent PAH profiles in the core samples are more similar to the 1987 samples and exhibit less variation than the 1993 and 1994 suspended particulate samples.

Alkyl PAHs were more minor constituents in suspended particulates from the Nunavut rivers, and were only detectable in the Coppermine and Hayes Rivers. Naphthalene and the molecular mass 202 PAHs (fluoranthene and pyrene) were the major PAHs is most cases. This, along with the general predominance of fluoranthene over pyrene, implicates combustion (presumably from long-range transport) as the major PAH source. The alkyl PAHs were often detectable in the corresponding water samples and the input of some petroleum is likely.

PCA Modelling

To provide a more comprehensive interpretation of the hydrocarbon data, several PCA models have been developed using different groups of parent and alkyl PAH variables. Preliminary PCA models identified differences between the NOGAP and NWRI samples that in some cases were quite substantial. Extensive work to confirm or disprove the differences has been completed. After substitution of new concentrations for benzo[b/j/k]fluoranthene, benzo[e]pyrene, 1,2/1,7-dimethylnaphthalene and 1,6-dimethylnaphthalene, the NOGAP and NWRI data sets are much closer together. Much of the variation in the ratios of benzo[b/j/k]fluoranthene/benzo[b/j/k]fluoranthene + benzo[e]pyrene (BF/BF+BeP) has also been removed. Nevertheless, the two data sets still show differences in PAH composition. The more volatile and water soluble PAHs (naphthalene, and the mono- and dimethylnaphthalenes) proved to be too variable to be reliable indicators, and the final PCA model has been based on phenanthrene and the higher PAHs.

SPM samples generally vary the most in composition and show the largest scatter in the PCA model. The 1987 samples are more similar to the core samples from the deltaic lakes and exhibit less variation than the 1993 and 1994 SPM samples. The molecular mass 178 and 252 predominance of Mackenzie River samples contrasts markedly with the mass 202 and 252 predominance that is usually observed in areas that receive direct anthropogenic input. Suspended particulate samples collected in March 1994 had elevated proportions of both the fluoranthene/202 ratio and of molecular mass 202 (fluoranthene and pyrene) at Inuvik, Aklavik and Arctic Red River. The indeno[1,2,3-*cd*]pyrene/276 ratio was also high at Arctic Red River, but indeno[1,2,3-*cd*]pyrene was undetectable in the other two samples. Fluoranthene and indeno[1,2,3-*cd*]pyrene proportions are elevated in the long-range transported aerosol (with its associated combustion PAHs) that manifests as Arctic haze in late winter. Because the river SPM is still low at this time, atmospheric PAHs may have a detectable influence on the river PAH composition.

Naphthalene and the molecular mass 202 PAHs (fluoranthene and pyrene) were the major PAHs in the Nunavut rivers. This, along with the general predominance of fluoranthene over pyrene, implicates combustion (presumably from long-range transport) as the major PAH source. Higher molecular weight PAHs were only trace constituents in most samples; the highest amounts were present in the Back River sample, where the molecular mass 252 PAHs were one-half the concentration of the mass 202 PAHs.

“Fort Good Hope” Project

SPMDs from the Norman Wells oil refinery effluent contained potent MFO inducers, equivalent to 18,000–39,700 pg TCDD per g SPMD. SPMDs from the Mackenzie River, 0.5 km downstream of the refinery outfall also induced MFO, but at one-twentieth to one-fortieth of the potency of the effluent SPMDs. Rainbow trout exposed to refinery effluent showed only a three-fold induction compared to control fish. While mono-, di- and trimethyl PAHs were present in the SPMD extracts, it is unknown which compounds caused the MFO induction (Parrot *et al.* submitted).

Expected project completion date: March 31, 1998

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DEPOSITIONAL TRENDS–LAKE AND MARINE SEDIMENTS

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OBJECTIVES

1. To obtain sediment core samples from a grid of arctic headwater lakes in sufficient quantities to permit determinations of layer ages using radionuclide concentrations and down-core profiles of polycyclic aromatic hydrocarbons, organochlorines, and metals. In addition, sediments from marine locations will also be taken when ships and equipment are available. The target collecting program has been 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, and more recent work has been in the western NWT and Yukon.

2. To derive the LRTAP input rates of each contaminant at each site, set current rates of supply in the context of those which have been taking place over the last century and longer, and compare accumulations with information on sources and transport processes. Knowledge of past and present loadings of chemical contaminants provides the best basis we have for predicting future loadings. When sufficient sites have been studied for both sediments and fish, it will be possible to tell how well the history of contaminant supply is related to contaminant levels in the fish.

   In the instances of metals and PAHs, there are both natural and anthropogenic components and core records offer one of the few technologies to gain insight into the relative importance of each.

DESCRIPTION

Lake sediment cores have been collected from several locations in the Northwest Territories and the Yukon Territory over the period from 1987 to the present, partly under the Northern Contaminants Program and partly under the previous program. A list of cores taken to date is given in Appendix 1. (A similar list is given in the Yukon report for cores taken there.) Coring arctic lakes has usually been done through the ice uses a box corer or a large-diameter KB-corer; these corers obtain quantities of sediment sufficient to permit dating and chemical analyses of individual slices. Cores are sliced at the time of collection and slices are returned to the laboratory for dating using radiochemical analyses before being analysed for a selected metals, hydrocarbons and organochlorines. Time intervals for the deposition of each slice are estimated from the lead-210 and cesium-137 profiles using several models (some supplied by Dr. J. Robbins, NOAA, Ann Arbor) that account for mixing of the upper layers. Dating allows the calculation of the rate of sedimentation at the core site. An estimate of the actual net rate of delivery of a contaminant to the site can be obtained from the sedimentation rate and the concentration of the contaminant. Making this calculation for different slices provides a measure of the changes in the rate of supply of the contaminant over time. Unless some factor intervenes to change the rate of supply, then it offers a realistic basis for predicting future inputs.

In 1992 and 1993 marine cores were obtained by participating with DFO cruises to Hudson Bay. In 1994, we were also able to obtain cores from Lake Winnipeg using the Coast Guard ship *Namao*. Cores taken from ships were obtained using oceanographic box corers, with 10-cm diameter push cores being taken from the box cores after they were on deck. We hope to extend the geographic coverage throughout the Canadian Arctic and to compare the 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 and some Ukrainian cores were obtained through a project with the International Development Research Centre.

ACTIVITIES IN 1995/96

There were no field collections after March, 1995 under the Northern Contaminants Program. A list of cores obtained with NCP support studies is appended (Appendix 1). Since March, 1995, the emphasis has been on the analysis of samples of sediment cores already on hand. In view of the amount of material to analyse (Appendix 1), this work will continue for some time beyond 1997/98. Our procedure has been to obtain slice dates and then proceed with other analyses if chronologies are credible.

RESULTS

Pb-210 and Cs-137 in cores

The fundamental measurements that make cores more valuable than simple grab samples are those that permit dating of slices, namely lead-210 and cesium-137. Lead-210 is a natural radioisotope formed by the decay of radon gas and cesium-137 is derived from atmospheric testing of nuclear bombs. Cesium-137 should peak in about 1963 just before atmospheric testing of bombs was stopped by most countries. The Pb-210 and Cs-137 profiles for a selection of NWT lakes are shown in Figure 1.

Metals

The principal focus of the report this year is on metals because several of these have been analysed but not been reported previously. Metals are among the most important measurements made, especially mercury, because it has been found often in northern fish and marine mammals at concentrations above those considered safe for human consumption. The implications for the fish and marine mammals themselves are speculative. At any given site mercury (or other natural elements) can be composed of contributions from natural geological sources within the watershed, from local human activities within the watershed and from local or distant sources of mercury deposited by atmospheric fallout. With mercury, cores offer the best insight we have regarding the relative contributions of natural and anthropogenic activities. Similarly with lead, there are both natural within-basin supplies and external fallout supplies. With lead, however, both core profiles and isotope ratios can offer insights into natural and anthropogenic sources. Resolution of the relative importance of natural and anthropogenic sources is important because countries throughout much of the world are trying to determine whether more stringent controls are needed on emissions of several metals. Generally the three metals of greatest concern are mercury, lead and cadmium. Our results for mercury in northern cores were presented at the Fourth International Conference on Mercury as a Global Pollutant in Hamburg in August, 1996 and have now been accepted for publication (Lockhart *et al.* Biogeochemistry, in press).

Amituk Lake Metals

In addition to our own cores, several cores from Amituk Lake have been analysed for Pb-210, Cs-137 and metals for Dr. R. Semkin, Environment Canada, Burlington, ON. Slices 1-34 of our core A have been analysed for Al, Cd, Cu, Fe, Hg, Mn, Ni, Pb, Ti, V, and Zn and these have not been reported previously (Figure 2). The resolution achieved with this core is relatively coarse since it was sliced a 1-cm intervals. Furthermore, the cesium-137 peak was in the top slice apparently deposited in the late 1970s and 1980s. This is too recent for bomb fallout and so the lead-210 dates and sedimentation rate for this core must be viewed circumspectly. The core shows an increase in mercury in uppermost slices and this is consistent with the other cores from that lake. There may also be a small increase in lead. Neither lead nor mercury are believed to be mobile in cores (EPRI 1996, Blais 1995) and so these increases probably reflect increased loadings to the site. Increases in manganese and iron are often observed in our cores; these are interpreted as within-core redistribution processes, not as indications of increased loadings with Mn or FE. The increases in nickel and zinc were confined to two slices and they appear too sharp to be the result of atmospheric fallout; they may represent some local event or possibly within-core redistribution like that that of manganese. Mercury levels in Amituk Lake arctic char were sometimes quite high with levels as high as 2 $\mu g \cdot g^{-1}$ being found in muscle and as almost 7 $\mu g \cdot g^{-1}$ in liver.

Lac Belot Metals

Belot core KB-1 had a satisfactory lead-210 profile with a maximum for Cs-137 in the mid-1960s. Slices 1-46 of core KB-1 were analysed for Cd, Hg, Al, Ti, Fe, Mn, Ni, Zn and Cu. There were no increases of Cd or Hg in the near-surface slices suggesting that this site reflects natural geological fluxes of these metals with little or no added loading due to anthropogenic sources. Increased concentrations of Fe and Mn in the upper slices are taken as within-core redistributions which occur commonly with these metals. Core 2 which has not been dated yet showed a more distinct increase in Hg in the upper few slices. However, lake trout from this lake had low levels of mercury in spite of being among the oldest fish we have analysed. For example, one fish was 55 years old and had a mercury level of only 0.18 $\mu g \cdot g^{-1}$.

Colville Lake Metals

The PB-210 profiles for these cores were interpreted readily but the Cs-137 profiles were highly unusual. Colville Lake core KB-1 was taken from very sandy sediment and core KB-2 was highly organic in nature. In some settings Cs-137 profiles are not preserved well and other studies have shown that, when they do not agree, the Pb-210 gives better agreement with

Table 1. Estimates of fluxes of mercury to the upper parts of the cores deposited since the 1950s (recent flux) as compared with fluxes to the deepest slices in the same cores (historic flux). The anthropogenic flux is taken as the excess of the recent flux over the historic flux. (See also Yukon report).

Site	Core	Time interval used to calculate recent	Mean HG concentration in slices since 1950s $ng\cdot g^{-1}$ dry wt.	Recent flux of Hg $\mu g\cdot^{-2}\cdot y^{-1}$	Mean Hg concentration in deepest 5 slices $ng\cdot g^{-1}$ dry wt.	Historic flux of HG $\mu g\cdot m^{-2}\cdot y^{-1}$	Excess of recent flux over historic flux of Hg $\mu g\cdot m^{-2}\cdot y^{-1}$
Amituk	KB1	since 1957, slices 1-4	49.5	3.9	16.4, slices 31-37	1.8	2.1
Belot	KB1	since 1954, slices 1-5	62.8	2.1	53.1, slices 42-46	1.8	0.3
Buchanan	KBA	since 1950, slices 1-16	98.8				
Far	BCA	since 1949, slices 1-4	89.0	3.1	31.6, slices 21-25	1.1	2.0
Great Bear	KB1	since 1950, slices 1-5	77.9	4.3	52.1, slices 17-23	2.8	1.5
Hazen	BCB	since 1963, slices 1-5	65.3	23			
Kusawa	KB1	since 1951, slices 1-5	35.8	10	22, slices 25-29	6.2	3.8
Lake 375	BCA	since 1953, slices 1-6	155	16	67, slices 25-29	7.0	9.0
Laberge	KB3	since 1951, slices 1-12	25.8	18.4	22.4, slices 22-26	16.0	2.4
Little Atlin	KB1	since 1950, slices 1-22	87.8	51	78.6, slices 38-42	45.6	5.4
Lindeman	KB1	since 1951, slices 1-23	23.1	9.6	15.8, slices 36-40	6.6	3.0
Ste Therese	KB1	since 1953, slices 1-10	152	29	130, slices 29-33	25.1	3.9
Trout	TL12	since 1952, slices 1-10	159	17	69.6, slices 32-36	7.7	9.3
Winnipeg South	7A	since 1949, slices 1-15	125	114	58.0, slices 34-38	52.7	61.3
Winnipeg North	2A	since 1952, slices 1-13	45.0	26	22.0, slices 38-42	12.7	13.3
Yaya	KB1	since 1951, slices 1-10	98.4	28	92.1, slices 24-28	29.8	
Hudson Bay	H4	since 1949, slices 1-6	23.0	6.0	16.2, slices 34-38	4.2	1.8
Hudson Bay	F4	since 1955, slices 1-5	35.2	16.2	24.9, slices 31-35	11.4	4.7

Anthropogenic loadings to Lake Winnipeg are too high to be consistent with atmospheric loadings. The likely contributors to these high loadings are the large population and extensive industrial and agricultural activities in the Red/Assiniboine drainage.

independent measurements such as *Ambrosia* pollen. Consequently, we have estimated dates and sedimentation based on Pb-210. Core KB-1 has been analysed for mercury only and core KB-2 has been analysed for Pb, Cd and Hg. Both cores show an increase in mercury in uppermost slices suggesting some anthropogenic loading with Hg. There is also a tendency for slightly higher concentrations of lead in the upper slices of core 2. We have only a few (8) lake trout from this lake, but they are richer in mercury than they are from nearby Lac Belot, the maximum being 0.45 $\mu g\cdot g^{-1}$.

Far Lake and Hawk Lake (Saqvaqjuac) Metals

Both these small lakes on the west coast of Hudson Bay had interpretable Pb-210 profiles with Cs-137 peak activities in the 1960s. Furthermore both these sites had trace quantities of Cs-134 in their top slices, indicating a small input of fallout from Chernobyl. These cores were taken in 1988 and the Chernobyl accident occurred in 1986. Far Lake Core A and Hawk Lake Core A have both been analysed for Pb, Cd, Hg, Al, Fe and Mn. (Figure 3). The Far Lake core showed distinct increases in the top few slices of Pb and Hg. Cd in Far Lake showed a sub-surface peak several slices deep; estimated dates place the peak in the 1930s and so we have wondered whether it reflects fallout from early smelters in southern Canada. Hawk Lake also showed three near-surface increases in Pb and Hg, and also in Cd. In Hawk Lake also the Al plot was surprisingly variable suggesting significant changes in the nature of the drainage, probably several hundred years ago. The near-surface variation in Fe and Mn probably reflects oxygen tensions but the deep peaks in these two metals, and probably also in Cd, may reflect the same drainage change that was indicated by Al. There was a striking increase in Cd in the uppermost slices similar to that from Far Lake but continuing almost to the sediment surface. Mercury data on these lakes was published by Lockhart *et al.* (1993, 1995). Mercury in a small (8) sample of lake trout from Hawk Lake ranged up to 0.5 $\mu g\cdot g^{-1}$.

Giauque Lake Metals

Giauque Lake, some 84 km north northeast of Yellowknife, is of particular interest with regard to mercury because it was the site of the Discovery mine. This is the first core we have examined from the NWT where a source of contamination was known to be localized within the basin. The mine produced gold from 1950 to 1968 using processes with cyanide and mercury to recovery gold from the ore. Approximately 2.5 tons of mercury were used during the operation. (Moore *et al.* 1978, Coedy 1994) and, although most of it was recovered, some escaped to the lake. Fish from Giauque have high levels of mercury with maximum levels reported to be 12.3, 4.8 and 2.6 µg/g for lake trout,

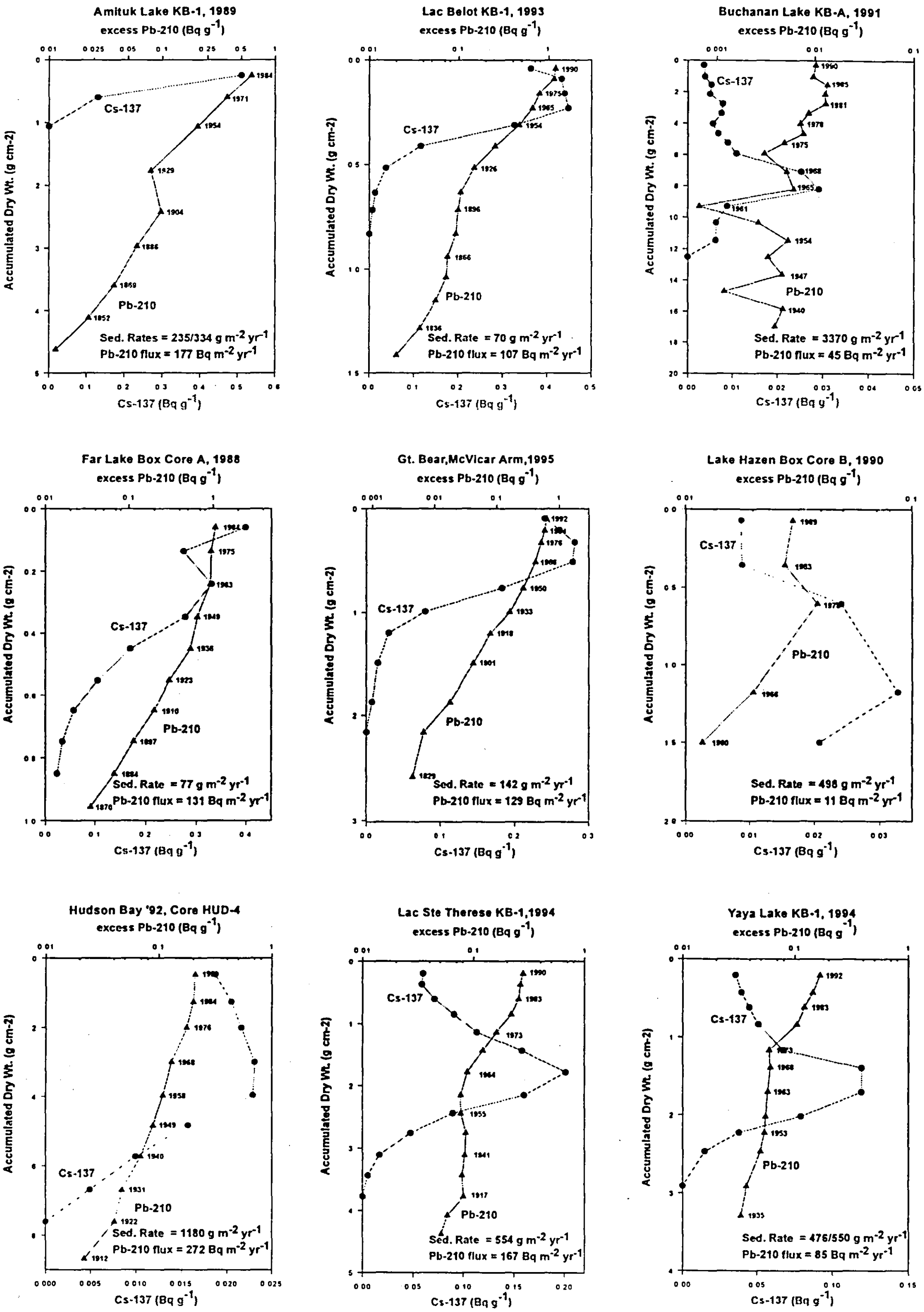


Figure 1. Pb-210 and Cs-137 in sediment core clices from lakes in the Northwest Territories.

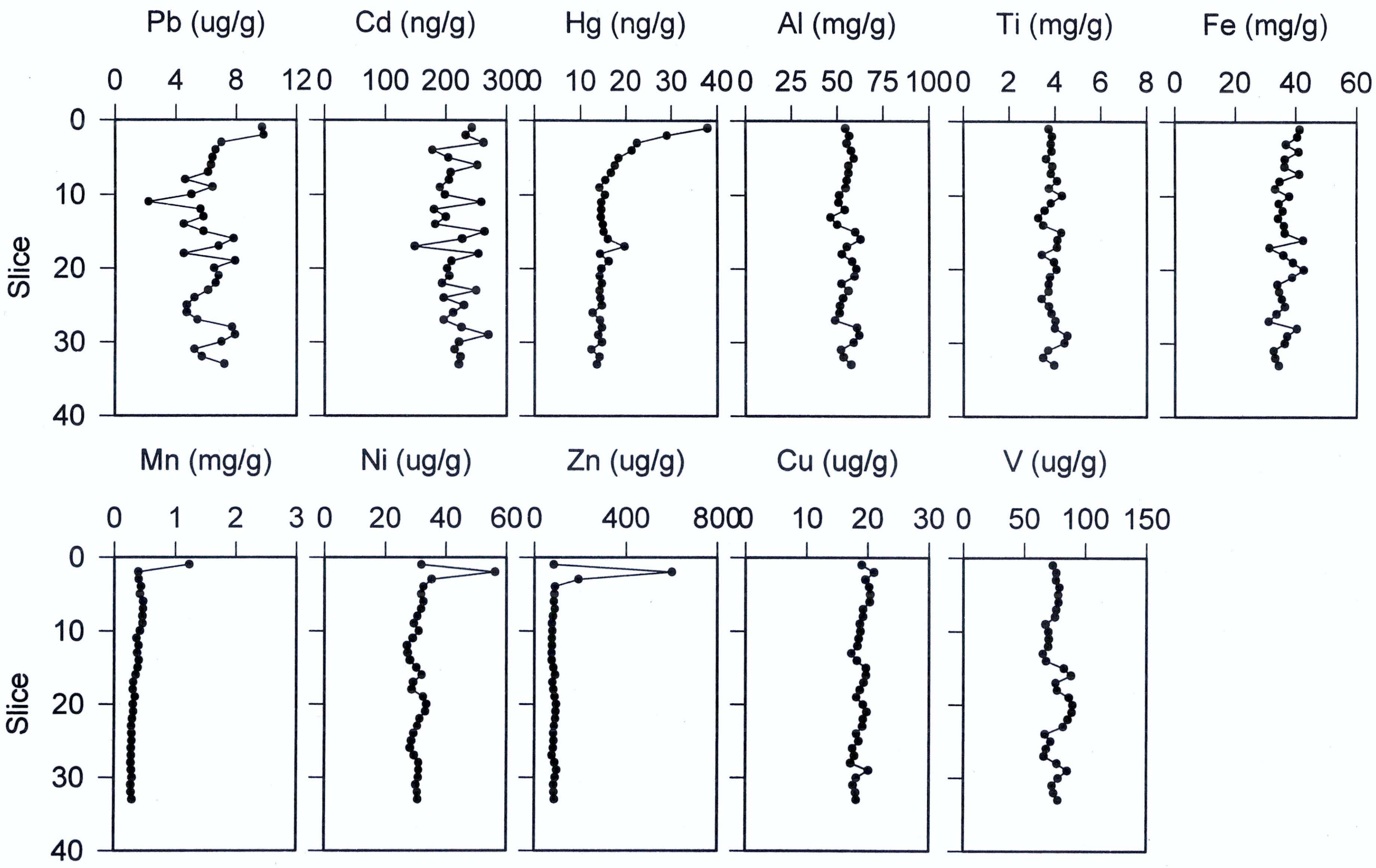


Figure 2. Metals in Amituk Lake, NWT, Core ALKB-A, June, 1989 (bottom slice omitted due to aberrant values, slice to be re-analysed.

northern pike and round whitefish respectively (Moore *et al.* 1978). A large "tailings fan" was formed by the deposition of tailings into the lake and several metals have been measured in near-surface samples from the tailings deposit (Moore *et al.* 1978). The core profiles (Figure 4) show increases in loadings of lead and mercury and also probably with gold. Mercury in tailings samples ranged averaged over 700 ng/g with a maximum of 2700 ng/g (Moore *et al.* 1978), as compared with basal levels in the lower part of the core of only about 30 ng/g. Lead in tailings ranged averaged 71 µg/g while in the bottom of the core lead concentrations were below 15 µg/g. Consequently, elevations in sediment mercury and lead could be explained most simply by treating the tailings as the source. Gold was not analysed in the tailings but the core results suggest that it too was lost due to mining activities. These three metals all show increased inputs several slices deep, with lead and mercury dating from approximately the 1950s (Figure 1); all but the top 4 slices were below our detection limit of 20 µg/g gold and so we can be confident that gold had increased by 1970s but we cannot tell how much earlier it began to increase. In addition to the metals shown in Figure 4, silver was also measured but it was below the detection limit of 20 µg/g in all slices.

Core 2 was taken in the deepest (66 m) central portion of the lake several km from the tailings fan and so material eroding from the tailings may have taken some time to reach the core site. Peaks in iron and manganese probably represent within-core redistributions rather than contributions from the tailings. Nickel sometimes increases much like manganese, presumably for similar reasons but it can also reflect contamination; We cannot tell which is the case here. The average Ni concentration in the tailings was 66 µg/g which is the same as levels deep in the core. It does seem likely that the increase in Ni in the top of the core can be explained by a simple mechanism of tailings dispersal. Increases in cadmium, zinc and copper were also noted in the top few slices but their profiles were different from those of lead, mercury and gold. Zinc and copper were present in the tailings with average concentrations of 183 µg/g (Zn) and 68 µg/g (Cu), both slightly above the respective levels deep in the cores. The tailings samples were all below detection in Cd. The profiles for Ni, Zn and Cu may reflect contamination with tailings and but they may also reflect some redistribution within cores since their profile shapes differ from those of Pb, Hg and Au.

Cobalt showed no increase throughout the core and concentrations in the tailings were about the same as those in the core. Aluminum and vanadium also showed no trend with depth in the core and core concentrations exceeded slightly those in the tailings.

Lac Ste Therese Metals

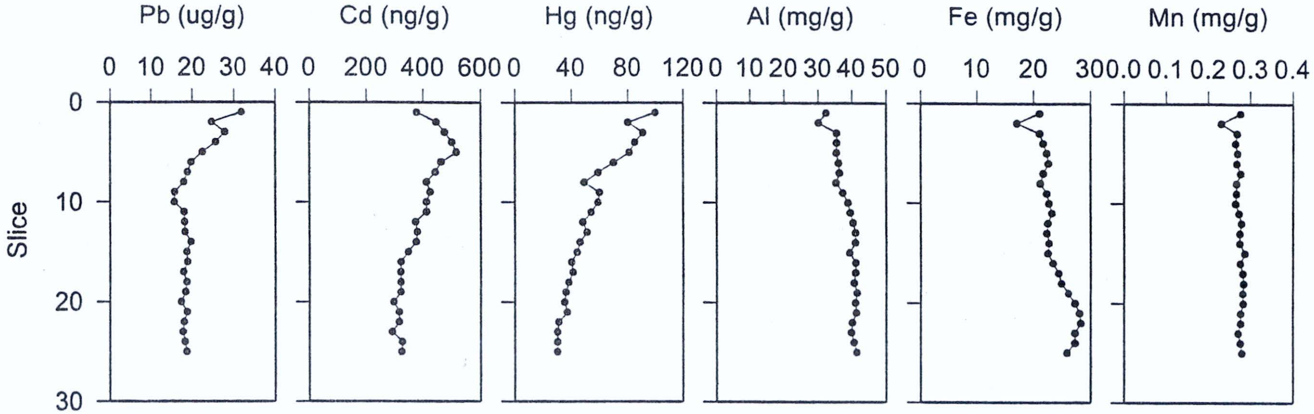
Previous studies by DIAND had shown that fish from Lac Ste Therese have high levels of mercury and so that lake was chosen for core studies. The Pb-210 and Cs-137 profiles for three of the cores are shown in Figure 1. We interpret the Pb-210 profile from core 1 to indicate a sedimentation rate of 554 $g \cdot m^{-2}\ y^{-1}$ (not corrected for focusing) and this interpretation estimated the date of the Cs-137 peak to be in the early 1960s, indicating credible dates. However, there has clearly been some spreading of the Cs-137, probably both upwards and downwards, since trace amounts were detected in slices earlier than the 1940s. A set of profiles for core 1 for several metals is given in Figure 5 and there was very little recent increase in inputs of mercury. The apparent increase in mercury just above the bottom of the core would have been two centuries or more ago and not an indication of an increase anthropogenic impacts. Similar profiles for core 3 are shown in Figure 6 with similar results except that the recent increase in mercury is more obvious. Lake trout, walleye and northern pike and walleye from this lake all had high mercury concentrations with individuals from all three species having as much as 2 $\mu g \cdot g^{-1}$.

YaYa Lake Metals

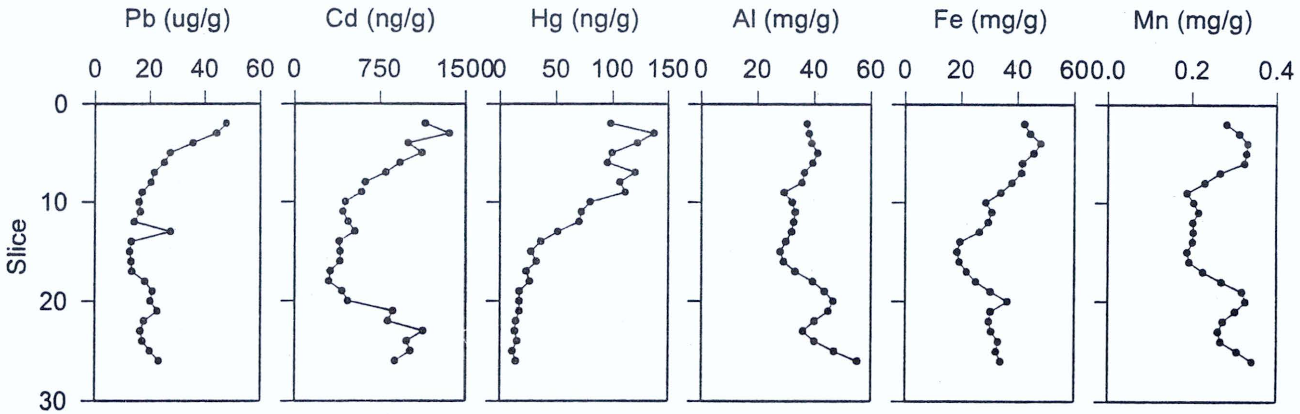
The Pb-210 and Cs-137 profiles for YaYa lake are shown in Figure 1. All three cores had interpretable profiles but core 1 was taken as two separate sedimentation patterns, an upper rate of 476 $g \cdot m^{-2}\ y^{-1}$ and a deeper one of 550 $g \cdot m^{-2}\ y^{-1}$. The Cs-137 peak was found to be in the mid-1960s for all three cores and so the dates were considered acceptable. The core profiles for core 1 for Pb, Cd, Hg, A.l, Ti, Fe, Mn, Ni, Zn, and Cu showed little or no increase in Pb, Cd or Hg in the upper slices. This is interpreted as evidence that the site has received little or no recent anthropogenic enrichment of these metals over basal geological levels. As in a number of other cores the increases in Mn and Fe are not taken as indicators of loadings but rather as indicators of movements within the sediment. Mercury has been analysed in lake trout and inconnu from this lake and levels were under the criterion of 0.5 $\mu g \cdot g^{-1}$ for commercial sales, but some lake trout fell only slightly under that level.

Anthropogenic fluxes of mercury

Taking the NWT, Yukon and some southern sites together, we have calculated the natural and anthropogenic fluxes of mercury to most of the sites where we obtained interpretable lead-210 profiles. We have also corrected the fluxes for within-lake focusing by comparing the flux of lead-210 with that expected for the region. The results are listed in Table 1 and shown in the map in Figure 7 (both taken from Lockhart *et al.*



Far Lake, NWT., Core A, April, 1988



Hawk Lake, NWT., Core A, May, 1988

Figure 3. Metals in Far and Hawk lakes, NWT, 1989.

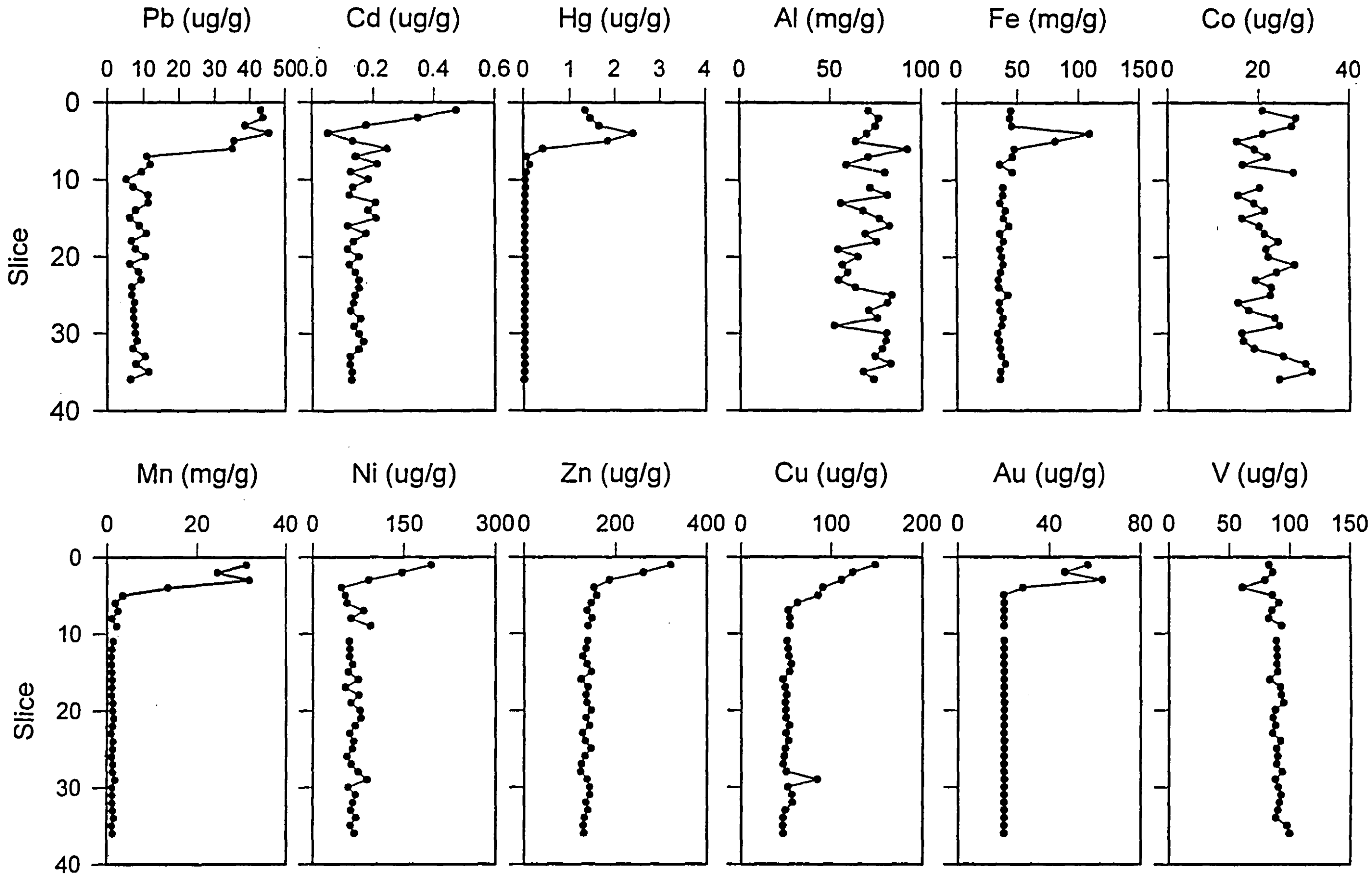


Figure 4. Metals in Giauque Lake, NWT (Discovery mine), Core 2, March 1995.

Table 2. Polycyclic aromatic hydrocarbons (PAHS) measured in the top 12 and in the 15th slices of Lac Ste Therese, core 1.

Naphthalene	2-methylnaphthalene	1-methylnaphthalene	Dibenzofuran
Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene
Anthracene	Fluoranthene	Pyrene	Retene
Benzo(a)anthracene	Triphenylene	Chrysene	Benzo(b)fluoranthene
Benzo(k)fluoranthene	Benzo(e)pyrene	Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene
Dibenzo(ah)anthracene	Benzo(g,h,i)perylene	Dibenzothiophene	Perylene

Biogeochemistry, in press). We were not confident in the lead-210 dating of cores from Lake Hazen on northern Ellesmere Island and Lake Buchanan on Axel Heiberg Island and so we did not make estimates of anthropogenic loadings there. However, down-core profiles of mercury in these lakes gave no indication of recent increases. Giauque Lake was also excluded because it had very high loadings due to contamination with mercury in waste from the Discovery mine. Anthropogenic fluxes had a small range from undetectable at Yaya Lake in the Mackenzie Delta up to 9 $\mu g \cdot m^{-2} \cdot y^{-1}$ in northwestern Ontario, in good agreement with other studies in north/central North America and Alaska. Similar conclusions have been derived from studies on lakes in the Belcher Islands (Hermanson 1993) and central Quebec (Ouellet and Jones 1983.

Quality Assurance (metals)

We participated in the external QC/QA interlaboratory comparison on marine sediments described as NOAA-10, operated by NRC (Willie and Berman 1996). This program is aimed at helping to bring laboratories in the NAFTA countries towards common levels of performance. There were 30 laboratories from USA, 4 from Canada, 1 from Mexico and 5 from Australia. This was our first experience with the NOAA program and we were the only Canadian Government laboratory involved this year. Our results were within the ranges expected.

PAHs

Lac Ste. Therese

Measurements of polycyclic aromatic hydrocarbons (PAHs) in the top 12 and in the 15th slices of Lac Ste Therese are shown in Table 2. These compounds originate largely from the combustion of carbon-based fuels, especially coal, but also wood (including forest fires) and oil. They are also present naturally in coal and petroleum and some are found in plant remains. The down-core profiles of several PAHs are shown in Figure 8. The sum (without perylene, retene, dibenzofuran and dibenzothiophene) for PAHs was about 350 ng/g which is similar to levels found for almost the same suite of compounds at Hawk Lake, NWT. and about half those from Lake 375 in the Experimental Lakes Area of Northwestern Ontario and (Lockhart *et al.* 1993). However, the down-core profiles from Lac Ste Therese show little or no trend for the PAHs to increase or decrease over time. The 12th slice of this core should date to the early part of the 20th century (Figure 1) and so the mid-century peak often found in other sites further south is absent. Both Hawk Lake and Lake 375 showed sub-surface peaks of PAH inputs. The profiles for Lac Ste Therese suggest that inputs of PAHs reflect the conditions of the basin with little influence from 20th-century combustion or other processes. PAHs in air tend to be associated with particulate matter, especially those compounds with three or more ring structures. Probably most PAH-bearing particles generated long distances away fall out before they reach this lake.

Yaya Lake

A similar set of PAHs was measured in the slices of core 1 from Yaya Lake (Figure 9) and most of the values were substantially higher than corresponding ones from Lac Ste. Therese. Peak values approached 1000 ng/g, similar to those seen much further south at the Experimental Lakes Area (Lockhart *et al.* 1993) with current values at about 500 ng/g. Yunker and Macdonald (1995) obtained similarly high PAH values for suspended particulate matter sampled in the Mackenzie Delta in 1987. We can compare directly the two sets of results for the group of PAHs identified as phenanthrene to benzperylene (molecular mass 178-278); with those PAHs the river sediment in 1987 contained 970 ng/g and the lake sediment reported here contained about 300 ng/g (Figure 9, ΣPhn-Bpe). In addition to the relatively high concentrations of PAHs, the lake sediment profiles generally displayed sub-surface maxima suggesting that inputs to the site peaked some time ago. The site where core 1 was taken was the first deep basin (150 feet) in the lake nearest the stream connecting the lake to the Mackenzie River. Such a location would probably be dominated by the river more than by its own watershed and would trap more sediment from the river during spring flood than other deep zones further removed from the river. If the period of increased deposition is taken as approximately slices 4 to 11, then the lead-210 dates indicate a period from the 1940s to 1970s. The pattern

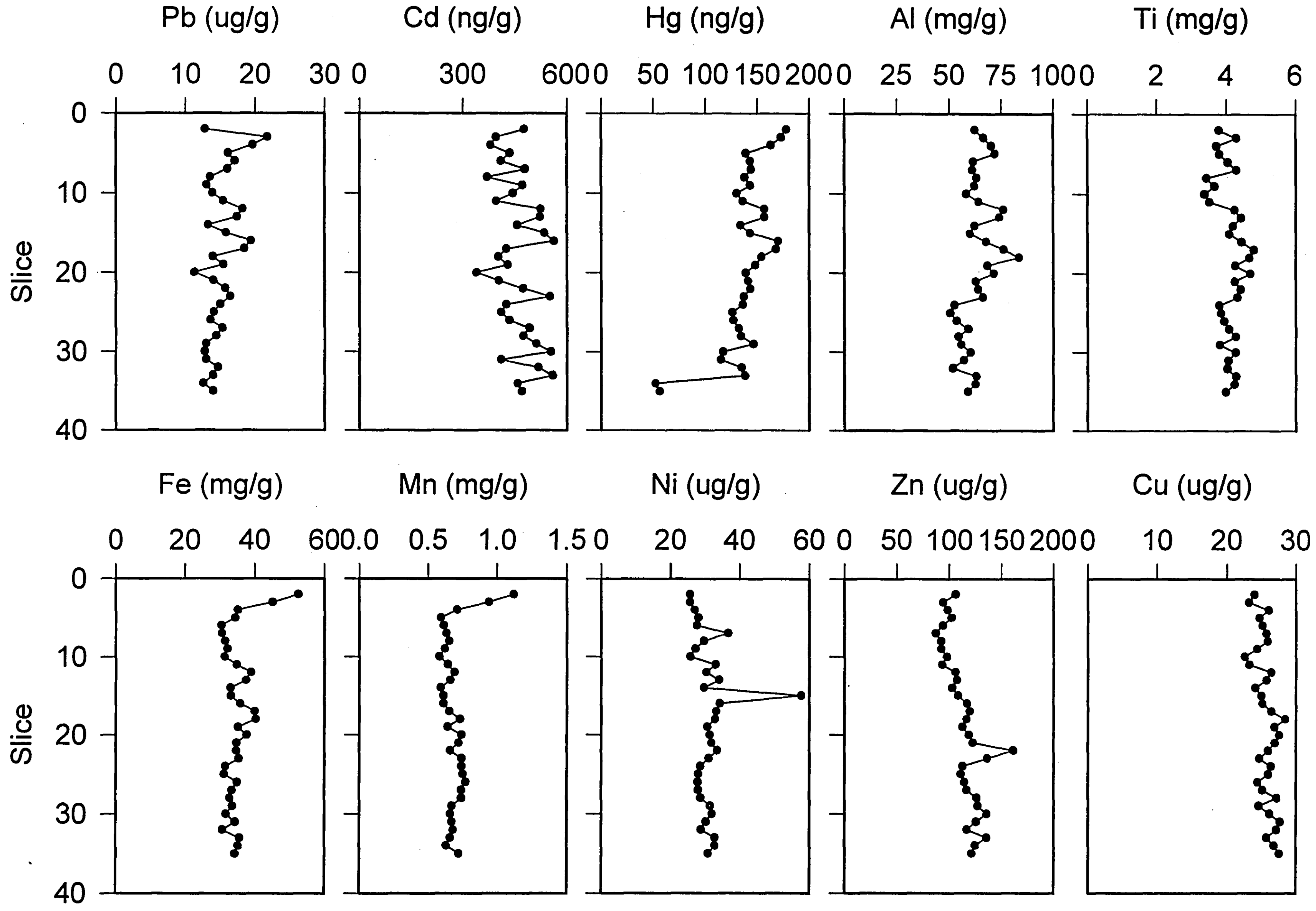


Figure 5. Metals in Lac Ste Therese, NWT, Core 1, April 1994

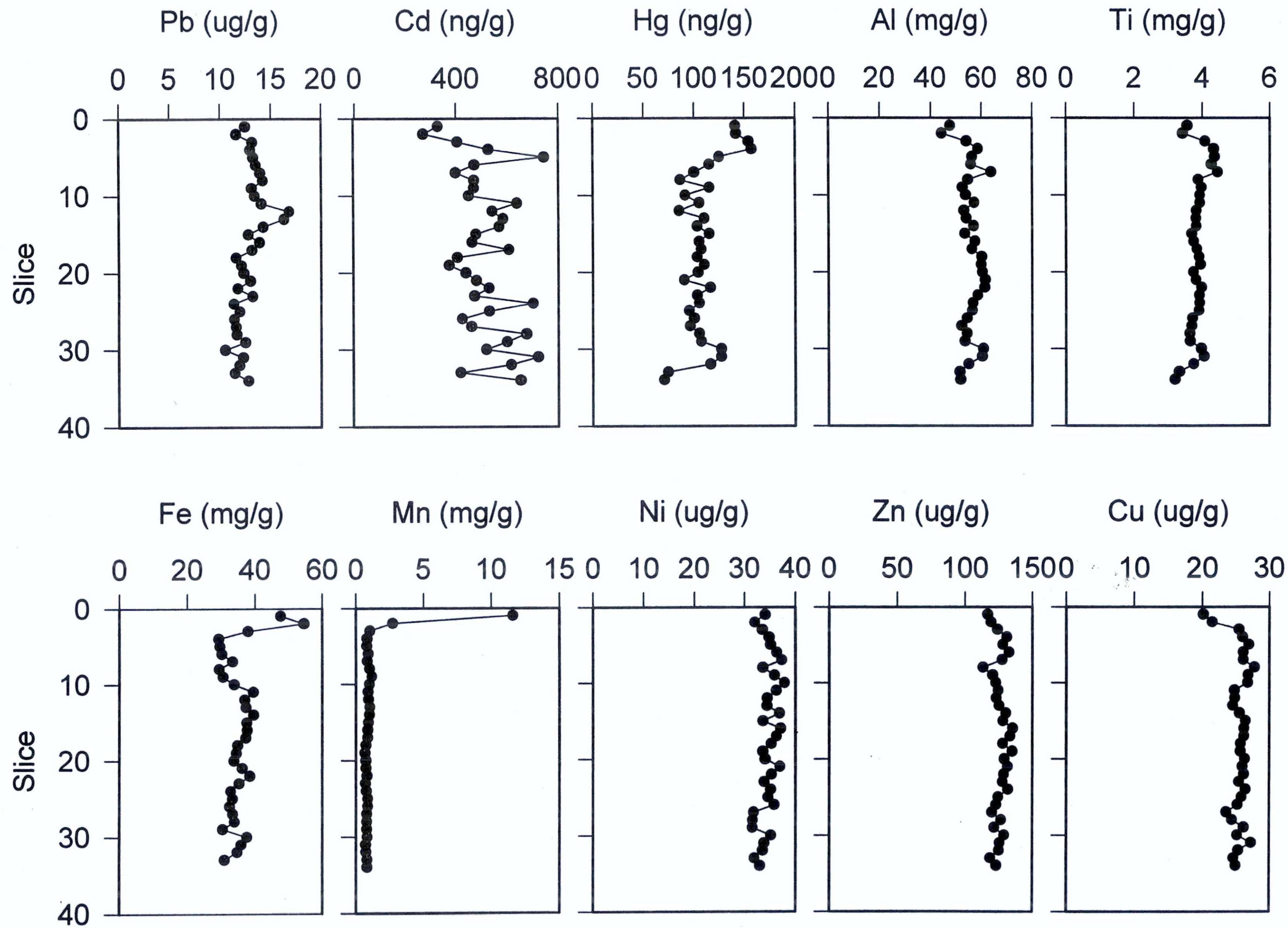


Figure 6. Metals in Lac Ste therese, NWT, Core 3, April 1994.

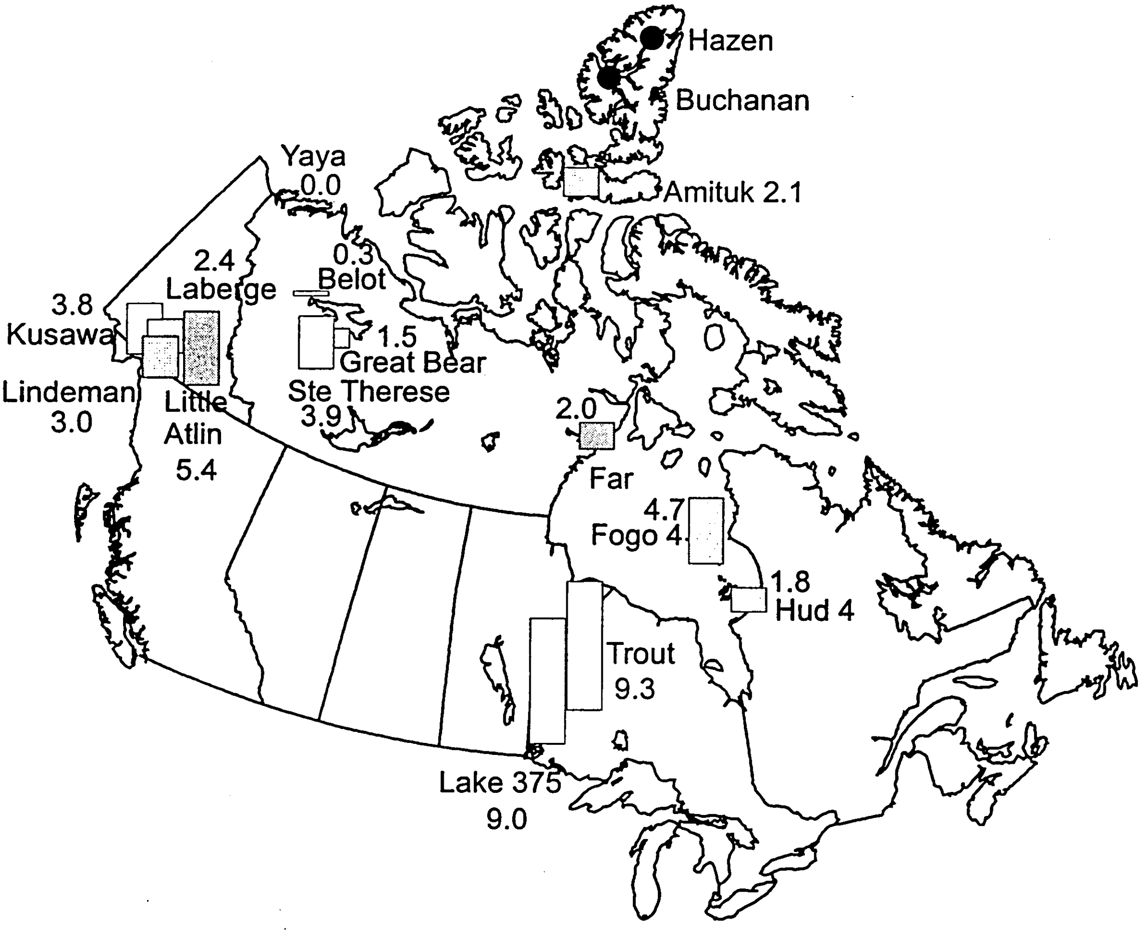


Figure 7. Estimated focus-corrected anthropogenic fluxes of mercury to relatively isolated lakes in Canada. Anthropogenic fluxes were estimated using slices dating since approximately 1950 with fluxes to deeper slices, taken as natural sources, subtracted.

of sub-surface maxima has been reported at a number of sites in North America but the unusual feature about Yaya Lake core 1 is the nearly complete return to basal levels in the top slices.

Organochlorines

Data on organochlorine compounds in several of these cores have recently been published (Muir *et al.* 1996). These compounds have the advantage that they are entirely of anthropogenic origin, and generally have not been used within the watersheds studied. Consequently, like cesium-137, synthetic organochlorines provide a clear and unambiguous indication of loadings originating from outside the watershed. Sediment extracts were analysed for up to 90 PCB congeners by capillary GC-ECD with confirmation by GC-high resolution MS. Total PCB (PCB) concentrations in surface slices (0-1.3 cm depth) ranged from 2.4 to 38.5 ng/g (dry wt.) and showed no latitudinal trend (Muir *et al.* 1996) (Figure 8). The proportion of di/trichloro- congeners of PCB also increased significantly with latitude, while total octachlorobiphenyls declined. Maximum PCB concentrations were observed in subsurface slices dating to the 1960-70s in most lakes except those in the high Arctic, where maxima were generally in surface slices. The onset of elevated PCB deposition was delayed in the high Arctic (1950-60s) relative to the mid-latitude and sub-arctic lakes (1930-40s) (Figure 10). The high proportions of lower chlorinated congeners and the delayed appearance of PCBs are consistent with predictions of the global fractionation model of Wania and Mackay (1993). These trends were originally observed for Lakes Belot, Ste. Therese, Far, Hawk, kusawa, Amituk, Sophia and Hazen but have now also been observed in more recently analysed cores, Yaya and Great Slave Lake 19B (from the study by Evans 1996).

Concentrations of total DDT (ΣDDT) in surface sediments declined significantly with latitude from 9.7 ng/g (dry wt.) in ELA sediments to 0.10 ng/g in Lake Hazen. HCB levels showed a reverse trend; organic carbon normalized concentrations increased with latitude. Concentrations of other OC pesticides (total HCH, total chlordane, toxaphene and dieldrin) were generally in the range of 0.1 to 3 ng/g with the sites at 63 N and 75 N generally having the highest levels (Muir *et al.* 1995).

Fluxes ($ng \cdot m^{-2} \cdot yr^{-1}$) and inventories of sPCB, as well as total tetra- to octachlorobiphenyls, declined significantly with increasing north latitude while those for di/trichlorobiphenyls showed no latitudinal trend. Focus-corrected fluxes of ΣPCB in 18 lakes from 49 to 82° N were found to decline 15-fold over 30 degrees latitude (Figure 11). This decline is statistically significant ($r^2 = 0.61$) and greater than we previously reported (Muir *et al.* 1996) using 11 lakes plus results for Siskiwit Lake (Isle Royale) and Lake Superior.

Fluxes of ΣDDT also showed a significant decline with north latitude ($r^2 = 0.73$) with a 70-fold decline over 30 N (Figure 9). The profiles of ΣDDT and total chlorobenzenes in all the mid-continental lakes showed maxima in slices dated to late the 1970-80s which is about 5 to 10 years later than reported for Lake Ontario.

The declining fluxes of ΣPCBs and ΣDDT between temperate and arctic lakes parallels observed declines in organochlorines in air. Bidleman (1997) reviewed existing data on PCB, DDT and chlordane levels in air in North America. There is a 7x decline in air concentrations of PCBs between southern Ontario and Alert NWT (82° N) and a 40x decline in DDT. The greater decline observed for PCBs fluxes to lake sediments may be due to a number of factors that vary with climate. Small arctic lakes have relatively low efficiency of trapping of contaminants as a result of rapid melting during the short spring period, poor mixing of melt waters with the lake and low concentrations of sinking particles (Diamond 1995). The lakes are icecovered for long period (up to 10 months in the high arctic) which limits inputs via gas exchange and direct precipitation.

DISCUSSION/CONCLUSION

Mercury concentrations were generally higher in surface sediments than deep sediments and this was interpreted as an indication of increased loadings in more recent time, most likely due to human activities. Lakes in southern Canada had higher recent inputs of mercury than those in the North, in common with other contaminants. The exception to this is Giauque Lake where there have been high recent inputs not only of mercury but also of lead and even gold due to the disposal of mine tailings in the lake.

PAH inputs, based on limited data to data, are clearly present throughout the North but anthropogenic inputs appear to be limited in comparison with more temperate locations. PAHs were relatively high in Yaya lake sediments, probably as a result of high spring flows in the Mackenzie River which also has high PAH concentrations associated with suspended matter.

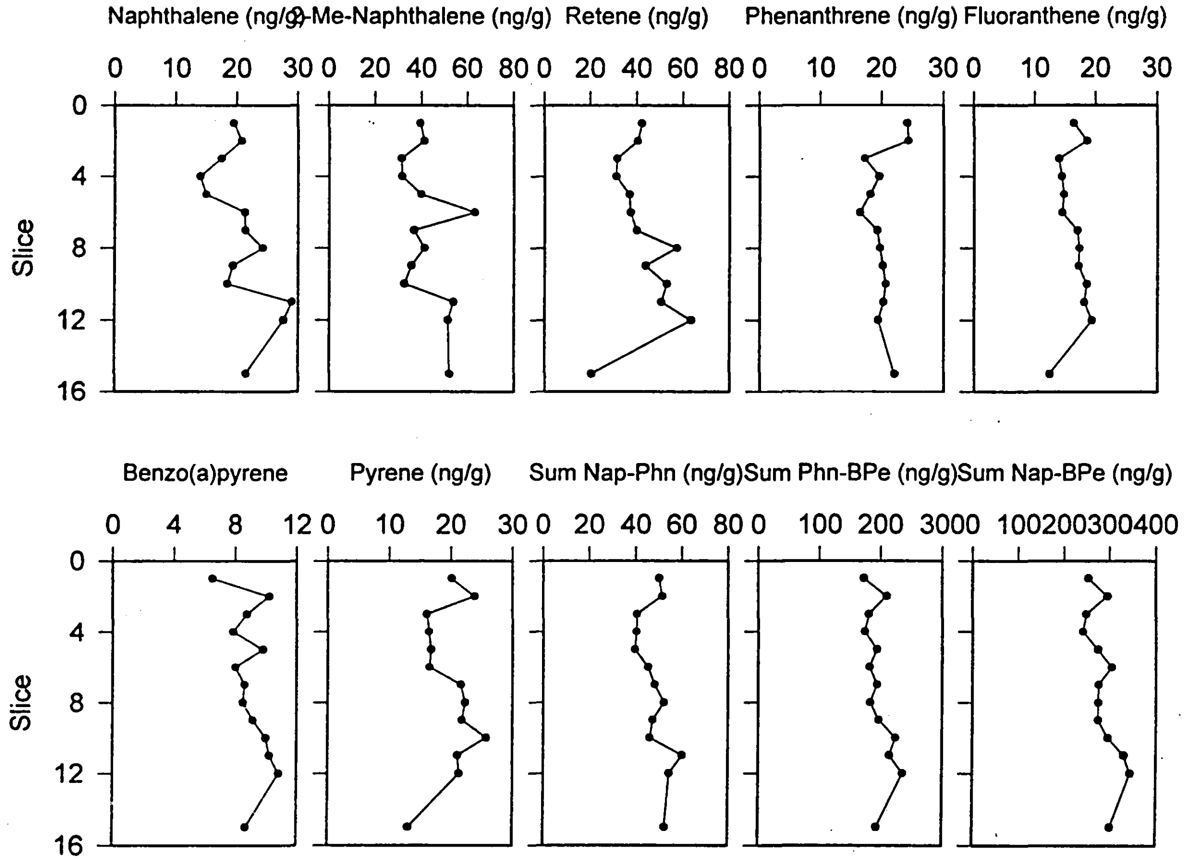


Figure 8. Polycyclic aromatic hydrocarbons in upper slices of Core 1 from Lac Ste Therese, NWT, April 1994.

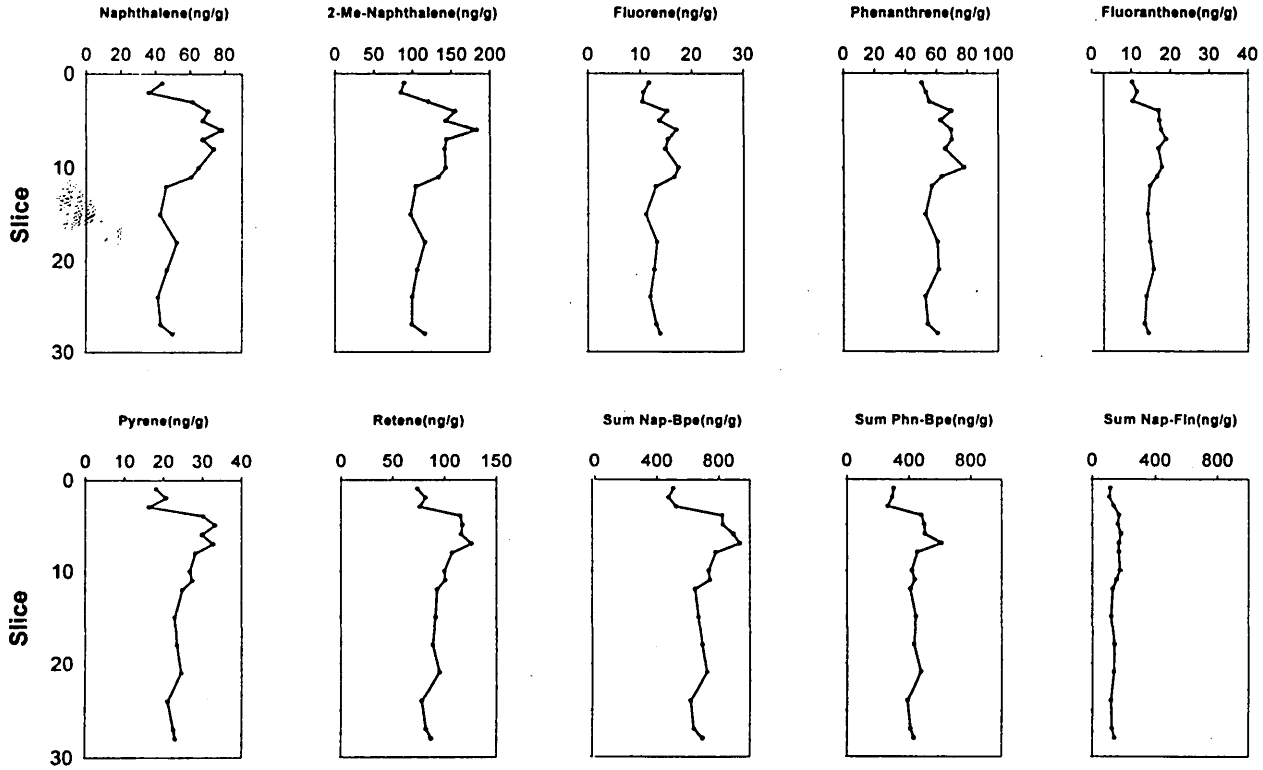


Figure 9. Polycyclic aromatic hydrocarbons in sediment core slices from YaYa Lake, NWT, September, 1994.

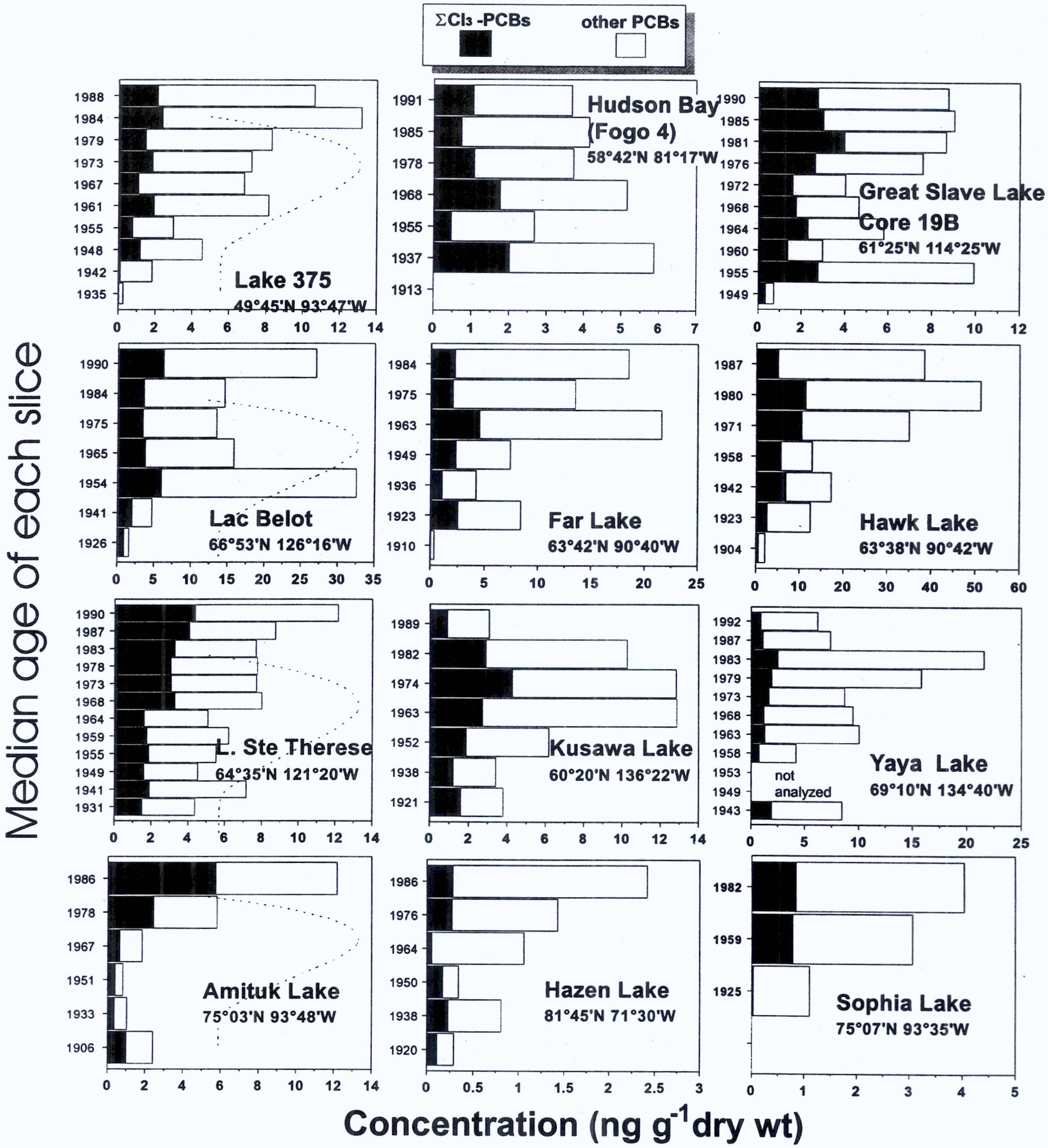


Figure 10. Sediment down-core profiles of PCBs from NWT and comparison with L375 in NW Ontario. Black protion of bar represents trichlorobiphynyls, which ahve been found to increase in proportion to total PCBs with nothern latitude. Entir bar represents "source function", i.e. relative level of production in the US starting in the late 1930s with maximum in the late 1960s. Results from Great Slave Lake core 19B are from the study by Evans (1996).

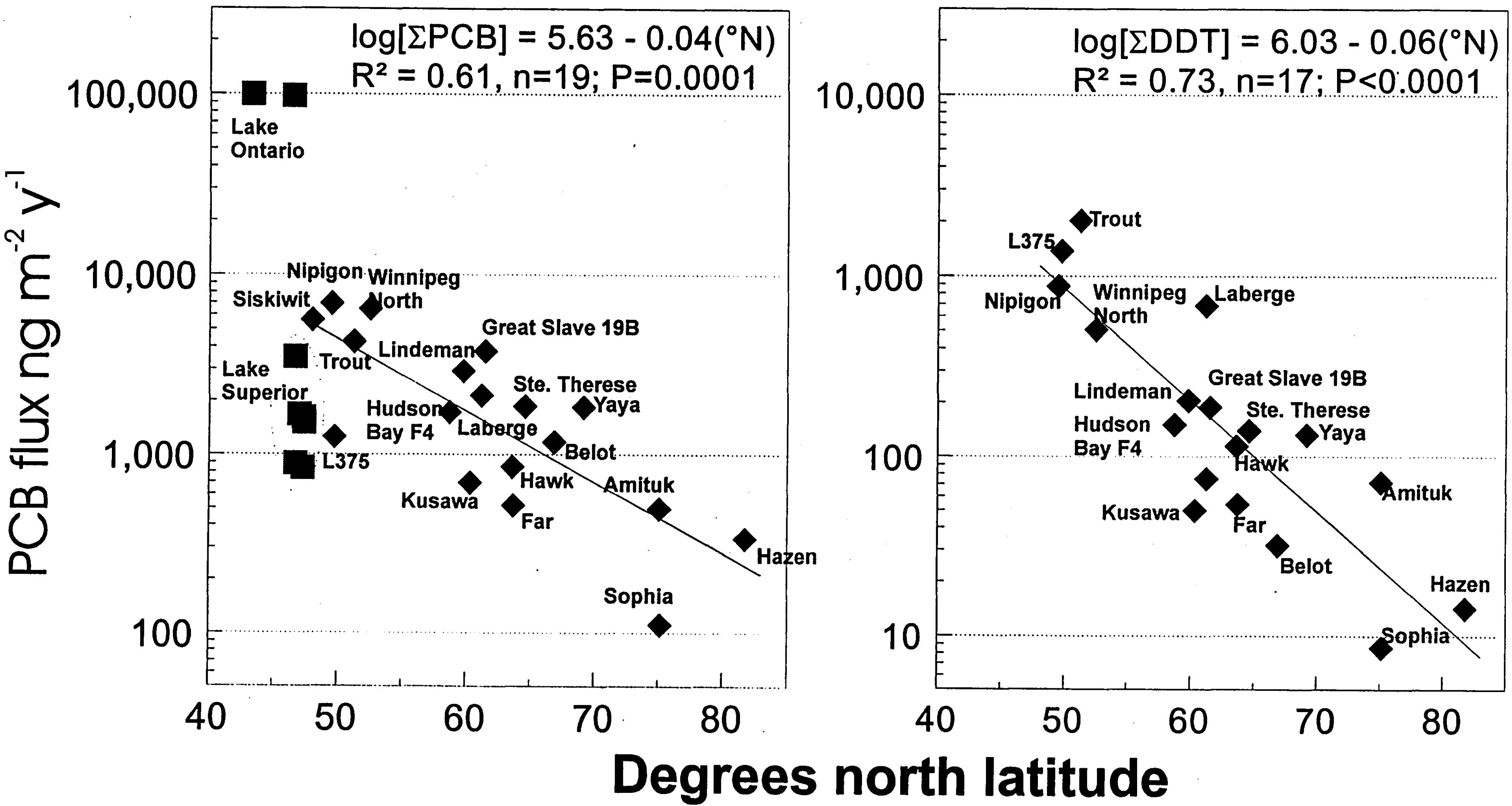


Figure 11. Latitudinal trends in focus-corrected fluxes of total PCBs and total DDT in arctic and north temperate lakes in Canada. Regressions of PCB and DDT vs latitude are made only with NW Ontario and arctic lakes. Results for PCBs in Lake Superior from Jeremiason *et al.* 1994, Siskiwit Lake, Swackhamer *et al.* 1988 and for Lake Ontario, Eisenreich *et al.* 1989.

Fluxes (ng·m^{-2}·yr^{-1}) and inventories of ΣPCB, as well as total tetra- to octachlorobiphenyls, declined significantly with increasing north latitude while those for di/trichlorobiphenyls showed no latitudinal trend. Focus-corrected fluxes of sPCB in 18 lakes from 49 to 82 N were found to decline 15-fold over 30 degrees latitude. Fluxes of ΣDDT showed a significant decline with north latitude (r^2 =0.73) with a 70-fold decline over 30 N (Figure 9.). The profiles of ΣDDT and total chlorobenzenes in all the mid-continental lakes showed maxima in slices dated to late the 1970-80s which is about 5 to 10 years later than reported for Lake Ontario.

Expected project completion date: This project has been completed. Several cores have been archived and analyses of these have not begun. Completion of the remaining cores depends on the priority given to this type of work.

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Appendix 1. Cores taken from Lakes in the Northwest Territories, Northern Contaminants Program and DFO LRTAP program, 1988 - 1995.

Lake	Core	Sample Date	Sample Latitude	Sample Longitude
Amituk	ALKB-A	1-Jun-89	75 28 40 N	093 49 00 W
	ALKB-B	3-Jun-89	75 28 40 N	093 49 00 W
Alexie	ALX-1	16-Apr-94	62 40 37 N	114 06 15 W
	ALX-2	19-Apr-94	62 41 10 N	114 05 57 W
Belot	BEL-1	16-Apr-93	66 57 14 N	126 17 37 W
	BEL-2	15-Apr-93	66 57 47 N	126 20 32 W
	BEL-3	15-Apr-93	66 54 11 N	126 19 28 W
	BEL-4	14-Apr-93	66 52 53 N	126 18 39 W
	BELBC-1	18-Apr-93	66 57 14 N	126 17 45 W
	BLKB-A	18-May-91	79 27 00 N	087 40 00 W
	BLKB-B	20-May-91	79 27 00 N	087 40 00 W
	BLKB-C	21-May-91	79 27 00 N	087 40 00 W
Colville	COL-1	19-Apr-93	67 03 51 N	125 59 43 W
	COL-2	19-Apr-93	67 07 46 N	125 55 16W
Far	FL-A	30-Apr-88	63 39 N	090 39 W
	FL-B	1-May-88	63 39 N	090 39 W
Great Bear	GB-1	13-Mar-95	65 05 49 N	120 47 00 W
Great Slave (Taken for Dr. M. Evans, DOE, Saskatoon)	GSL-1	1-Jul-93		
	GSL-10	16-Mar-95	61 40 27 N	114 03 13 W
	GSL-11	17-Mar-95	61 26 58 N	113 48 55 W
	GSL-12	17-Mar-95	61 53 06 N	113 39 55 W
	GSL-2	1-Jul-93		
	GSL-7	11-Mar-95	62 31 47 N	110 26 24 W
	GSL-8	16-Mar-95	61 37 05 N	113 53 17 W
	GSL-9	16-Mar-95	61 44 57 N	113 52 28 W
Hazen	HAZBC-A	14-May-90	81 47 N	071 30 W
	HAZBC-B	14-May-90	81 47 N	071 30W
	HAZBC-C	15-May-90	81 47 N	071 30 W
	HAZKB-A	12-May-90	81 47 N	071 30 W
	HAZKB-B	13-May-90	81 47 N	071 30 W
Hawk Inlet	HI-A	4-May-88	63 39 N	090 39 W
	HI-B	5-May-88	63 39 N	090 39 W
Hawk Lake	HL-A	2-May-88	63 39 N	090 39 W
	HL-B	3-May-88	63 39 N	090 39 W
Hudson Bay	Hud-1	15-Aug-92	55 17.284 N	77 49.387 W
	Hud-2	16-Aug-92	55 20.15 N	77 46.07 W
	Hud-3	17-Aug-92	55 14.32 N	77 58.96 W
	Hud-4	18-Aug-92	55 15.62 N	77 56.31 W
	Hud-5	18-Aug-92	55 15.79 N	77 53.45 W
	Hud-6	19-Aug-92	55 32.79 N	77 34.31 W
	Hud-7	23-Aug-92	55 58.71 N	77 09.63 W
	Hud-8	24-Aug-92	56 05.45 N	76 56.26 W
	Hud-9	26-Aug-92	55 21.46 N	77 43.20 W
	Hud-10	28-Aug-92	55 32.78 N	78 44.80 W
	FOGO-1	3-Sep-93	54 44.622 N	80 37.770 W
	FOGO-2	4-Sep-93	55 24.224 N	81 18.491 W
	FOGO-3	7-Sep-93	56 45.12 N	79 44.07 W
	FOGO-4	8-Sep-93	58 00.79 N	81 16.68 W
	FOGO-5	9-Sep-93	60 55.59 N	78 56.17 W
	FOGO-6	13-Sep-93	62 41.62 N	78 03.97 W
Giauque	JQ-1	14-Mar-95	63 11 20 N	113 53 13 W
	JQ-2	14-Mar-95	63 10 39 N	113 49 56 W
Kellar	KEL-1	10-Mar-95	63 55 19 N	121 26 43 W
Lac Ste Therese	LST-1	13-Apr-94	64 37 32 N	121 39 10 W
	LST-2	13-Apr-94	64 37 32 N	121 39 10 W
	LST-3	14-Apr-94	64 37 33 N	121 31 06 W
	LST-4	14-Apr-94	64 38 01 N	121 35 24 W
Sophia	SLBC-A	30-May-89	75 06 N	094 35 W
	SLBC-B	31-May-89	75 06 N	094 35 W
	SLKB-A	28-May-89	75 06 N	094 35 W
	SLKB-B	28-May-89	75 06 N	094 35 W
YaYa	YA-1	1-Sep-94	69 10 27 N	134 39 45 W
	YA-2	1-Sep-94	69 12 13 N	134 38 05 W
	YA-3	1-Sep-94	69 11 19 N	134 37 22 W

LONG-RANGE TRANSPORT OF CONTAMINANTS TO THE CANADIAN BASIN

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OBJECTIVES

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

2. To provide an oceanographic and geochemical perspective for interpretation of the contaminant data.

3. 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. Our field work has been carried out in collaboration with the Canadian Coast Guard, who have provided icebreakers as oceanographic platforms, and with other AES workers; Smith and Ellis (radionuclides) and Bidleman and Jantunen (organic contaminants).

ACTIVITIES AND RESULTS IN 1996/97

For the most part, this has been a year of completing analyses on samples collected during previous cruises to the East Siberian Sea (Larsen-93), the Lincoln Sea (1994), the Arctic Ocean Section (AOS-94) and Beaufort Sea sections (Louis-95) with interesting results starting to emerge. Additionally, we have been working on syntheses of marine contaminant pathways for CACAR, AMAP, and PAME (cf. Barrie *et al.* 1997, Macdonald and Bewers 1996). In the following, we outline some of our recent findings which have been reported at the San Diego AGU Meeting in January 1996, and at the Gordon Conference in August 1996.

Arctic Ocean HCH sections and profiles

From our oceanographic sections we defined a region containing persistently high concentrations of HCH in the top 100m of the Beaufort Gyre (Macdonald *et al.* 1996). Several factors appear to contribute to what are some of the world's highest oceanic concentrations. In the Beaufort Gyre the permanent ice cover in winter combined with a shallow low-density surface layer produced by ice melt in summer limits the effectiveness of outgassing with the result that surface water reflects older, higher atmospheric HCH concentrations. This region seems to be one of very low vertical flux with the result that the Archipelago has become the main exit route for this HCH-enriched water. Clearly, for HCH and probably for other OCs that have low Henry's Law constants (e.g., toxaphene) oceanographic conditions provide controls for contaminant concentrations and trends in the top marine predators. To verify that the importance of the Archipelago as an outflow for contaminants, we have collected samples of the outflow water on the eastern side of Greenland (East Greenland Current).

Presently, the inflowing water to the Arctic Ocean from the Pacific and the Atlantic is low, reflecting modern atmospheric concentrations and rapid equilibration (Figure 1). However, as shown in previous sectional data, the reduced concentration in inflowing water is not yet having a discernible influence on the surface waters of the Canada Basin due primarily to manner in which these waters enter this basin interior. The HCH section in 1994 (Figure 2) shows two dominant features. First, the Eurasian Basin surface waters are relatively low in concentration, probably the result of a more rapid renewal by waters recently equilibrated. Second, the basin interiors tend to be higher than regions where boundary currents have provided more rapid transport of inflowing water. Because the AOS-94 section ran along the Canada Basin boundary, the HCH concentrations tend to be lower than we have observed in the interior and we have probably defined a region of transition from basin to margin/shelf. Figure 3 provides a summary of all the vertical profiles produced during sectional work from 1993 and 1994.

Using the above data together with other oceanographic parameters (S, Ba, CFCs; not illustrated here) we have reached the following conclusions. Seasonally ice-free regions are now an atmospheric source of HCH; surface waters (top 200m) under the permanent ice pack continue to have high HCH concentrations; the Arctic Ocean is not homogeneous- there are differences between boundary and interior regions and differences between basins; oceanographic processes are the pathway to set the time scale and provide a method of turndown (water mass production, loss, vertical-flux); HCH budgets suggest the archipelago is the most important escape route for transport of HCH out of the Arctic Ocean. Since about 1990, the Arctic Ocean appears to have been undergoing a dramatic change in circulation and the distribution of water masses (Macdonald 1996). We do not understand what is forcing this change, nor do we know what effect it will have on the redistribution of water properties including contaminants. This makes it all the more important to continue monitoring activities to observe the evolution of these changes and their downstream effects.

Processes affecting Cd distribution in Arctic sediments

Because it is one of the priority contaminant metals, and because high concentrations have been found in the organs of some marine mammals, we have been measuring Cd in sediment cores collected from a variety of coastal and basin locations. Our aim was not only to establish the sediment concentrations in the Arctic Ocean, but also to look for evidence of trends in the sediments both as a function of depth and as a function of location. It was a surprise, therefore, that we often found sub-surface Cd concentrations to be elevated above ocean disposal guidelines in many sediment cores. Detailed examination of the sediment geochemistry has shown these elevated concentrations to be produced by redox processes within the cores rather than by contamination (Gobeil *et al.* 1997). As a result, sediment records of Cd must be viewed with extreme caution and cannot be used directly to infer contaminant Cd fluxes.

Hydrocarbon (PAH) distributions in Arctic Ocean Sediments

PAHs are important POPs that can induce biological effects including toxicity. PAHs also have value as tracers of contaminant transport pathways and areas of accumulation (source/sink).

Work initiated on the Beaufort Shelf in the late 1980s has been expanded to include sediments from the East Siberian and Chukchi Seas, the Barents and Kara seas and from the Canada and Eurasian Basins. Detailed examinations of the PAH profiles both in terms of their compound compositions and their horizontal and vertical distributions in sediments (Figure 4) are suggesting the importance of ice as a transport mechanism (Yunker et al. 1996). The main findings have been that Arctic Basin locations influenced by the Transpolar Drift have higher hydrocarbon concentrations than locations influenced by the Beaufort Gyre. This probably reflects the direct connection between the Kara and Laptev shelves and the TPD whereas ice in the Beaufort Gyre has cleaner sediment sources, tends to recirculate more, and probably does not transport the quantities of material. PAHs in the Arctic Basins appear to derive predominantly from natural sources and reflect long-term inputs. The sediment concentrations are below the level where direct effects on biota are expected. However, some regions have a relatively high natural background (e.g., the Beaufort Shelf) and biota will be more susceptible to stress from additional contaminant loadings.

DISCUSSION/CONCLUSIONS

Future work should focus on:

- Time series measurements to monitor the anticipated downturn in contaminants. Oceanographic and biological processes are the link between the downturned atmospheric sources and the top predators of the food web.

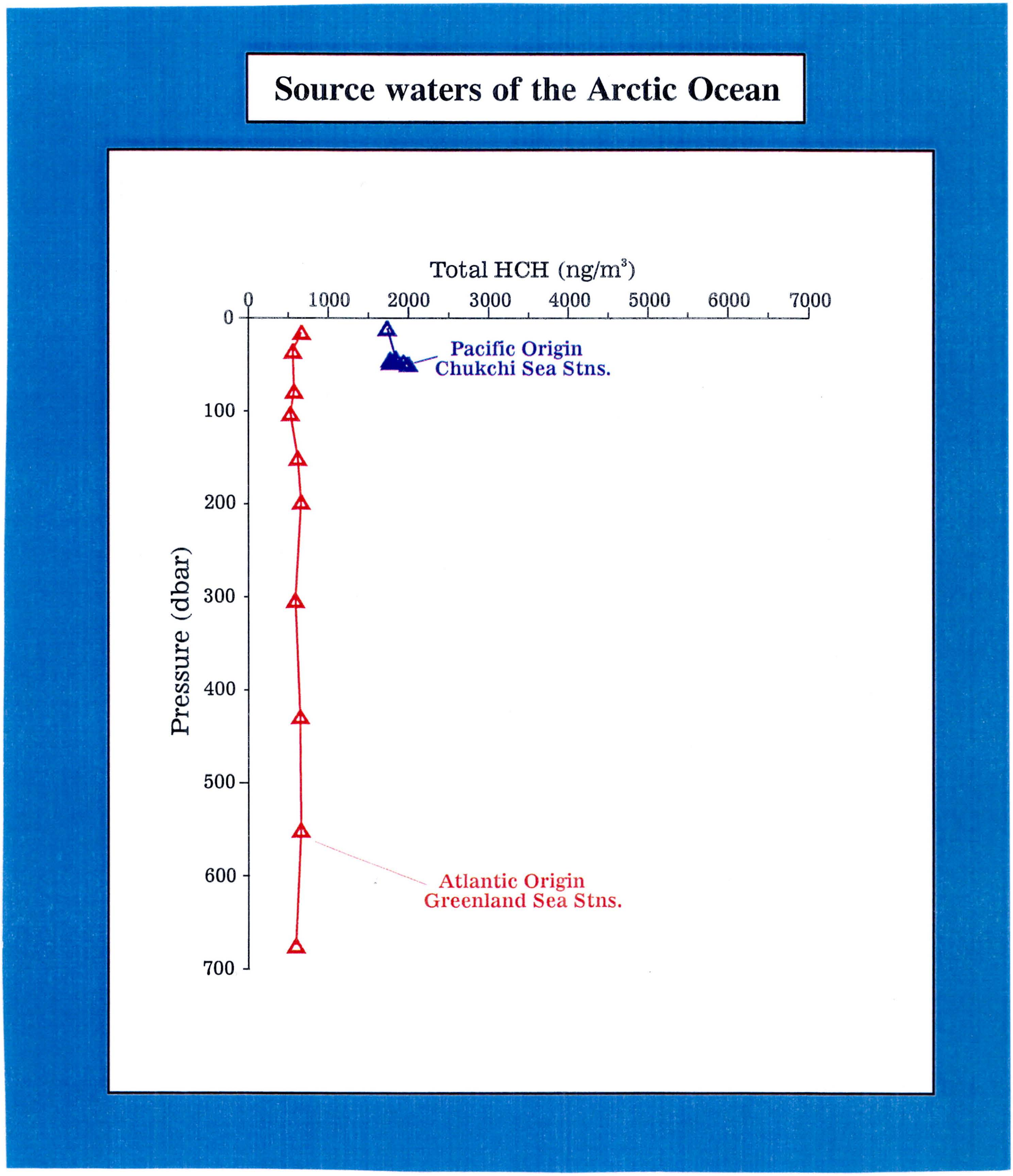

Figure 1. Vertical profiles of total HCH concentration in water from the two main entrances to the Arctic Ocean. Both profiles reflect the turndown in atmospheric HCH and show that water now entering the Arctic Ocean has much lower concentrations than the surface water of the Canada Basin.

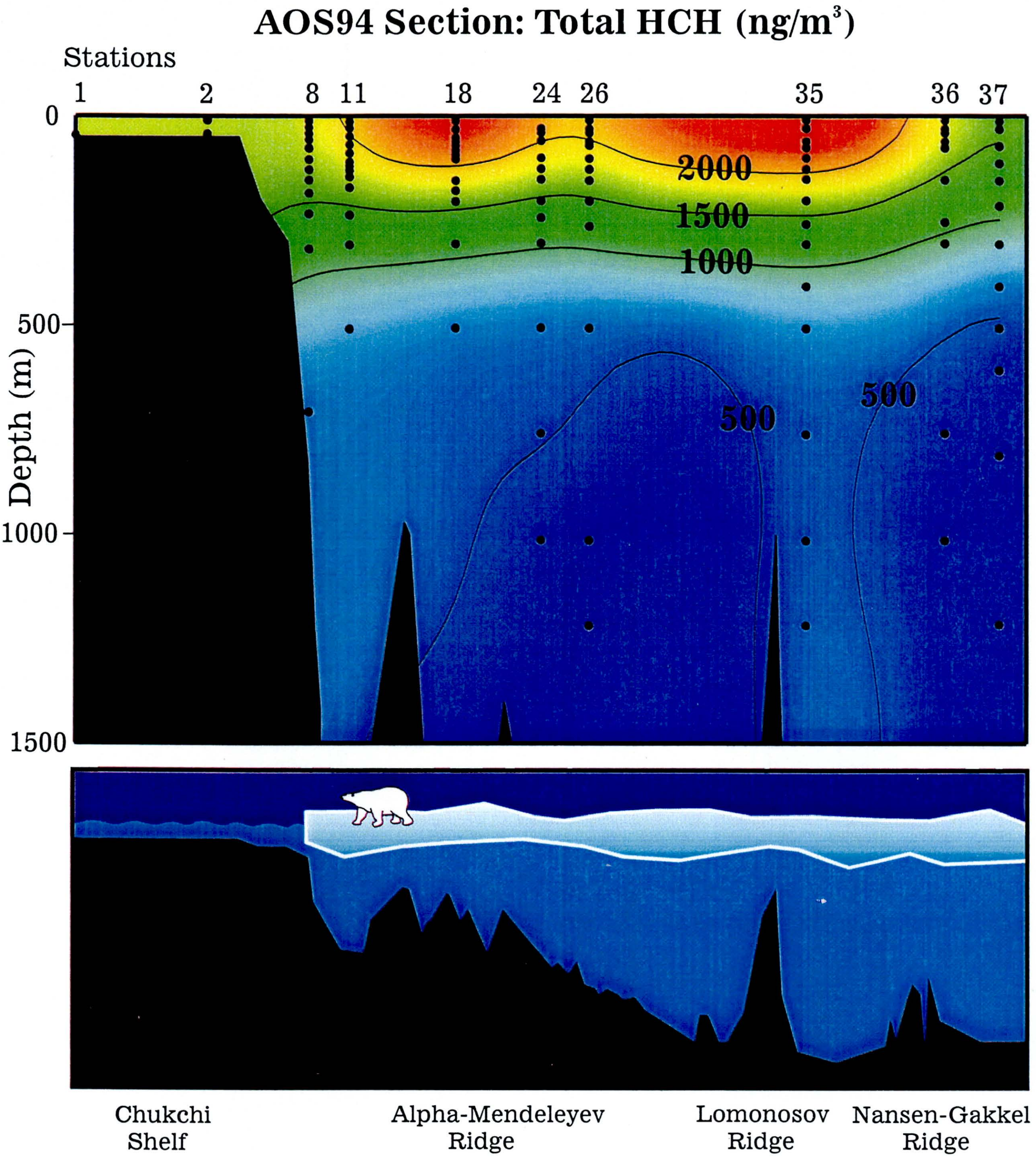

Figure 2. A sectional view of HCH concentration along the AOS-94 cruise track illustrating that most of the HCH burden is contained in the top 200–300m of the water column. The section shows lobes of higher concentration reflecting Canada Basin water, and lower concentrations in the Chukchi Sea and Eurasian Basin where air-sea exchange has taken place or where surface waters have been recently replaced by equilibrated water.

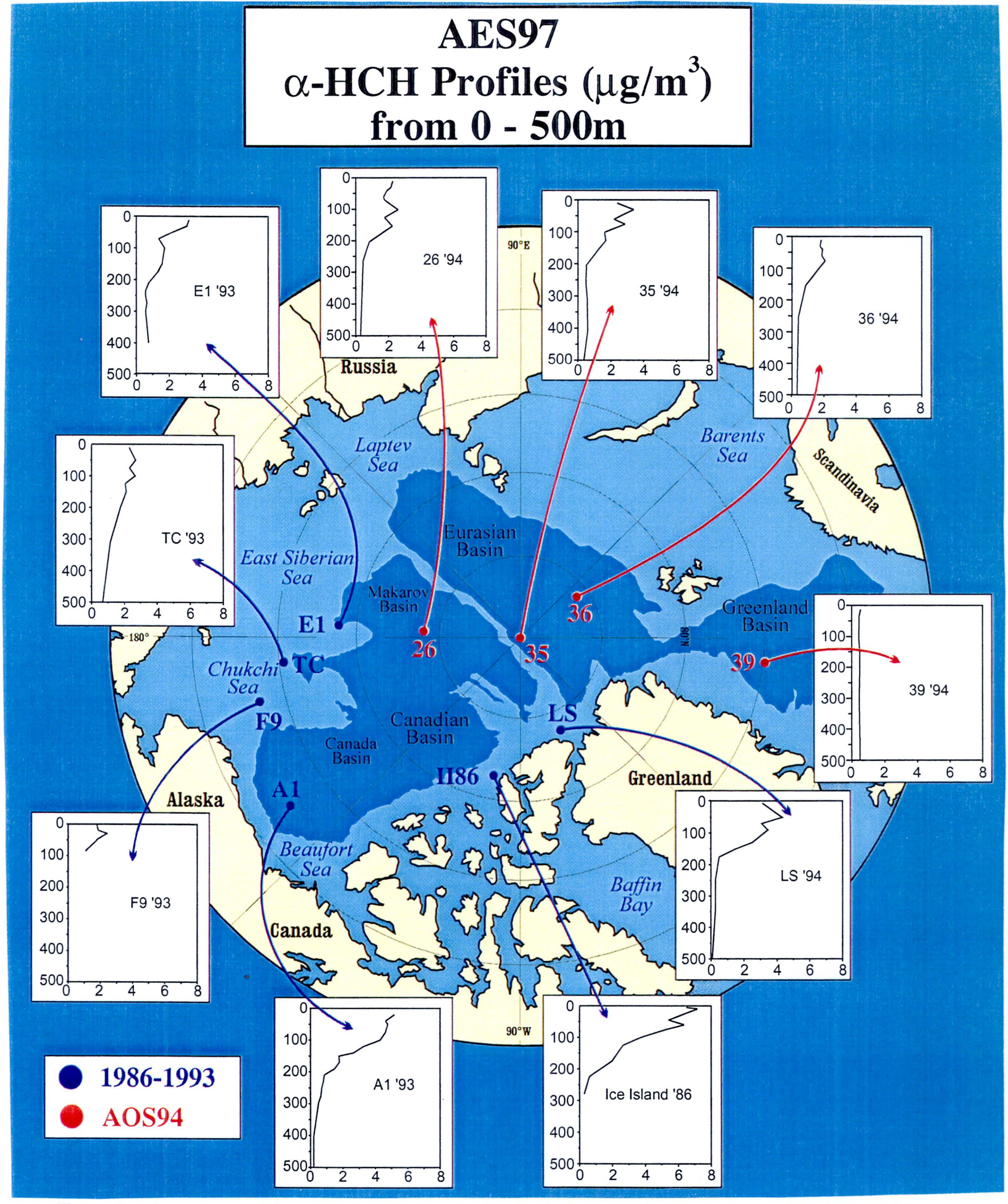

Figure 3. A summary of the vertical profile data for the Arctic Ocean including the Larsen-93, AOS-94, Lincoln Sea-94 and Ice Island data (Hargrave et al., 1988).

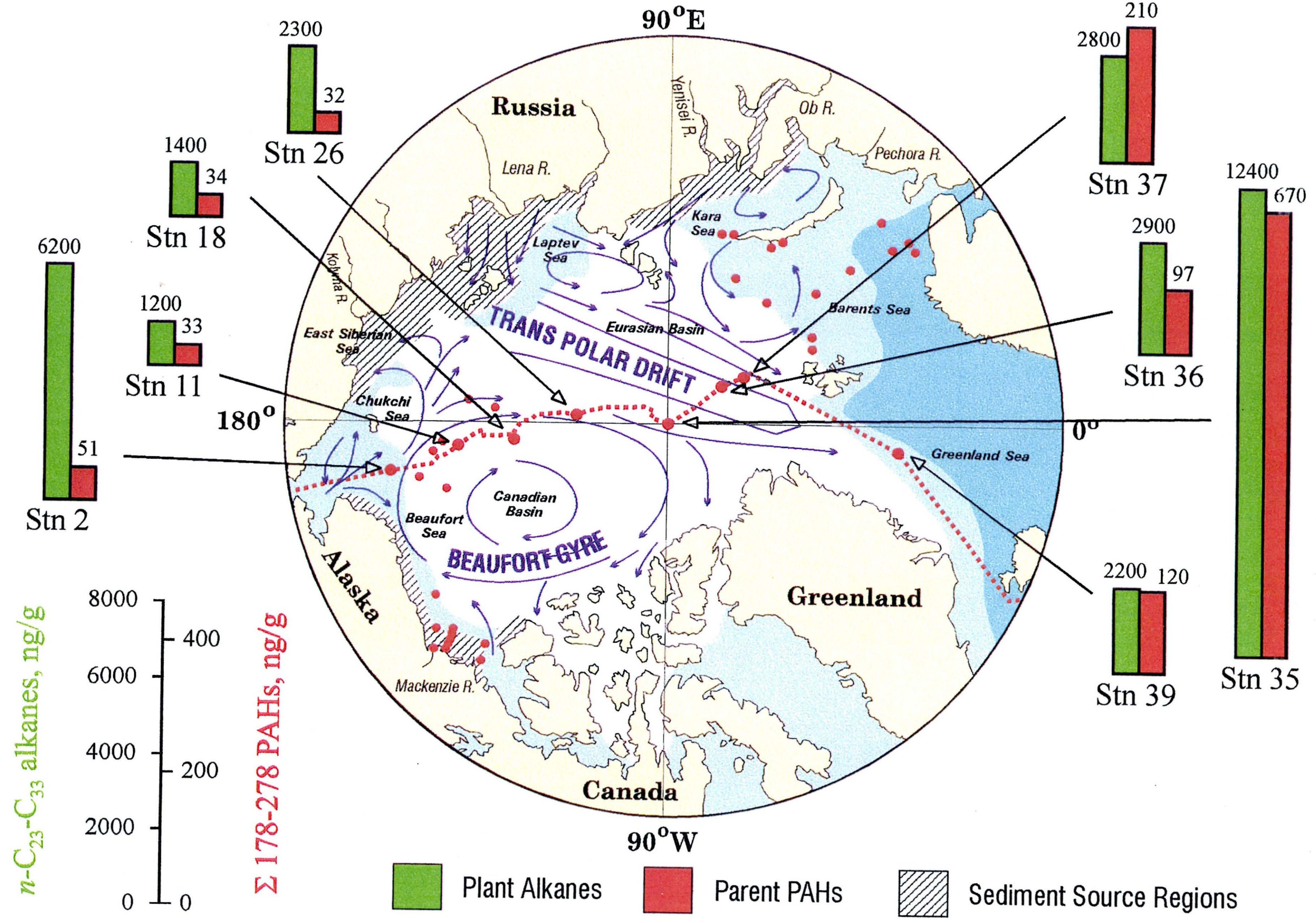

Figure 4. Arctic Ocean showing the major ice transport regimes, sediment source regions and PAH sampling locations (red dots). PAH and alkane concentrations for surface sediments at selected Arctic 94 stations are shown by vertical bars.

- The Archipelago together with the upstream pool (Canada Basin) is probably the most critical area for Canada to monitor into the future. Additional spatial measurements are required to define the extent of the high pool in the Canada Basin.
- Hg needs to be studied in an oceanographic context. Like the OCs, it is subject to long range transport, its travel northward is likely enhanced by the so-called cold condensation, and it biomagnifies. Presently, there exist no oceanographic data for the Arctic Ocean with which to make an assessment.
- PAH data are needed from important source regions like the Siberian and Eurasian Shelves. Such source data will aid in the development of source receptor models using multivariate statistics.

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DEVELOPMENT OF MODELS DESCRIBING THE LONG-TERM GLOBAL FATE OF PERSISTENT ORGANIC CHEMICALS, AND STUDIES OF THE INTERACTIONS BETWEEN ORGANIC CONTAMINANTS AND SNOW

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Project Team: Frank Wania, NILU, Trømso, Norway; Daryl Callcott, Eva Webster, Trent University; Wan Ying Shiu, Charles Q. Jia ,University of Toronto; Antonio Di Guardo, University of Milan

OBJECTIVES

1. To develop, test and validate mass balance models which will describe how emissions of persistent organic chemicals in various geographic locations world-wide, will result in concentrations in air, freshwater and marine water, soils, sediments and biota in distant locations, especially in the Canadian Arctic.

2. To investigate the sorption of organic compounds to ice surfaces (i.e., snow) and thus contribute to a more quantitative understanding of the depositional and post-depositional behaviour of contaminants in snow. These results will be used directly in the modelling project to improve predictions of contaminant fate in cold climates.

DESCRIPTION

To satisfy the first objective, two computer models are being developed. Both accept as input, year-by-year emissions of specified chemicals for defined geographic areas (e.g., Central America) then calculate the long-range transport of these chemicals to other regions, again on a year by year basis. It will thus be possible to assert that use of, for example, x tonnes of DDT in Mexico in 1980 would have resulted in the transport of 2% of this quantity to the Canadian Arctic over a period of five years, causing a concentration increase of y ng/g in a specified target species such as a fish or mammal. It is hoped that application of this model will result in policy changes that will restrict the global use of the more persistent organic chemicals that are susceptible to long-range global transport and accumulation.

In previous studies a nine-meridional segment global model was developed by Wania, details of which have been published in a series of papers in the refereed literature (Wania and Mackay 1995a). Work has continued on this model by Wania in collaboration with Bailey, the focus being on hexachlorobenzene (HCB) and hexachlorocyclohexanes (HCHs). This "Meridional Model" work is described below. A new, second model is being developed, largely by Calcott, Webster and Mackay that includes a larger number of segments that have explicit geographic locations such as e.g. Australia or the North Equatorial Atlantic Ocean. Land and ocean segments are treated separately, whereas in the meridional model they are lumped into one segment. This "Geographic Model" work is also described below.

In addition to these studies, work has been underway on aspects of the fundamental environmental properties of organic chemicals of relevance to Canadian Arctic contamination (especially as a function of temperature) and on processes experienced by organic chemicals, (especially interactions with snow). This work on physical chemistry of contaminants has been done primarily by Dr. W.Y. Shiu of the University of Toronto. Dr. J. Hoff of the University of Waterloo has continued an experimental study of the sorption of organic chemicals to the water and ice interfaces, including the measurement of surface areas of freshly fallen snow. These results are being used to develop predictive equations describing the deposition of organic chemicals in snowfall, and the post-depositional behaviour of the chemical—i.e., the extent to which it reacts, evaporates, leaches in melt water, or is retained in the snowpack. This aspect has, we believe, considerable relevance to the use of snowpacks and glacial snow/ice to establish the chronology of deposition over many years and decades.

ACTIVITIES IN 1995/96

Meridional Models

Selection of Degradation Data

The global model requires estimates of an overall first order degradation rate in each environmental medium of each climate zone. Early model calculations had relied on fairly haphazardly collected or estimated degradation data. In collaboration with B. Bailey (Bailey and Wania 1996), improved reaction half-lives were deduced and used in the model calculations.

The reaction of persistent organic contaminants such as HCHs and HCB in the atmosphere was assumed to be controlled by the reaction with hydroxyl radicals. The variable incidence of short wave-length sun light causes the atmospheric ·OH concentration to show a strong latitudinal dependence. Estimates of average ·OH levels for each climate zone were based on a globally averaged concentration reported by Prinn *et al.* (1992) and the latitudinal dependence given in Altshuller (1989). Reaction half-lives of HCB and HCHs were calculated by multiplying these ·OH concentrations with reaction rates derived using the Atmospheric Oxidation Program (AOP) of Meylan and Howard. Table 1 shows the estimated atmospheric half-lives for HCH and HCB.

Emission Estimates

On a very preliminary basis it was estimated that in 1990 the global emission of HCB was approximately 100 metric tonnes annually (Bailey *et al.* 1996). It was assumed that 33% of this emission occurred in the N-Subtropic zone, 25% each in the N-Temperate and N-Tropic zone, 10% in the S-Tropic, 5% in the S-Subtropic and 1% each in the N-Boreal and S-Temperate zone. It was further assumed that 55% of the HCB was emitted into soil, 40% into the atmosphere, and 5% into freshwater, which is based on the assumption that:

i) the HCB, which is a constituent of pesticides, is emitted mostly to soils, with some loss during application to the atmosphere and freshwaters, and

ii) the combustion derived HCB was emitted into air.

Based on work by Li and Voldner (Li *et al.* 1996, Voldner and Li 1995) global emissions of HCHs (α–and γ–HCH) (Table 2) were assumed to have occurred in 1980 and 1990.

Table 1. Estimated atmospheric half-lives

Contaminant		**Climate zone**			
		Polar	**Subpolar**	**Temperate**	**Subtropic**
Tropic					
HCH	1.6 years	1489 hours	350 hours	175 hours	88 hours
HCB	130 years	13 years	3.2 years	1.4 years	1 year

Table 2. Estimated global emission of α– and γ–HCH

	N-Boreal	**N-Temperate**	**N-Subtropic**	**N-Tropic**	**S-Tropic**	**S-Subtropic**	**Global**
1980	40	7621	14284	15601	2115	239	39900
1990	29	5501	10310	11261	1526	173	28800

Table 3. Results of the four scenarios

	Scenario	**Atmospheric concentration**	**Ocean water concentration**
A	18 to 24 pg/m^3	2 to 3 pg/L	
	B	38 to 45 pg/m^3	4 to 6 pg/L
	C	21 to 26 pg/m^3	2.5 to 3.5 pg/L
	D	40 to 45 pg/m^3	6 to 8 pg/L

It was further assumed that 85% of the HCH was emitted to agricultural soils, while 10% and 5% are lost to the atmosphere and to freshwater systems respectively during application.

New Calculations for HCB and HCHs

Using the new degradation half-lives and emission estimates a number of calculations were performed using the Global Distribution or Meridional Model (Wania and Mackay 1995a). The results were presented at an international conference on "The Future Uses of Chlorine" at Cambridge, Massachusetts (Bailey *et al.* 1996).

HCB

Having only emission estimates for a single year, the following scenarios for HCB were used as input for the model:

A: 20 years of "1990" emissions
B: 20 years of doubled "1990" emission
C: 10 years of doubled "1990" emission followed by 10 years of "1990" emissions
D: 10 year of ten-fold "1996" emission followed by 10 years of "1990" emissions

The calculated concentrations in air and ocean water of the three northernmost zones at the end of these 20-year periods are shown in Table 3.

The calculated values are lower than those typically measured in either the atmosphere or in ocean water, but they are within one order of magnitude. This indicates that the global emission estimate may be of the correct order of magnitude. The model results further suggest that very high past HCB emission could still have an impact on concentrations measured 10 years later (especially in ocean water, but less pronounced in the atmosphere), while slightly higher emissions in the past have a rather limited effect on present concentration levels.

The simulation results from "Scenario C" indicate that at the end of the 20-year emission period, most of the HCB is contained in agricultural soils (55%), the atmosphere (20%) and the surface ocean (18%). HCB is lost from the global environment primarily by degradation in the atmosphere (53%, mostly in the tropical atmosphere), degradation in agricultural soils (20%), and transport to the deep ocean water (22%). A major environmental pathway is evaporation of HCB from agricultural soils (i.e. soils which received direct input of HCB in connection with pesticide applications) and subsequent atmospheric advection.

HCHs

To make use of the emission estimates provided for the years 1980 and 1990, it was assumed that between 1970 and 1980 there had been a steady emission of HCHs on the level of the "1980" estimate, while for the following decade the estimates for 1980 and 1990 were linearly interpolated.

The annual average HCH concentrations in atmosphere and surface ocean of the Northern Hemisphere calculated for 1990 are shown in Table 4.

While atmospheric concentrations are within the range of measured values, ocean water concentrations are too low by one order of magnitude. They also fail to reproduce the observed latitudinal gradients with higher concentrations in arctic latitudes (Wania and Mackay 1996).

HCHs are mostly found in the soils of initial application (75%) and in fresh and ocean water (approx. 10% each). Its disappearance from the global environment is mostly due to degradation in soil (ca. 55%), and the atmosphere (ca. 30%), while the remaining loss is due to degradation in water phase. Because of its relatively high water solubility and thus limited tendency to sorb to particulate matter, sediment burial and transfer to the deep ocean are negligible loss processes for HCH. Besides degradation, major global pathways for HCHs are transport in the water phase (i.e. leaching from soils to freshwater, and further transport with freshwater to the oceans), and evaporation from agricultural soils and freshwater.

Currently, work is being performed using considerably more reliable and detailed HCH emission estimates compiled by Dr. Y.F. Li of AES in global model calculations. Results were presented at SETAC in the Fall of 1996 (Wania *et al.* 1996a).

In general, the model results are within an order of magnitude of observations, suggesting that:

i) emission data are within this level of reliability,
ii) chemical property data are fairly reliable, and
iii) that the fundamental equations for transport, transformation and partitioning reproduce the phenomena with adequate fidelity.

Clearly, we are now in a mode of refining the input data and seeking closer reconciliation between computed results and observations. At some point in the future, it should be possible to compare these model results with those obtained using the more detailed models being developed by AES and ORTECH as part of the overall program.

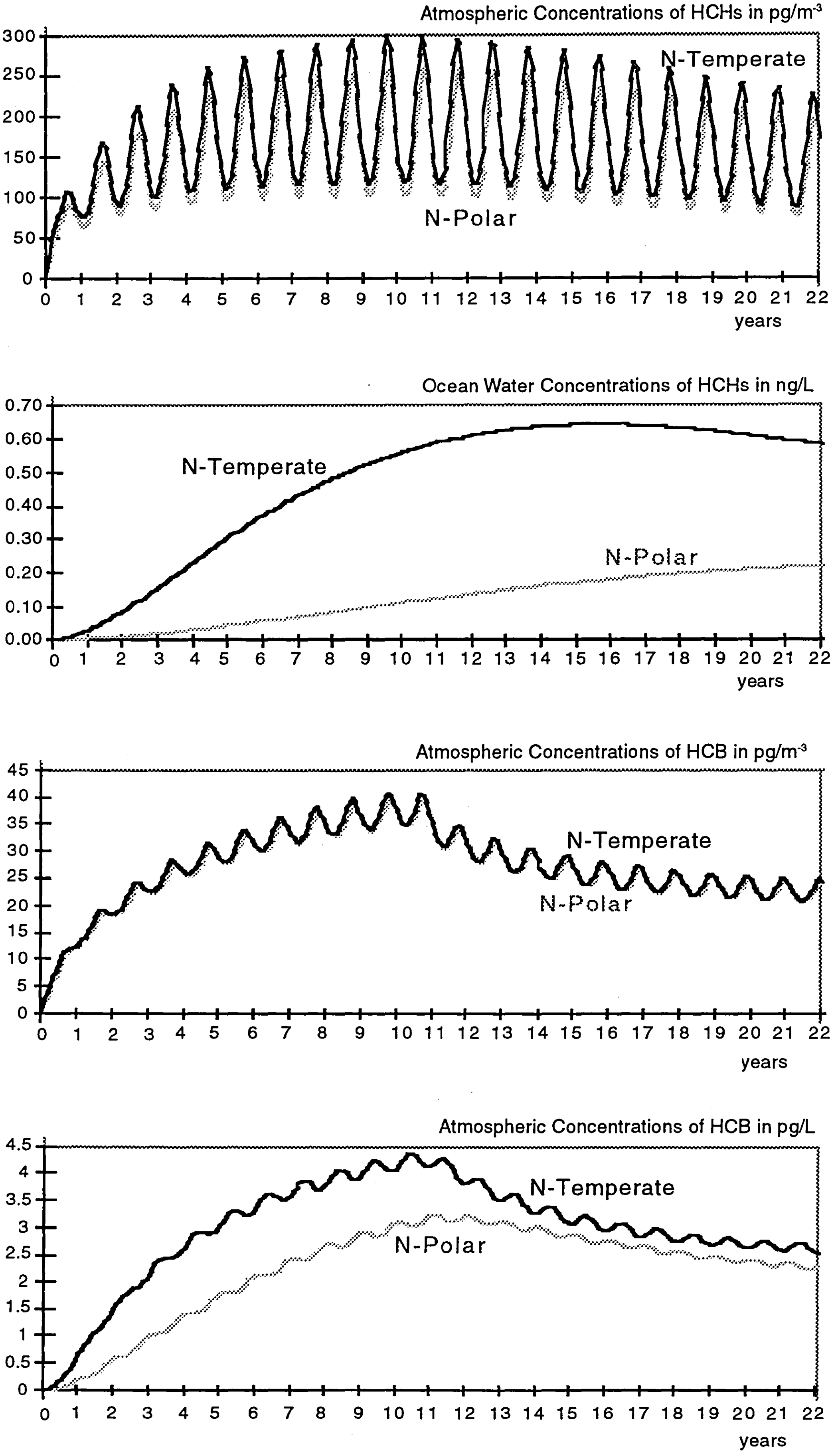
Atmospheric Concentrations of HCHs in pg/m^{-3}
300
250
200
150
100
50
0
N-Temperate
N-Polar
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22
years
Ocean Water Concentrations of HCHs in ng/L
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
N-Temperate
N-Polar
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22
years
Atmospheric Concentrations of HCB in pg/m^{-3}
45
40
35
30
25
20
15
10
5
0
N-Temperate
N-Polar
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22
years
Atmospheric Concentrations of HCB in pg/L
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
N-Temperate
N-Polar
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22
years

Figure 1.

Geographic Model

This model uses concepts similar to those used in the Meridional Model, but the segmentation is quite different. The Earth was first subdivided into 24 zones; 17 terrestrial and 7 oceanic zones. The selection of zone boundaries was a subjective decision, based on environmental, ecological and political criteria. Geographic areas of similar environmental attributes were grouped within a zone, however political boundaries were often used because environmental and chemical emissions data are often available as national values. Figure 2 depicts the terrestrial segmentation approximately.

For each of the zones, selected environmental attributes were determined and data were collected. These data included land and water areas, political units contained in each zone, population, vegetation characteristics, air height and volume, water depth and volume, air and water fluxes between zones, air and water temperatures, water discharge from terrestrial to aquatic zones, mean annual precipitation and evaporation, and soil organic carbon content. Since air and water temperatures and fluxes vary greatly between summer and winter, data were obtained for both seasonal conditions.

The information for each zone was stored within a Microsoft Access Database. The sources and techniques used in the collection of the data are discussed below for each set. The information was obtained from readily available sources. Should more detailed information be required in the future, this information may be inserted directly into the data base, thus requiring minimal changes to the model.

Area and Population

Data on terrestrial zone area and population was obtained from Stanford (1992), and Matthews and Morrow (1995) using statistics collected for each country within zones. Aquatic zone areas were collected from Couper (1990), by determining the percentage of the oceans contained within each zone.

Vegetation Cover

Vegetation cover for terrestrial zones was obtained from Bartholomew *et al.* (1990). The contribution of each vegetation type to the zone was determined by estimating percentage cover.

Freshwater Area

Information was obtained from Gleick (1993) for lakes of the world. In addition, data on freshwater coverage for Canada, characterized as having a large number of small lakes, was obtained from Matthews and Morrow (1995).

Discharge of Water from Terrestrial Zones

This information was obtained using the Global Environmental Monitoring System (GEMS) (1996) data base on rivers. The destination zone for the discharge was determined using Bartholomew *et al.* (1990).

Air Height

Air height values were adopted from Wania and Mackay (1995a).

Water Depth and Volume

Water depth for terrestrial zones with freshwater lakes was gathered from Gleick (1993). An effective ocean surface depth of 200m was adopted following Wania and Mackay (1995a). The volume of water within zones was determined from the surface area and depth.

Mean Air and Water temperature

Average temperatures for zones were determined from climate maps displayed in Bartholomew *et al.* (1990). The percentage coverage of a given temperature was determined and the average temperature for a zone was produced by summing the product of the temperature and percentage coverage. The surface water temperatures were determined using the same method, with information obtained from Couper (1990). Air and water temperatures were determined for both January and July.

Precipitation and Evaporation

Precipitation and evaporation values were obtained from Bartholomew *et al.* (1990). Values for zones were determined by summing the product of the precipitation or evaporation and percentage coverage.

Table 4. Computed air and ocean HCH concentrations

	N-Polar	N-Boreal	N-Temperate	N-Subtropic	N-Tropic
Air pg/m^3	136	141	152	139	29
Ocean ng/L	0.21	0.43	0.60	0.18	0.03

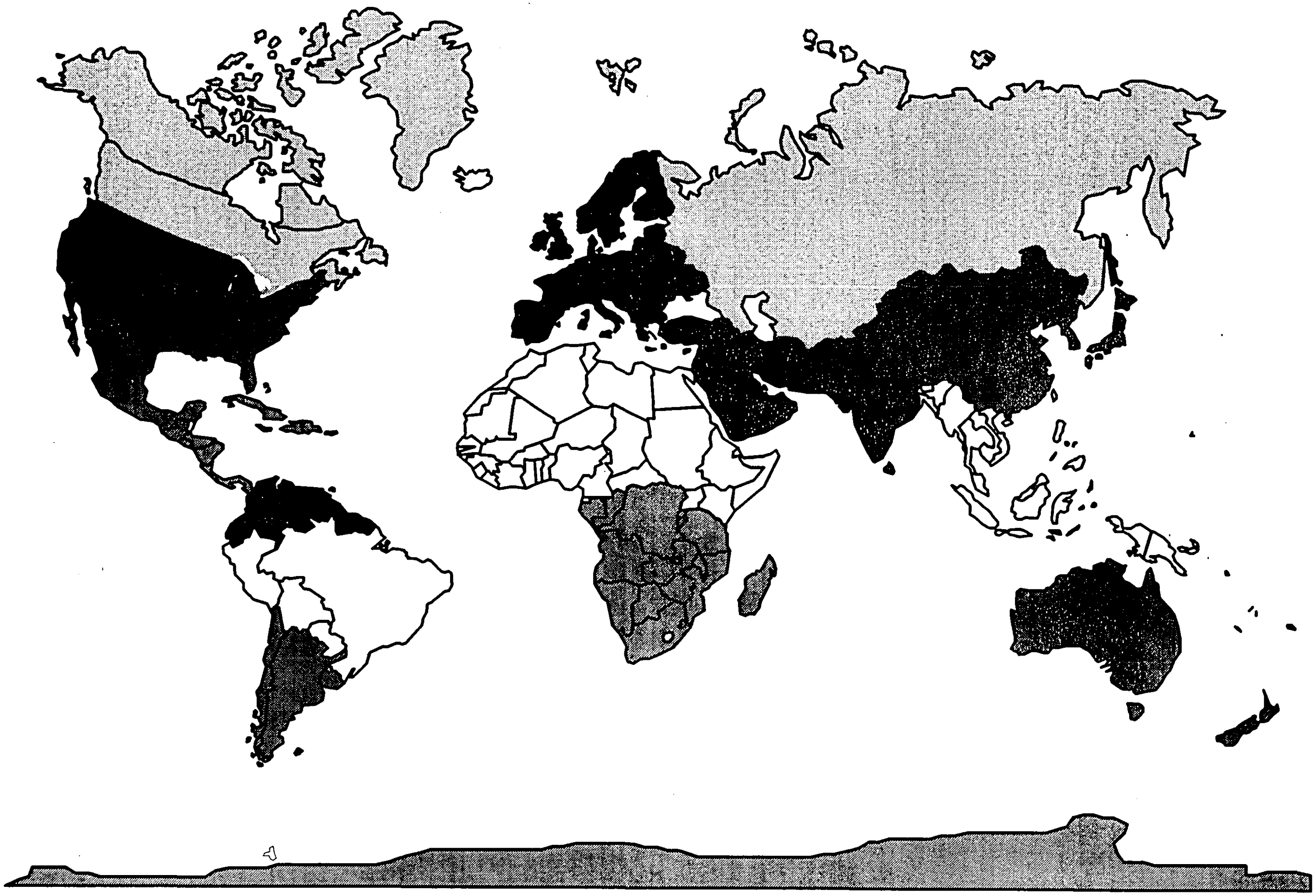

Figure 2. Approximate segmentation of global terrestrial environment. The oceanic segmentation is not shown.

Soil Organic Carbon Content

Information on soil types contained within zones was obtained from the United Nations' Food and Agriculture Organisation (FAO) (1991), while the organic carbon content for the soils in each zone was available through the FAO and UNESCO (1974). The percentage coverage of a soil type in a given zone was determined, and an average percentage of organic carbon determined by summing the product of the percentage coverage of a specific soil type, and the organic carbon content of that soil.

Air Fluxes

The movement of air between zones was estimated for July and January. The data were collected from Hasse and Dobson (1986), and were in the form of a vector map. The fluxes from zones were determined using the projection of vectors between zone boundaries.

Water Fluxes

Water fluxes between zones were estimated using information from Couper (1990), for both January and July. Again, fluxes between zones were determined using the projection of vectors to zone boundaries.

Second Data base

In addition to the 24-zone data base, a second data base containing 27 zones was also created, which is expected to give improved model performance. This is shown inTable 5. Within this data base, the tropical oceans zone (21) from the original collection was subdivided into North Tropical Indo-Pacific, North Tropical Atlantic, South Tropical Atlantic, and South Tropical Indo-Pacific. All of the characteristics from the original data base for tropical oceans were applied to the new zones, however the discharge from terrestrial zones was corrected to enter the correct tropical zone. The fluxes of water and air were also corrected for the new zones, and fluxes between zones were estimated. This change was largely due to separate the Atlantic and Pacific Ocean zones, as the Atlantic Ocean has been observed to have higher contaminant concentrations. In addition, the new segmentation gives better control of trans-equatorial transport.

Studies of fundamental aspects of contaminant behaviour at low temperatures and in the presence of snow

Interactions with snow

A major concern with these models is that they do not adequately describe the environmental fate of chemicals as influenced by snow. Experimental and theoretical studies are underway, supported in part by this program, to measure the surface area of snow and measure the partition coefficient between air and ice surfaces.. Most of this work is being done at the University of Waterloo by Dr. J. Hoff. Specifically, information on two key parameters, K_{ia} values for adsorption of organic compounds at the air-ice interface and the specific surface area (SSA) of snow, are needed to quantify the interaction of falling snowflakes with organic contaminants in the atmosphere (atmospheric scavenging) and for modelling the behaviour of contaminants in snow deposits on the ground. Information on mass transfer rates is also needed for modelling atmospheric scavenging. Improvements in the quality and quantity of knowledge of these aspects was made during 1995/96. In addition, this knowledge has been applied to elucidating the role of snow in modifying the behaviour of organic contaminants in the Arctic.

Progress in modelling adsorption at the air-water interface

The working hypothesis is that K_{ia} values for ice can be estimated by extrapolating values for water to lower temperatures.

A broader data base has been developed. K_{ia} data for 22 polar compounds have been added to the data previously considered (6 polar and 29 non-polar compounds). In addition, solute-water interfacial tension data for 12 compounds have been added to the data for 18 compounds previously considered.

A simple empirical formula relating the activity coefficient in the surface phase to that in bulk phase has been derived from this data. The significance is that the extent of partitioning can now be estimated with good precision for both polar and non-polar compounds using a single equation from the following empirical data: vapour pressure, solubility in water and surface tension of the compound. It is thus not necessary to have empirical data for solute-water interfacial tensions. This facilitates the estimation of K_{ia} because interfacial tension data are only available for a few compounds which are liquids at room temperature.

Further progress has been made towards developing practical methods for accurately estimating the enthalpy of adsorption, a parameter which is necessary for estimating the temperature dependence of K_{ia}.

Progress in measuring K_{ia} values for semi-volatile organic compounds

The objective is to obtain experimental K_{ia} values for compounds which have sub-cooled liquid vapour pressures in the range of 10^{-4} to 10^{-9} atm. These compounds are solids at room temperature.

Table 5. Global segmentation of the "Geographic Model".

Zone	Description	Area (km²)	Population (millions)
1	Canada-north	3246400	0.0085
2	Canada-south	5956600	27.2
3	USA	9363000	255
4	Central America	2688000	145.9
5	N. South America	2520000	55.2
6	Cen. South America	11167000	191.7
7	S. South America	4119000	54.6
8	Europe	5218700	578.7
9	Middle East	6693700	157.8
10	Former USSR	21693000	216.1
11	China	11739000	1358.2
12	South Asia	4402000	1169
13	South East Asia	4951000	454.2
14	Australiz/NZ	7952000	21.1
15	Afrrica N of equator	18594000	433.1
16	Africa S of equator	11260000	223
17	Antarctica	6500000	0
18	Arctic Ocean	23196850	0
19	N. Boreal oceans	14693720	0
20	N Temperate oceans	28235590	0
21	N tropic Indo-Pacific	124424390	0
22	N Tropical Atlantic	65530300	0
23	S. Tropical Atlantic	39727880	0
24	S Tropical Indo-Pacific	44046096	0
25	S Temperate oceans	65529000	0
26	S Boreal oceans	39728000	0
27	Antarctic oceans	58064000	0

A new method was developed that utilizes solid phase micro-extraction (SPME) to monitor and measure the contaminant concentration in the gas exiting a snow column. When the system has reached equilibrium, the concentration in the exiting gas is constant. After determining the equilibrium concentration in the gas, the snow is melted in the column and purged with the carrier gas. (The column is designed so that the snow can be melted and purged *in situ*) By measuring the exponential rate of decrease of contaminant concentration in the purge gas exiting the column, the quantity of contaminant in the snow can be calculated. K_{ia} is calculated as the ratio of the concentration in the snow to the concentration in the gas at equilibrium with the snow.

Using this novel method, experimental K_{ia} values have been obtained for dichloro-, trichloro- and pentachlorobenzene. The experimental values are within a factor of two of the estimated values. The K_{ia} value for pentachlorobenzene at −10°C is 2.2 cm, which represents an extension of the measured range of K_{ia} values by nearly two orders of magnitude.

One of the main limitations of the method is the coefficient of variation of SPME measurements, which seems to increase as the concentration of contaminant (the vapour pressure of the compound) decreases. We suspect that we are approaching the limit of the method to measure large K_{ia} values and yet we want to determine K_{ia} values that are several orders of magnitude larger. Good results have been obtained by Tom Harner at AES in measuring K_{oa} (octanol-air partition coefficient) values for semi-volatile organic compounds at low temperatures using a C-18 trap. We plan to adapt this method for measuring K_{ia} values for snow.

Progress in modelling the removal of organic vapours from the atmosphere by falling snowflakes: Estimating mass transfer rates

A model has been developed for estimating the characteristic time τ for equilibration of a falling snowflake with lindane in the atmosphere. τ is calculated as the sum of the contributions from surface accommodation, internal diffusion and external diffusion taking into account fluid dynamic effects. The approach to equilibrium is calculated using a conventional first order approach.

It is assumed that: a snowflake is considered to be a porous spherical aggregate of ice crystals with SSA of 0.1 m²/g; the snowflake diameter ranges from 1 to 10 mm; the snowflake porosity ranges from 0.7 to 0.9. The height of the cloud base (falling distance) is taken to range from 500 to 3000m.

The calculations indicate that the finite rate of mass transfer is important for larger snowflakes. The approach to equilibrium for 10 mm snowflakes is 3% to 38%.

Measurement of the Specific Surface Area (SSA) of Snow

Scant data exists for the SSA of snow and the extant values date from the 1960s. The SSA of snow is expected to depend on meteorological conditions during formation and on metamorphic conditions such as temperature and length of time spent on the ground. A method of determining SSA experimentally has been developed based on a commercial surface area analyzer and which utilizes the nitrogen adsorption technique, the most widely used and accepted technique for measuring specific surface area.

Precision: A Monte Carlo study of the effect of random error in raw adsorbed volumes on the precision of the determination of SSA (obtained by fitting BET-transformed adsorbed volumes to relative pressures) indicates that a relative standard deviation of 20% for snow SSA can be achieved by measuring adsorbed volumes at seven equally spaced relative pressures between 0.05 and 0.35.

The largest source of error in the accuracy of measurement of snow SSA is the free space correction. Simulations suggest a factor of two uncertainty in SSA is due to the uncertainty in the free space correction factor.

The limitations imposed by the small SSA, small bulk density and small BET C constant of snow can be overcome by the use of larger sample vials, an increase in the bulk density by compacting the snow in the vial at dry ice temperature, minimizing the free space difference by using equal quantities of snow in the vials, and optimizing number and placement of data points. More work is required to determine the best method of free space correction.

The results obtained to date suggest that the SSA of snow are likely to range from 0.1 to 0.3 m^2/g

Comparison with literature data

The older literature values for the SSA of snow are 0.2, 0.4, 1.3, and 7.8 m^2/g. Optical microscope images of individual snow crystals (or replicates thereof) indicate that the geometric surface area ranges from 0.03 to 0.80 m^2/g with median values close to 0.1 m^2/g. Recent SEM images of snow crystals are consistent with the above estimates but also reveal parasitic growths on larger snow crystals with SSA as high as 1.0 m^2/g. Cloud drop size distributions (which are relevant for rime) indicate medians between 0.12 and 0.60 m^2/g. These studies suggest that the SSA of snow is essentially that which is revealed by optical and scanning electron microscope images.

Our data together with literature data and other evidence cited above, suggest that the SSA of fresh snow is of order 0.1 m^2/g and has a natural variability of about one order of magnitude. SSA values greater than 1.0 m^2/g are considered unlikely.

In conclusion, we now have better estimates of (i) the sorption partition coefficient of organic contaminants from the gas phase to ice surfaces, and (ii) the area of ice in snow. The product of these two quantities expresses the "capacity" of snow to sorb and retain contaminant and is a fundamental quantity in any model or assessment of the role of snow for contaminant transport. All indications are that snow is an effective and under-estimated vehicle for transport.

Physical Chemical Data

The global models show clearly that temperature plays an important role in determining the fate of contaminants. Especially important are processes which involve equilibrium between the atmosphere and water or soil in which there is a large enthalpy change such as heat loss on condensation. This translates into a marked dependence of partition coefficients on temperature, as is suggested by LeChatelier's Principle and the Clapeyron Clausius equation. Data are being gathered on the temperature dependence of partitioning quantities and a paper on this topic is being prepared for the *Journal of Physical and Chemical Reference Data* (Shiu *et al.* 1996).

Finally, discussion of the issue of long-range transport of contaminants to the Arctic continues in the international scientific literature, a recent example being a feature article in *Environmental Science and Technology* by Wania and Mackay (1996). An extended abstract in a NATO publication also examines aspects of this issue, especially the role of snow (Jia *et al.* 1996). We believe that it is important not only to conduct sound scientific studies, but also to disseminate the results and their implications as broadly and expeditiously as possible.

CONCLUSIONS

In general the projects are proceeding according to plan and significant progress is being made on all fronts. It is clearly important to continue to develop and improve the models, incorporate into them the latest information on contaminant fate at low temperatures, and steadily refine our understanding and predictive capability.

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MODELLING THE GLOBAL DISTRIBUTION OF HEXACHLOROCYCLOHEXANE (HCH) USING A THREE-DIMENSIONAL ATMOSPHERIC TRACER MODEL

Project Leaders: Janusz A. Pudykiewicz and A. Koziol, Atmospheric Environment Service

OBJECTIVES

The main objective of numerical modelling of pathways of toxic substances is to investigate their spatial and temporal distributions in different components of the global environment.

DESCRIPTION

The modelling approach presented here permits the analysis of the transport of contaminants without investing a considerable amount of money required to perform measurements at multiple locations. The high resolution three-dimensional (3-D) transport model is a suitable tool for both the evaluation and the prediction of spatial and temporal trends of toxic species in the Arctic environment including air, snow, ice and the ocean.

The global 3-D HCH transport model based on a system of the advection-diffusion equations in spherical coordinates was developed and tested for a period of two years using real meteorological data. The model simulates transport of toxic substances on a global scale, while allowing them to interact with the earth's surface, clouds, and precipitation. The transport equations are solved using the semi-Lagrangian algorithm formulated in spherical coordinates. The meteorological input data used in our calculation consists of the objectively analysed wind components, geopotential, temperature, and humidity. The model is able to perform simulations of the spatial and temporal distribution of atmospheric γ– and α–Hexachlorocyclohexane (HCH). HCH has been chosen as the compound of interest because of its wide use as a pesticide in the past. The generalization of our model for other toxic materials is also possible.

In the first step, the global 3-D HCH model was applied in order to determine the concentration of HCH emitted into the atmosphere from oceans during one year. This modelling scenario is particularly important because the major part of HCH accumulated in the environment is stored in aquatic systems. The global distribution of HCH in the ocean waters was obtained by mapping experimental data onto a latitude-longitude grid using an interpolation with the polynomial weight function. After defining the state of HCH concentrations in surface reservoirs (land, snow and surface waters) as a function of location, the global tracer model was run for one year. The source term in the advection-diffusion equation was derived from the forcing by the surface fluxes of HCH. The model results were verified using the data from Arctic monitoring stations.

The general conclusion from the above simulation is that the model is not able to reproduce observed concentrations of HCH without the explicit information about the current emission. In our initial test runs, it was also noted that the model responds to the emission inputs from the aquatic system with the delay of five to six months. We decided, therefore, to run the model for two years in order to investigate in a more realistic manner the interaction between various chemical, meteorological and the oceanographic processes. We used a currently available inventory of the annual usage of HCH on a global grid in order to estimate a global seasonal emission inventory. The gridded seasonal emissions of HCH obtained in this way was then included in the database of the model in a manner analogical as in other atmospheric tracer studies.

The results of more realistic simulations were presented in detail during the Arctic Monitoring and Asessment conference in Trømso. Upon these results, we conclude that the combined information about the actual emissions of HCH and the background concentrations of HCH emitted from the oceans into the atmosphere largely improve the model results. Further, we expect that the current accuracy of computer simulations is sufficient to consider the use of such models for the prediction of spatial and temporal trends of toxics in the Arctic. The major deficiency of the model was overprediction of the concentration of γ–HCH. This fact could be explained relatively well by the simplified treatment of the soil in our global 3-D model.

In order to perform the prediction of trends of HCH concentrations with more certainty we need to expand the 3-D global toxics model by including the soil module. The work in this direction has been already initiated and the major tasks which have been acomplished are as follows:

- Investigation of the state of the art in soil modelling.
- Search for physical constants characterizing α– and γ–HCH necessary to apply in the soil module.
- Investigation of soil properties to be included in the soil module.
- Preparing numerical subroutines with which to model the physical processes in the soil like diffusion, advection and disintegration of pesticides.
- Calculating fluxes of pesticides from the soil to the atmosphere.
- Designing the numerical code to calculate the upper boundary conditions of the soil module.
- Performing tests with different parameterizations of the boundary conditions.

The soil model will be included in the global 3-D HCH model and the results of a long-term simulation with the realistic 3-D multicompartment model will be reported in a scientific paper.

ATMOSPHERIC MERCURY MEASUREMENTS AT ALERT

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

Project Team: A. Steffen (Professional Services Contract); W.H. Schroeder; T. Lees (Co-Op Student, U. of Waterloo; Jan.–April, 1996); V. Grande (Co-Op Student, U. Of Waterloo; Sept. 1996 – April 1997); D. Schneeberger (Tekran Inc. of Toronto); C. Lamborg, G. Vandal and W. Fitzgerald (University of Connecticut); M.-D. Cheng (Oak Ridge National Laboratory)

OBJECTIVES

1. To obtain a baseline data set on the temporal (diurnal, seasonal, annual) variability of total gaseous mercury (TGM) at Alert, NWT.
2. To gather information about atmospheric emission sources, pathways/processes/behaviour and removal mechanisms for airborne mercury in the Canadian High Arctic troposphere.

DESCRIPTION

The arctic ecosystem is exhibiting increasingly disturbing evidence of contamination by a host of persistent, bioaccumulative toxic substances, including 'heavy metals' such as mercury (Barrie *et al.* 1997). Prior to 1992, no data existed on atmospheric concentrations of mercury in the Canadian Arctic. The first data set of atmospheric mercury concentrations in the Canadian Arctic consisted of a series of exploratory total gaseous mercury (TGM) measurements carried out at Alert (82°28'N, 62°30'W) between August 1992 and August 1993. This historic data set (Schroeder *et al.* 1995a, Schroeder 1996a) was obtained using weekly integrated manual sampling (in duplicate), followed by thermal desorption of the mercury amalgamated on the sample traps and subsequent detection by Cold Vapour Atomic Fluorescence Spectrophotometry (CVAFS) similar to the methodology described by Fitzgerald and Gill (1979 and by Bloom and Fitzgerald (1988). Our measurement results have recently been used to identify possible source regions of atmospheric mercury emissions likely to contribute to the concentrations of this metal observed at Alert, using a numerical modelling technique called the "Potential Source Contribution Function" (PSCF) source-receptor model (Cheng *et al.* 1993, Cheng and Schroeder 1996).

At the time that our manual method atmospheric TGM measurements were in progress at Alert, a Canadian company located in Toronto (Tekran Inc.) was developing an automated atmospheric mercury vapour analyzer. During fiscal year 1994/95, with funding from the Northern Contaminants Program (NCP), we assessed the suitability and reliability of this new, sophisticated Canadian instrument—the Tekran (Model 2537A) Mercury Vapour Analyzer—for application to TGM measurements in the arctic environment. This instrument assessment was performed in three phases: (1) Laboratory-based testing and evaluation (under controlled conditions of operation); (2) An initial field trial at a rural/remote location in North-Central Wisconsin in which the automated analyzer was intercompared with the traditional *manual* sampling and analytical methodology developed by Bill Fitzgerald's group at the University of Connecticut; (3) Testing and evaluation, under harsh winter conditions, at Alert during January 1995.

The results from the aforementioned instrument assessment have been reported (Schroeder 1996a). A paper on this work was presented at the 10th International Conference on Heavy Metals in the Environment which was held in Hamburg, Germany, during September 1995 and has been published in the Proceedings of this conference (Schroeder *et al.* 1995b).

Under the aegis of the federal NCP, this research project is a significant component of the current scientific efforts designed to advance our (as yet rather incomplete) understanding of the emission sources contributing to the burden of mercury present in the arctic atmosphere, which is strongly coupled with the northern biosphere. Furthermore, it is making a substantial contribution to our current knowledge of the atmospheric transport, transformation and removal/deposition mechanisms and processes operating on mercury which is present in the arctic troposphere due to releases from either natural or anthropogenic emission sources in the circumpolar regions (Mackay *et al.* 1995).

ACTIVITIES IN 1995/96

Buoyed by the success of the three-pronged evaluation performed on the Tekran automated mercury vapour analyzer, we began atmospheric TGM measurements at Alert with this instrument in January 1995. The distinguishing feature of these ongoing observations, compared with the exploratory, manual 1992/1993 measurements, is that the new data are characterized by a much higher temporal resolution (30-minute rather than weekly integrated sampling periods).

With the assistance of D. Schneeberger (Tekran Inc., Toronto) and a Co-Op student from the University of Waterloo (T. Lees), the data acquired during 1995 have been processed, quality-assured and analysed, both statistically and graphically. These results provided the material for an oral presentation at the "Fourth International Conference on Mercury as a Global Pollutant", which was held in Hamburg, Germany, from August 4–8, 1996 (Schroeder and Schneeberger 1996).

ACTIVITIES IN 1996/97

Surface-level atmospheric measurements of total gaseous mercury concentrations, which were initiated at Alert in January 1995 utilizing an automated Tekran mercury vapour analyzer, were continued during fiscal year 1996/97 (Schroeder and Schneeberger 1996, Schroeder 1997a, 1997b, 1997c). The distinguishing feature of these ongoing observations, compared with the exploratory, manual method TGM measurements that were undertaken during 1992–1993 (Schroeder *et al.* 1995a), is the much higher temporal resolution of the current data (based on 30-minute rather than on weekly integrated sampling periods). With the assistance of a Co-Op student from the University of Waterloo (V. Grande), the data acquired during 1995 and 1996 have been processed and analysed, both statistically and graphically.

Because funding was not provided by the Department of Indian and Northern Affairs (DIAND), to conduct a regular sampling program for particulate-phase mercury in ambient air, nor for mercury in precipitation, only intermittent collection of environmental media other than air was possible during fiscal year 1996/97 at Alert.

In a concurrent activity, the 1992/1993 atmospheric TGM measurement results from Alert were used to identify possible source regions of atmospheric mercury emissions likely to contribute to the concentrations of this heavy metal observed at Alert. This collaborative work with Oak Ridge National Laboratory (Tennessee, USA.) involved the application of a numerical modelling technique called the "Potential Source Contribution Function" (PSCF) source-receptor model (Cheng and Schroeder 1996). A paper describing this method and the results derived from its application has been accepted for publication (Cheng and Schroeder 1997).

RESULTS

During 1995 measurements of total gaseous mercury in ambient air were carried out at Alert, located at the northern tip of Ellesmere Island, where the Atmospheric Environment Service of Environment Canada operates a baseline tropospheric chemistry observatory. Results were obtained using a Tekran (Model 2537A) automated mercury vapour analyzer (Schroeder 1996a). The instrument operating parameters were set up to collect half-hourly integrated air samples onto a gold-mesh cartridge which retains vapour-phase mercury species contained in the air through a process of amalgamation. Thermal desorption of the mercury collected, followed by cold-vapour atomic fluorescence spectrophotometry are employed for the analytical procedure. A distinguishing feature of these TGM measurements, compared with the earlier exploratory series of manual atmospheric mercury measurements at Alert (Schroeder *et al.* 1995a), is their significantly higher time resolution.

Figures 1 and 2 show the total gaseous mercury concentrations (consisting predominantly of elemental mercury vapour) which were observed at Alert during 1995 as a function of time, on a season-by-season basis. One interesting feature of this time series, which will be discussed later, is the much greater variability which characterizes the results for the April to June 1995 period (Spring) especially when compared with the Winter and the Fall periods of the year.

Meteorological data, such as temperature, wind speed and wind direction, are monitored routinely at the Alert baseline chemistry observatory. The data for the year 1995 were obtained from Mr. D. Worthy (pers.comm 1996) for the purpose of facilitating the interpretation of the atmospheric mercury measurements. For example, using wind direction data recorded at Alert, we have plotted the median values of total gaseous mercury concentrations that are associated with different wind directions. These results are depicted in Figures 3 and 4.

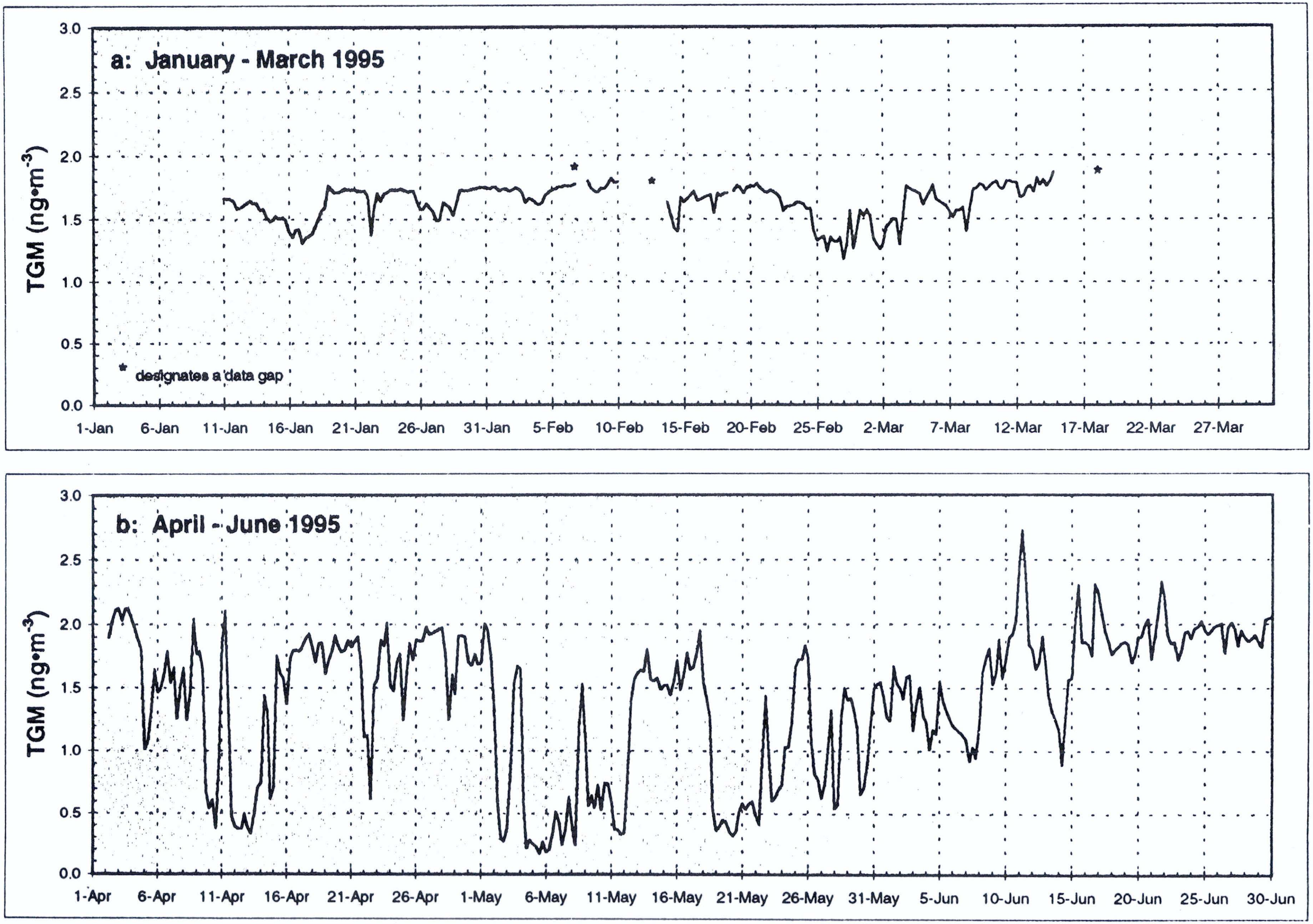


Figure 1. Atmospheric concentrations (6-hour averages) of total gaseous mercury (TGM) measured at Alert, NWT during 1995 (January to June).

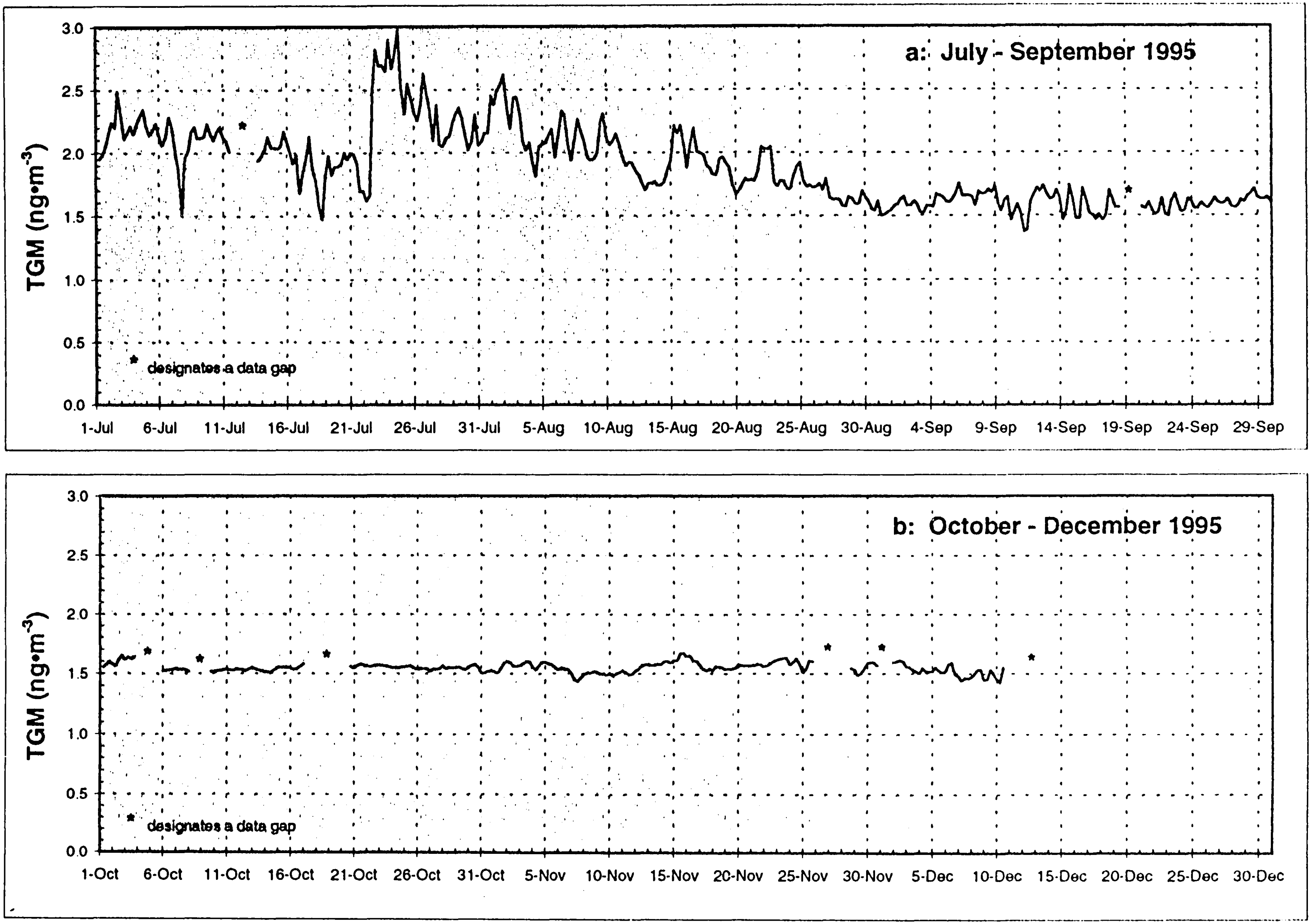


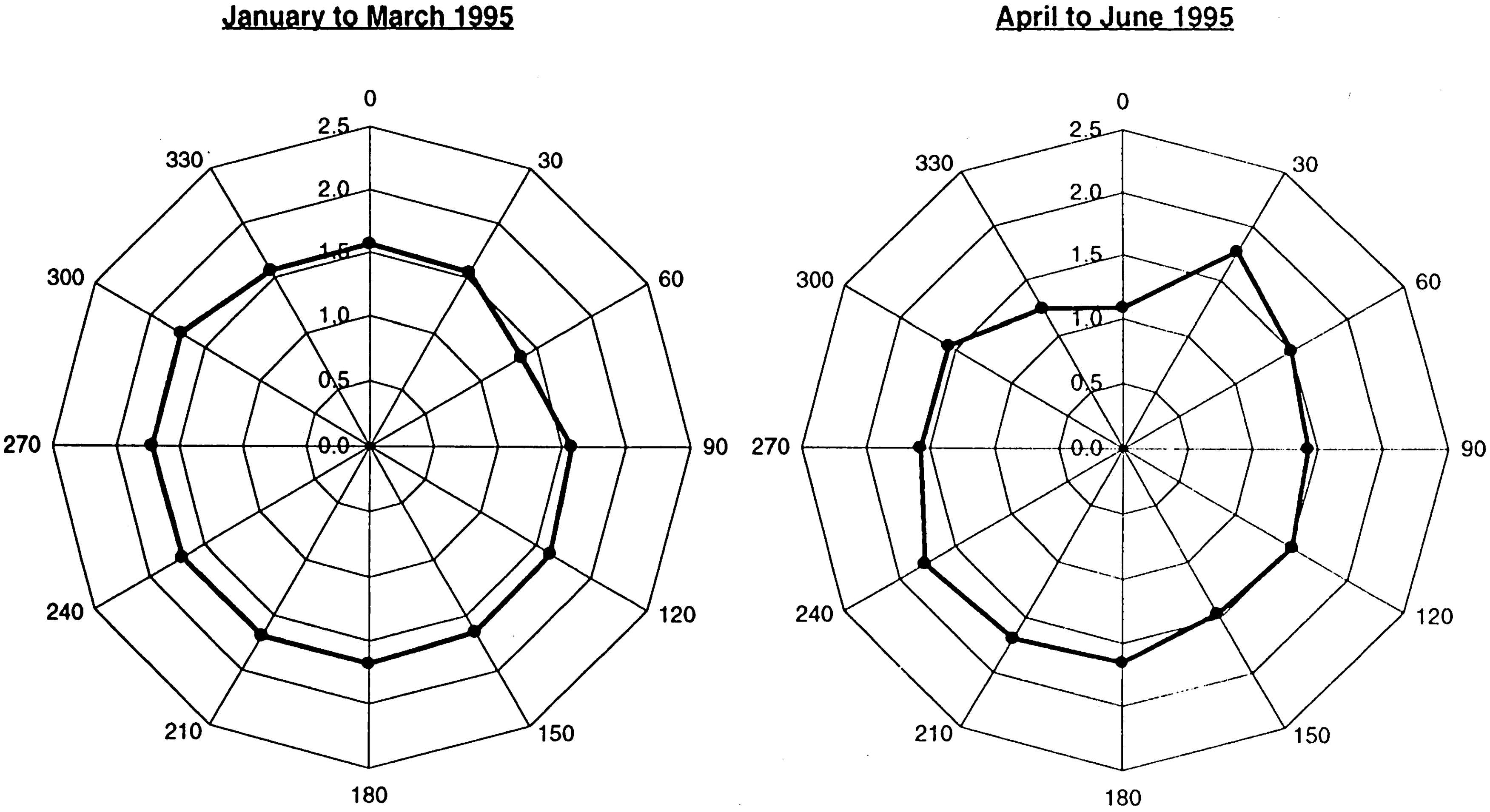
Figure 2. Atmospheric concentrations (6-hour averages) of total gaseous mercury (TGM) measured at Alert, NWT during 1995 (July to December).

Surface-level ozone is one of a number of air quality parameters that are being measured at Alert (pers. comm. *et al.* 1994). These ozone concentration data are plotted, along with the measured TGM concentrations, in Figure 5 and Figure 6. A striking similarity is evident in the observed concentration profiles of these two air contaminants. This covariance of ozone and surface-level total gaseous mercury is supported by the method-of-least-squares linear correlation plots which are shown in Figures 7 and 8 and will be discussed in the next section.

The 1995 data set of near-surface tropospheric mercury levels at Alert shows a very pronounced increase in the variability of the total gaseous mercury concentrations which occur after polar sunrise. Furthermore, there is a striking similarity in the TGM and near-surface ozone (O_3) concentration patterns observed at Alert (Schroeder *et al.* 1997, Schroeder, this report). In 1996, following polar sunrise, a similar temporal pattern of TGM concentrations was observed: the variability of the air concentration data is much greater, and relatively low (<1 ng·m^{-3}) ambient air concentrations of TGM occur much more frequently, during the spring (late March–April–May–early June) than at other times of the year (Figures 9 and 10). It is expected that the mercury vapour concentration pattern will again resemble that of near-surface ozone which consistently shows dramatic episodes of depletion of its ambient air concentration during the two- to three-month period following polar sunrise (Barrie *et al.* 1988, Anlauf *et al.* 1994). In the case of ozone, this depletion is known to be associated with the photochemical production of very reactive chemicals (notably halogen species) that destroy ozone, but the reason(s) for the depletion of mercury vapour in the near-surface air at Alert during late winter and spring is not yet known.

One possibility for the surprisingly low values of TGM that occur at Alert after polar sunrise is a sampling/measurement artifact: a so-called gold cartridge "passivation" or "blocking effect" (Brosset and Iverfeldt 1989, Schroeder *et al.* 1995a). Such an artifact could result from incomplete collection of mercury vapour by the pre-concentrating gold cartridges in the automated analyzer, caused by the presence of reactive chemical species which are produced through chemical/photochemical processes taking place in the polar atmosphere during that time of the year. Another (less likely) possibility could be quenching of the fluorescence signal measured by the instrument, owing to incomplete flushing of the air (or a chemical 'contaminant') introduced into the instrument with the sample being analysed. Hence, during March/April 1997 (in conjunction with *Polar Sunrise Experiment 1997*), a variety of tests and diagnostic experiments/procedures were performed at Alert to either confirm or rule out the existence of a sampling/measurement artifact. Two Tekran mercury vapour analyzers were operated in parallel (with sample integration periods reduced from 30 minutes to 5 minutes). "Standard additions" of known amounts of mercury vapour were periodically 'spiked' into the ambient air sample of one of the instruments near the end of the sampling period. As can be seen in Figure 11, the expected instrument response (i.e., the TGM concentrations of about 18 ng·m^{-3} determined for the 'spiked air' standard addition samples) was registered consistently, even at times when depletion events were occurring. These diagnostic field experiments provide conclusive evidence that the unusually low concentrations of TGM associated with the springtime (post-polar sunrise) mercury vapour depletion events—which coincide with surface-level ozone depletion—are indeed real and are not caused by a sampling/measurement artifact affecting the automated instrumental procedure.

Using a novel method recently developed at the Atmospheric Environment Service (AES) (Schroeder 1996b, Lu 1997, Lu *et al.* 1997), alongside the traditional weekly integrated sampling procedure, particulate-phase mercury samples were also collected at Alert during April and May 1997. Preliminary results (Figure 12) indicate that the concentration of particulate-phase mercury increases substantially during those times following polar sunrise when the TGM concentrations are well below 1 ng·m^{-3} (i.e., during TGM depletion episodes). This is exactly what would be expected if a chemical reaction mechanism (converting gaseous, elemental mercury into one or more particulate-phase mercury species) is responsible for the observed depletion of the gaseous-phase mercury in the ambient air. In this scenario, one or more of the highly reactive chemical species that are known to be produced in the arctic troposphere after polar sunrise (Barrie *et al.* 1988, Bottenheim *et al.* 1990, Li *et al.* 1994, Mozurkewich 1995) reacts with and oxidizes the normally inert, gaseous mercury fraction (consisting mainly of elemental mercury vapour) to one or more compound(s) of mercury with vapour pressure(s) substantially below that of Hg^{o}. The much less volatile compound(s), such as a mercury halide or an oxide, would preferentially exist in the particle-phase rather than in the gas-phase under the environmental conditions prevailing in the Arctic.


January to March 1995

April to June 1995

Figure 3. Pollution rose of median TGM concentrations found in 30° wind direction sectors. TGM values are shown in ng·m^{-3}. (each bin represents ± 15 degrees from each datapoint).

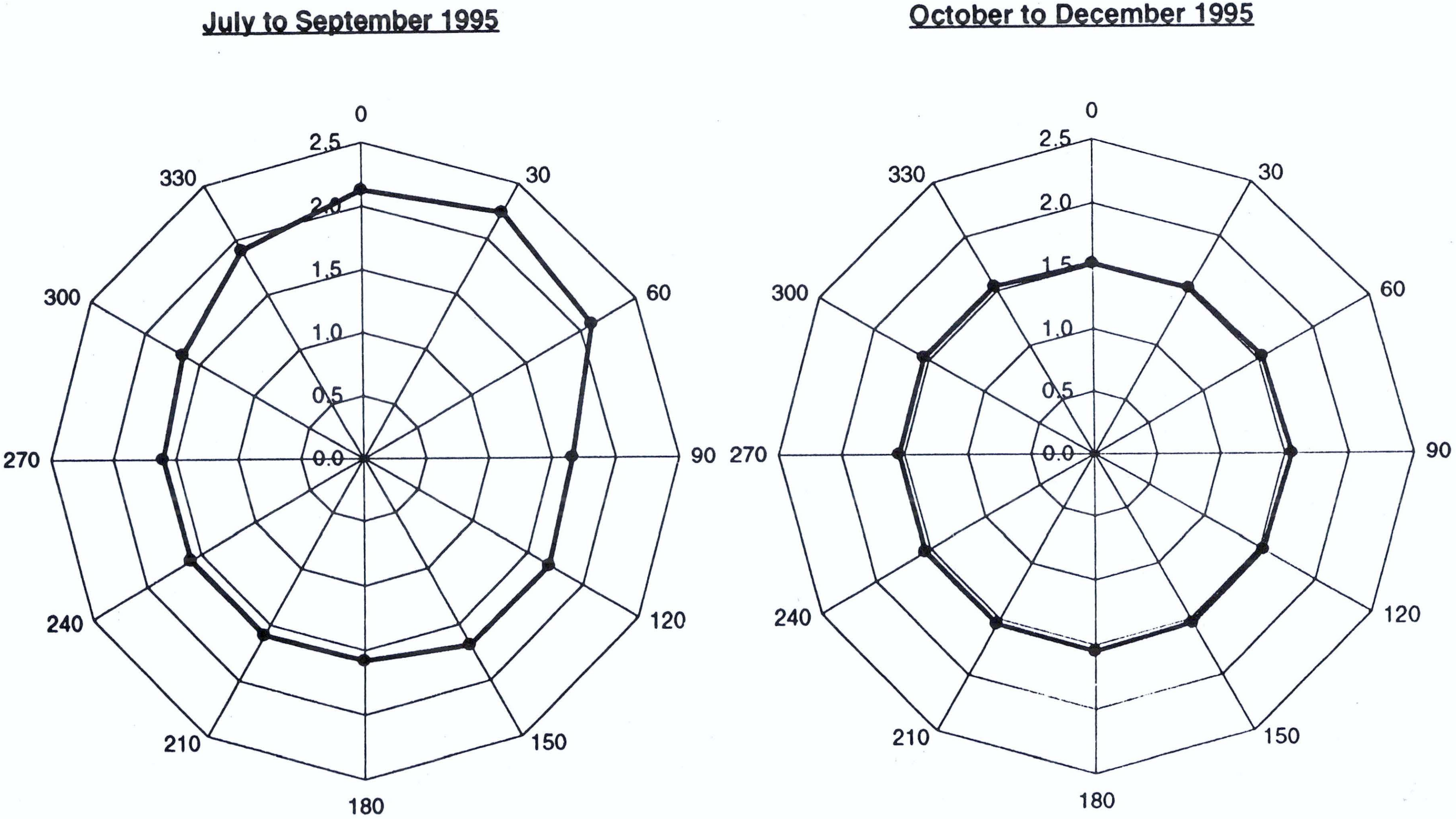


Figure 4. Pollution rose of median TGM concentrations found in 30° wind direction sectors. TGM values are shown in ng·m^{-3}. (each bin represents ± 15 degrees from each datapoint).

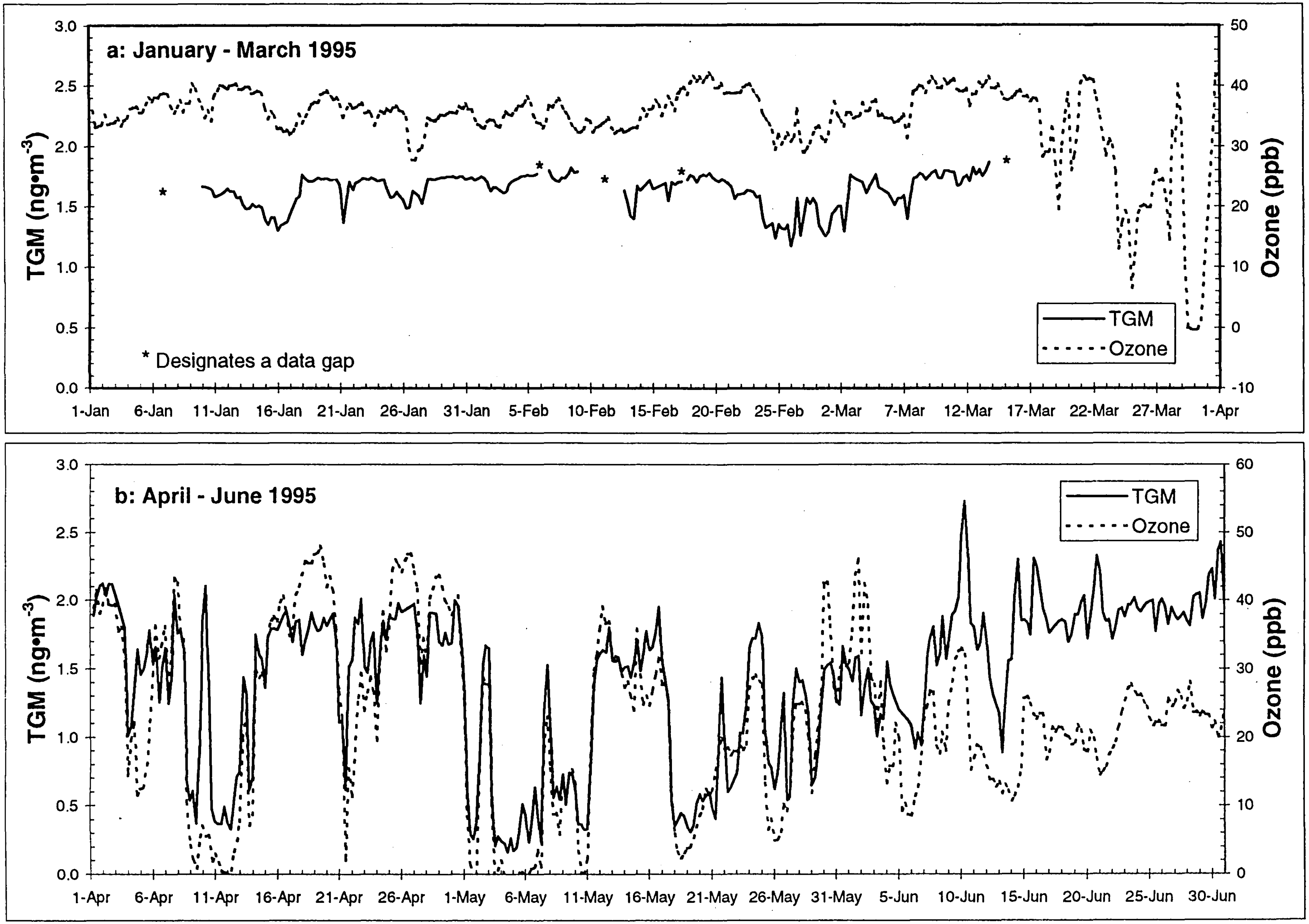


Figure 5. Atmospheric concentrations (6-hour averages) of total gaseous mercury (TGM) and ground level ozone measured at Alert, NWT during 1995 (January to June).

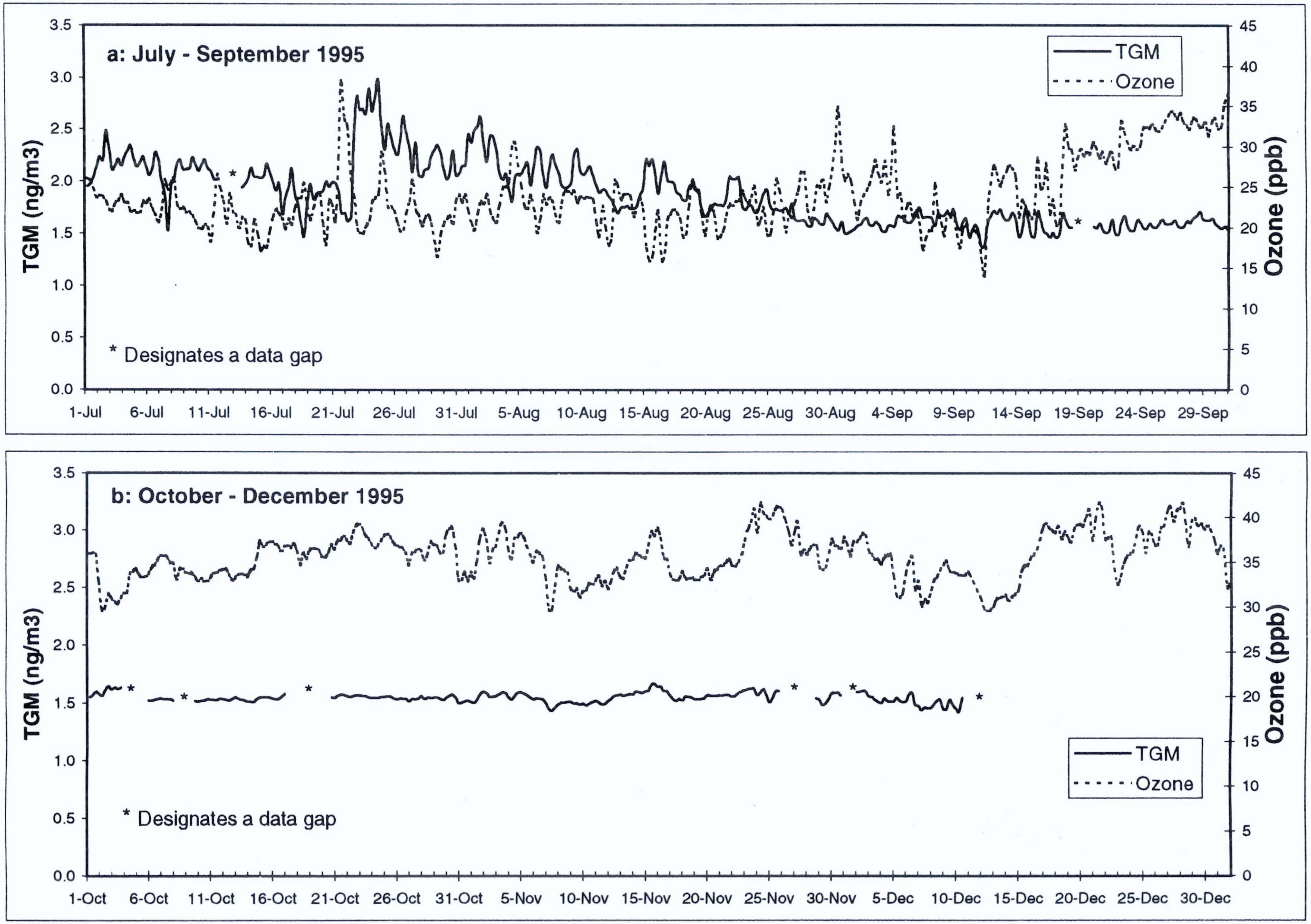


Figure 6. Atmospheric concentrations (6-hour averages) of total gaseous mercury (TGM) and ground level ozone measured at Alert, NWT during 1995 (July to December).

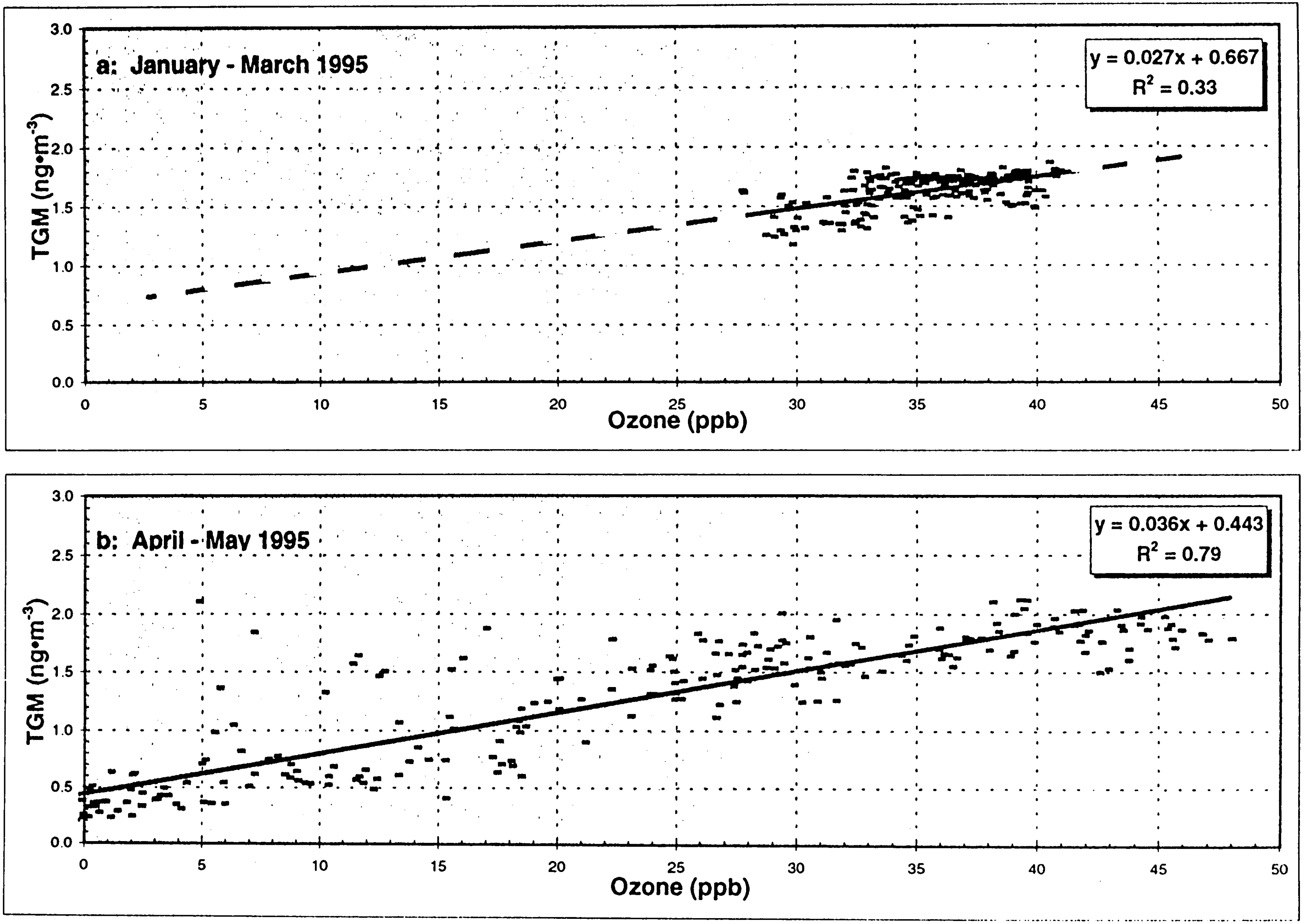


Figure 7. Correlation of ground level ozone and TGM concentrations (6-hour averages) measured at Alert, NWT during 1995 (January to June).

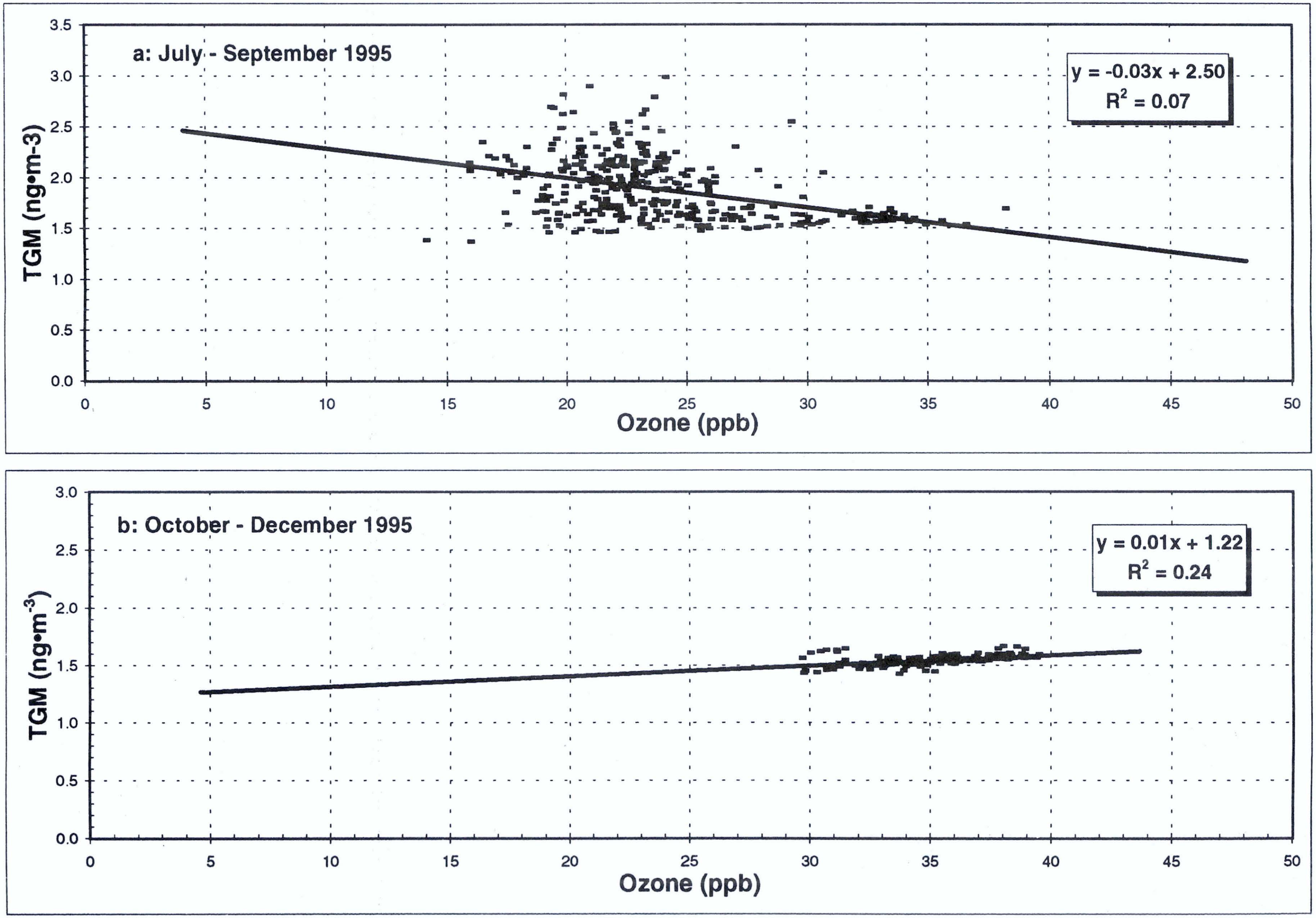


Figure 8. Correlation of ground level ozone and TGM concentrations (6-hour averages) measured at Alert, NWT during 1995 (July to December).

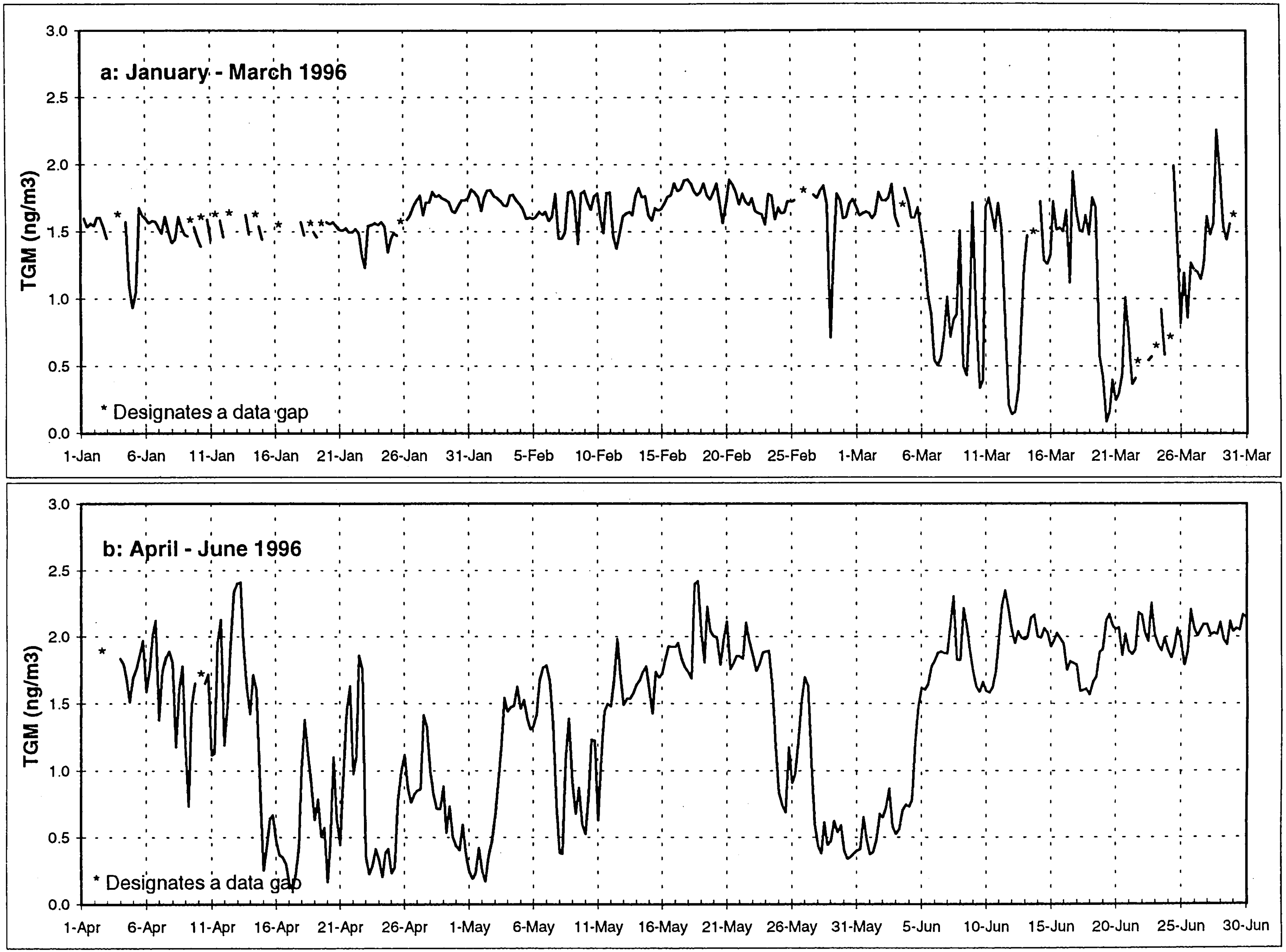
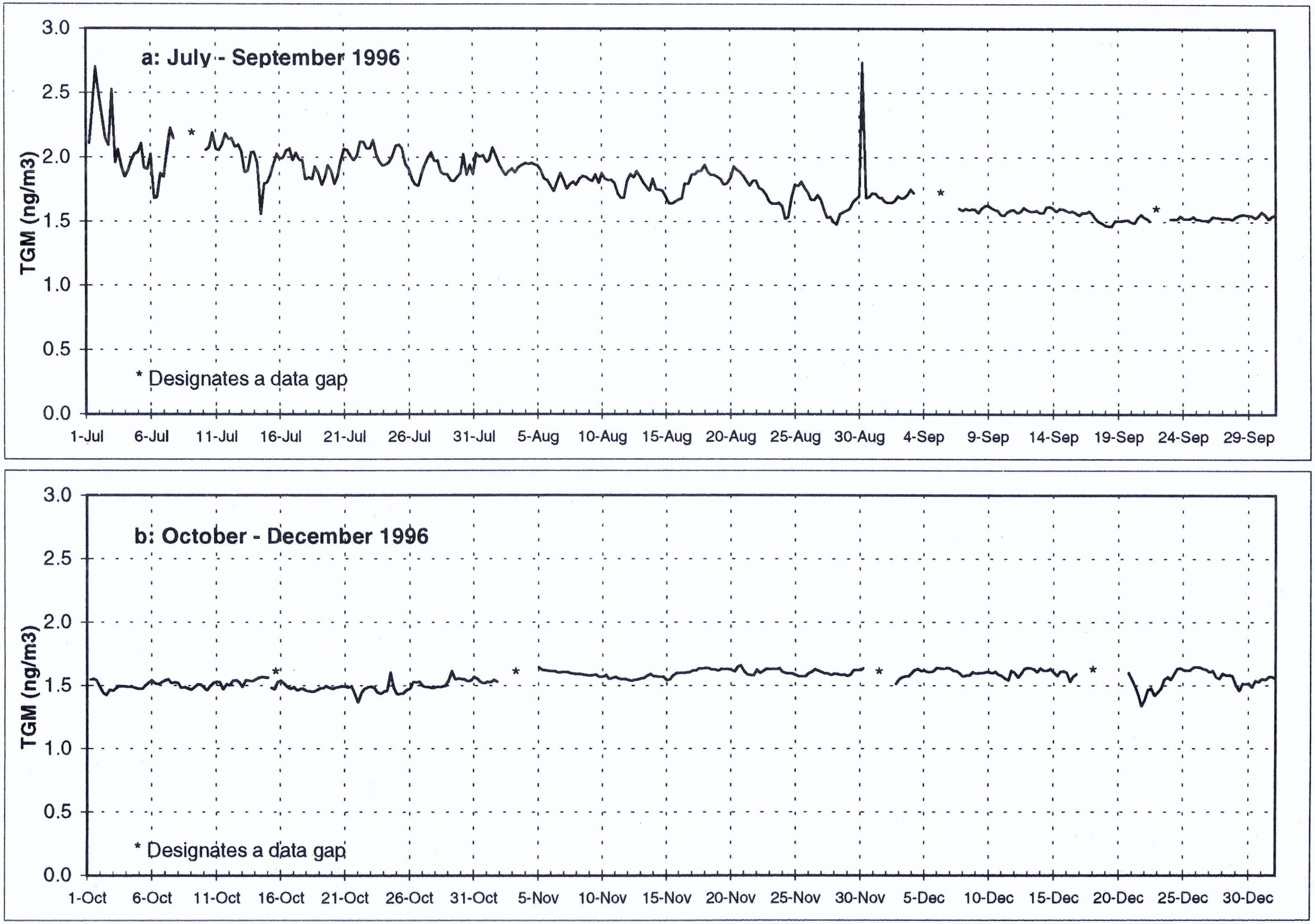


Figure 9. Atmospheric concentrations (6-hour averages) of total gaseous mercury (TGM) measured at Alert, NWT during 1996 (January to June).


a: July - September 1996

b: October - December 1996

Figure 10. Atmospheric concentrations (6-hour averages) of total gaseous mercury (TGM) measured at Alert, NWT during 1996 (July to December).

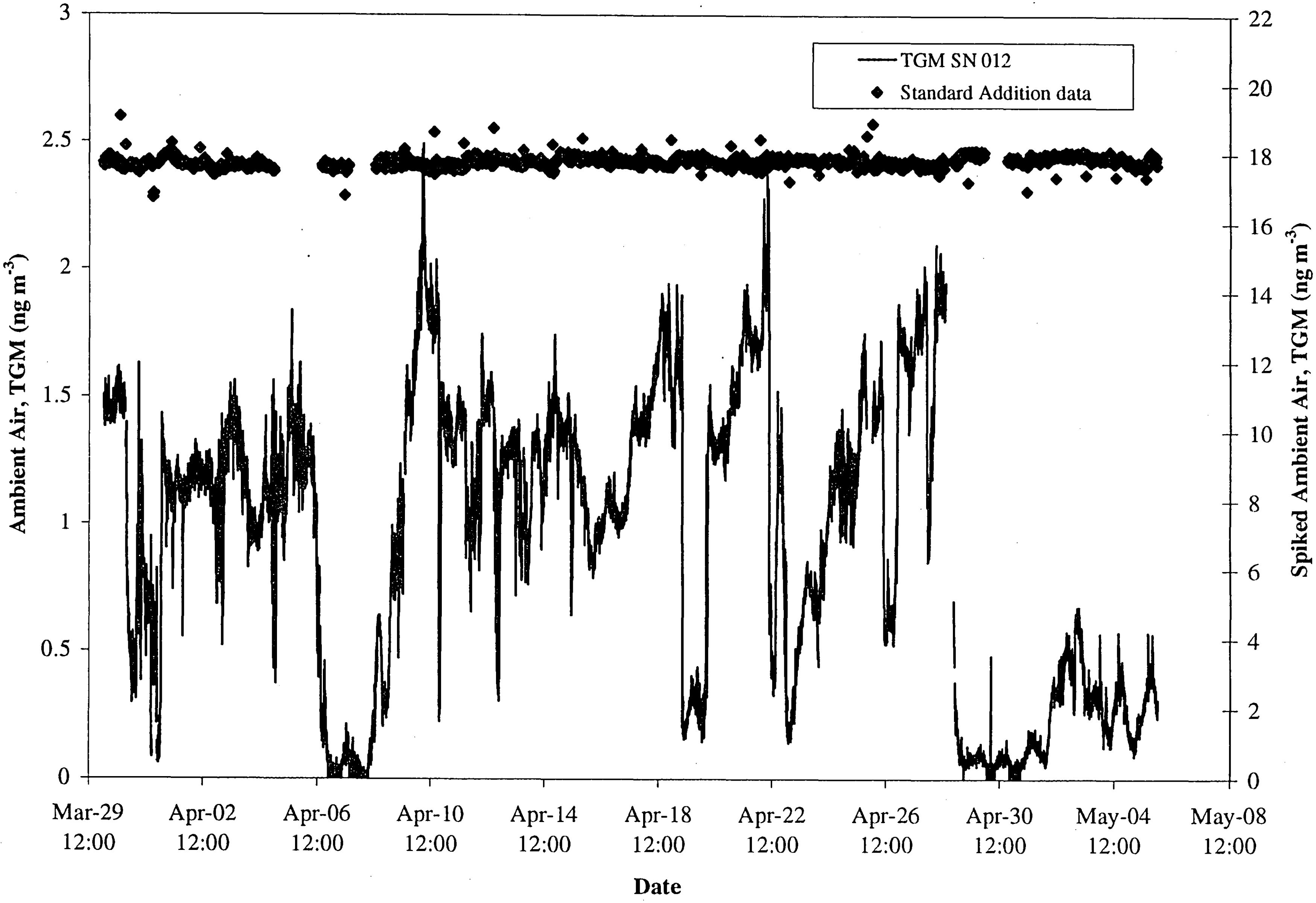


Figure 11. Results of standard addition diagnostic tests performed on Tekran Mercury Vapour Analyzer at Alert during late winter and spring 1997.

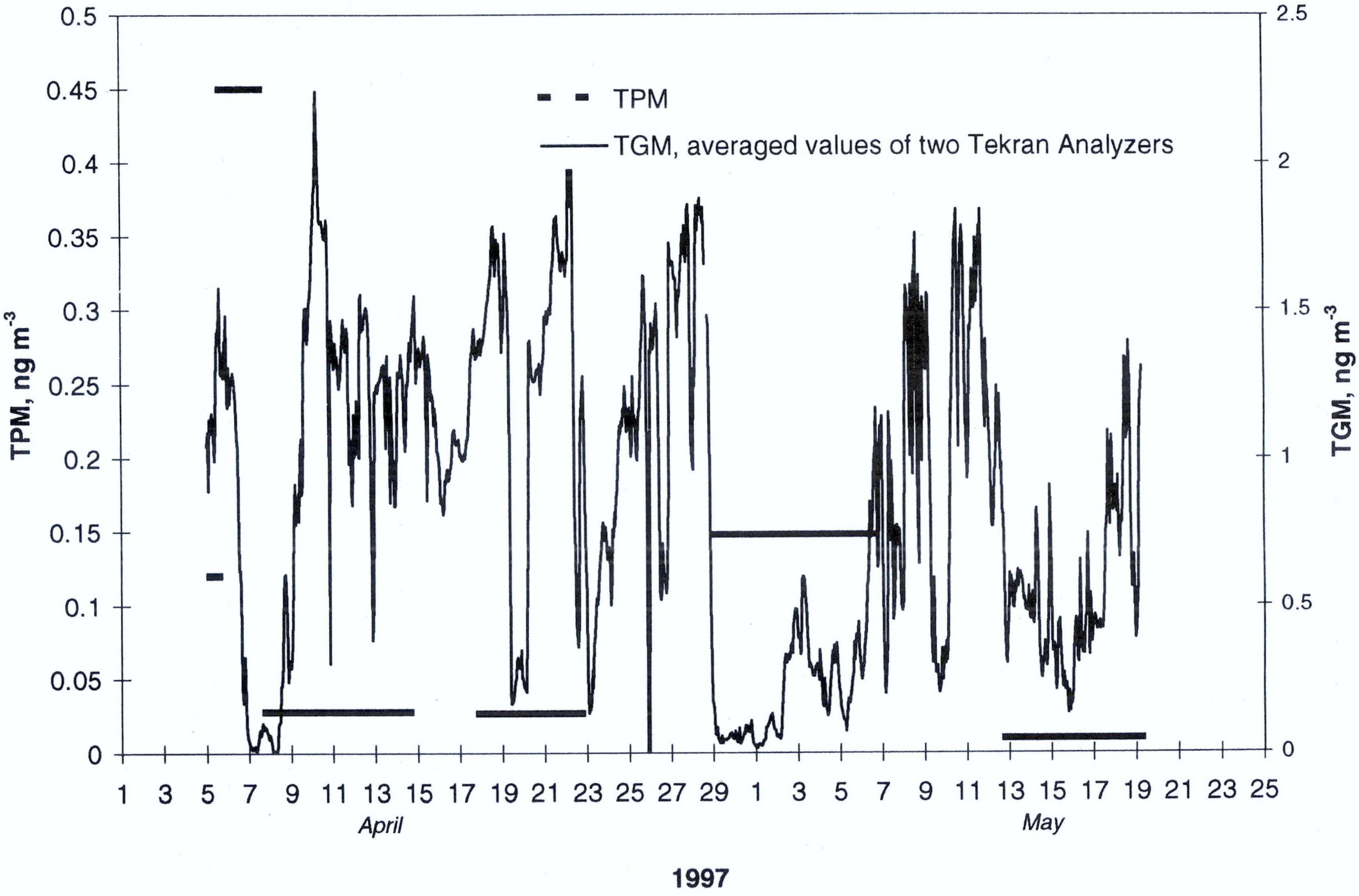


Figure 12. Results of concurrent measurements of total gaseous mercury (TGM) and total particulate mercury (TPM) concentrations in ground level ambient air at Alert during April and May 1997.

DISCUSSION/CONCLUSIONS

A comparison of the TGM concentrations observed in air at Alert during 1995 – see Figures 1 and 2 – reveals the existence of distinctly different patterns ("signatures") during different times/seasons of the year. Whereas the six-hour mean concentrations of TGM all fall between 1.0 and 2.0 ng·m^{-3} during the winter months (January through March), there occurs much more variability in the April to June period (spring 1995), with concentrations at times falling even below 0.5 ng·m^{-3} and rising significantly above 2.0 ng·m^{-3} at other times, especially in June. During July, August and September, TGM concentrations at Alert generally exceeded values of 1.5 ng·m^{-3}, reaching a maximum value of 3 ng·m^{-3} towards the end of July. It can also be seen that the variability in the instrument response dropped off considerably after the latter part of August. During the fall (October to December), the instrument response remains quite consistent with an average air concentration of TGM in the vicinity of 1.5 ng·m^{-3}. TGM values between 1 and 2 ng·m^{-3} are typical of rural or remote continental locations (Fitzgerald *et al.* 1991, Iverfeldt 1991).

Figure 3 and Figure 4 show the median values for total gaseous mercury concentrations associated with different wind directions measured at Alert. For a relatively long-lived gaseous air pollutant such as elemental mercury, which is estimated to have a global atmospheric residence time of the order of 1 year, one might expect to find a rather uniform distribution of air concentrations as a function of direction, at least at a remote arctic site such as Alert. This hypothesis is supported rather well by the pollution roses for January to March and for October to December, which are nearly symmetrical in their shape. For the summer months (July to September 1995) higher air concentrations of TGM are mainly associated with winds from the northwest, north and northeast directions. In 1995, during the period from April to June, northerly winds generally contained lower concentrations of TGM than winds from other directions. Analysis of the atmospheric mercury measurement data set will be extended in the future through the use of air parcel backward trajectories, once their quality-assured versions for the year 1995 are available to us.

Inspection of Figures 5 and 6 shows that during the period from March to June, noticeably more so than at any other time of the year, the atmospheric concentrations of TGM are much more variable and surprisingly low concentrations (values below 0.5 ng·m^{-3}) are not uncommon. This is also the time of the year during which severe ground-level ozone depletion episodes have been observed at Alert (Anlauf *et al.* 1994). In the case of ozone, the depletion has been attributed to advection from over the Arctic Ocean of a shallow layer of air in which O_3 has been consumed through its interaction with other chemicals (especially inorganic bromine- and, possibly, iodine-containing species). These highly reactive halogen species are generated in the lower troposphere when sunlight returns to the Arctic after several months of continuous darkness (Barrie *et al.* 1988, Barrie *et al.* 1994). The reason(s) for the highly variable and, at times surprisingly low, TGM concentrations observed at Alert following polar sunrise are not yet known, but plans are being developed to further investigate this phenomenon during the winter and spring of 1998.

The significance of the observed spring-time depletion events of TGM concentrations at Alert (and most likely at other locations in the arctic environment as well) lies in the fact that the associated reaction(s) provide(s) an environmental pathway for converting the normally inert (hence long-lived) and relatively insoluble gaseous form of mercury (viz., Hg^{o}), which constitutes the predominant species of mercury in the atmosphere, to the particulate phase which has a much shorter atmospheric residence time, since it is more readily deposited from the atmosphere to (arctic) terrestrial and aquatic ecosystems. Probably of even more importance for the arctic environment and its biosphere/food chain is that this chemical transformation of Hg^{o} yields Hg(II), which is the substrate (i.e., starting material) for the biological (and abiotic) methylation of inorganic mercury to organometallic methyl mercury, the most toxic form of this heavy metal (Fitzgerald *et al.* 1994). It is the methyl mercury species which has the unique ability to bioaccumulate in the human food chain and cross the blood-brain barrier as well as the walls of the placenta. This invasive potential of the methylated form of mercury has, of course, considerable ecological/ toxicological implications.

Expected project completion date: March 31, 2002.

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PROCESSES AND FLUXES OF CONTAMINANTS IN AQUATIC SYSTEMS

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OBJECTIVES

1. To investigate and quantify the major processes affecting contaminant transformation, transport and fate in the Amituk Lake watershed.
2. To develop and calibrate contaminant transport models utilizing the data from Amituk Lake and to compare the results with other basin studies.
3. To utilize the study results from all basins studied in the Arctic for model development and calibration in order to estimate contaminant transport and flux in larger northern aquatic systems.

DESCRIPTION

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

Amituk Lake is located on the eastern coast of Cornwallis Island at latitude 75°02' 57" and longitude 93° 45' 51". The basin is underlain by Ordovician and Silurian carbonate rocks, 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 1995/1996

No field activities were conducted at Amituk Lake in 1995/96. The work effort was directed to the completion of chemical analyses for mercury and organochlorine compounds and to data processing. The mercury study at Amituk Lake will be the focus of this synopsis.

METHODS

Snow and surface water samples were collected for total mercury analysis during the 1994 field season (June–August). Using a teflon-lined box corer and a CREEL snow corer (for depths >1.5m), 22 samples were taken from the pre-melt snowpack at Amituk Lake. Water samples from the six influent streams and the lake outflow were collected frequently (every 1–2 days) during the high spring flows and at least weekly during low flows. Amituk Lake was sampled four times from June 15 to August 7 at 1m intervals (0–5m) and at 10, 20, 30 and 40m. In total, 149 and 40 stream and lake samples were submitted for total Hg content. Additional duplicate and Hg- spiked samples were utilized for QA/QC purposes. All samples were placed in acid-washed teflon bottles and preserved with high-purity acid in the field. Total Hg analyses were carried out at the clean laboratories at MOEE, Dorset, Ontario. The methodology involved sodium borohydride reduction to elemental Hg, Hg° purging and collection on gold-coated sand, and thermal desorption followed by detection with atomic fluorescence.

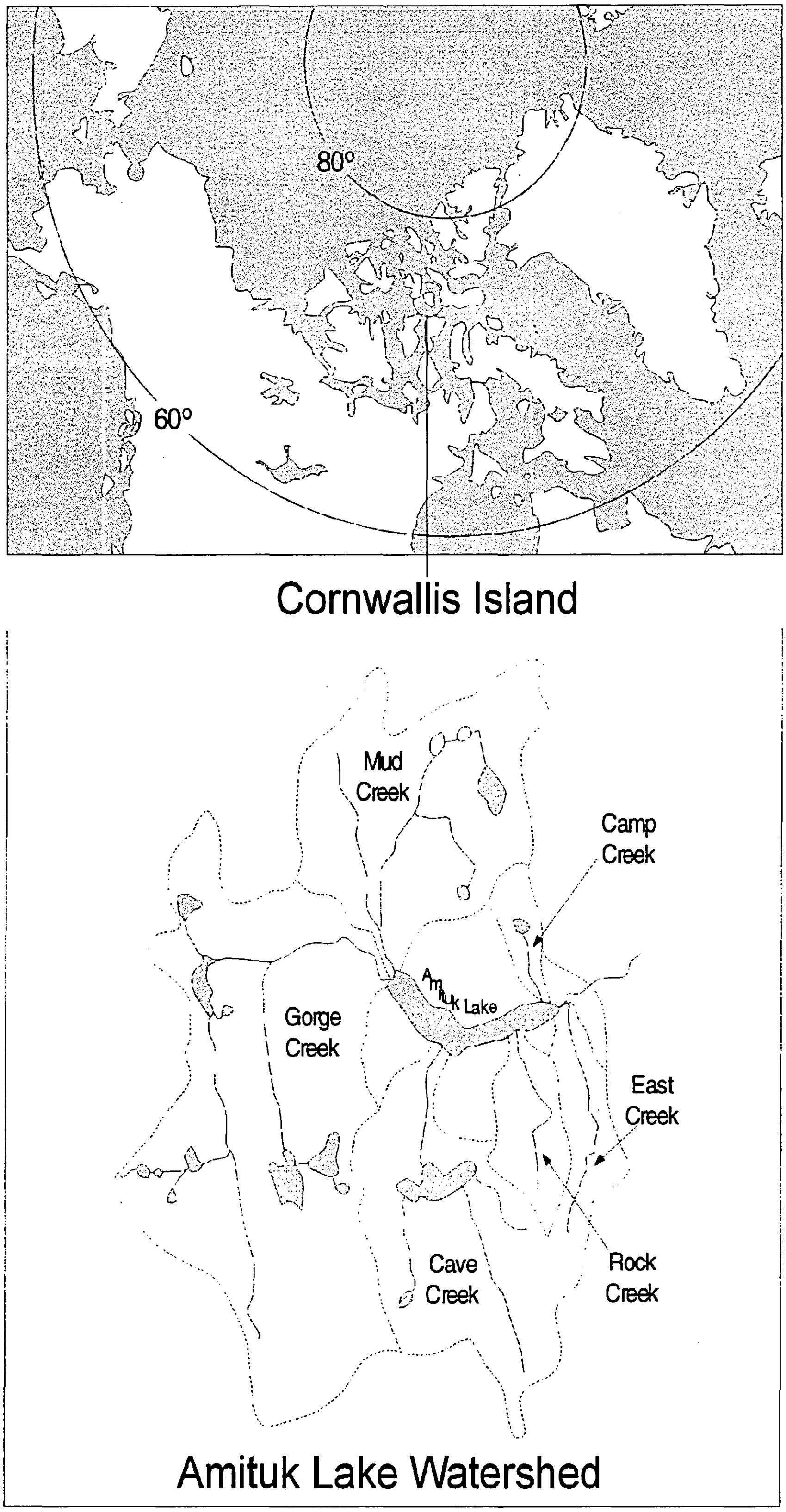


Figure 1. Location of Study Site in the Canadian Arctic.

Table 1. Snowpack and Surface Water Chemistry[1], Amituk Lake 1994

	Shallow Snowpack	Valley Snowpack	Stream[2] Inflow	Amituk Lake	Lake[2] Outflow
H^+μeq.L^{-1}	0.0782	0.3415	0.0085	0.0048	0.0071
pH	7.11	6.47	8.07	8.32	8.15
Cond μS·cm^{-1}	21.5	18.3	102.8	138.2	116.1
Ca^{2+}	2.57	0.87	15.69	20.59	17.83
Mg^{2+}	0.54	0.55	3.08	4.20	3.34
Na^+	0.73	1.23	1.01	1.48	1.23
K^+	0.08	0.19	0.15	0.17	0.18
NH_4^+ -N	0.008	0.031	0.007	0.002	0.005
Alk meq.L^{-1}	0.137	0.031	0.986	1.320	1.105
SO_4^{2-}	0.56	0.87	1.26	2.09	1.38
NO_3^- -N	0.029	0.041	0.031	0.015	0.022
Cl^-	1.68	3.34	2.29	3.15	2.77
SiO2	0.171	0.086	0.321	0.267	0.412
DIC	1.78	0.59	11.59	16.31	12.81
DOC	0.853	0.433	0.670	0.625	0.657
POC	0.616	0.437	0.097	0.037	0.078
TOC	1.447	0.870	0.767	0.705	0.736
TP	0.0043	0.0044		0.0210	
TN	0.136	0.184		0.078	
Org N	0.099	0.120		0.060	
PON	0.019	0.023	0.007	0.006	0.010
DON	0.080	0.099		0.054	
Susp. Solids	21.8	26.0	4.44	3.96	2.88
Hg ng·L^{-1}	1.25	4.21	0.76	0.33	0.52

[1] Concentrations as mg·L^{-1} unless otherwise specified.

[2] Stream and lake outflow concentrations are discharge-weighted.

In addition to the total Hg determinations, snow and surface water samples were analysed for major ions and nutrients. Daily streamflows were calculated from discharge measurements and the automated stream level recorders. Limnological surveys at Amituk Lake included profiling of temperature and specific conductance.

RESULTS AND DISCUSSION

The snowpack at Amituk Lake can be differentiated into two types based on physical and chemical attributes. In 1994, the shallow snowpack on the lake ice and on the upland plateaux recorded an average depth of 0.47m, density of 0.433 and snow water equivalent (SWE) of 204 mm for 49 samples, whereas the snowpack in the six stream valleys was much deeper (z = 2.76m), denser (p = 0.642) and obviously of a higher water content (SWE = 1803 mm). The shallow snowpack was more alkaline with a higher pH and Ca^{2+} content; the valley snowpack revealed higher concentrations of Na^+ and Cl^- (Table 1). A temporal variability in the time of snow deposition was suggested by these chemical differences. Furthermore, recent work by S. Kinney (personal communication) used isotopic signatures to support an early winter formation of the shallow snow cover and a late winter deposition of the valley snow. Total mercury also varied in the two snowpacks—from 1.25 ng·L^{-1} in the shallow to 4.21 ng·L^{-1} in the valley snowpack.

Stream and lakewater chemistry at Amituk Lake was alkaline - pH >8.0, high Ca^{2+} and alkalinity, and was reflective of extensive limestone weathering in the basin (Table 1). With the exception of nutrients, which are utilized in biological production in the lake, the concentration of major ions in the lake water column and in the lake outflow generally exceeded levels in the cumulative stream input. While cryo-concentration may have resulted in an increase in lake concentrations during the formation of a thick ice cover (2.2m), the higher lake values were primarily related to groundwater input.

Streamflow into Amituk Lake was initiated with snowmelt in mid-June; the stream hydrographs peaked over a three-week period (Figure 2). The cold, relatively dilute meltwater entered Amituk Lake just beneath the ice cover and mixed only minimally with the lake water column as indicated by the isopleths of temperature and specific conductance (Figure 3). At this time, most chemicals solubilized in the snowmelt passed directly through Amituk Lake to the lake outflow. Not until the end of July did isothermal conditions develop in Amituk

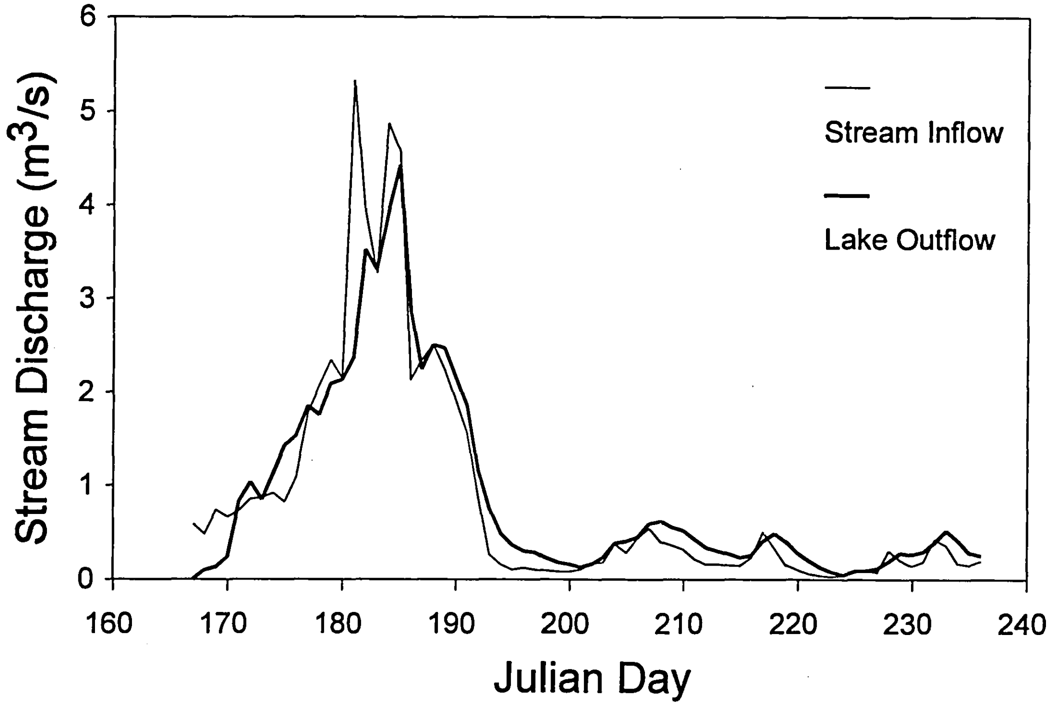


Figure 2. Amituk Lake Hydrology

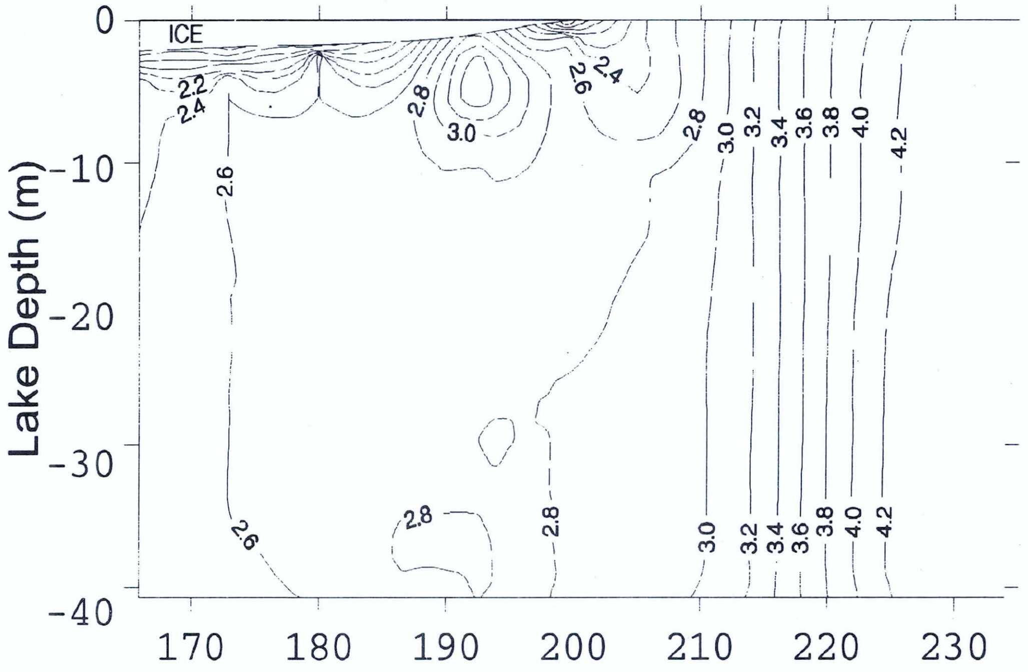
Lake and did complete mixing of the influent streamwater and lakewater occur. It was also when the groundwater contribution was most significant in terms of subsurface flow volume and in the ability to effect chemical changes in the lake water column. This was readily evidenced by the substantial increase in major ions such as SO_4^{2-}, Ca^{2+} and alkalinity in lakewater compared to the inflowing streams.

The discharge - weighted concentration of total Hg averaged 0.76 ng·L^{-1} in the six streams and 0.52 ng·L^{-1} in the lake outflow. The total Hg level in the lake water column was calculated to be 0.33 ng·L^{-1} on August 7 (Table 1). Overall, the surface water concentrations of total Hg were at the lower end of the spectrum reported for other remote sites (Table 2).

Elevated levels of total Hg in streamwaters were associated with the major influx of meltwater from the ablating snowpack (Figure 4). Depending upon the meteorological conditions and the physical constraints within the snowpack, e.g., snow/ice dams and ice lenses, regulating the production and routing of snowmelt, the pattern of chemical release to the streamwaters could be quite variable. Rock Creek first flowed on June 20. At this time, elevated levels of total Hg were observed in the initial streamwaters followed by reduced concentrations with diminishing flow (Figure 5). This behaviour was very similar to that previously reported for major ions and dissolved nutrients in snowmelt at Amituk Lake (Semkin 1996). The chemical elution of total Hg from the snowpack suggested that a high proportion existed in dissolved form - probably $Hg(OH)_2$, based upon the high pH and chemical make-up of the streamwaters (see Lindqvist and Rodhe 1985). In addition, a strong relationship between total Hg and dissolved organic carbon (DOC) was recorded in Rock Creek during the melt period: Hg_T (ng·L^{-1}) = 0.94* DOC (mg·L^{-1}) + 0.02, $r^2 = 0.70$ (Figure 6). The importance of DOC in the transport and bioavailability of mercury in freshwater ecosystems has been documented in other studies (Driscoll *et al.* 1994).

At lower flows in the summer, peaks in total Hg concentrations were also observed in Rock Creek and in the other streams. In most cases, the elevated Hg levels were associated with relatively high concentrations of suspended solids and quite often with high levels of total iron. Whether this represented adsorption to mercury or some iron compound or whether we were simply sampling mineral particulate matter (e.g., Fe-Hg sulphide grains) of geologic origin is unknown.

a) Temperature (°C)



b) Specific Conductance (µS/cm)

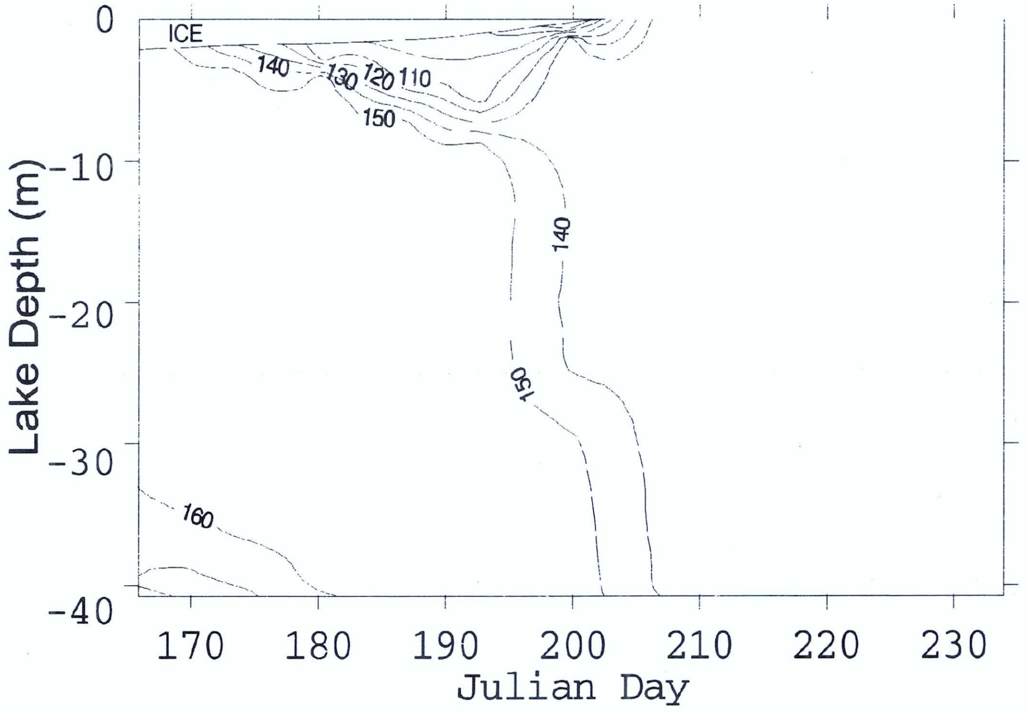


Figure 3. Temperature (a) and Specific Conductivity (b) Isopleths in Amituk Lake 1994.

Table 2. Total Mercury Levels ($ng{\cdot}L^{-1}$) in Remote Areas

Site	Precipitation[1]	Lakewater	Reference
Harp Lake, Ontario	10.2 (m)	1.6-3.2	Mierle 1990
Adirondack Lakes		0.8-5.3	Driscoll *et al.* 1994
Minnesota Lakes	16.8-24.2 (m)	0.9-7.0	Sorensen *et al.* 1990
Wisconsin Lakes	10.5 ± 4.8 (r) 6.0 ± 0.9 (s)	0.7-2.1	Watras *et al.* 1994
Lakes in Sweden		1.35-15	Lee and Iverfeldt 1991
Lakes in Finland	1.2–2.9 (r) 5.9–11.1 (s)	1.3-7.2	Verta *et al.* 1994
Lake Baikal, Russia	8–60 (s)	0.14-0.77	Meuleman *et al.* 1995
Worldwide			
–oceanic	6 (r)		N.D. Johnson cited in Stein *et al.* 1996
- rural areas	16 (r) 5 (s)		

[1] Precipitation type: r = rain; s = snow; m = mixed.

Meltwater entering Amituk Lake produced a Hg-rich lens (up to 0.67 $ng{\cdot}L^{-1}$ total Hg) just beneath the ice cover (Figure 7). Although a significant portion of the mercury in streamwater exited via the outflow, the lake still appeared to act as a sink for Hg_T as indicated by the reduced outflow concentration (0.52 $ng{\cdot}L^{-1}$) compared to levels in the influent streams (0.76 $ng{\cdot}L^{-1}$). Part of the "lost" mercury entered the lake water column and generated an increase in whole-lake Hg_T from 0.23 $ng{\cdot}L^{-1}$ on June 15 to 0.33 $ng{\cdot}L^{-1}$ on August 7; however, most of the incoming mercury would have been deposited to the lake sediments. What portion of this Hg deficit could also be explained by uptake by lentic biota or by volatilization to the atmosphere requires further investigation.

CONCLUSIONS

Research in the Amituk Lake basin has provided insight into the distribution and behaviour of mercury, a contaminant of some concern in the Arctic environment. The following conclusions can be made:

1. The level of total mercury in the snowpack and in the surface waters at Amituk Lake was at the lower end of the concentration range reported for other remote sites.

2. Spring snowmelt was the main transport conduit for mercury entering Amituk Lake.

3. Based on the relative concentrations in the influent streams and in the lake outflow, more than 50% of the total Hg input to Amituk Lake exited via the outlet. The mercury remaining in Amituk Lake increased the water column concentration and was also deposited to the bottom sediments.

Expected project completion date: March 31, 1997

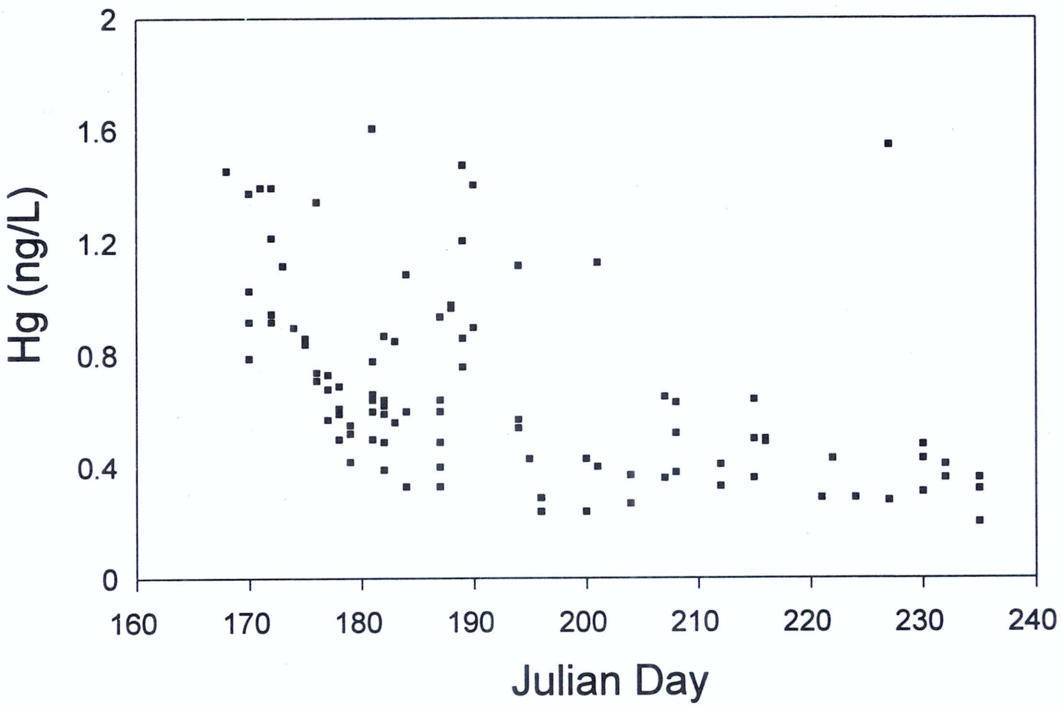


Figure 4. Total Hg in streamwaters, June 16 – August 23, 1994

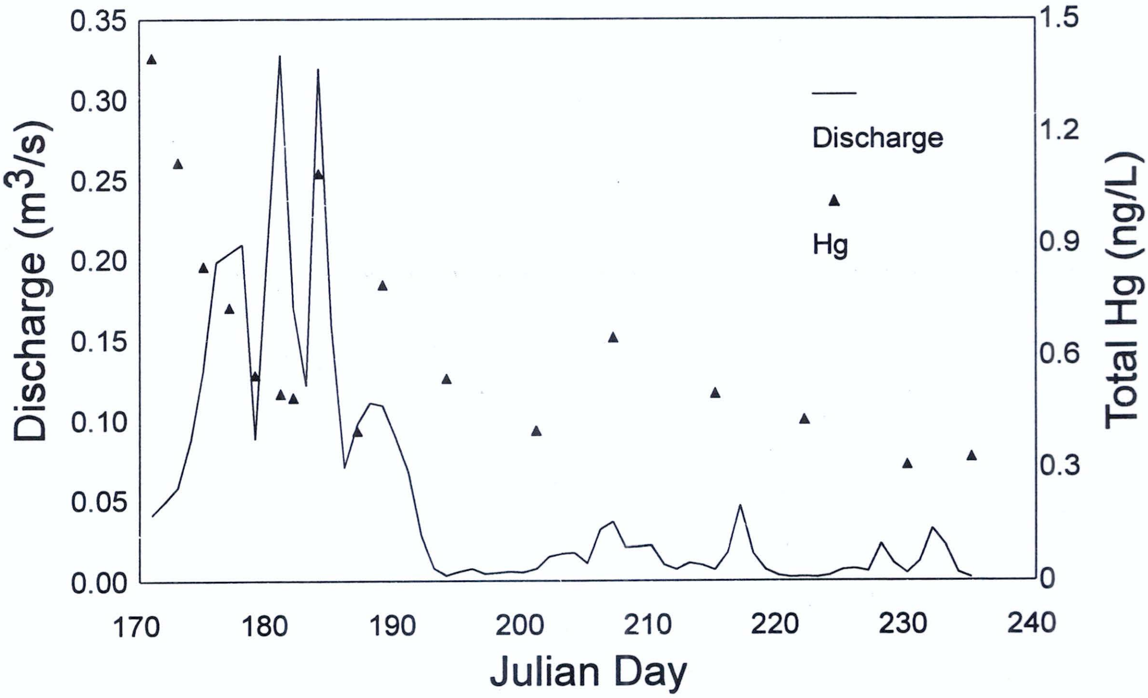


Figure 5. Total Hg in Rock Creek, 1994

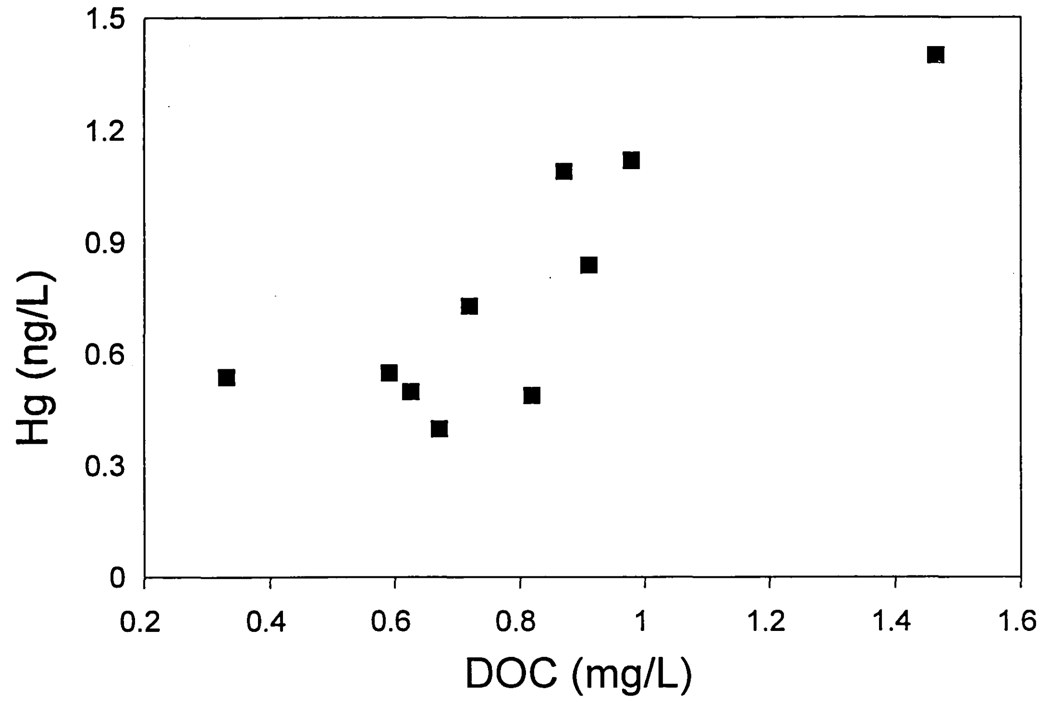


Figure 6. Total Hg-DOC in Rock Creek during spring melt, 1994.

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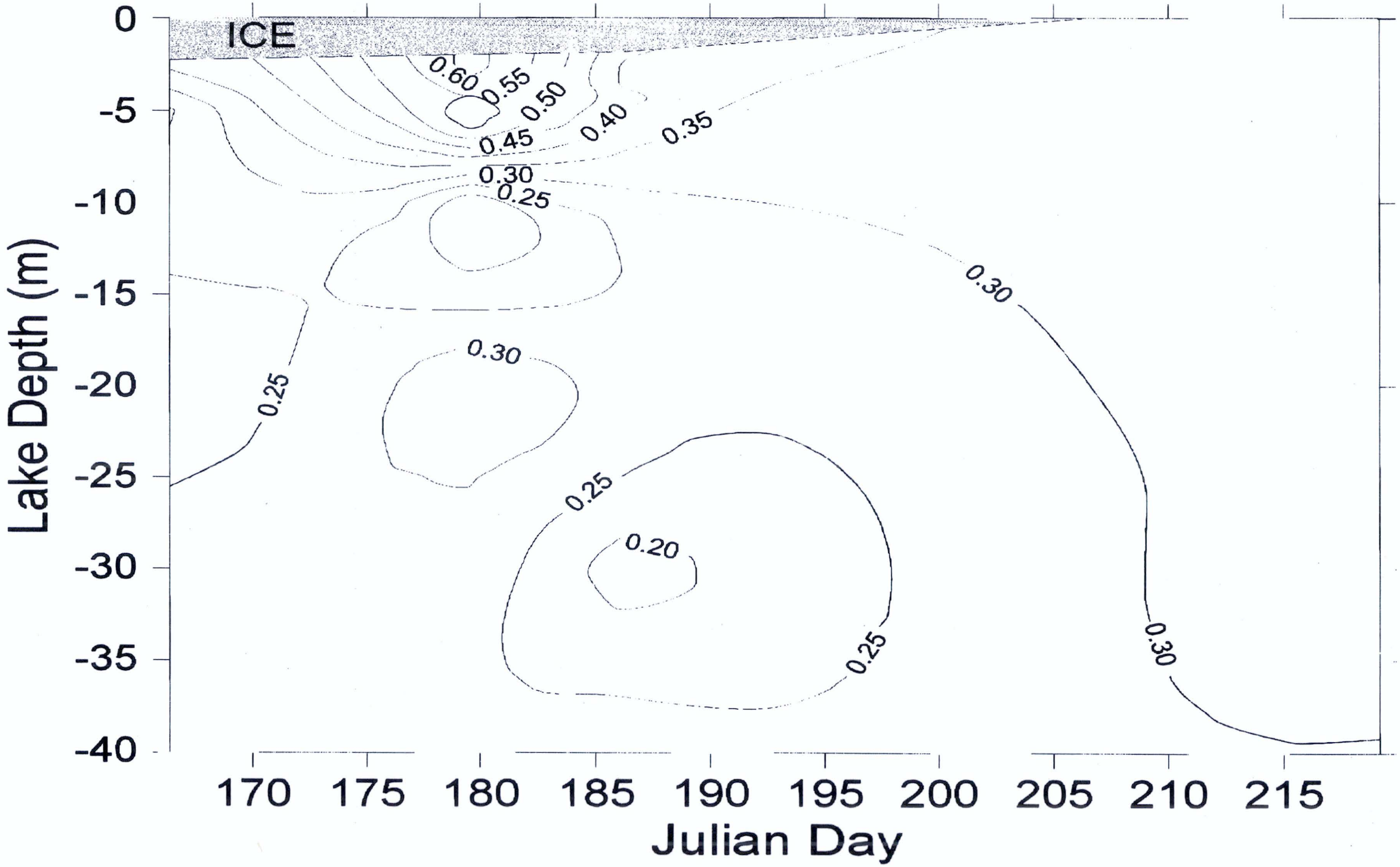

Figure 7. Total Hg (ng/L) in Amituk Lake, 1994.

MEASUREMENTS OF RADIOACTIVE CONTAMINANTS IN THE ARCTIC OCEAN

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

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, Tromso, Norway); L. Kilius, (University of Toronto)

OBJECTIVES

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

DESCRIPTION

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 provides 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 are also used as tracers to estimate inorganic and organic contaminant fluxes in collaboration with other investigators.

ACTIVITIES IN 1995/97

Arctic activities in 1995/97 included:

(a) radionuclide analyses of sediment, seawater and biota samples collected in 1993-96 in the Barents and Kara Seas in the Russian Arctic;

(b) radionuclide analyses of sediment and seawater samples collected aboard the CSS Louis S. St. Laurent during the Arctic Ocean Section (AOS) cruise in 1994 and the Beaufort Sea cruise in 1995;

(c) the collection and analysis of seawater samples from the central Arctic Ocean in 1995 and 1996 from the US Navy nuclear submarines, USS Cavalla and USS Pogy;

(d) the collection of seawater and sediment samples in Kola Bay and off Novaya Zemlya in the Barents Sea in 1996 in collaboration with Russian scientists (Okeangeologia, St. Petersburg); and

(e) publication of a series of papers and reports on these arctic activities and the presentation of these results at several international meetings.

RESULTS

Cruise Activities

Several oceanographic sampling programs were carried out in 1995-96:

(1) Samples were collected for radionuclide analyses during the cruise of the CSS Louis S. St. Laurent in the Beaufort Sea and Canada Basin in collaboration with scientists from the Institute of Ocean Sciences (B.C.). Two scientists from the Bedford Institute of Oceanography (BIO) accompanied the CSS Louis S. St. Laurent and collected seawater sample profiles on the Canadian continental slope and shelves of the Beaufort Sea. The purpose of this work is to determine radionuclide (^{137}Cs, ^{90}Sr, ^{129}I, ^{239,240}Pu) distributions and transport through the Arctic Ocean. 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 one litre samples were collected for ^{129}I analyses (Smith and Ellis, 1995). Four Challenger in-situ pumps were deployed, as on the 1994 AOS cruise, and used to process the large (> 300 L) volumes of seawater required to measure radio-

nuclides 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 permit estimates of organic and inorganic fluxes through the halocline.

(2) Seawater samples were collected from the two US Navy nuclear submarines, USS Cavalla and USS Pogy for ^{137}Cs and ^{129}I analyses during their respective cruises in 1995 and 1996 in the Central Arctic Ocean. Samples were collected through the hull of the submarine down to depths of 240 m. The submarines surfaced through the ice on numerous occasions during which time samples were collected to depths of 800 m from the surface of the ice. 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 by pathways indicated in Figure 1 and to evaluate any environmental impacts on the North American continental shelf.

(3) Collaborative cruises with other scientists in 1995-97 include a cruise to the Kara Sea (National Research Laboratory, Wash. DC) in 1995 and to the Nansen Basin (Lund Univ., Sweden) in 1996. Seawater samples collected on these cruises have been analysed for ^{137}Cs and ^{129}I in order to determine input functions for these tracer isotopes in the Arctic Ocean.

Analytical Work

Central Arctic Ocean

More than 200 sediment and seawater samples collected during the *CSS Louis S. St. Laurent* cruise across the Arctic Ocean in 1994 were analysed between 1995 and 1997 (Ellis *et al.* 1995). Measurements of ^{210}Pb, ^{137}Cs and ^{239,240}Pu conducted on sediment samples from box cores collected on slope/shelf regions of the Makarov, Canada and Eurasian Basins reveal elevated radionuclide levels in slope/shelf compared to deep basin sediment regimes owing to preferential scavenging in the former regions (Schlosser *et al.* 1995). Radionuclide

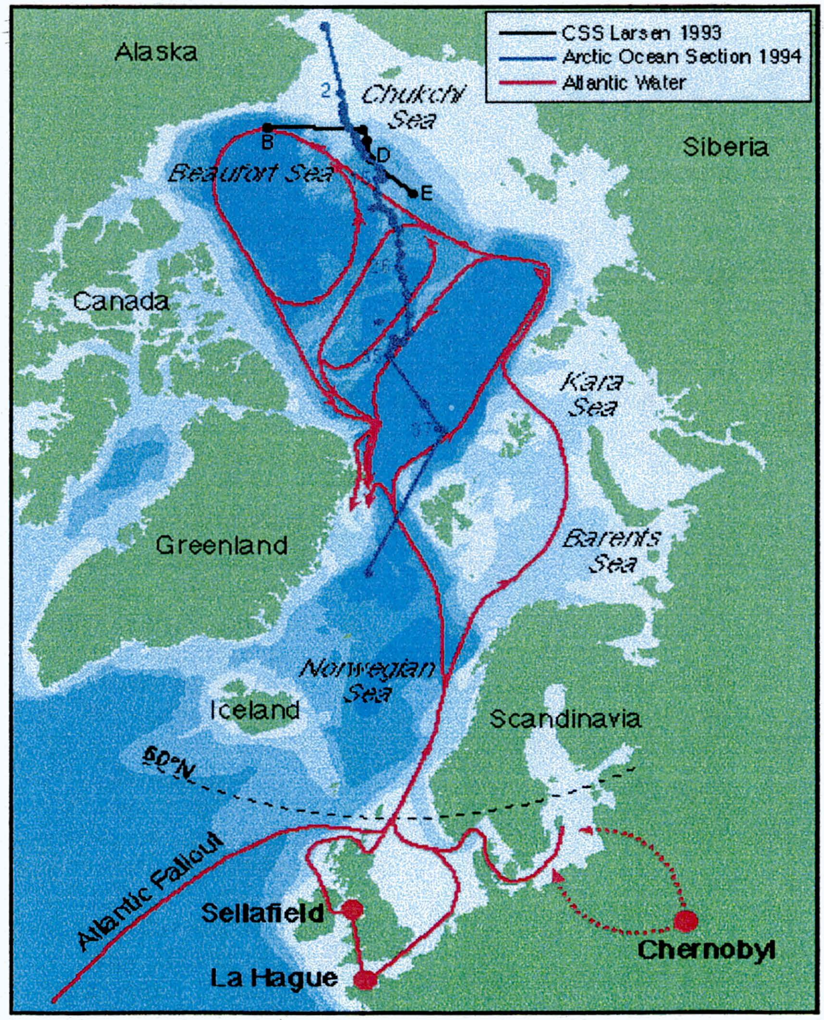

Figure 1. ^{129}I and ^{137}Cs from Sellafield, La Hague, and Chernobyl (from the Baltic Sea) enter the Arctic Ocean, with Atlantic-origin water, via the Norwegian and Barents Seas and can be used as tracers for transit times from a 60°N reference point in the Norwegian Coastal Current. Also shown are the cruise tracks for ice-breaker cruises of the *CSS Larsen* in 1993 and the *CSS St. Laurent* in 1994.

sediment-depth profiles have been introduced into biodiffusion models to constrain sedimentation and bioturbation rates. ^{129}I and ^{137}Cs analyses of seawater samples from both the icebreaker and submarine cruises clearly delineate the plume of Sellafield and Cap La Hague contaminants being transported across the Arctic Ocean (Smith *et al.* 1990). The ^{129}I section (Figure 2) for the *CSS Louis S. St. Laurent* cruise shows a "front" between Atlantic-origin water, labelled with reprocessing plant signals and Pacific-origin water distinguished mainly by fallout from weapons tests which is positioned over the Mendeleyev Ridge. This front is delineated in surface mixed layer and upper halocline water by a decrease in ^{129}I levels from >80 x 107 at/l in Atlantic-origin water over the Makarov Basin to <10 x 107 at/l near the continental slope of the Chukchi Sea. The front is displaced easterly (towards North America) with increasing water depth. The highest ^{129}I levels at each station appear to be associated with lower halocline water whose isopycnals (34-34.7 psu) slope downward from the Makarov into the Canada Basin (Carmack *et al.* 1995; MacLaughlin *et al.* 1995). Elevated levels of ^{129}I are observed at depths of 1000 m in the Makarov Basin indicating the recent descent of Atlantic water to these depths.

In 1995, one litre water samples were collected for ^{129}I analyses during the *USS Cavalla* (SCICEX-95) submarine cruise in the Central Arctic Ocean. The 1^{291} distributions contoured at a water depth of 59 m (Figure 3) clearly shows that the "front" between Atlantic-origin water, having elevated ^{129}I concentrations and Pacific-origin water is aligned along the length of the Mendeleyev Ridge. Further, the position of the front is displaced in an easterly direction with increasing water depth in the halocline. These fronts are also congruent with the salinity interface (S = 34.2 psu) between lower halocline and upper halocline water outlined in MacLaughlin et al. (1995).

Barents and Kara Seas

Radionuclide measurements have been continued on

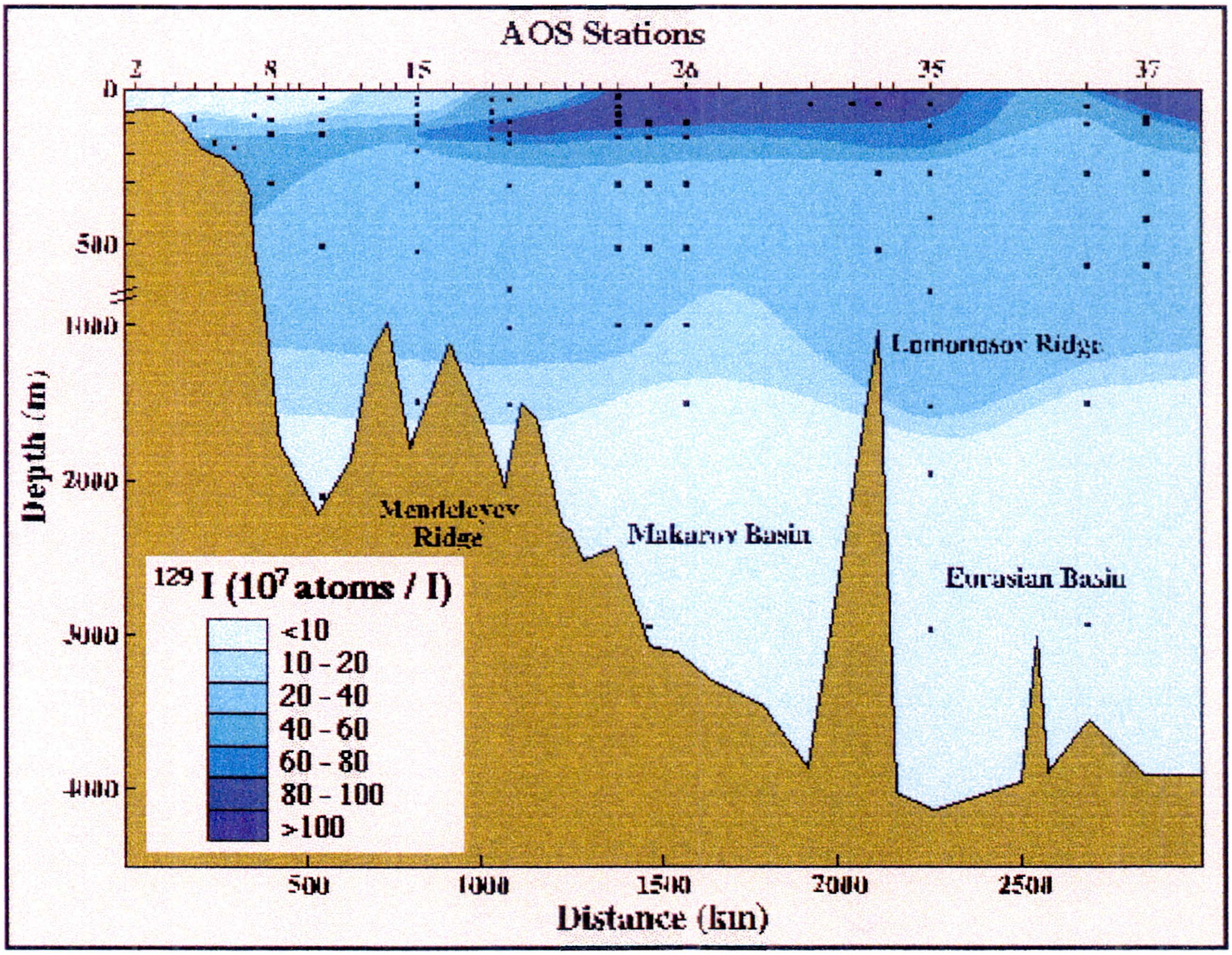

Figure 2. An ^{129}I section for the 1994 AOS cruise shows elevated elvels in surface mixed layer and Atlantic-origin water over the Mendeleyev and Lomonosov Ridges, extending to depths of 1000 m in the Makarov Basin owing to transport from European reprocessing plants. Reduced ^{129}I levels in surface and halocline waters of pacific origin in the Chukchi Sea (Sta. 2–8) are associated mainly with fallout.

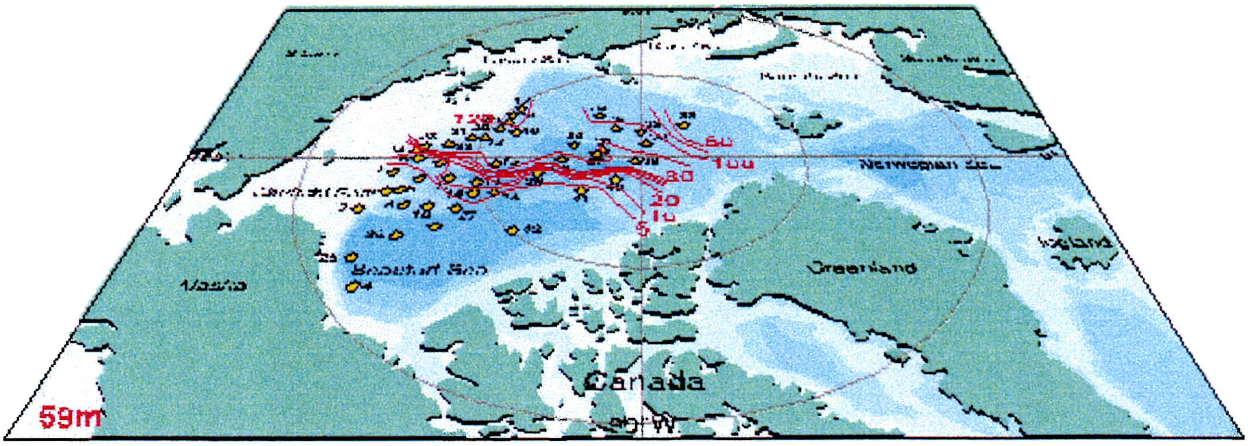

Figure 3. ^{129}I contours in units of at/l x 10^7 are shown for samples collected at a water depth of 59 m during the 1995 USS Cavalla submarine cruise. The steep ^{129}I gradients are distinguished by order of magnitude changes in concentrations alogned over the Alpha-Mendeleyev Ridge. These data reveal features of Atlantic water circulation (particularly the structure of the Atlantic-Pacific "front" over the Mendeleyev Rdige) that are uniquely defined by ^{129}I tracer distributions and best measured by submarine sampling.

samples collected between 1993 and 1995 in the Barents and Kara Seas. Sediment and seawater samples collected from Chernaya Bay, Novaya Zemlya in collaboration with Russian scientists from Okeangeologia in St. Petersburg and the Murmansk Marine Biological Institute were analysed for ^{137}Cs, ^{239,240}Pu, ^{60}Co and ^{210}Pb. Chernaya Bay is the site of at least two underwater nuclear weapons tests conducted by the former Soviet Union in the 1950s. Levels of ^{239,240}Pu in the sediments caused by fallout from these tests are among the highest recorded anywhere in the world and are equivalent to levels measured at the US nuclear test site in the Marshall Islands, in the Pacific Ocean (Smith *et al.* 1995). The sediment-depth distributions of radioactivity have been modelled using ^{210}Pb profiles and a biodiffusion model in order to predict the rates of burial and potential release of radioactivity from these highly contaminated regimes. Measurements of radioactivity were also conducted on several species of sediment in fauna in order to estimated rates of uptake of radioactivity into the food chain. Trace metal analyses of these sediment samples have also revealed unusually high levels of As which are clearly associated with the weapons tests. The inventories of radioactive and metal contaminants are almost entirely restricted to the upper 20 cm of sediment.

In 1993, 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. Radionuclide analyses on these samples indicate that there is negligible release of radioactivity from the dumpsite. However, the analysis of 12 sediment cores proximal to the dumpsite has revealed a significant Holocene depositional event that has affected the sediment regime throughout the Novaya Zemlya Trough. Measurements of ^{129}I and ^{137}Cs in the water column proximal to the dumpsite indicate that these contaminants are derived from European reprocessing plants with smaller inputs coming from the Ob River. The analysis of seven sediment cores collected in 1993 in the Ob and Yenesei River estuaries was continued through 1995/96. Elevated levels of ^{137}Cs and ^{60}Co in sediments at the mouth of the Yenesei River have also been traced to the Krasnoyarsk nuclear complex located several thousand kilometers upstream. This represents one of the few cases in which releases from upstream nuclear facilities in Russia have been shown to produce significant contamination in downstream estuaries.

DISCUSSION/CONCLUSIONS

Kara and Barents Sea

Elevated levels of plutonium in Chernaya Bay indicate that this fiord represents a potential source of radioactivity contamination to the Barents Sea and Arctic Ocean. Measurements of the distribution of Pu and ^{241}Am with distance from Chernaya Bay into the Barents Sea reveal that approximately 25% of the plutonium originally produced in the weapons tests has been transported out of Chernaya Bay to distances as great as 100 km from the test location. This indicates that Chernaya Bay could remain to be a significant source of radioactivity to the Arctic Ocean for many years in the future. Further, extremely elevated levels of plutonium measured in organisms from Chernaya Bay indicate that significant uptake is occurring into lower trophic levels. It will be important to determine whether there have been any significant long-term biological or toxicological effects associated with the dissemination of radioactivity through the fiord.

Studies of radionuclide distributions in sediments and seawater in the vicinity of the scuttled ship loaded with radioactive wastes in the Novaya Zemlya Trough indicate that radionuclide levels are governed by transport from European reprocessing plants and that there are only negligible, local releases of radioactivity. Although it appears that measures taken to isolate the radioactive wastes from dissolution in seawater have been effective, it is difficult to predict the time-table for future releases and continued monitoring of this dumpsite will be probably be required. However, this represents a far less severe radioactive contamination site that those within the Novaya Zemlya fiords where fuelled nuclear reactors were deposited on the sea bed.

Radioactivity results from the 1994 and 1995 *CSS Louis S. St. Laurent* cruises and the 1995 *USS Cavalla* submarine cruise have revealed the broad distribution of signals from European reprocesing plants throughout the Arctic Ocean. These results provide a clear outline of the "front" between Atlantic and Pacific-origin water in the western Arctic Ocean and show that this "front" is aligned along the Mendeleyev Ridge. They also provide evidence of the subsurface transport of Atlantic water as a boundary current along the continental margin of the Makarov and Canada Basins. These tracer distributions are very useful because they delineate the pathways that contaminants from European sources will likely follow as they circulate through the Arctic Ocean. Comparisons of the ^{129}I/^{137}Cs ratios measured in water samples with source function data permits estimates of time scales for the transport of Atlantic water through the Arctic Ocean. 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.

Expected project completion date: March 31, 1998

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II ECOSYSTEM CONTAMINANT UPTAKE AND EFFECTS

LONG-TERM TRENDS IN ORGANOCHLORINE (OC) RESIDUES IN WESTERN ARCTIC SEAL (*Phoca hispida)* BLUBBER

Project Leader: R.F. Addison (DFO, IOS, Sidney)

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

OBJECTIVES

1. To record trends in organochlorine concentrations in blubber of ringed seal (*Phoca hispida)* from Holman, NWT.

DESCRIPTION

The ringed seal population from Holman, NWT, has been studied by the Department of Fisheries and Oceans (DFO) since the early 1960s, and thus provides a source of samples in which to determine long-term trends in arctic contaminant concentrations. Previous studies have shown that concentrations of the polychlorinated biphenyls (PCBs) declined from the early 1970s to the early 1980s, most probably in response to the global ban on manufacture and use of these compounds; in contrast, DDT-group concentrations stayed fairly constant during that interval, suggesting that these compounds continued to enter arctic ecosystems, most probably by atmospheric transport from the far east (Addison *et al.* 1986).

During the past year, work on this topic has involved three activities:

a) Changes in PCB and DDT-group concentrations, 1972–1989

The measurement of trends in OC concentrations over long intervals is confounded by changes in analytical methods. The prime example of the difficulty is in PCB measurement, which the early 1970s was carried out by gas chromatography (GC) on packed columns followed by electron capture detection (ECD); nowadays, it is routinely carried out by GC on capillary columns with mass spectrometric (MS) identification and measurement. The two approaches yield quite different kinds of information: the former gave an estimate of total PCB contamination expressed as commercial PCB mixtures (e.g., "Aroclor 1254"), whereas the latter gives concentrations of specific PCB congeners (e.g., 2,4,5,2',4',5'-hexachlorobiphenyl). Because of changes in the distribution of PCB congeners caused by environmental "weathering" or metabolism, the sum of individual congeners in an environmental samples does not necessarily equal estimates of the total PCB mixture. In this work, we have compared DDT-group and PCB concentrations in ringed seal blubber analysed in 1972 and 1981 using packed column methods with samples taken in 1991 and analysed by modern methods. None of the original samples of 1972 was available, but samples from 1981 had been archived. The approach taken was therefore to re-analyse some 1981 sample using modern methods, compare "old" and "modern" analyses of 1981 samples, to establish a relationship between "old" and "modern" PCB estimates, and re-calculate 1972 and 1981 data in terms of modern analyses and compare these with 1991 data.

The results of this exercise led to the following conclusions:

(i) modern approaches to analyses of DDT-group residues yield results not significantly different from "old" analyses: DDT-group data are therefore directly comparable;
(ii) individual congener analyses of PCBs can be compared between 1982 and 1991;
(iii) total PCBs in 1982 and 1989 samples can be expressed as Aroclor 1254 for comparison with 1972 analyses; 1972 data must be reduced by X 0.65 to allow comparison with more recent data.

When the accumulated data are examined after appropriate corrections, the following conclusions emerge:

(i) total DDT-group concentrations have declined between 1972 and 1991: concentrations were significantly higher in 1972 than in 1981, and marginally higher in 1981 than 1991 (Figure 1);
(ii) the small decline between 1981 an 1991 was accounted for mainly by changes in p,p'-DDT; p,p'-DDE concentrations remained more or less constant;
(iii) PCB concentrations declined between 1972 and 1981, but have "levelled out" between 1981 and 1991 (Figure 2).

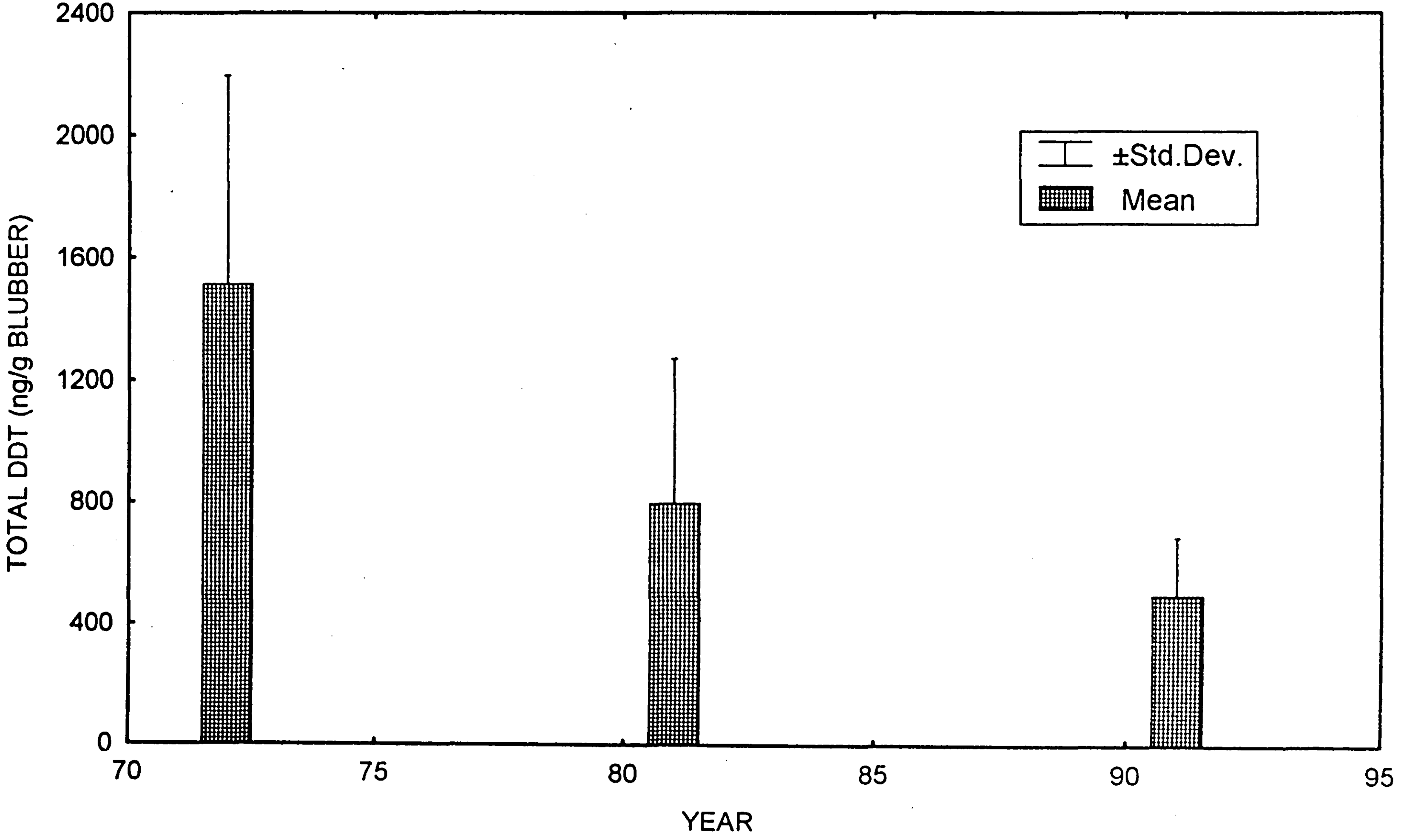

Figure 1. Total DDT in Holman Island ringed seal (m) (1972–1991)

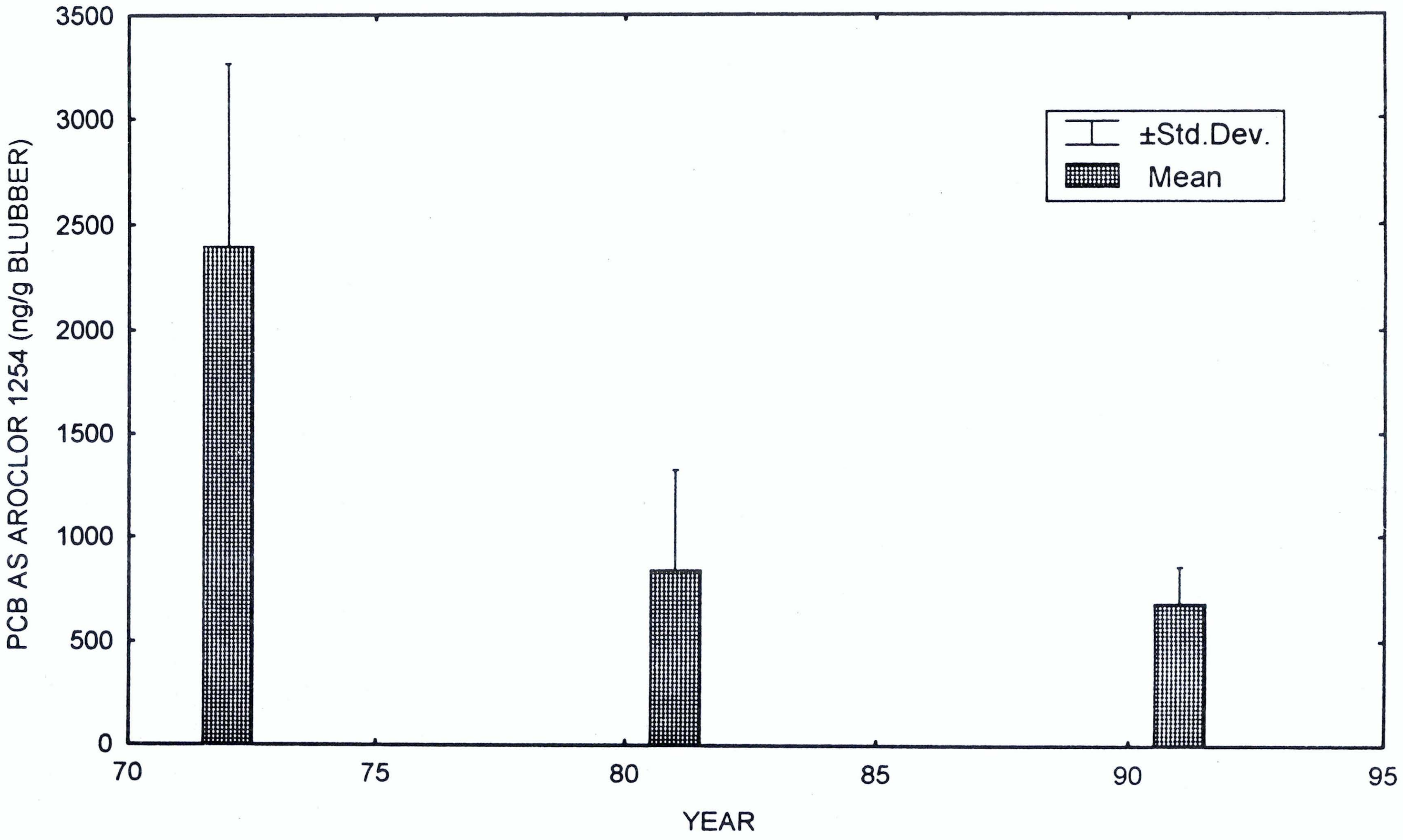

Figure 2. PCB in Holman Island ringed seal (m) (1972–1991)

The declines in PCB concentrations between 1972 and 1981 presumably reflect the global cessation of PCB manufacture and use during the 1970s. However, the fact that PCB concentrations appear not to have declined significantly after 1981 suggests that some constant supply of PCBs to the Arctic (presumably by atmospheric transport from the south?) may continue. The DDT data are more difficult to interpret: the significant decline between 1972 and 1981 probably reflects some restriction on the use of DDT in North America and Europe during the 1970s (though as we noted previously, the difference between 1972 and 1981 data becomes less significant if differences in condition are considered: Addison *et al.* 1986). The small decline between 1981 and 1991 may reflect some reduction in DDT use over that interval, though the fact that p,p'-DDE concentrations did not decline suggests that any such reduction must be small.

b) Changes in other OC concentrations, 1981–1989

Concentrations of I-hexachlorocyclohexane (I-HCH) and of K-HCH usually did not differ significantly in either sex. However, concentrations of hexachlorobenzene (HCB) fell by 1989 to about 50% of their 1981 values.

The trend in Holman seal HCB concentrations probably reflects the general trend in total chlorobenzene production (of which HCB is one component). Chlorobenzene manufacture in the US reached a peak around 1965–1970 and thereafter declined until the 1980s (Rapoport and Eisenreich 1988).

The absence of a decline in HCH concentrations in Holman seals between 1981 and 1989 is at first sight inconsistent with the observation that HCH concentrations in arctic air (Bering and Chukchi Seas and Canada Basin) declined about three-fold between 1979 and 1993 (Jatunen and Bidleman, 1995) reflecting global reductions in HCH use. However, since HCH concentrations in arctic seawater were over-saturated until after 1988, the supply of HCH to the seals (via adsorption to small particulates and entry to the food web) would have been constant until then. This leads us to predict that the "outgassing" of HCH from arctic seawater which began in the early 1990s should result in declining supplies of HCH to marine food webs; this might be reflected in falling HCH concentrations in younger Holman seals by the mid-1990s.

The results in (a) and (b) above have been published as a data report and have been submitted to *Arctic* for publication (July 1997).

(c) Changes in PCDD/F concentrations, 1981–1996

Samples of 1981 and 1991 blubber from male Holman Island ringed seals (selected for similar age range) were analysed for residues of PCDD/F at the IOS Regional Dioxin Laboratory using high resolution GC and MS. The results showed that:

(i) PCDD/F concentrations in Arctic ringed seals were low, in comparison to those in west coast harbour seal samples;
(ii) total PCDD concentrations declined between 1981 and 1991 (just statistically significant); total PCDF concentrations were lower in 1991, though not significantly so;
(iii) the "fingerprint" of PCDD/F congeners suggested that at least some of the residues appeared to arise from pulp and paper industry emissions.

Since the major declines in PCDD/F emissions from the pulp and paper industries took place in the late 1980s, these data imply that atmospheric transport to the Arctic and uptake by the ringed seal must be a relatively rapid process. This inference is supported by some recent data from the Netherlands which suggest that PCDD are turned over in harbour seals much more rapidly than (say) PCBs.

In May 1996, a further sample of 40 animals was collected from Holman with age, sex and condition recorded. These samples are now in the "pipeline" for PCDD/F analysis in the DFO Regional Dioxin Laboratory at IOS.

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FORT RESOLUTION DOMESTIC FISHING ZONE CONTAMINANTS RESEARCH

Project Leaders: Maurice Boucher, Fort Resolution Environmental Working Committee;
M. S. Evans, National Hydrology Research Institute

Project Team: P. Simon, Fort Resolution Environmental Working Committee, Deninu Ku'e First Nation, Aboriginal Harvester's Working Committee; G. Lowe, Department of Fisheries and Oceans (DFO); D. Muir, National Water Research Institute; W. L. Lockhart, Freshwater Institute

OBJECTIVES

1. To determine organic contaminant and metal concentrations in fish harvested from the Fort Resolution Domestic Fishing Zone.

2. To improve community expertise in research sampling.

3. To educate community members through increased involvement in various aspects of research studies.

4. To improve community confidence in the results of research studies by having its members be part of the process—from study design to the presentations and discussions of results.

DESCRIPTION

Fort Resolution has a domestic fishery that is of vital importance in providing fish for members of the community. The Domestic Fishing Zone is recognized by the Department of Fisheries and Oceans (DFO) and is not available to the commercial fisheries. Fish are harvested from Resolution Bay, the Little Buffalo River, and the Slave River. The community is anxious to protect the sustainable harvest of this fishery for the future. It has worked with Fisheries and Oceans, Hay River, to assess the important fish stock such as walleye/pickerel, pike/jack, burbot/loche, and inconnu/connie.

The community was aware of the research done by M. Evans and D. Muir investigating organic contaminant concentrations in fish such as whitefish, lake trout, and burbot/loche in Great Slave Lake. While they were supportive, they wished to have a greater participation in these studies. In particular, they wanted to integrate the organic contaminant work being conducted by these researchers with the fish assessment program being conducted in Resolution Bay (in collaboration with DFO). It was felt that this process would provide the community with a greater opportunity to be involved in research studies, including the selection of fish, tissues, and contaminants to be analysed. The community would become better educated in environmental studies and begin developing its own expertise in such studies. Finally, the community would have a greater confidence in the results of the studies and researchers would be more certain that their studies were addressing local needs. Accordingly, a proposal was submitted to the Northern Contaminants Program (NCP) to conduct a research study of contaminants in fish from the Fort Resolution Domestic Fishing Zone.

ACTIVITIES IN 1996/1997

After the funding for the study was approved, discussions were held with P. Simon (Fort Resolution Environmental Working Committee) and M. Evans to make the final selection of the fish species to be analysed, the tissues, the number of replicates, and the actual contaminants to be measured. Based on the budget, the community decided that it could afford approximately 40 analyses for organochlorine contaminants such as PCBs and toxaphene. It then decided to focus its effort on walleye/pickerel, pike/jack, burbot/loche, and inconnu/connie. These are predatory fish and should have higher concentrations of organic con-taminants such as PCBs and toxaphene than non-predatory fish such as whitefish and suckers.

The community next decided to analyse the muscle of five specimens of each of the four species: this represented 20 of the 40 possible analyses. Five replicate liver samples were next selected for walleye, jack, and burbot, bringing the total analyses to 35. Next, pike stomachs, which are eaten by many people, were selected bringing the total to 40. With further discussion, the community decided to include one composite sample of pike gall bladder. The reason for this was to see whether or not contaminants were being lost from the liver with the bile.

The community decided that, in addition to having fish analysed for organochlorine contaminants, they wanted the same tissues analysed for metals. Metals were of concern because of the presence of the decommissioned Pine Point Mine site, to the west of the community. Since the early 1970s, when the first environmental studies were conducted (Stein and Miller 1972), the community has expressed various concerns relating to the mining operation and metal contamination. More recently, a report published by Klaverkamp and Bacon (1996) suggested that burbot/loche collected from the Slave River delta had high concentrations of metallothionein. They suggested that these high levels were occurring because burbot/loche were exposed to high concentrations of metals, possibly from the Pine Point mine.

The budget was sufficient for six metals to be analysed. Lead, copper and zinc were selected for analyses because of concerns related to the decommissioned Pine Point mine (Stein and Miller 1972). Arsenic, cadmium, and mercury were also selected because they can be toxic in very low concentrations. Receveur *et al.* (1996), with CINE, have indicated that some communities in the Northwest Territories may, on occasion exceed their tolerable daily intake for arsenic, cadmium, and mercury when consuming certain fish species.

With the collaboration of DFO, Hay River, 10 specimens of each fish species were harvested from the Domestic Fishing Zone and shipped to the Freshwater Institute. Five were selected for analysis and the remainder archived for possible later study.

Continuing discussions were held with Evans through the summer to design a second study to investigate whether the decommissioned Pine Point mine had contaminated or was contaminating the water, sediments, and fish in the Resolution Bay area with metals such as lead, zinc, and copper. A proposal was developed to investigate this issue and submitted to the Water Resources Program, in Yellowknife. The Water Resources Program requested that a another component be added to this study, i.e., a metal-metallothionein study, focusing on burbot from the Slave River. This overall study design was approved and funding provided to Evans. Evans visited the community in August to finalize sampling sites and then conduct the study with the assistance of community members. One community member assisted during a one-day cruise to sample water and lake sediments. Two community members assisted with sampling fish in the Little Buffalo and Slave Rivers. Burbot/loche could not be collected during this trip. One community member, in collaboration with a DFO contract worker, completed the loche sampling in the Slave River in December.

Two interim reports (Evans *et al.* 1997 a, b), based on the Domestic Fishing Zone Study and the Pine Point Mine Study, have been submitted to the community (M. Boucher) for comments. In addition, a presentation of the results to date was given to community members in August. This study led to the development and submission of a new proposal to NCP by Evans and Boucher. This proposal is based on concerns that metals may, on occasion, occur in high concentrations in Slave River waters (Jensen *et al.* 1997). The community is concerned that the water treatment plant operation may not be effective in removing these metals. Other concerns relate to possible lead leaching from potable-water holding tanks and pipes and the desire to develop a long-term water quality monitoring program for Resolution Bay. The community was involved in water-quality sampling during M. Evans' August trip to Great Slave Lake and wishes to continue building on this experience.

RESULTS

Metals

Analyses of metals in fish collected from Resolution Bay in summer 1996 (Table 1) have been completed. Data interpretation is ongoing, including comparisons with similar collections made during the Pine Point study, historic values from Great Slave Lake, and comparisons with other regions of the Northwest Territories and the Yukon. Therefore, only descriptions of the data are presented in this report.

Arsenic tended to occur in low concentrations in all tissues, relative to other metals. The highest concentrations were found in loche liver and gall bladder. Cadmium concentrations also were low and sometimes below detection limits (0.001 μg/g). Copper concentrations were low in muscle but higher in liver. Lead was always below detection limits (0.05 μg/g).

Mercury concentrations generally were low and tended to be higher in muscle than in liver. However, the recommended maximum mercury concentration for those who are engaged in subsidence fisheries is 0.25 μg/g (Jensen *et al.* 1997). Four of the five jack and two of the five pickerel analysed (muscle tissue) exceeded this level.

Table 1. Mean concentrations of metals in the tissues of four species of fish collected from Resolution Bay, Summer 1996. Concentrations are in µg/g (parts per million) wet weight

Fish	Tissue	Arsenic	Cadmium	Copper	Lead	Mercury	Zinc
Pike/Jack	Muscle	0.15	<0.001	0.2	<0.05	0.25	3.7
	Liver	0.15	0.10	16.0	<0.05	0.10	34.2
	Stomach	0.38	0.03	1.1	<0.05	0.06	797.3
Walleye/Pickerel	Muscle	0.08	<0.001	0.2	<0.05	0.18	3.0
	Liver	0.51	0.25	1.4	<0.05	0.05	18.4
Burbot/Loche	Muscle	0.13	<0.001	0.3	<0.05	0.08	3.0
	Liver	0.89	0.07	9.0	<0.05	0.03	17.9
	Gall bladder	0.87	0.01	1.9	<0.05	0.03	14.2
	Bile	0.30	0.003	1.0	<0.05	0.01	2.2
Inconnu/Connie	Muscle	0.32	<0.001	0.4	<0.05	0.11	2.7

Zinc was the most abundant metal analysed. Concentrations were higher in liver than in muscle. Jack stomach had surprisingly high concentrations of zinc. In their interim reports (Evans *et al.* 1997 a, b) indicated that there was no evidence that the Pine Point mine had measurably contaminated water, sediments, and fish with metals. Metal concentrations that were observed appeared to be at background levels. Nevertheless, some metal concentrations may be sufficiently high to be of concern to human health, for example, mercury in jack and pickerel muscle. Health Canada will be provided with copies of these data and asked to assess potential health concerns. The community realizes that it is not the mandate of Environment Canada and Fisheries and Oceans to utilize data collected for scientific/research purposes for human health assessments.

Organochlorines

Organochlorine analyses are complete with the exception of pickerel and loche liver. For the purposes of comparison, loche muscle and liver data from 1993 collections are included in Table 2. There was insufficient tissue for the analysis of loche gall bladder. Data interpretation is ongoing, including comparisons with similar collections made in other regions of Great Slave Lake and other regions of the Northwest Territories and the Yukon. Therefore, only descriptions of the data are presented in this report.

Dieldrin concentrations were low. For jack, concentrations were markedly higher in the stomach than in muscle and liver. Dieldrin appeared to occur in higher

Table 2. Mean concentrations of chlordane, dieldrin, total DDTs, PCBs, and toxaphene in the tissues of four species of fish collected from Resolution Bay, Summer 1996. Concentrations are in ng/g (parts per billion) wet weight. N. A. means data not available.

Fish	Tissue	Dieldrin	Chlordane	Total DDTs	Total PCBs	Toxaphene
Pike/Jack	Muscle	0.2	2.3	2.7	5.3	23.2
	Liver	0.7	7.3	3.4	13.0	24.8
	Stomach	7.8	36.3	12.9	39.4	106.6
Walleye/Pickerel	Muscle	0.1	1.6	2.3	5.4	21.7
	Liver	N. A.	N. A.	N. A.	N. A.	N. A.
Burbot/Loche - 1996	Muscle	0.1	0.8	0.8	2.9	3.0
	Liver	N. A.	N. A.	N. A.	N. A.	N. A.
Burbot/Loche - 1993*	Muscle	0.1	0.3	0.3	1.6	0.8
	Liver	5.1	61.2	26.7	74.5	244
Inconnu/Connie	Muscle	0.9	6.8	4.4	11.5	31.3

* data from Evans (1996)

concentrations in liver than in muscle (pickerel and loche). Dieldrin concentrations appeared similar in jack and loche liver.

Chlordane also appeared to occur in higher concentrations in liver than in muscle (jack and loche): concentrations appeared higher in loche than jack liver. Dieldrin concentrations also were high in jack stomach. Loche muscle had the lowest chlordane concentrations of the four species analysed.

Total DDTs occurred in lower concentrations in loche muscle than in jack, pickerel, and connie muscle. DDTs appeared to occur in slightly higher concentration in jack liver than muscle (although these differences may not be statistically significant): concentrations were even higher in jack stomach. DDTs occurred in substantially higher concentrations in loche liver than muscle.

Toxaphene occurred in very low concentrations in loche muscle. Concentrations were seven to ten times greater in jack, pickerel and connie muscle. Toxaphene concentrations were similar in jack muscle and liver but higher in jack stomach. There was a marked difference in toxaphene concentration in loche tissues: loche liver has substantially greater toxaphene concentrations than muscle.

DISCUSSION/CONCLUSIONS

This study, which was developed by the community of Fort Resolution, investigated contaminants in fish harvested from the Domestic Fishing Zone. During this study, the community became more experienced with research study design, sampling, and data interpretation. Comparisons of metal concentrations were made in fish species and their tissues. There were several interesting observations including relatively high levels of zinc in jack stomach, higher levels of copper and zinc in jack, pickerel, and loche muscle than liver. While a companion study provided no evidence of localized contamination resulting from the decommissioned Pine Point mine, mercury levels in some pickerel and walleye muscle were above guidelines for subsistence consumption. Data from these studies will be made available to Health Canada for further assessment.

The study also has provided preliminary information on organochlorine concentrations in fish harvested from the Domestic Fishing Zone. It was interesting to observe that jack stomach tended to have higher concentrations of organochlorines than the muscle or the liver. It was also interesting to note that while loche liver had relatively high concentrations of organochlorines, muscle concentrations were low—in fact lower than in jack, pickerel, and connie.

The community will further consider the results of the metal and organic contaminant study from a consumption viewpoint. It recognizes that it is not the mandate of Environment Canada and DFO to utilize data collected for scientific/research purposes for human health assessments. Data will be made available to Health Canada for such considerations.

From a research perspective, these data will be combined with the larger data sets from Great Slave Lake to further investigate why different species of fish have different concentrations of contaminants. These data also will be analysed to investigate regional differences in contaminant concentrations in the lake, for example, between Fort Resolution and Lutsel K'e for those species of fish that were harvested from both regions.

Overall, this study progressed well and the community is interested in further community–research partnerships. It has submitted a new proposal to NCP based on the success and new understandings gained from this study.

Expected Project Completion Date: March 1999.

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CONTAMINANTS IN WATERFOWL FROM NORTHERN CANADA

Project Leader: B.M. Braune, Environment Canada, Canadian Wildlife Service, National Wildlife Research Centre, Hull, Quebec

Project Team: Malone Associates (contractor)

OBJECTIVES

1. To determine the levels and geographical distribution of contaminants in arctic wildlife with particularly emphasis on avian species.
2. To provide a data set on contaminants in waterfowl and other game birds used as food by native people to Health Canada so that potential health risks to the human consumer may be evaluated.

DESCRIPTION

Up until recently, there has been little information available on contaminants in arctic wildlife potentially consumed by humans. Waterfowl, terrestrial game birds, shore birds and sea birds (and their eggs) are harvested to varying degrees by native people for consumption (Coad 1994). A survey of contaminants in harvested avian species in the Canadian Arctic has been a part of a larger national survey since 1988. Each year, a different arctic region has been subject to intensive study. In 1991/92, the Nunavik Region of northern Quebec was surveyed. Data collected from that survey was submitted to Health Canada in December 1992 for evaluation of risk to human health of consuming harvested waterfowl. The Nunavik survey was followed by a survey in Labrador in 1992/93, the Northwest Territories in 1993/94, and the Yukon Territory in 1994/95.

The specific objectives for 1995/96 and 1996/97 were to complete all chemical residue analyses, statistically analyse the data collected from northern Canada, and to submit any data not yet analysed for risk to human consumers to Health Canada for evaluation.

ACTIVITIES IN 1995/96

Chemical residue analyses were completed for all remaining samples of breast muscle and egg contents. Samples were analysed for PCBs, organochlorines, mercury, cadmium, lead and selenium at the CWS laboratories at NWRC. The entire data set was proofed and exploratory statistics carried out. The results have been included in *the Canadian Arctic Contaminants Assessment Report (CACAR)* and the *Arctic Monitoring and Assessment Program (AMAP) Assessment Report.* All data not yet reviewed by Health Canada were submitted for evaluation of risk to human consumers eating waterfowl and/or their eggs.

ACTIVITIES IN 1996/97

Statistical analyses of the data were completed and progress was made on the production of a technical report containing all of the data. The final evaluation report containing recommendations on whether or not the birds were safe for human consumption was received from Health Canada. The results of the survey and Health Canada's recommendations were summarized in a one-page information sheet which was sent to all northern communities through the NWT Contaminants Committee.

RESULTS

The birds were grouped according to trophic level as follows:

Browsers:
ground dwellers such as grouse and ptarmigan that feed mainly on terrestrial vegetation;
Grazers:
geese that graze mainly on aquatic and terrestrial vegetation; *Ominivores* - surface-feeding ducks with a varied diet consisting mainly of aquatic vegetation;
Molluscivores:
diving ducks feeding mainly on invertebrates;
Piscivores:
diving ducks feeding mainly on fish.

Northern collection sites were grouped into western Arctic (north of 60°N west of 95°W) and eastern Arctic (north of 55°N east of 95°W, so as to include Hudson Bay, northern Quebec and northern Labrador) (Figure 1). Baker Lake was kept with the eastern sites because of its proximity to Hudson Bay, and Spence Bay was kept with the western sites because of the influence of western arctic waters.

Levels of organic contaminants found in breast muscle of harvested birds were generally quite low (Table 1). The highest organochlorine residue levels were found in birds feeding at the higher trophic levels, the piscivores and molluscivores. The browsers and grazers contained the lowest levels of organic contaminants. The highest residue levels were found for ΣPCB and ΣDDT in piscivores and molluscivores collected from eastern Arctic communities. Birds collected from eastern locations generally contained higher levels of organic contaminants than comparable collections made from western sites. Total toxaphene levels in 12 pooled waterfowl samples from the Yukon Territory ranged from non-detectable to 9.4 ng·g^{-1}, with the highest levels found in Oldsquaw.

Metal levels found in breast muscle were also generally quite low (Table 2). Lead concentrations were not included because the presence of lead shot embedded in muscle interfered with the determination of biologically incorporated lead in breast muscle. Total mercury concentrations increased with trophic level, whereas cadmium levels were highest in plant-eating species such as ptarmigan, and in benthic feeders such as eiders.

DISCUSSION/CONCLUSIONS

Many of the bird species are migratory, breeding in the north and overwintering in more temperate, industrialized

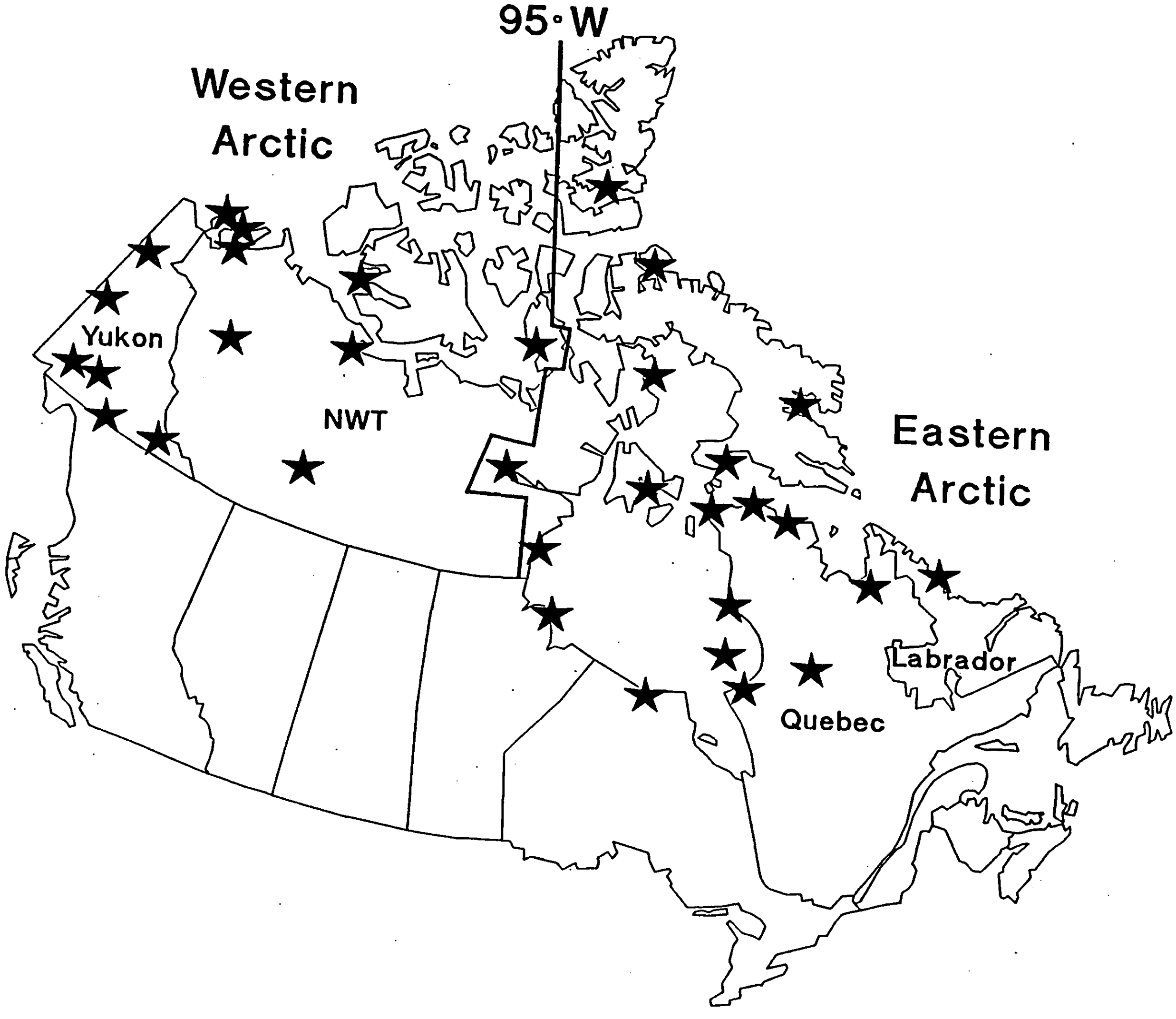

Figure 1. Locations of sampling sites for waterfowl and game birds analysed for organochlorines

Table 1. Range of organochlorine residue levels in breast muscle of waterfowl and game birds harvested in northern Canada in 1988-94 (μg/kg or ppb wet wt.)

Birds *	Region **	N ***	ΣPCBs	ΣDDTs	ΣCHL	ΣCBz	ΣHCHs	ΣMirex	Dieldrin
Browsers	East	(5, 9, 39)	<1.0–3.1	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	West	(12, 22, 91)	<1.0–9.6	<1.0–1.5	<1.0–2.5	<1.0–1.9	<1.0	<1.0	<1.0–5.0
Grazers	East	(16, 39, 234)	<1.0–44.9	<1.0–30.0	<1.0–4.5	<1.0–1.6	<1.0	<1.0	<1.0–3.2
	West	(7, 11, 59)	<1.0	<1.0–3.1	<1.0–4.7	<1.0–1.9	<1.0	<1.0	<1.0–2.0
Omnivores	East	(2, 4, 30)	<1.0–87.0	<1.0–31.5	<1.0–2.3	<1.0–2.0	<1.0	<1.0–1.6	<1.0–1.3
	West	(8, 31, 149)	<1.0–115	<1.0–650	<1.0–12.8	<1.0–62.4	<1.0–1.0	<1.0–1.6	<1.0–15.9
Molluscivores	East	(14, 30, 175)	<1.0–1076	<1.0–403	<1.0–102	<1.0–35.9	<1.0–27.8	<1.0–222	<1.0–120
	West	"(12, 42, 178)"	<1.0–129	<1.0–127	<1.0–13.2	<1.0–15.4	<1.0–26.5	<1.0–1.7	<1.0 -3.8
Piscivores	East	"(7, 16, 55)"	<1.0–1695	<1.0–951	<1.0–105	<1.0–120	<1.0–2.4	<1.0–268	<1.0–54.7
	West	"(2, 5, 5)"	1.1–909	32.0–530	2.9–75.7	1.6–18.3	<1.0–9.9	<1.0–9.2	1.0–17.4

* Birds are grouped by feeding habit:
Browsers (grouse, ptarmigan)
Grazers (geese, tundra swan)
Omnivores (black, mallard, teal, pintail, wigeon, shoveller)"
Molluscivores (eider, scoter, scaup, oldsquaw, ring-necked duck, goldeneye, bufflehead, canvasback)
Piscivores (mergansers, loons)

** Birds are grouped into eastern and western collections by collection site (see Figure 1)

*** Numbers in brackets refer to : (total # of sites, total # of collections, total # of birds)

ΣCBz = Sum of 1,2,3,5 & 1,2,3,4 Tetrachlorobenzene, Pentachlorobenzene and Hexachlorobenzene
ΣHCHs = Sum of α–, β– & γ– hexachlorocyclohexanes
ΣCHL = Sum of oxy-, trans- & cis-chlordane, trans- & cis-nonachlor and heptachlor epoxide
ΣDDTs = Sum of p,p'-DDE, p,p'-DDD and p,p'-DDT
ΣMirex = Sum of Photo-mirex and Mirex
ΣPCBs = Sum of PCB congeners , standardized to the following 29 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 2. Range of metal residue levels in breast muscle of waterfowl and game birds harvested in northern Canada from 1988-94 (ug/kg or ppb wet wt.)

Trophy	R	N	Hg	Se	Cd	As
Browsers	East	(5, 9, 39)	<30–58	60–241	18–437	2–20
	West	(12, 22, 91)	<60	<30–527	<50–583	<70
Grazers	East	(16, 39, 234)	<130	38–826	<20–40	3–900
	West	(7, 11, 59)	<30–156	105–781	10–30	<100
Omnivores	East	(2, 4, 30)	202–230	183–520	<250	<40
	West	(8, 31, 149)	24–665	<100–2076	<10–80	<30–110
Molluscivores	East	(14, 30, 175)	35–455	314–1751	20–707	<30–600
	West	"(12, 42, 178)"	<20–369	<100–5787	<10–510	<30–426
Piscivores	East	(7, 16, 55)	74–1232	373–1240	<30–110	7–723
	West	(5, 5, 5)	258–1932	254–1512	<65–438	<30–232

Detection Limits - shown as (<value). Detection limits with trace metals analysis are very variable, being highly dependent on the individual sample matrix.

* Birds are grouped by feeding habit:
Browsers (grouse, ptarmigan)
Grazers (geese, tundra swan)
Omnivores (black, mallard, teal, pintail, wigeon, shoveller)
Molluscivores (eider, scoter, scaup, oldsquaw, ring-necked duck, goldeneye, bufflehead, canvasback)
Piscivores (mergansers, loons)

** Birds are grouped into eastern and western collections by collection site (see map)

*** Numbers in brackets refer to : (total # of sites, total # of collections, total # of birds)

As = Arsenic; Se = Selenium; Hg = Total Mercury; Cd = Cadmium

latitudes. The birds pick up contaminants through the food on their southern wintering grounds or from sites along the migration pathway. Historically, some of the eastern overwintering areas such as the Great Lakes – St. Lawrence River have been much more contaminated than some of the western areas. This is clearly illustrated by mirex, a contaminant characteristic of the lower Great Lakes (Comba *et al.* 1993). Mirex is virtually undetectable in western Arctic birds but is quite measurable in eastern Arctic birds (Table 1).

In addition to atmospheric transport of metals, metals also occur naturally in the mineral resources of the Canadian North. Some of the activities associated with mineral extraction mobilize the metals making them more bioavailable (Thomas *et al.* 1992). Metals are often transported via riverine sediments. Therefore, those birds which are predominantly benthic feeders may be subject to a greater exposure to metal contamination since they eat prey associated with bottom sediments where metals may settle out. As well, plants absorb metals, particularly cadmium, from soil and water (Singh 1994) which could explain the measurable levels in the browsers and grazers.

All chemical data on the birds collected from both the Yukon and Northwest Territories between 1993 and 1995 was submitted to Health Canada in January 1996 for evaluation of risk to human health of eating those harvested birds and eggs. Health Canada's final evaluation of those data was received in January 1997. With the exception of some concerns about contaminant levels in some seabird species, Health Canada has advised that ducks, geese and other game birds analysed in this survey, are safe to eat. Those recommendations have been forwarded to the appropriate local authorities.

Expected project completion date: March 31, 1997

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IDENTIFICATION OF BASELINE LEVELS AND SPATIAL TRENDS OF ORGANOCHLORINE, HEAVY METAL AND RADIONUCLIDE CONTAMINANTS IN CARIBOU *(Rangifer tarandus)*

Project Leader: B.T. Elkin, Department of Resources, Wildlife & Economic Development, Government of the Northwest Territories

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

Prior to the AES Northern Contaminants Program, information on contaminant exposure in caribou in the Canadian Arctic and subarctic was extremely limited, and data on temporal trends were nonexistent (Wong 1985, Thomas *et al.* 1992). The scarcity of metal or organic residue data for terrestrial mammals was identified as a data gap in Arctic contaminant research (Wong 1985). The few analyses that had been conducted on terrestrial species indicated that a wide range of organochlorine, heavy metal and radionuclide contaminants were present and warranted more comprehensive studies to establish baseline levels. Caribou are a major component of the traditional diet in communities across the NWT and an important component of the terrestrial food web, highlighting the need for baseline data in this important country food species.

Barren ground caribou (*R.t. groenlandicus*) 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). The defined ranges and distribution of caribou herds across the Canadian north make it a good species for the examination of geographical variation in terrestrial contaminant deposition. The simple plant-herbivore food chain and the pan-arctic distribution of caribou make it a useful species for monitoring spatial and temporal trends in arctic terrestrial ecosystem contamination.

This study was designed to provide important baseline levels and spatial trends of organochlorine, heavy metal and radionuclide contaminants in caribou from 10 major barren ground caribou herds across the NWT. The spatial trends in contaminant residues contributed to understanding of contaminant deposition and distribution within the Arctic terrestrial ecosystem. The results of this work also identified some specific contaminants that warrant further study and provided a starting point for more specific ongoing monitoring efforts in the future to assess temporal trends. Samples collected as part of this work were also provided for a CWS study on PCDD/Fs, and an AECL study on ^{210}Po and ^{210}Pb in caribou.

The specific objectives for 1995/96 and 1996/97 were (1) to complete all caribou field collections, (2) to determine organochlorine, metal and radionuclide residues in several caribou tissues from all remaining samples, and (3) to complete evaluation and communication of the study results.

ACTIVITIES IN 1995/96 AND 1996/97

Field Sampling

In 1995/96, the last of the field sampling was completed.

Collections have now been completed in cooperation with local Hunters' and Trappers' organizations at Arviat, Cambridge Bay, Cape Dorset, Coral Harbour, Fort Smith, Inuvik, Lake Harbour, Ndilo/Fort Rae, Pond Inlet, and Taloyoak (Figure 1). Samples were collected from the Bathurst herd at several different times throughout the year to assess seasonal variation in contaminant levels. 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

In 1995/96, analyses were completed on all remaining and banked samples. 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. Further detail on sample collection and analysis can be found in Elkin and Bethke (1995).

Data Analysis and Communication of Results

All data analysis and interpretation was completed in 1996/97. Public information materials were developed, and the results of the study were communicated to both the communities involved and to wildlife co-management boards and communities across the NWT.

RESULTS

Contaminant residue analyses have been completed for all 10 caribou herds sampled, and a wide range of organochlorine contaminants were detected. Most compounds were found at very low levels, with the more volatile and less persistent compounds HCB and HCH predominating, as seen in other terrestrial herbivores in the Canadian north (MacNeil *et al.* 1987, Thomas *et al.* 1992, Salisbury *et al.* 1992). 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. Total HCH (ΣHCH) ranged from 3.3 $ng \cdot g^{-1}$ (lipid corrected) in fat from Inuvik caribou to 40.0 $ng \cdot g^{-1}$ at Cape Dorset, and consisted almost entirely of α-HCH. HCB residues ranged from a mean of 20.3 $ng \cdot g^{-1}$ in fat of Taloyoak caribou to 129.4 $ng \cdot g^{-1}$ in Lake Harbour animals. HCB and α-HCH were detected in fat samples from all caribou at all 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 suggest a direct air-plant-animal pathway into the terrestrial food chain (Thomas *et al.* 1992). Woodland caribou in the Yukon have similar ΣHCH and HCB levels to western NWT barren ground herds (Gamberg and Scheuhammer 1994).

Oxychlordane, a major metabolite of several compounds in the pesticide technical chlordane, was the major chlordane-related compound detected in caribou liver. Total chlordane levels ranged from 0.1 $ng \cdot g^{-1}$ in Inuvik caribou to 5.0 $ng \cdot g^{-1}$ 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 from 0.1 $ng \cdot g^{-1}$ in Beverly caribou to 2.6 $ng \cdot g^{-1}$ at Cape Dorset. The levels found in this study were consistent with those found in Baffin Island caribou by Muir *et al.* (1988). Total toxaphene levels found in 12 pooled fat samples from 4 sites ranged from non-detectable to 23 $ng \cdot g^{-1}$.

Total PCB (ΣPCB) residues (sum of 43 congeners) ranged from a mean of 1.0 $ng \cdot g^{-1}$ (lipid corrected) in fat of Inuvik caribou to 31.7 $ng \cdot g^{-1}$ at Cape Dorset. The CB congener patterns were similar at all sites, with greater accumulation of more highly chlorinated congeners. CB-153 was bioaccumulated to the greatest extent at all sites. The results were consistent with Muir *et al.* (1988) who found that caribou muscle had low levels of a broad spectrum of congeners which resembled PCB mixtures more closely, while six or seven congeners made up the major portion of ΣPCB in marine mammals. Higher levels of trichlorobiphenyl and tetrachlorobiphenyl compounds in caribou relative to other terrestrial mammals and birds may be a result of the direct air-lichen-caribou food chain. The results of this study suggest that the source of contamination in terrestrial herbivores is atmospheric particulate-bound PCBs which are deposited on plant surfaces. Regional differences in both PCB and DDT distribution appear to be more marked than the other organochlorine compounds, possibly reflecting a North American origin or different deposition mechanisms (Thomas *et al.* 1992).

Figure 1. Sites in the Northwest Territories where caribou collections were conducted between 1991 and 1996.

PCDD/Fs in caribou have been found to be very low (<1 pg·g^{-1} for total PCDD/Fs at most sites), and TCDD TEQs in caribou have been attributed mainly to non-ortho and mono-ortho PCB congeners (Hebert *et al.* 1995).

Barren ground caribou from all sites had moderately elevated levels of cadmium in both kidney and liver tissue. Levels in kidney tissue ranged from 7.49 µg·g^{-1} dry weight in Taloyoak caribou to 42.70 µg·g^{-1} at Inuvik, and levels in liver ranged from 0.98 µg·g^{-1} at Pond Inlet to 5.83 µg·g^{-1} at Inuvik. The levels detected are similar to levels found in other barren ground caribou in the NWT and Yukon, and woodland caribou from the Bonnet Plume herd in the Yukon (Gamberg and Scheuhammer 1994). These levels are comparable to those found in caribou in northern Quebec and reindeer in Norway (Froslie *et al.* 1986, Scanlon *et al.* 1988, Crete *et al.* 1987, 1989), and moose and white tail deer from Ontario and Newfoundland (Gloshenko *et al.* 1988, Brazil and Ferguson 1989). These cadmium levels are considered normal because of their relatively high levels on a circumpolar basis.

Mercury levels were generally low in all caribou herds, with means in kidney ranging from 0.52 µg·g^{-1} in Bathurst caribou to 2.93 µg·g^{-1} in Arviat animals (Figure 3). Mercury levels were generally lower in liver than in kidney, ranging from 0.16 to 0.92 µg·g^{-1}. 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 µg·g^{-1} and 0.24 µg·g^{-1} respectively (Froslie *et al.* 1984, Erikson *et al.* 1992). Analyses of methylmercury levels in kidneys of Finlayson caribou indicated that virtually all of the mercury present occurs in the relatively non-toxic inorganic form (Gamberg and Scheuhammer 1994).

Radionuclide levels were generally low or nondetecable in caribou muscle, with the exception of cesium-137 (^{137}Cs), cesium-134 (^{134}Cs), and potassium-40 (^{40}K) (Figure 4). ^{137}Cs was the most predominant radionuclide, with activity ranging from 2.83 Bq·Kg^{-1} at Inuvik to 184.10 Bq·kg^{-1} in Lake Harbour caribou. These are lower than ^{137}Cs levels found in northern Quebec herds in the late 1980s (Marshall and Tracey 1989). Levels of ^{134}Cs ranged from <0.37 Bq·Kg^{-1} in Bathurst caribou to <0.71 Bq·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 1989, consistent with the view of declining ^{137}Cs levels in the Arctic. The levels of ^{134}Cs in this study were very low, and most likely derived from the Chernobyl accident, although much lower than levels observed in reindeer from northern Europe after Chernobyl.

Potassium-40 (^{40}K), a naturally occurring radionuclide with a very long half-life, was consistently found in all samples at about 100 Bq·Kg^{-1}, similar to levels reported for moose in southern Manitoba (Zach *et al.* 1989). The naturally occurring radionuclides lead-210 (^{210}Pb) and polonium-210 (^{210}Po) have also been detected in NWT caribou herds (Macdonald *et al.* 1996). Highest levels of ^{210}Pb were found in bone, and large differences in concentrations were observed between animals within the same herd and between herds. The Lake Harbour herd had the highest ^{210}Pb and ^{210}Po levels, but no consistent geographical trends were observed. Macdonald *et al.* (1996) concluded that radiation doses for Lake Harbour caribou, due mainly to ^{210}Po, were high relative to other mammals in Canadian environment. The animals have presumably adapted to the radiation stress from these natural sources, although the potential effects of the high doses on the animals are not clear.

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 cadmium in kidney and liver from caribou in the NWT are comparable with findings in other big game species in Canada, and these levels are considered natural given the general elevation on a circumpolar basis.

Radionuclides are important contaminants in caribou, and information is available on temporal trends for some compounds for more than 30 years. The levels of ^{137}Cs, the predominant radionuclide in this study, are up to 10 times lower than during the 1960s, supporting the conclusion that levels of ^{137}Cs are steadily declining in the Canadian Arctic. Caribou also receive relatively high doses of natural radiation from ^{210}Pb and ^{210}Po.

The comparatively low levels of contaminants detected,

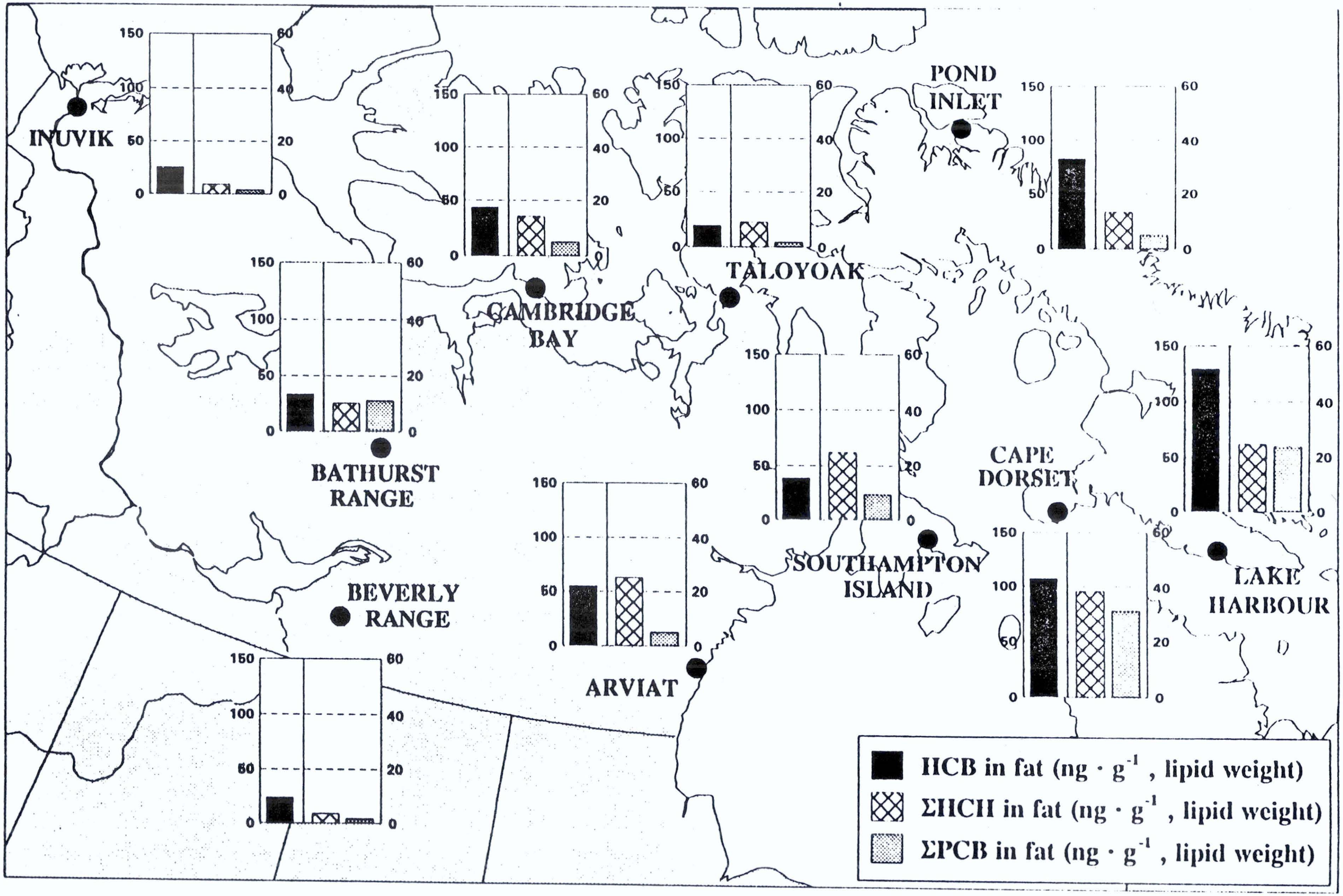

Figure 2. Concentrations of HCB ΣHCH and ΣPCB in fat of caribou collected in the Northwest Territories, 1991–1996.

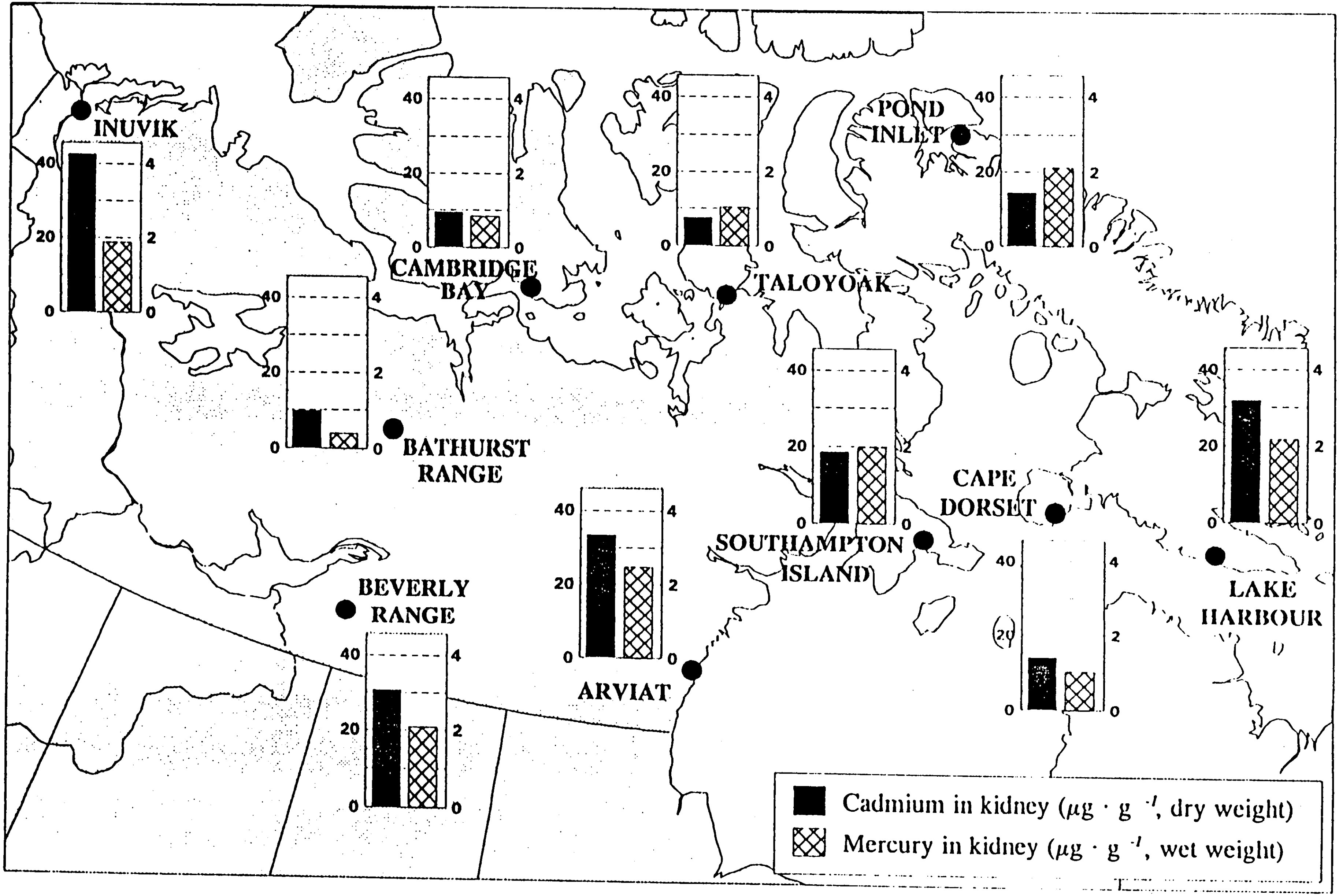

Figure 3. Cadmium (CD, dry wt. in kidney) and mercury (HG, wet wt. in kidney) levels in caribour collected in the Northewest Territories, 1991–1996.

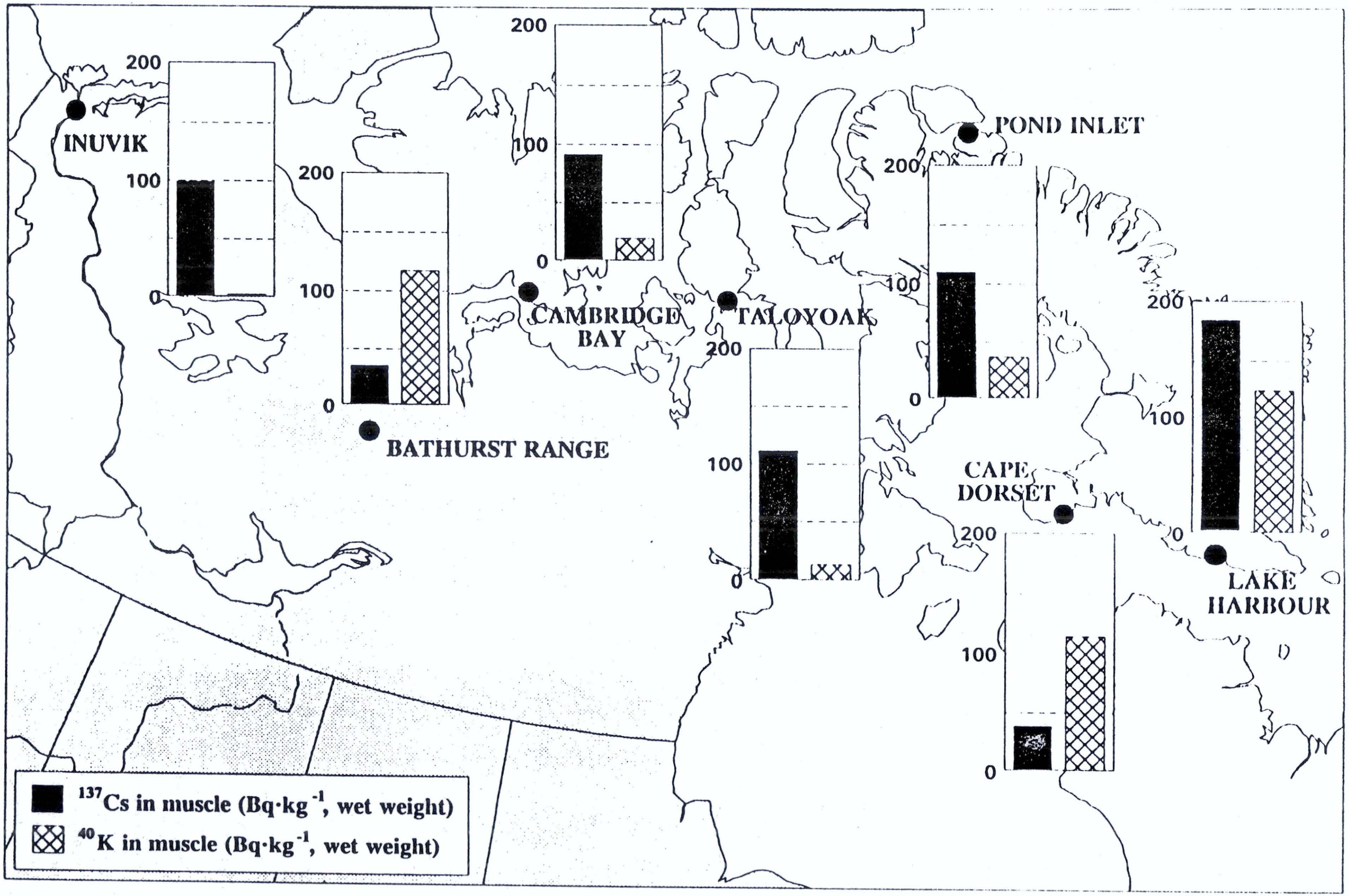

Figure 4. Cesium-137 and Potassium-40 (wet wt. in muscle) activities in caribou collected in the Northwest Territories, 1991–1996.

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 has 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.

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ORGANOCHLORINE, HEAVY METAL AND RADIONUCLIDE CONTAMINANT TRANSFER THROUGH THE LICHEN–CARIBOU–WOLF FOOD CHAIN

Project Leader: B.T. Elkin, Department of Resources, Wildlife & Economic Development, Government of the Northwest Territories

Project Team: R. Bethke, C. Macdonald, Local Hunters' and Trappers' organizations

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 NWT.

DESCRIPTION

Prior to the AES Northern Contaminants Program, information on contaminant exposure in caribou (*Rangifer tarandus*) and other terrestrial wildlife species in Canadian arctic and subarctic regions was extremely limited (Wong 1985, Thomas *et al.* 1992). The scarcity of metal or organic residue data for terrestrial mammals was identified as a data gap in Arctic contaminant research (Wong, 1985). The limited work that has been done has indicated the presence of wide range of contaminants, including cadmium, mercury, HCH, HCB, PCBs, 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. They accumulate atmospheric contaminants in a non-selective manner, resulting in a contaminant load similar to atmospheric input. 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 (Kelsall 1968, Parker 1978). In Arctic areas of the NWT, caribou has been shown to be the predominant food item of wolves (*Canis lupus*). This short and simple food chain provides an opportunity to evaluate and quantify the transfer of contaminants through three trophic levels to the top of the chain. The direct lichen–caribou–wolf food chain may also serve as a useful monitor of contaminant deposition in the terrestrial ecosystem.

This study was designed to provide baseline data on organochlorine, heavy metal and radionuclide contaminant levels in several tissues at all three trophic levels of this terrestrial food chain. This data was used to evaluate the transfer of specific contaminants through the lichen–caribou–wolf food chain. The defined ranges and distribution of caribou herds across the NWT also allowed for comparison of potential spatial variation in contaminant exposure or food chain dynamics. Regional differences in residue levels may help define the sources of contaminants and relative levels of inputs at the three sites. Samples were collected near Ndilo/Fort Rae (Bathurst herd), Cambridge Bay (Victoria Island herd), and Inuvik (Bluenose herd) (Figure 1).

ACTIVITIES IN 1995/96 AND 1996/97

This study was initiated in 1992/93, and 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

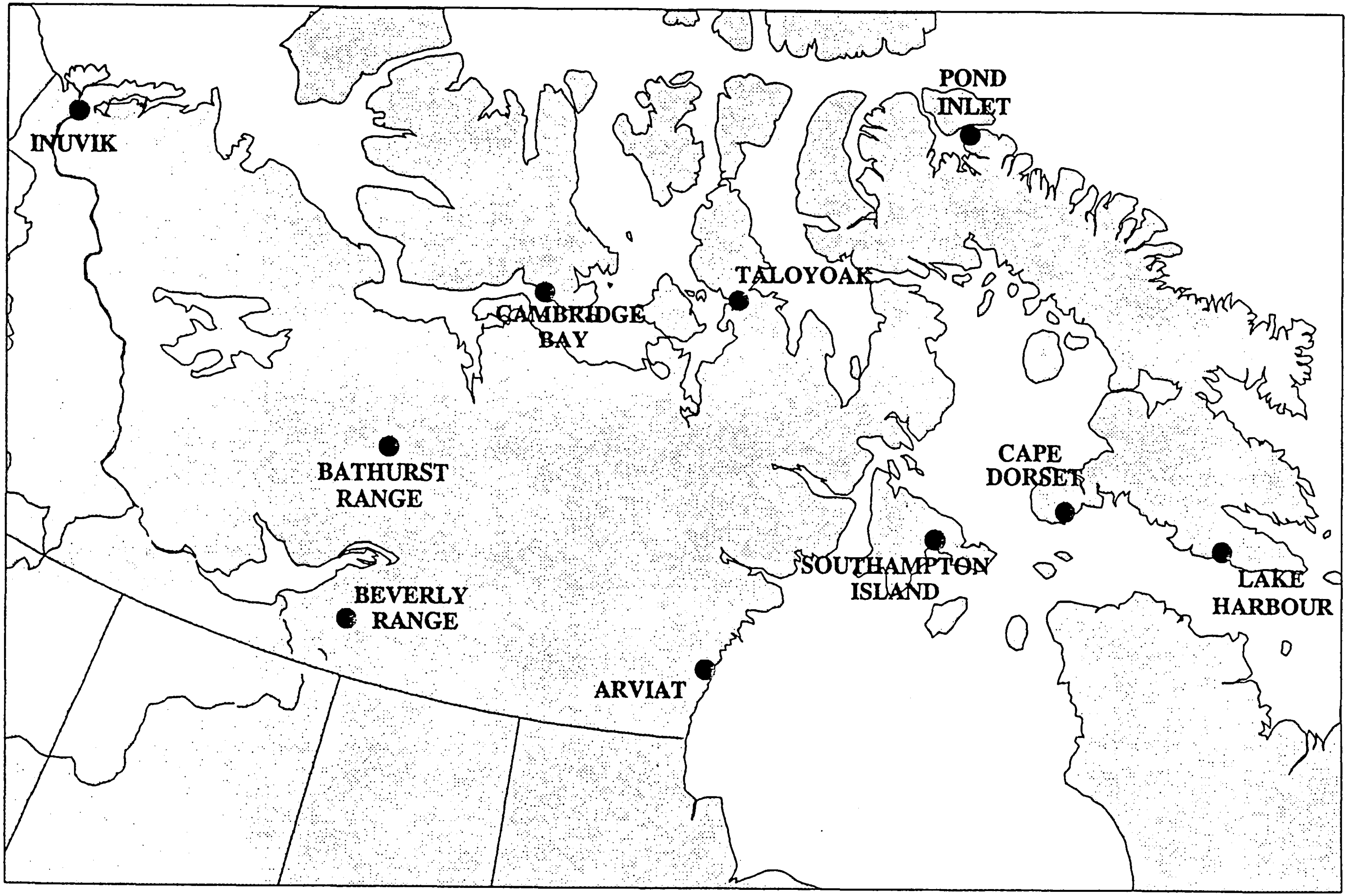

Figure 1. Sites in the Northwest Territories where caribou collections were conducted between 1991 and 1996.

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 aging purposes, and a variety of biological and morphometric measurements were taken. Samples of three common lichen species (*Cladina mitis, Cladina rangiferina, Cetraria nivalis*) that are important in the diet of barrenground caribou 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 and muscle samples from caribou and wolves were also analysed for radionuclides at AECL Whiteshell Laboratories in Pinawa, Manitoba.

All data analysis and interpretation was completed in 1996/97. Public information material are being developed, and the results of the study will be communicated to both the communities involved and to wildlife co-management boards and communities across the NWT.

RESULTS AND DISCUSSION

Contaminant analyses of lichen, caribou and wolf samples from the Bathurst, Bluenose and Victoria Island samples were all completed in 1995/96. 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).

Organochlorines

Chlorobenzenes (ΣCbz) were one of the dominant contaminant groups in lichen, caribou and wolf tissues. ΣCbz concentrations in caribou fat (35–40 $ng \cdot g^{-1}$ lipid weight) were approximately two-fold fold higher than ΣHCH and ΣPCB, the other two major residues. ΣCbz was also the dominant residue group in wolf fat (30–70 ng lipid weight), with levels slightly higher than ΣPCB (20–65 $ng \cdot g^{-1}$ lipid weight). The ΣCbz/ΣPCB ratio remained constant at 1.2 to 1.5 in wolf fat for the three sites.

Hexachlorocyclohexanes (ΣHCH) were one of the residue groups detected most consistently in lichen (1–2 $ng \cdot g^{-1}$), and were also seen at relatively constant concentrations in caribou and wolf. The major HCH component in lichen was α-HCH (75% of ΣHCH); γ-HCH comprised approximately 25% of ΣHCH, and β-HCH levels were nondetectable. In caribou fat, the α-HCH congener still predominated. β-HCH concentrations increased markedly relative to lichen, with its contribution to ΣHCH approaching 25%. γ-HCH comprised less than 5% of ΣHCH in caribou fat. This trend continued in wolves, with ΣHCH composed of approximately equal amounts of α- and β- isomers.

The concentration of ΣPCB was very low (<0.20 ng-1 dry weight) in lichen, but increased in concentration through the food web to become one of the major residues in wolf tissues. ΣPCB concentration remained generally low in caribou, with much higher levels observed in wolves There was a consistent trend of increasing proportions of higher chlorinated congeners in each successive step up the food chain.

Chlordanes (CHL) were a minor residue group in lichen, but were one of the dominant residues in caribou and wolf tissues. The relative proportions of individual chlordane isomers changed markedly within the lichen–caribou wolf food chain. Chlordane isomers detected in lichen were cis-chlordane, cis-nonachlor and heptachlor epoxide, which together contributed about 60% of ΣCHL. Trans-chlordane was not detected in lichen at any of the sites. In caribou and wolves, the dominant isomers were oxy-chlordane and heptachlor epoxide, with trans-nonachlor comprised a minor but consistent fraction of ΣCHL.

Residue levels in caribou and wolf adipose tissue clearly show the biomagnification of some OCs from caribou to wolf. Magnification of individual compounds between trophic levels was examined by calculating concentration ratios (CR), which showed that the major increases in the lichen–caribou–wolf food chain occur between lichen and caribou. The largest differences between trophic levels were observed in liver tissue. In the case of chlordane, biomagnification was due to accumulation of the persistent metabolite oxychlordane in wolf relative to caribou. Caribou liver:lichen CRs for oxychlordane ranged from 1000 to 4900. Further increases to wolf liver of 20 to 30 times resulted in wolf liver:lichen ratios up to 15000. β-HCH increased by 250 to 800 times between lichen and caribou liver, but showed little further accumulation in wolves. PCBs increased steadily through the food chain, with higher chlorinated PCB congeners were present at much higher proportions relative to the recalcitrant congener PCB 153

(2,4,5,2',4',5'-hexachlorobiphenyl) in wolf in comparison with caribou or lichen. Initial CRs of 50–100 between caribou fat and lichen increased by a further 50 to 400 times in wolves for several PCB congeners.

Metals

All 10 metals were observed above detection limits in lichen, caribou and wolf at all three locations. Cadmium (Cd) concentrations were significantly higher in caribou than wolf, significantly higher in kidney than liver, and significantly higher in the Bluenose compared to the Bathurst and Victoria Island herds. In the Bluenose herd, Cd concentrations were 31.2 $\mu g \cdot g^{-1}$ (dry weight) in caribou kidney and 2.41 $\mu g \cdot g^{-1}$ (dry weight) in wolf kidney, giving a caribou kidney : wolf kidney ratio exceeding 12:1. A consistent relationship was observed between liver and kidney concentration indication a consistent relationship between the tissues for both wolves and caribou. Total mercury (Hg) concentrations remained low in all samples, although significant differences were observed between sites, species and tissues. Concentrations in caribou kidney ranged from 1–2 $\mu g \cdot g^{-1}$ dw, while the concentrations in wolf kidney at the same sites were less than 0.15 $\mu g \cdot g^{-1}$ dw. A positive correlation was found between Hg and Cd in both caribou liver (r=671) and wolf liver (r=0.670).

Radionuclides

The only two radionuclides consistently observed in caribou or wolf were ^{137}Cs and ^{40}K. Cesium- 137 was the only nuclide consistently observed in lichen, ranging from 45.0–55.6 $Bq \cdot kg^{-1}$ ww. Cesium-137 concentrations in caribou muscle were generally lower than in lichen, ranging from 2.5–38.5 $Bq \cdot kg^{-1}$ ww. There were no significant difference between sexes, and no correlation between ^{137}Cs concentration and age. ^{137}Cs concentrations in wolf muscle showed considerable variation between sites. On Victoria Island, ^{137}Cs levels in wolves (15–20 $Bq \cdot kg^{-1}$ ww) were not significantly different than in caribou. In the Bluenose herd, mean ^{137}Cs levels in wolves (73.3 $Bq \cdot kg^{-1}$ ww) was about 30-fold higher than in caribou. In the Bathurst herd range, concentrations in wolves (364 $Bq \cdot kg^{-1}$ ww) were about 10 times higher than in caribou at the same site. Potassium-40 concentrations were consistent between sites, with levels of <30.0 $Bq \cdot kg^{-1}$ ww in lichen, 100 $Bq \cdot kg^{-1}$ ww in caribou, 115–122 $Bq \cdot kg^{-1}$ ww in wolves.

Expected project completion date: Field collections and contaminant analyses have been completed at all three sites. Data evaluation and interpretation, preparation of public information materials, and community consultation will continue in 1996/97.

BIOMAGNIFICATION OF PERSISTENT ORGANIC CONTAMINANTS IN GREAT SLAVE LAKE

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

Project Team: D. Muir, National Water Research Institute, and W. L. Lockhart, Freshwater Institute

OBJECTIVES

1. To investigate the role of the Slave River as a source of persistent organic contaminants to Great Slave Lake.
2. To determine the concentrations of organic contaminants in fish commonly consumed by Indigenous people inhabiting various regions of the lake.
3. To investigate factors affecting organic contaminant concentrations in such fish including food web biomagnification and the influence of the Slave River.

DESCRIPTION

This project, which is in its fourth year, is multidimensional. The underlying basis of the study is the investigation of the influence of the Slave River on the contaminant loading to and biomagnification within Great Slave Lake. As such, the study is investigating the potential implications of increased development in the Great Slave Lake drainage basin on contaminant loading to the lake. Ultimately, down-river transport (via) the Mackenzie River may result in increased contaminant loading to the Arctic Ocean. The biological focus of the study is the investigation of organic contaminants in fish which are important in indigenous diets and to the commercial fisheries. Invertebrates and forage fish also are being analysed in order to investigate why organic contaminant concentrations are higher in some species of predatory fish than others.

The project is considering three classes of contaminants: persistent organochlorine compounds (POCs), polynuclear aromatic hydrocarbons (PAHs), and polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs). Most of the focus has been on POCs.

POCs include PCBs, toxaphene, DDT, HCH, and dieldrin. These compounds strongly biomagnify in food webs. Long-range atmospheric transport is believed to the primary source of these compounds to Great Slave Lake. POCs may be deposited directly onto the lake surface or onto the watershed and ultimately transported into the lake by riverine inflow, primarily by the Slave River. The Slave River is the major river flowing into Great Slave Lake with an annual water inflow of 135 km^3 and a suspended sediment load of 2.72 - 6.72 kg x 10^{10}/y (Evans *et al.* 1996). This river is formed by the confluence of the Peace and Athabasca rivers. Because Slave River inflow dominates the limnology of the West Basin of Great Slave Lake, it may be the primary source of contaminants to this region of the lake. Some Slave River water flows into the East Arm. Thus, the river may also be a significant source of contaminants to this region of the lake.

PAHs are produced by combustion; they also are produced as byproducts of the oil and gas industry (Bjorseth and Ramdahl 1985). There are numerous potential sources of PAHs to Great Slave Lake. The southern regions of the Peace and Athabasca watersheds are rich in oil and gas deposits (Northern River Basins Study 1996). PAHs may be eroded from these watersheds into the Peace and Athabasca rivers and ultimately be deposited into Great Slave Lake via the Slave River system. In addition, there may be anthropogenic sources of PAHs associated with the oil and gas industry. PAHs are not strongly biomagnified in aquatic food webs. Nevertheless, their presence in the environment is of concern because some compounds have carcinogenic properties.

PCDDs and PCDFs are produced by combustion and as byproducts of the pulp and paper mill industry (Safe and Hutzinger 1990). Pulp and paper mills along the Peace and Athabasca rivers may be a significant source of PCDDs and PCDFs to Great Slave Lake. PCDDs and PCDFs are of concern because of their carcinogenic properties (Safe 1990).

Our research on Great Slave Lake has considered all three classes of organic contaminants. With funding from the Northern Contaminants Program (NCP), we have focused our research on the investigation of contaminants in biota, primarily POCs. We also have received funding through the Northern Water Resources Studies (AES Program, Yellowknife); this funding has been applied towards sediment analyses, including PAHs, PCDDs and PCDFs. Funding also has been provided for core (March 1995) collection. The Northern River Basins Study (NRBS) provided funding to collect (March 1994) a series of cores in the West Basin; funding also was provided to date and analyse some of these cores for selected contaminants. NRBS was particularly concerned with PCDDs, PCDFs, and PAHs. In 1996/1997, new studies were initiated to consider metals. These studies focused on concerns related to the decommissioned Pine Point mine near Fort Resolution. They were initiated by the community and involved close, collaborative efforts. Funding was provided by the community and by the Northern Water Resources Program (Yellowknife). Fish, sediments, water, and a core sample were analysed as part of these efforts.

ACTIVITIES IN 1995/1996

This was a successful and productive year. Two field trips were conducted in 1995 and a major report submitted to NRBS presenting the results of sediment studies to date (August 1993 to March 1994 collections).

In March 1995, we continued our coring studies in Great Slave Lake. We attempted to collect a series of cores in the East Arm; several sites were sampled over two days with little success. Sediments were either too hard-packed or of insufficient consistency to be retained by the corer. Only one marginal core was obtained in the vicinity of Lutsel K'e. Accordingly, the remaining two days of aircraft time were used to collect an additional series of five cores offshore of the Slave River mouth and to the east of the cores collected during the March 1994 NRBS study. Three of the five cores were dated and found to be in high depositional areas. Sedimentation rates ranged from 1 910–3 190 $\text{gm}\cdot\text{m}^{-2}\cdot\text{yr}^{1}$ versus 343–692 $\text{gm}\cdot\text{m}^{-2}\cdot\text{yr}^{1}$ observed to the east of the river outflow (Evans *et al.* 1996). Sediment deposition was considerably more dynamic than at the sites investigated in March 1994 with strong sediment focusing (a factor of 2.8–3.0). Two of the cores were analysed for POCs and PAHs. The upper slice from all six cores collected during this sampling trip were analysed for PCDDs and PCDFs.

In August 1995, we conducted a cruise which expanded upon our previous summer's collections. We focused our research effort on obtaining more information on organic contaminants in biota at the base of the food web—i.e., plankton, mysids, amphipods. A full series of samples was collected at Resolution Bay (immediately west of the Slave River mouth) and, with the exception of the number of mysid replicates, at Lutsel K'e in the East Arm. In addition, plankton were collected in Christie and McLeod bays (East Arm) to obtain a broader spatial coverage of contaminant concentrations in Great Slave Lake relative to distance from the Slave River. Fish sampling was broadened to include small fish not previously sampled. Gill nets were set in Resolution Bay, near Lutsel K'e, and in the Hearne Channel; cisco, long nose suckers, and additional lake trout and whitefish were caught. A small number of spottail shiners, emerald shiners, sculpins and dace were collected by beach seining in Resolution Bay; emerald shiners and juvenile suckers were obtained by beach seining at Lutsel K'e. The community at Lutsel K'e provided us with additional whitefish and lake trout, but was unable to provide any burbot. Additional whitefish and burbot, primarily from Windy Bay, were provided by a commercial fisherman.

Conductivity, temperature, and oxygen profiles with depth were collected at several locations in the East Arm in order to trace the movement of river water from the West Basin to the Channel Islands, Christie Bay, and McLeod Bay. Water was also collected for nutrient and chlorophyll analysis. Sediment traps were left at two stations offshore of the Slave River mouth. Surficial sediment samples were collected at 17 sites to investigate the movement of river-born sediments and contaminants from the West Basin into the East Arm. (Sites suitable for coring were identified during these collections.) We had intended to collect additional surficial sediment samples in the West Basin. Unfortunately, the charted vessel ran aground offshore of the Simpson Islands, effectively terminating the cruise.

A major report was written for NRBS presenting the results of the August 1993 surficial sediment sampling offshore of the Slave River mouth and the March 1994 coring studies in the West Basin (Evans *et al.* 1996). The report concluded that contaminant concentrations are low in West Basin sediments in comparison to regions such as the Great Lakes. There was some evidence of recent increases in the depositional rates of contaminants; however, interpretation of the time trends was difficult given the small magnitude of increase and the limited number of cores examined. There was strong evidence that the Slave River is a significant source of POCs and PAHs to Great Slave Lake. There also was some evidence that PAHs occurred in greater concentrations in West Basin than East Arm sediments. The sample series analysed was insufficient to detect spatial patterns in POCs, PCDD, and PCDF concentrations.

ACTIVITIES IN 1996/1997

Our 1996/1997 research on Great Slave Lake had three major funding sources in addition to direct support provided by the National Hydrology Research Institute and Freshwater Research Institute. With our NCP (Ottawa) funding, we focused our research on the investigation of contaminants in the biota, primarily POCs. Most of these samples were collected in 1995 and included a wide variety of fish species and various invertebrates. However, a large archive of samples remains. Some fish analyses included comparisons of contaminants in various tissues; these fish were collected from Lutsel K'e, in the East Arm, and Windy Bay, on the extreme western end of Great Slave Lake. The second funding source was the community of Fort Resolution. With this study, we investigated organochlorine and metal concentrations in pike, walleye, burbot, and inconnu. The third study was supported by the Northern Contaminants Program in Yellowknife and investigated various aspects of concern related to the decommissioned Pine Point mine, west of Fort Resolution. This study was conducted on behalf of the community and with their collaboration.

RESULTS

Limnology – August 1995

There was a strong decrease in water conductivity from the West Basin (ca. 0.24 mS·cm^{-1}) into the Hornby Channel (ca. 0.18 mS·cm^{-1}). Conductivity increased in Christie Bay (ca. 0.21 mS·cm^{-1}) for reasons that are not yet clear. Conductivity in McLeod Bay, the region most isolated from the West Basin, was ca. 0.05 mS·cm^{-1}. Conductivity in the Hearne Channel was ca. 0.22 mS·cm^{-1}. Spatial gradients in turbidity and Secchi disc depths between the West Basin and the East Arm were more pronounced than conductivity gradients. These data, along with nutrient and chlorophyll data, are being examined in more detail to infer the movement of Slave River water into the East Arm.

Polynuclear aromatic hydrocarbons

PAHs were the most abundant contaminant in Great Slave Lake sediments with concentrations generally exceeding 100 ng·gm^{-1} (dry weight). Concentrations were high to the west of the Channel Islands (300–500 ng·gm^{-1}) then decreased into the East Arm; lowest concentrations were observed in Christie (22–105 ng·gm^{-1}) and McLeod (53–53 ng·gm^{-1}) bays. Total PAH concentrations at 10 sites in the immediate vicinity of the Slave River mouth ranged from 466–727 ng/gm while concentrations further offshore in depositional areas ranged from 1172–1481 ng·gm^{-1} (Evans *et al.* 1996). PAH concentrations in sediment traps (August 1994) averaged 833 ng·gm^{-1}. These data suggest that the Slave River is a significant source of PAHs to Great Slave Lake with the highest West Basin concentrations located in depositional areas. Concentrations decreased over thirty-fold in the East Arm, presumably due to a weakening Slave River influence.

PAH analyses have been conducted on a subset of biological samples. Concentrations in amphipods averaged 568 ng·gm^{-1} (wet weight) for animals collected in Resolution Bay, 325 ng·gm^{-1} for animals collected offshore of Hay River but only 167 ng·gm^{-1} for animals collected at Lutsel K'e. Regional differences in PAH concentrations appear to be related to regional differences in sedimentary PAH concentrations.

Mysids collected at Resolution Bay had 80 ng·gm^{-1} PAH, a value some 7 times lower than that of amphipods. Mysids may contain lower concentrations of PAHs than amphipods because mysids spend little or no time in the sediments; amphipods are strongly benthic in habitat. Mysids also are more effective than amphipods in eliminating PAHs such as benzo(a)pyrene and, presumably, other PAHs (Frez and Landrum 1986, Evans and Landrum 1989).

PAH concentrations were relatively low in Lutsel K'e fish averaging 2.65 ng·gm^{-1} in whitefish muscle, 2.39 ng·gm^{-1} in lake trout muscle, and 2.44 ng·gm^{-1} in burbot muscle. Analyses of fish collected from the West Basin are ongoing. Overall, PAH concentrations were substantially lower in fish than in invertebrates, indicating weak biomagnification.

PCDDs and PCDFs

PCDDs and PCDFs occurred in very low concentrations in Great Slave Lake surficial sediments. PCDD concentrations tended to be lower in West Basin than East Arm sediments. Highest concentrations were observed in McLeod Bay. PCDDs were dominated by HpCDD and OCDD, which is suggestive of a combustion source. DiCDD, which is suggestive of a pulp and paper mill source, was detected only at the seven stations closest to the Slave River mouth. PCDD concentrations in sediment traps (August 1994) collections averaged 80.0 pg·gm^{-1}; surprisingly, DiCDD was not detected.

PCDF concentrations were substantially lower than PCDD concentrations. Moreover, concentrations were much higher in the West Basin than the East Arm. The lower chlorinated PCDFs, prevailed, particularly in the West Basin, again suggesting a pulp and paper mill source. PCDF concentrations in sediment traps averaged 41.0 pg·gm^{-1}; lower chlorinated PCDFs prevailed in the upper trap and higher chlorinated PCDFs in the deeper trap.

Limited PCDD and PCDF analyses have been conducted on biota. PCDD concentrations averaged 45.3 pg·gm^{-1} (wet weight) in plankton. PCDD concentrations were substantially lower in fish, indicating weak biomagnification. Concentrations averaged 0.1 pg·gm^{-1} for whitefish muscle, 0.2 pg·gm^{-1} for lake trout muscle, and 1.1 pg·gm^{-1} for burbot liver from fish caught in the West Basin. Concentrations were 0.0 pg·gm^{-1} for whitefish and lake trout and 0.6 pg·gm^{-1} for burbot from Lutsel K'e. In comparison, PCDD concentration in burbot liver from the Slave River averaged 4.3 pg·gm^{-1} (Peddle *et al.* 1996).

PCDF concentrations averaged 22.8 pg·gm^{-1} for plankton versus 0.9 pg·gm^{-1} for whitefish muscle, 1.0 pg·gm^{-1} for lake trout muscle, and 2.7 pg·gm^{-1} for burbot liver from Fort Resolution; concentrations averaged 0.6 pg·gm^{-1} for whitefish muscle, 0.7 pg·gm^{-1} for lake trout muscle, and 12.6 pg·gm^{-1} for burbot liver from fish from Lutsel K'e. It is not clear why PCDF concentrations were higher in Lutsel K'e than Fort Resolution burbot liver. PCDF concentration in burbot liver from the Slave River averaged 15.2 pg·gm^{-1} (Peddle *et al.* 1996).

Persistent organochlorine contaminants

PCBs were the most abundant of the POCs analysed in lake sediments (toxaphene was not analysed in these studies). PCB concentrations were lower in the East Arm than the West Basin (Figure 1). In the East Arm, concentrations ranged from 0. 5–1.5 ng·gm^{-1} with the lowest concentrations occurring in Christie Bay. Concentrations at the 10 stations sampled offshore of the Slave River mouth (August 1993) ranged from 2.9–8.3 ng·gm^{-1} and averaged 4.1 ng·gm^{-1}. These values are lower than our previously reported concentrations of 4.8–15.2 ng·gm^{-1} (mean = 9.8 ng·gm^{-1}, Evans *et al.* (1996)). The re-analysed values, while lower, are ca. 4 times higher than the East Arm series. Overall, these data suggest, and in contrast to the conclusions of our Northern River Basin Study (NRBS) report, that the Slave River may be an enriched source of PCBs to Great Slave Lake.

Sedimentation rates, as estimated from dated cores, were highest offshore of the Slave River mouth (Figure 2). Rates decreased to the west but were still higher than in the single core dated from the East Arm. PCB flux rates, estimated from the product of PCB concentrations and sedimentation rates were highest offshore of the Slave River mouth (Figure 3). Fluxes were substantially lower to the west, indicating a weaker Slave River influence. The lowest flux rate was in the East Arm. This again indicates that the Slave River is a significant source of PCBs to Great Slave Lake.

In August 1995, plankton were collected for PCB analyses in four regions of the lake. PCB concentrations (wet weight) in plankton collected in Resolution Bay averaged 1.2 ng·gm^{-1} versus 3.0 ng·gm^{-1} for plankton collected offshore of Lutsel K'e, 2.4 ng·gm^{-1} for plankton in the open waters of Christie Bay, and 2.4 ng·gm^{-1} for plankton in McLeod Bay. Relatively low concentrations of PCBs in plankton from Resolution Bay may be due to the fact that a significant fraction of PCBs were adsorbed onto the high concentrations of suspended sediments in Resolution Bay waters. Alternately, differences may have been related to the composition of the plankton. Stable isotope analyses will help resolve these differences. In Evans (1996), we reported PCB concentrations of 4.5 ng·gm^{-1} for plankton from Fort Resolution and 4.7 ng·gm^{-1} for plankton from Lutsel K'e. These values were not appreciably different from Kidd *et al.*'s (1996) mean value of 5.1 ng·gm^{-1} for plankton from Lake Laberge and 4.3 ng·gm^{-1} from Fox Lake but higher than their 1.2 ng·gm^{-1} value for plankton from Kusawa Lake.

In August 1995, amphipods from Resolution Bay had a mean PCB concentration of 1.8 ng·gm^{-1} compared with 1.4 ng·gm^{-1} for amphipods collected from Lutsel K'e. Amphipods collected in August 1994 from the two sampling locations also had similar PCB concentrations (Evans 1996).

Interpretation of the larger data sets (organochlorines and stable isotopes) for the fish collections made during 1995 and 1996 (Fort Resolution studies) are ongoing and are not reported here. However, organochlorine and metal data based on the Fort Resolution fish studies are presented in a separate chapter in this highlights report (see "Fort Resolution Domestic Fishing Zone Contaminants Research").

DISCUSSION/CONCLUSIONS

The results of our study support earlier observations that organic contaminants occur in relatively low concentrations in the Great Slave Lake ecosystem. Nevertheless, there appear to be important regional variations in contaminant concentrations. Biological data (invertebrates, fish) collected in 1996 appear to support the observation that PCB concentrations are higher in biota from the East Arm than the West Basin. This occurs despite the fact that our most recent data indicate that PCB concentrations are higher in West Basin than East Arm sediments. Possibly, the high suspended sediment

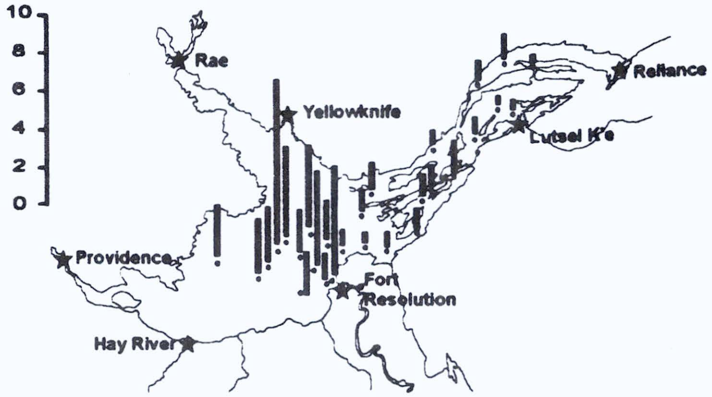

Figure 1. Total PCB concentration (ng/g dry weight) in surficial sediments.

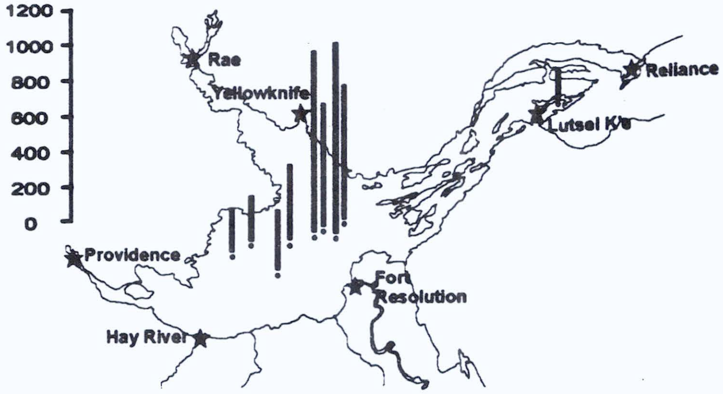

Figure 2. Sedimentation rate (g/m²/y).

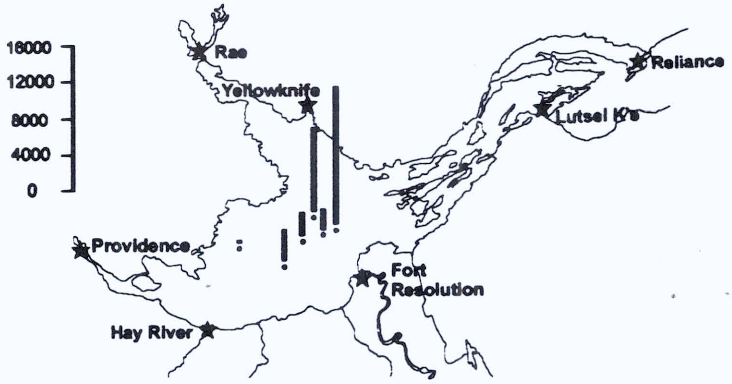

Figure 3. PCB flux rate (ng/m²/y) corrected for sediment movement, Great Slave Lake.

load associated with the Slave River dilutes PCB concentration on particulates in the water column. This, in turn, may result in lower PCB concentration in plankton in the West Basin than the East Arm. This may also account for the fact that PCB concentrations tend to be higher in whitefish, lake trout, and burbot from the East Arm than West Basin.

PAH concentrations were higher in West Basin than East Arm sediments, suggesting that, like PCBs, the Slave River is an enriched source of these contaminants. However, the source of these PAHs has yet to be determined, i.e., anthropogenic (combustion, oil and gas industry) or natural (seepages from oil and gas deposits). A significant component of the PAH input into Great Slave Lake does appear to be anthropogenic in origin because PAH concentrations have increased in recent years in two cores analysed from the West Basin (Evans *et al.* 1996).

PAH concentrations were greater in amphipods from the West Basin than the East Arm, reflecting regional differences in PAH concentrations in sediments. PAHs concentrations were lower in mysids and even lower in fish confirming that this class of compounds is not strongly biomagnified in food webs. Continuing analyses of plankton, mysids, and fish will help confirm regional differences in PAH concentrations.

PCDD and PCDF concentrations were low in the sediments. There was strong evidence of regional differences in PCDD and PCDF concentrations. There was also some evidence that lower chlorinated PCDDs and PCDFs occurred in higher concentrations in the West Basin than East Arm. Such differences are suggestive of a pulp and paper mill influence.

PCDDs and PCDFs were not strongly biomagnified in the food web. There were no clear differences in PCDD and PCDF concentrations in fish collected from the West Basin and East Arm. PCDD and PCDF concentrations in burbot muscle from these two regions were similar to concentrations in burbot collected from the Slave River.

Our ongoing research will focus on elucidating regional differences in contaminant concentrations and the role of the Slave River in affecting such differences. We also will continue to compare contaminant biomagnification in different regions of the lake and the factors affecting such differences.

Expected project completion date: March 1999.

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SOURCES AND SINKS OF ORGANOCHLORINES IN THE ARCTIC MARINE FOOD WEB

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OBJECTIVES

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

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

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

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

DESCRIPTION

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

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

While the present distribution and mechanisms for transfer of OCs between various compartments of the arctic marine environment and food web are poorly understood, it is known that concentrations of organic matter (particulate and dissolved) in the Arctic Ocean are extremely low (Gordon and Cranford 1985). Since there is no photosynthesis during months of darkness, marine organisms must store energy-rich lipids to survive. The high fat content of tissues used for lipid synthesis and storage make these organisms more likely to accumulate OCs that have a high fat solubility. This in turn may result in a greater bioconcentration of these contaminants by higher trophic levels than that which 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 logistics of sampling throughout the year. The main objective for this project in 1996 was to complete analyses of samples collected over 12 months in 1993 to provide the first seasonal measurements of OCs in seawater and lower trophic level marine organisms in the Barrow Strait/Resolute Bay region. The distribution and relative concentrations of OCs and PCBs in air, snow, seawater and various marine food web organisms sampled earlier from the Ice Island (Hargrave *et al.* 1988, 1989) over a restricted range of seasons could be compared with the new data set covering a full annual period. In addition, large scavenging amphipods were collected from deep water in the Canada Basin during 1997 during SCICEX-96, a US project using a nuclear-powered submarine.

ACTIVITIES 1995/96 AND 1996/97

No new sample collection was undertaken during 1995 but samples collected during 1993 and held frozen were analysed for various OCs during 1996 to complete the seasonal data set. Specimens of *Eurythenes gryllus* (a large deep-water scavenging amphipod) were collected during SCICEX-96 (September–October 1996) using the nuclear-powered submarine USS Pogy. A portable electric winch constructed at the Bedford Institute of Oceanography was specifically designed to use 440 V power supplied by the submarine while it occupied surface ice stations. Baited traps were constructed and deployed on the seabed for 3 to 6 hours at a depth of 3600 to 3700 m at three stations in the Canada Basin in late September and early October 1996. Amphipods trapped using protected bait to prevent ingestion were analysed for OCs during 1997. A total of 32 biota samples (planktonic and benthic (amphipod) crustaceans and arctic cod tissues) were analysed under contract (Axys Analytical Services, Ltd., Sidney) for 16 chlorinated pesticides, toxaphene and PCBs during 1996 and 1997. The analyses complete the annual (12 month) data set for the 1993 study in Barrow Strait which now includes various sample types (air, snow, ice melt water, seawater at various depths, epontic particulate matter, various size classes and species groups of planktonic and benthic crustaceans and fish)(data summarized in Tables 1 and 2). The new results for *E. gryllus* obtained during 1996 can be compared with OC measurements for this species collected from the Alpha Ridge during the CESAR project in 1983 (Table 3).

Written contributions summarizing results from this project were prepared for Chapter 2 ("Sources and Sinks") and Chapter 3 ("Ecosystem Uptake and Effects") of the *Canadian Arctic Contaminants Assessment Report*. A primary paper on digestion and lipid storage of bait consumed by the Arctic abyssal scavenging amphipod *Eurythenes gryllus* was published in *Deep Sea Research* (Hargrave *et al.* 1995). This widely distributed deep-water amphipod has high lipid content and its diet as a scavenger of fish and mammal tissues makes it suitable as a sentinel organism for following temporal and spatial trends in OCs transferred from surface to deep water biota in the Arctic Ocean. A manuscript co-authored by L. Barrie, T. Bidleman (DOE, Downsview, Ont.) and H. Welch (DFO, Central and Arctic Region) was accepted for publication in *Environmental Science & Technology*. The paper compares seasonal changes in air-sea fluxes of OCs derived from fugacity ratios calculated from OC gradients in the arctic atmosphere and surface seawater of the Canadian archipelago using Henrys Law coefficients for various OCs.

RESULTS

Five classes of compounds (hexachlorocyclohexanes, cyclodienes, isomers of DDT and its metabolites, and congeners of PCBs and toxaphene (PCCs)) have been detected in various sample types collected between 1986 and 1993 (Table 1). Results for lower trophic level biota (Table 2) are summarized from Hargrave *et al.* (1992) with additional data provided from the seasonal study (POLARPRO) carried out in Barrow Strait/Resolute Bay in 1993 and for scavenging amphipods collected during SCICEX-96. PCCs, PCBs, isomers of DDT and DDE, chlordane, dieldrin, endosulfan-I, HCB and α–HCH were present in quantifiable levels in most sample types. Traces of β– and γ–HCH and the cyclodienes aldrin, endrin, heptachlor, heptachlor epoxide, methoxychlor and mirex were also usually present but small sizes of some sample types (epontic particles and smaller zooplankton size fractions) did not allow OC concentrations to be accurately determined.

Levels of the most abundant OCs (PCCs, PCBs, and DDTs) in *E. gryllus* collected during SCICEX-96 (Table 3) are within the range of values (2 to 30 $\mu g \cdot g^{-1}$ lipid) previously reported for specimens of this species from deep water collected in 1983 (Table 2). Concentrations in a second species (*Anonyx nugax*) with smaller body size found in more shallow continental shelf areas such as Barrow Strait/Resolute Bay are lower than those in *E. gryllus*. In shallow water, these smaller sized amphipods are important food resources for fish such as arctic cod and seals. *E. gryllus* is restricted in its distribution to deep water where there is probably a refuge from predation due to a low abundance of fish.

Table 1. Ranges or mean values for various OCs (hexachlorocyclohexane [a–HCH and g–HCH]), hexachlorobenzene (HCB), dieldrin (DIEL), endosulphan I (ENDO), cis-chlordane (cis-CHL), trans-chlordane (trs-CHL), total DDT (DDT), total PCBs (PCB)(as Aroclor 1254 equivalents), toxaphene (PCC) (sum of congeners) were measured in air vapour, dissolved in snow and ice-melt water, seawater (upper 60 m mixed layer) and surficial (upper 1 cm layer) sediments from the Arctic Ocean (Ice Island) and Canadian archipelago (Barrow Strait/Resolute Bay) between 1986 and 1993.

Sample type	α–HCH	γ–HCH	HCB	DIEL	ENDO	cis–CHL	trs–CHL	DDT	PCB	PCC
Air Vapour (pg · m^{-3})	13–115 (352)	2–28 (44)	17–86 (68)	0.4–2.4 (<12)	2–6 (3)	0.3–2.4 (1)	0.1–1.4 (0.5)	(0–4) (2)	(0–32) (<9)	0.8–16 (NA)
Snow Melt (pg · L^{-1})	170–2600 (1335)	75–740 (428)	0–41 (33)	40–290 (192)	30–210 (114)	5–40 (27)	5–86 (30)	(3–36) (14)	(20–36) (102)	NA (NA)
Ice (pg · L^{-1})	60–1700 (1320)	69–240 (186)	0–7 (<2)	5–8 (6)	0 (0)	0–5 (5)	0 (0)	7 (<5)	(0) (<2)	NA (NA)
Seawater (Surface Mixed Layer) (pg L^{-1})	2100–4400 (4465)	77–140 (610)	12–18 (20)	10–20 (14)	0–6 (9)	0.8–2 (2)	0.4–3.4 (3)	0.4–3.2 (<1)	4–47 (<10)	10–130 (NA)
Sediment (pg · g^{-1} dry sediment)	(240)	(15)	(17)	(<6)	(2)	(18)	(<4)	(<2)	(<1)	(NA)

Numbers in parentheses are mean values taken from data collected from the Canadian Ice Island (1986–1989).
Data is summarized from Hargrave *et al.* (1988 and 1997).
Air vapour (seasonal ranges) are from unpublished data collected at Alert during 1993 (L. Barrie, AES, personal communication to B. Hargrave 1995) as summarized in Hargrave *et al.* 1997.
NA = not analysed. Data from snow and ice melt, seawater and sediments has not been corrected for percent recovery during ECD/MS analyses of extracted samples. The recovery efficiency for analyses carried out prior to 1993 was 64%–98%. Recovery efficiency for samples collected in 1993 was 98%–100%.

Although sample sizes are small (n=6 to 12 individuals), the results from 1996 show ranges of OC concentrations in *E. gryllus* from the Canada Basin in 1996 that are from >50% lower than values observed in 1983 for the same species collected on the Alpha Ridge. With the data currently available, it cannot be determined if the difference is related to geographic location or the time (13 years) between the two sets of observations.

DISCUSSION/CONCLUSIONS

The OCs in samples of epontic particles, pelagic and benthic crustaceans collected during the POLARPRO study in Barrow Strait/ Resolute Bay (Table 2) are also present in the arctic atmosphere, particulate and dissolved fractions of snow, ice melt water and seawater samples collected from the Ice Island between 1986 and 1988 (Hargrave *et al.* 1988) (Table 1). The data show that small-bodied organisms which are short-lived generally have a lower lipid content for storage of OCs than larger sized animals. The large storage potential for OCs in lipids of fish, seal and mammal tissues, where lipid content may amount to <50% of tissue fresh weight contrasts average values for lipid expressed as a percentage of wet weight in benthic amphipods (6.4%), zooplankton (3.1%) and epontic particles (<1%) melted from the under-surface of the ice.

Seasonal differences in bioaccumulation of OCs occur in the arctic marine food web as the source of primary production shifts from under-ice epontic algae in the late spring (May to June) to phytoplankton during the summer open water period (July through September). The 1993 sampling program in Barrow Strait/Resolute Bay provided the first opportunity for seasonal measurements of the major OCs in any arctic marine area. Results show that seasonal differences occur in OC concentrations in pelagic and benthic biota which may be compared with variations in air-sea exchanges in the Arctic archipelago (Hargrave *et al.* 1997). Air concentrations of all OCs decreased from maximum levels in April-May to minimum values in June followed by an increase during the open water period and a decrease after freeze-up in October. Seasonal changes in concentrations in surface (1 m) and subsurface (50 m) seawater were

Table 2. Ranges of concentrations (µg · 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. 1989, 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 25-215µm	Zooplankton >509µm	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	3.5-23.8	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	0.05-0.1	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	0.14-0.1	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)

Table 3. Ranges of concentrations (µg · g^{-1} lipid) of organochlorines (OC) and PCBs in two species of benthic amphipods (*Eurythenes gryllus* and *Anonyx nugax*) collected in various regions of the Arctic Ocean between 1983 and 1996.

Location (Year/Species)	Depth (m)	PCC	ΣPCB	ΣDDT	ΣCHL	ΣHCH	HCB
Alpha Ridge (1983/*E. gryllus*)	2025	3–35	6–34	2–26	0.8–5	0.006–0.4	0.06–0.3
Ellef Ringnes Is. (1986-1989/*A. nugax*)	500	3–10	5–12	0.5–12	0.5–2	0.003–0.1	0.03–0.1
Barrow Strait (1993/*A. nugax*)	85	0.2–4	0.05–2	0.02–2	0.03–1	0.1–8	0.01–0.2
Canada Basin* (1996/*E. gryllus*)	3700	1–4	0.5–3	0.2–2	0.2–2	0.005–0.02	0.03–0.2

* Data from SCICEX-96

correlated suggesting that water mass advection was a major process for transporting OCs through the archipelago. Seasonal changes in seawater concentrations were smaller than those in air, but as in air, high levels in seawater during spring also decreased during July and August when maximum phytoplankton growth and biomass occurred. Results show that outgassing rates of over-saturated OCs occurred primarily during June.

Data obtained in Barrow Strait/Resolute Bay in 1993 form a comparative baseline for a planned study in 1998/99 to examine seasonal changes in OC transport through the Canadian archipelago. The new study will determine the importance of water flow from the permanently ice-covered central Arctic Ocean vs. changes in atmospheric levels of OCs for seasonal variations in air-sea deposition and volatilization observed for different OCs.

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BIOMARKERS AND STRESS EFFECTS IN ARCTIC MARINE MAMMALS

Project Leader: W.L. Lockhart, Freshwater Institute (FWI) Winnipeg, Man.

Project Team: D. Metner (chemist), C. Hyatt (graduate student)

OBJECTIVES

The objectives of this project have been to try to identify and measure biological responses to chemical contaminants in arctic fish and marine mammals. The responses sought are generally at sub-cellular levels since these are closest to the actual modes of action of contaminants, although they need not be biochemical.

Short-term

1. To define levels of biochemical stress responses in marine mammals as functions of contaminant concentrations measured in the same animals.

2. To define the influences of normal biological and habitat variables (e.g., sex, age, size, etc.) on the ranges of bioindicator values.

Long-term

1. To understand the implications of contaminants (PCBs, chlorinated dioxins and furans, polycyclic aromatic hydrocarbons, heavy metals) for the health of individual arctic marine mammals, using the liver microsomal mixed function oxidase system and other biological responses as appropriate for the mode of toxic action of the contaminant under study.

DESCRIPTION

It is well established that arctic marine mammals contain a range of chemical contaminants. This project asks whether these contaminants matter to the animals by examining them for subtle indicators of biological responses (biomarkers or bioindicators) to contaminants. The biological responses selected for these animals have established sensitivities (in laboratory animals) to the same contaminants measured in arctic marine mammals, notably several PCB congeners, chlorinated dioxins and furans, and polycyclic aromatic hydrocarbons including petroleum oil. Experimental studies directly on seals have also shown that they respond in the same manner as laboratory mammals. For several years this project has examined fish and marine mammals for indications of responses to chemical contaminants being measured in related projects describing residues in fish and marine mammals. The principal biomarker being used is the microsomal monooxygenase system since it has been associated both with exposures to planar aromatic compounds and with a cascade of other biological responses. Evidence has been accumulating from studies of beluga whales (Lockhart and Stewart 1993), ringed seals (Lockhart 1994, White *et al.* 1994), burbot (Lockhart *et al.* unpublished) and most recently from polar bears (Norstrom 1996) that contaminant levels are associated with subtle responses in these animals. This project was the first one in the Canadian Arctic to indicate that some of the stable organic contaminants may be having biological effects on arctic marine mammals.

Recently mercury has been detected at high levels in blood and brain of beluga whales (Hyatt *et al.* 1996). Both brain and blood levels are high enough to induce biological effects in laboratory animals. However, it is not known whether the beluga are suffering any biological effects of mercury. A striking observation is the close correspondence in molar amounts of mercury and selenium. For this project in 1996/97 we examined some liver samples histologically to see whether structures could be detected that would be consistent with compounds of mercury and selenium. This work was done jointly with a project run internally by the Department of Fisheries and Oceans and one supported by the Fisheries Joint Management committee.

This project was not funded in 1995/96 but partial funding was restored in 1996/97.

ACTIVITIES IN 1995/96 AND 1996/97

Since polycyclic aromatic hydrocarbons can induce some of the same responses as PCBs, we wanted to examine beluga tissues for PAHs since these compounds have been detected in the Mackenzie River and southern Beaufort Sea (Yunker *et al.* 1991, 1993). The methodology used for PAH analysis is described in some detail in Appendix 1. Also, since the beluga from the western Arctic have high and apparently increasing levels of mercury, we have been examining beluga for mercury and selenium in organs that are targets of the toxic actions of mercury, namely the brain.

RESULTS

PAHs

Two beluga samples were analysed for hydrocarbons and two tissues (muscle and blubber) were used. The MEOH/KOH reflux method was used on muscle samples and the Ball Mill method was used on the blubber. An extensive list of PAH, alkylated PAH and alkanes were analysed for by GC/MSD in SCAN and SIM mode. Sample #9503043 (95-HI-5) and #9503049 (95-HI-11) showed no PAHs above blanks and peaks that appeared in the same time windows as anthracene (mz 178) and p-terphenyl d14 (mz 244) when run in SCAN mode, appeared to be related to organochlorines. The SCAN also identified a large peak as the isoprenoid squalene. Failure to identify PAHs is in arctic beluga was not unexpected in view of the active mixed-function oxygenase system in these animals, but it was necessary to check the possibility. Hellou *et al.* (1990) identified low but detectable amounts of PAHs in muscle tissue of several marine mammal species from waters of Newfoundland and Labrador but we have been unable to detect those compounds in the Mackenzie Delta samples to date. No alkylated PAHs were present above the levels in a blank. A peak that appeared in the C3 phenanthrene window (mz 220) was also identified by SCAN as an organochlorine.

Alkanes also did not show any positive results except for a large peak (mz 268) that was identified by SCAN as the isoprenoid pristane.

Beluga Liver Histology

Beluga liver samples taken in 1995 (with the support of FJMC and DFO projects) were fixed in 10% buffered formalin, embedded in paraffin and sectioned to a thickness of 7 µm. The sections were mounted on glass slides and stained with H&E. The samples from whales with higher levels of mercury showed an increasing number of macrophages (Kupffer cells) (Figure1). Macrophages are phagocytic cells which partly line the hepatic sinusoids. They frequently contain granules of pigment, engulfed erythrocytes in various stages of disintegration, and granules containing iron. These cells are fixed in place but are located where toxic agents circulating in the blood can contact them. Within the macrophages appear to be dark granules which we hypothesize may be particles of mercury selenide. This may indicate that the methylmercury in the blood is being taken into the liver where some of it is converted to mercuric selenide and stored in the macrophages. Nigro (1994) reported the presence of mercuric selenide in the macrophages of striped dolphins (*Stenella coeruleoalba*). Currently, a number of slides have been sent to a laboratory in Denmark for special staining, which may reveal more about the intracellular distribution of mercury.

Selenium and mercury

Previous studies with mammals have reported a protective effect of selenium against the toxicity of mercury (Thompson 1990), and hence accumulation mercuric selenide granules could be an adaptation to high dietary intake of mercury. We investigated the relationship between mercury and selenium in beluga blood, brain, spinal cord and liver (Figure 2). Work by Ms. Carissa Hyatt (M.Sc. student) on samples obtained in 1996 confirmed her earlier 1995 results. Analysis of brain for selenium and mercury revealed a almost a 1:1 molar ratio of mercury to selenium (Figure 2, upper right). A similarly strong association between mercury and selenium was noted in spinal cord (Figure 2, lower left) and, somewhat less strikingly, in liver (Figure 2, lower right). However, there was no relationship between mercury and selenium in blood (Figure 2, upper left). In most cases with other species, inorganic mercury cannot pass the blood/brain barrier and if this applies to the whales, then the mercury must enter the brain as methylmercury from the blood and then be demethylated to inorganic mercury within the brain. Some of the brain samples had levels over 10 ppm a level high enough to cause symptoms of mercury poisoning in some mammals. However, some earlier studies with laboratory mammals have indicated that most of the blood and brain mercury is in the form of methylmercury. In beluga the mercury in blood is almost all methylmercury but much of the mercury in brain exists as inorganic mercury. In fact, brain total mercury levels appear to be related to methylmercury levels such that high total mercury levels correspond to low percentages of total mercury occurring as methylmercury. Analysis of the whale brains also revealed a form of organic mercury which was not methylmercury. We hypothesize that this may represent an intermediate stage in the conversion of methylmercury to mercury selenide.

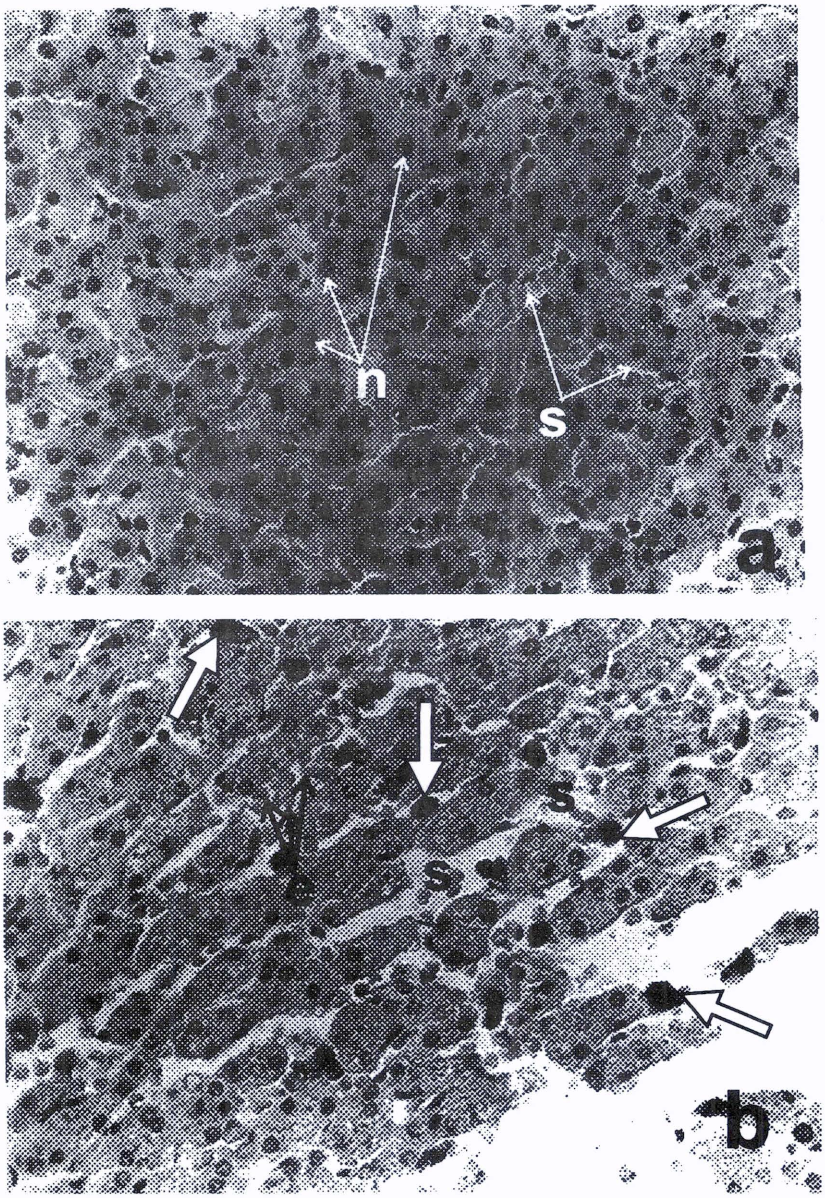

Figure 1. Light micrographs of beluga whale livers: (a) with a total mercury level of 5.65 µg/g, and (b) with a total mercury level of 59.6 µg/g showing numerous macrophages (large white arrows). Both livers were stained with H & E (x 250; e, erythrocytes; s, sinsoids; n, nuclei).

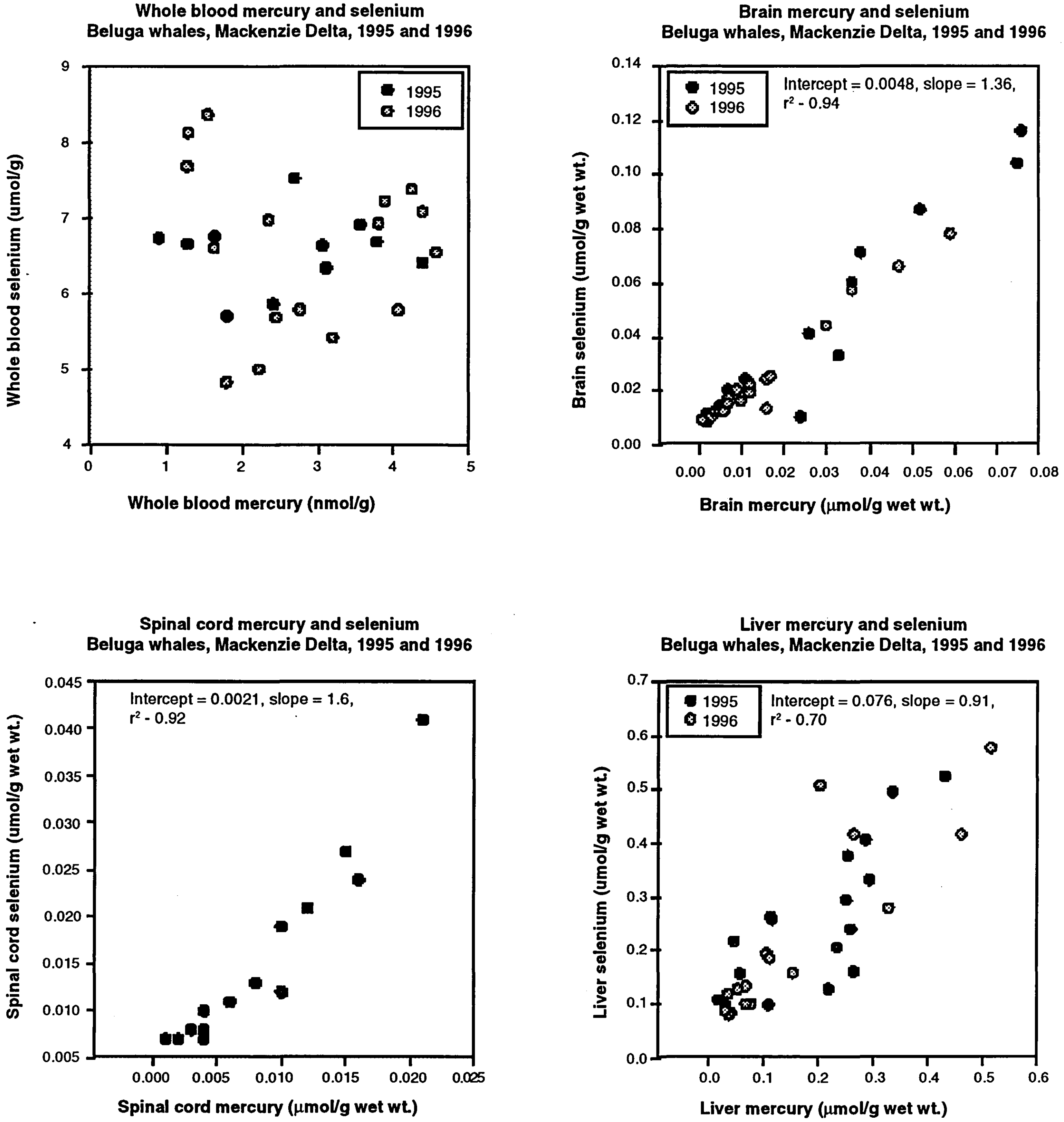

Figure 2. Molar quantities of total mercury and selenium in tissues of beluga whales from the MacKenzie delta.

QUALITY ASSURANCE

Histology slides were examined by the student doing the project and by a histologist of long experience (R.E. Evans). Both total mercury and selenium were included in the NOAA-10 interlaboratory comparison study and results were within the acceptable ranges. There are no interlaboratory comparisons available for methylmercury in tissues. For PAHs, we have participated in interlaboratory comparisons of PAHs in water and sediment in the past but not for biological tissues for this project. We have described the methodology in detail (Appendix 1).

DISCUSSION/CONCLUSION

We found no evidence of polycyclic aromatic hydrocarbons in the muscle samples of beluga whales from the Mackenzie Delta, in spite of the fact that low levels of hydrocarbons are known to be present in other media in the area. This is in contrast to whales from Newfoundland/Labrador where low levels of PAHs were reported.

Brain levels of mercury in beluga are quite variable, with some individuals having levels over 10 $ug \cdot g^{-1}$. This level in brain is enough to cause mercury toxicity in some other species of laboratory animals, and so the question is whether or not the arctic beluga are suffering any toxic effects of mercury. Selenium has often been reported to protect animals from the toxic effects of mercury and the beluga brains and spinal cords have a strong statistical correlation between selenium and mercury. The histology (Figure 1) suggests that the individuals with high mercury contents have greater frequencies of dark-staining granules which may represent mercury selenide. We suspect that beluga accumulate selenium as a protective response to high dietary intakes of mercury.

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APPENDIX 1

PAHs and Alkanes in Hendrickson Island Beluga Tissues

The extraction procedure used for fish and invertebrates has been modified from Warner (1976). Briefly, 5-10 grams of tissue was digested with 150 mL of methanol and 7 to 10 grams of potassium hydroxide. This mixture was refluxed for four hours and then extracted with hexane. Fractionation was carried out by column chromatography using silica/alumina.

This extraction method is used to isolate PAHs quantitatively from insoluble samples, such as beluga muscle, where hydrolysis is an absolute necessity. For beluga blubber samples it was found that in using a MEOH/KOH reflux not all the fat was saponified, causing cleanup problems. For beluga blubber lipids, which are completely soluble in a solvent mixture such as dichloromethane:hexane (1:1), the hydrolysis step is not necessary.

The following Ball Mill Extraction method from Muir *et al.* (1990), which has been used for the extraction of organochlorines from high lipid samples proved to be effective for PAHs. Recoveries of deuterated internal standards were in the range of 80% to 120%. Into a clean stainless steel ball mill, weigh out 2.2 grams of blubber plus 10 grams of sodium sulfate. Add 25 mL of (1:1) DCM:hexane plus a spike of 100 ng of the recovery deuterated internal standard. Shake on a wrist-action shaker for 15 minutes and let stand for 4 hours. Centrifuge at 2000 rpm for 10 minutes and decant the solvent into a 250 mL round bottom flask. Repeat the shaking step with 25 mL of fresh solvent, centrifuge (no standing time) and decant into the same flask. Rotavap the solvent down to approximately 5 mL and volume to 11 mL in a conical graduated test-tube. Pipette 1 mL into a weighed aluminum pan and evaporate to dryness in a fumehood and weigh for total lipid. In the case of beluga blubber total lipid is approximately 95%. Add deuterated internal standard for quantitation and evaporate to 5 mL. Cleanup on a gel permeation column (S-X3 Biobeads) with 300 mL of (1:1) DCM:hexane, discarding the first 125 mL. The remaining 175 mL was evaporated on a Rotavap to 1mL and then follow the usual fractionation on Si/Al columns. Detection was by GC/MSD in SIM and SCAN modes using separate methods for PAH, alkylated PAH and alkanes.

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

Project Leaders: W.L. Lockhart and G. Stern, Freshwater Institute, Winnipeg, Man. and D.C.G. Muir, Canada Centre for Inland Waters, Burlington.

Project Team: B. Grift, B. Rosenberg, D. Metner and R. Danell (biomarkers); B. Billeck (PAH analyses, sediment collection); P. Wilkinson (radionuclides and sediment collection); K. Kidd (U of Alberta, collections of fish)

OBJECTIVES

1. To determine temporal trends in supplies of organochlorines and several metals to Yukon lakes by retrospective analysis of fish samples and by analysis of dated lake sediment cores.
2. To investigate further the increased inputs of lead inferred from a core taken from Hanson Lake near Mayo by collecting cores from two additional lakes in the area.

DESCRIPTION

Reports of high levels of organochlorine compounds in fish from Lake Laberge (Kidd *et al.* 1995) prompted the analysis of fish from a number of other Yukon lakes. Sediment cores have also been examined in efforts to reconstruct the histories of chemical contamination of these lakes. PCBs in one Yukon lake, Kusawa, have been described recently by Muir *et al.* 1996. Previous reports have described the results obtained with fish and this report will describe sediment core results. The focus of the report this year is on metals because many of the measurements have not been reported previously.

ACTIVITIES in 1995/96 and 1996/97

There were no field activities in 1995/96 or 1996/97. The emphasis for 1995/96 was on the analysis of samples of cores on hand from previous collections. In view of the amount of material to analyse, this work will continue for several years. Yukon cores on hand are listed in Appendix 1.

RESULTS

Lead-210 and cesium-137 in Yukon cores

The fundamental measurements on the cores are the isotopes lead-210 and cesium-137 since these determine whether time periods can be calculated for the deposition of individual slices. The down-core profiles for those isotopes in Yukon cores completed to date are shown in Figure 1. If the dates derived from the excess Pb-210 indicate that peak Cs-137 occurred in the 1960s, then the dates are taken to be credible.

Metals

Bennett Lake

Pb-210 and Cs-137 activities for Bennett Lake core 1 are shown in Figure 1. In this core the Pb-210 dates indicated that the Cs-137 peak was in the early 1960s and so the dates are taken to be credible. The sedimentation rate was calculated to be relatively high at 1140 $g \cdot m^{-2} \cdot y^{-1}$ with a Pb-210 flux of 261 $Bq \cdot m^{-2} \cdot y^{-1}$ indicating considerable sediment focusing. This core from has been analysed for 10 metals, namely Pb, Cd, Hg, Al, Ti, Fe, Mn, Ni, Zn, and Cu; the down-core profiles of these are shown in Figure 2. Several of these were highly variable but no clear trends were evident. Cores often show peaks in iron and manganese near the sediment/water interface and this core shows such a peak for manganese due to processes within the sediment. The peak in manganese in slices 5–7 is not interpreted as increased inputs of Mn but rather as redistribution within the sediment. There were also sharp peaks in copper (slices 7–9) and nickel (slices 7–9). We interpret these as products of within-core processes; we are not aware of any local source in the late 1960s or early 1970s which could have produced these peaks. The metals of greatest interest as contaminants are lead, cadmium and mercury and the results indicated no striking changes in any of these metals over the history spanned by this core. Of these three, lead and mercury are generally thought to have very little mobility within sediments but the status of cadmium is less well known.

Fox Lake

Pb-210 and Cs-137 results for Fox Lake cores 1 and 2 are included in Figure 1. Both Pb-210 plots were interpretable with sedimentation rates of 119 $g \cdot m^{-2} \cdot y^{-1}$

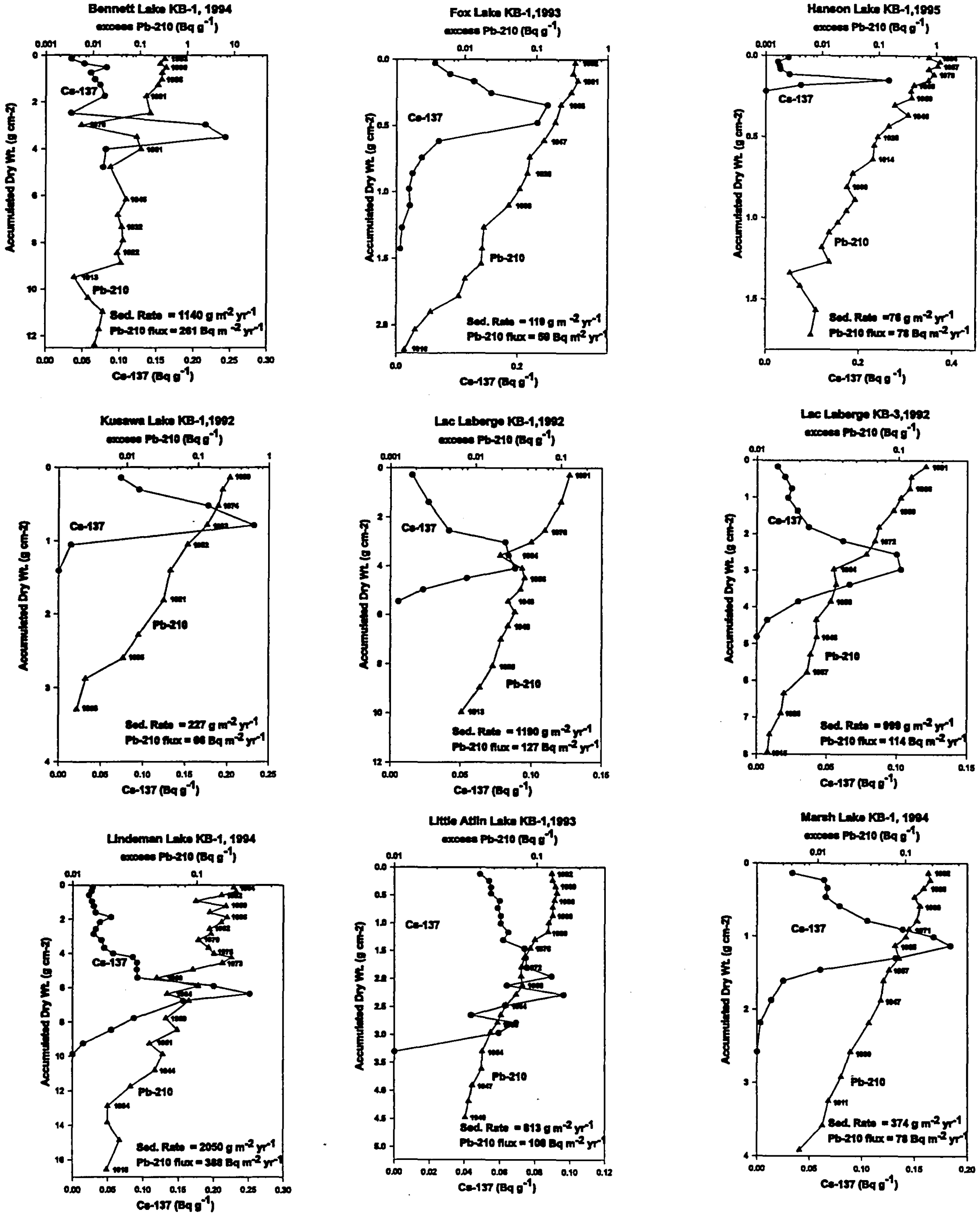

Figure 1. Sediment down-core profiles of lead-210 and cesium 137 from several lakes in the Yukon.

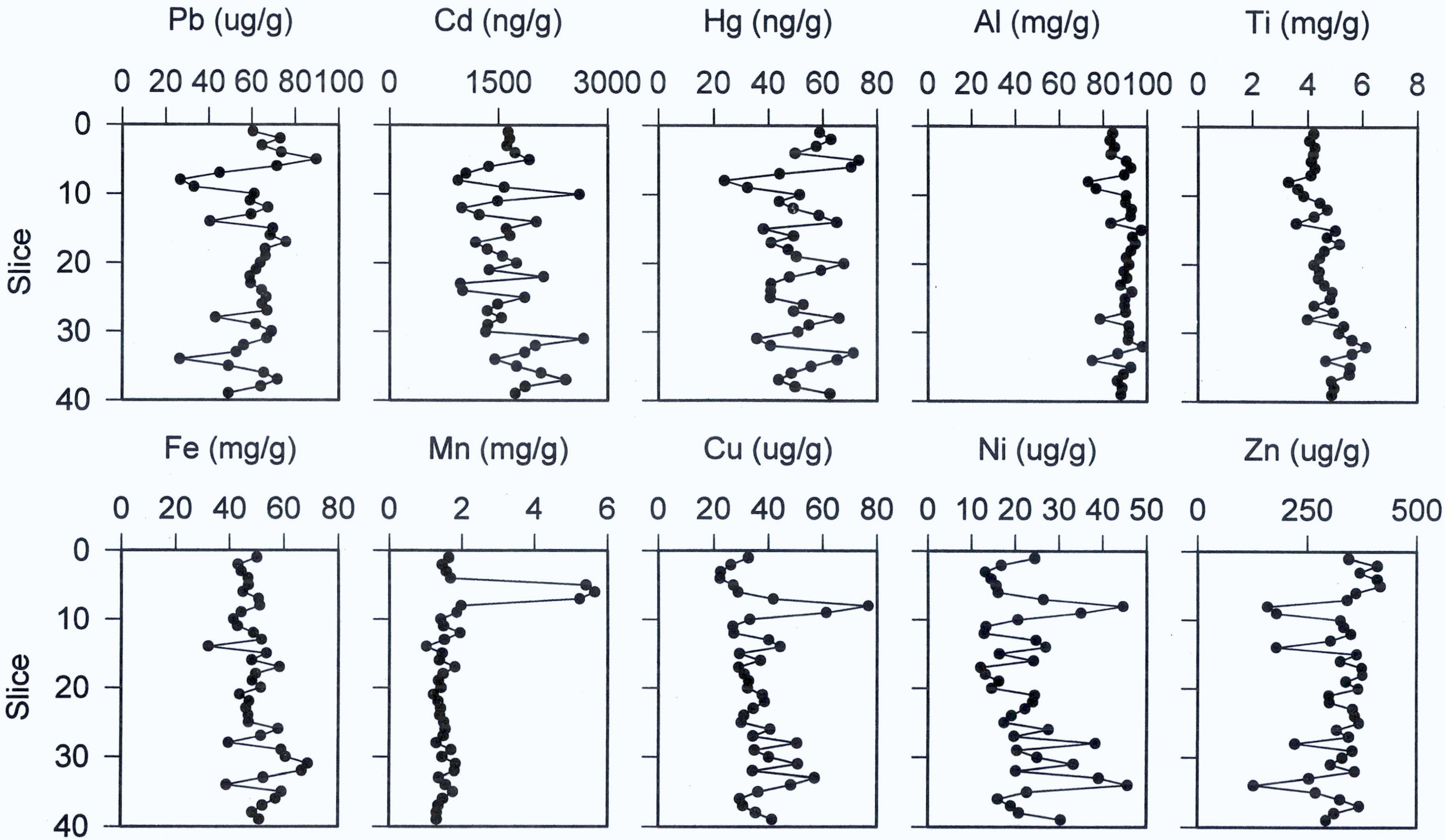

Figure 2. Bennett Lake, Yukon, Core 1, March, 1994

for core 1 and 81·g m^{-2}·y^{-1} for core 2. Lead-210 fluxes were both very low at 59 and 46 Bq·m^{-2}·y^{-1} respectively, so low indeed that the sites may have been subject to erosion. The Pb-210 dates indicated that peak Cs-137 counts were in the mid-1960s. There had clearly been some diffusion of Cs-137, probably in both directions, because trace quantities were detected in slices deeper than the 1940s, before atmospheric testing of fission bombs began. The top slice of core 2 showed a small increase in Cs-137 which may represent a signal from Chernobyl.

These cores have been analysed for eight metals (Figures 3 and 4). Core 1 showed a striking increase in lead starting in slice 8 (Figure 3) which was deposited in the 1930s or 1940s. A similar although less consistent increase in lead is evident in core 2 (Figure 4) from slice 6 which dates from the 1940s or 1950s. Core 2 also shows a distinctive change in inputs of aluminum in slice 6 and this probably indicated a change in the type of soil material being carried into the lake from the drainage. Core 1 also showed an increase in aluminum but only in the top slice. Taken together, these suggest that the increases in lead and aluminum were probably independent events. They may both be related to road building and transportation since the road to Mayo was built in the 1950s (Yukon State of the Environment 1996). The two cores are inconsistent with regard to mercury with core 1 showing a gradual increase over approximately a century but core 2 showing an unusually variable pattern with no clear trend. The pattern in core 2 was increasing prior to the change in erosion event signalled by aluminum. Probably loadings of mercury have increased somewhat to Fox Lake, but they have been obscured in core 2 by a change in erosion and the new sediment has diluted the original sediment. There were no striking increases in zinc in the upper slices of either of the cores. The increased manganese in the top slices of both cores probably reflect normal, within-core movements.

Hanson Lake

There was very little dry material from the Hanson Lake cores because the water content was so high, especially in the upper slices. The Pb-210 and Cs-137 dating has been completed for Core 1 (Figure 1). The core was interpretable with a Cs-137 peak in the 1960s and a sedimentation rate of 76 g·m^{-2}·y^{-1}. Again, there was a small increase in Cs-137 in the top slice which may indicate Chernobyl. Core 2 has not been dated yet, but both cores have been analysed for three metals, Pb, Cd and Hg (Figure 5). Given the small amount of material available, no further analyses for metals has been done since the priority is to analyse these cores for toxaphene. Core 1 showed an increase in lead in about the top 10 slices which would date from the 1940s. There was no corresponding increase in core 2, but this core has not been dated and so it cannot be interpreted yet. Mercury in core 1 was highly variable but it appears to have increased for a period covered by about the top 20 slices deposited over about the past century.

Kusawa Lake

Kusawa Lake core 1 had good profiles for both Pb-210 and Cs-137 (Figure 1). The sedimentation rate was calculated to be 227 g·m^{-2}·y^{-1}. Core 2 had a good Pb-210 profile but the Cs-137 profile was highly aberrant and we have not tried to interpret it. Where Pb-210 and Cs-137 disagree, investigations of discrepancies among dating techniques have shown that Pb-210 agrees better with independent markers like pollen (Blais *et al.* 1995). Core 1 has been analysed for nine metals (Pb, Cd, Hg, Al, Ti, Fe, Mn, Zn and Cu) (Figure 6). There was a large peak in Mn mid-way through the core and a gradual but consistent increase in mercury in about the top third of the core. The manganese peak is taken as a natural process, not an indication of loading. However, mercury appears to have increased for about a century with a plateau for about the past 30 years. This pattern for mercury is consistent with observations in eastern Canada where the source is fallout of atmospheric mercury. If the source to Yukon lakes is regional atmospheric fallout, then we should expect all the lakes to show it unless within-lake processes obscured it.

Lake Laberge

Four cores from Lake Laberge have been analysed for Pb-210 and two of them have been done for Cs-137 (example in Figure 1). Core 3 had a good pattern for both Pb-210 and Cs-137 with the peak for the latter falling in the early 1960s. The sedimentation rate for this core was high, 999 g·m^{-2}·y^{-1}. Core 3 was analysed for seven metals, Pb, Cd, Hg, Fe, Mn, Zn and Cu (Figure 7). Manganese had a large sub-surface peak often observed in cores. Lead levels showed an unusual step-like series of increases throughout most of the core with current levels about twice basal levels. Mercury concentrations were low and tended to increase only slightly towards the top of the core. The high sedimentation rate appears to have been only partially the result of focusing since the Pb-210 flux was 127 Bq·m^{-2}·y^{-1} and so the inputs of suspended matter from the watershed may have diluted and obscured inputs of anthropogenic mercury or lead.

Lindeman Lake

Both cores from Lindeman Lake in northern British Columbia had quite good profiles of Pb-210 and Cs-

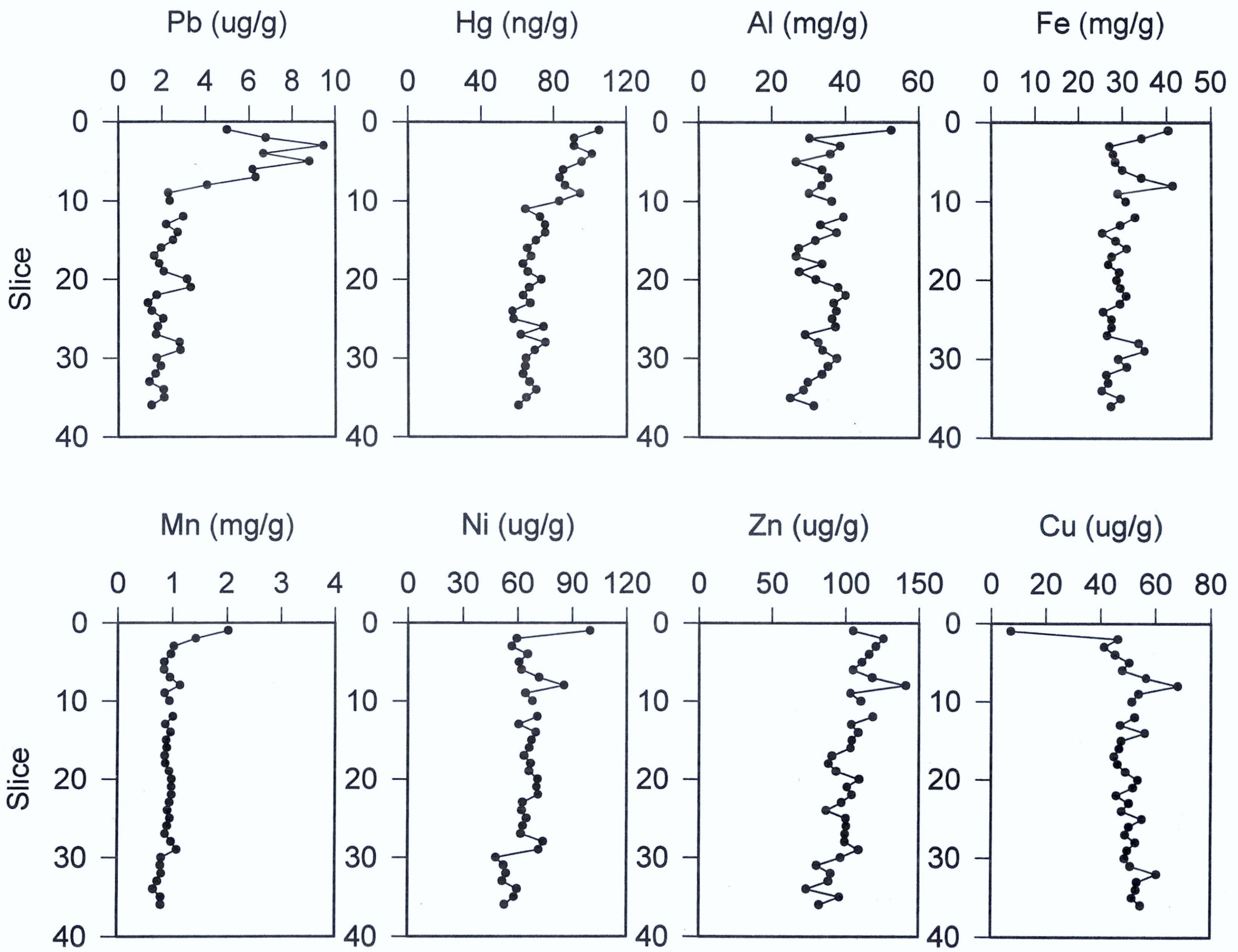

Figure 3. Fox Lake, Yukon, Core 1, March, 1993

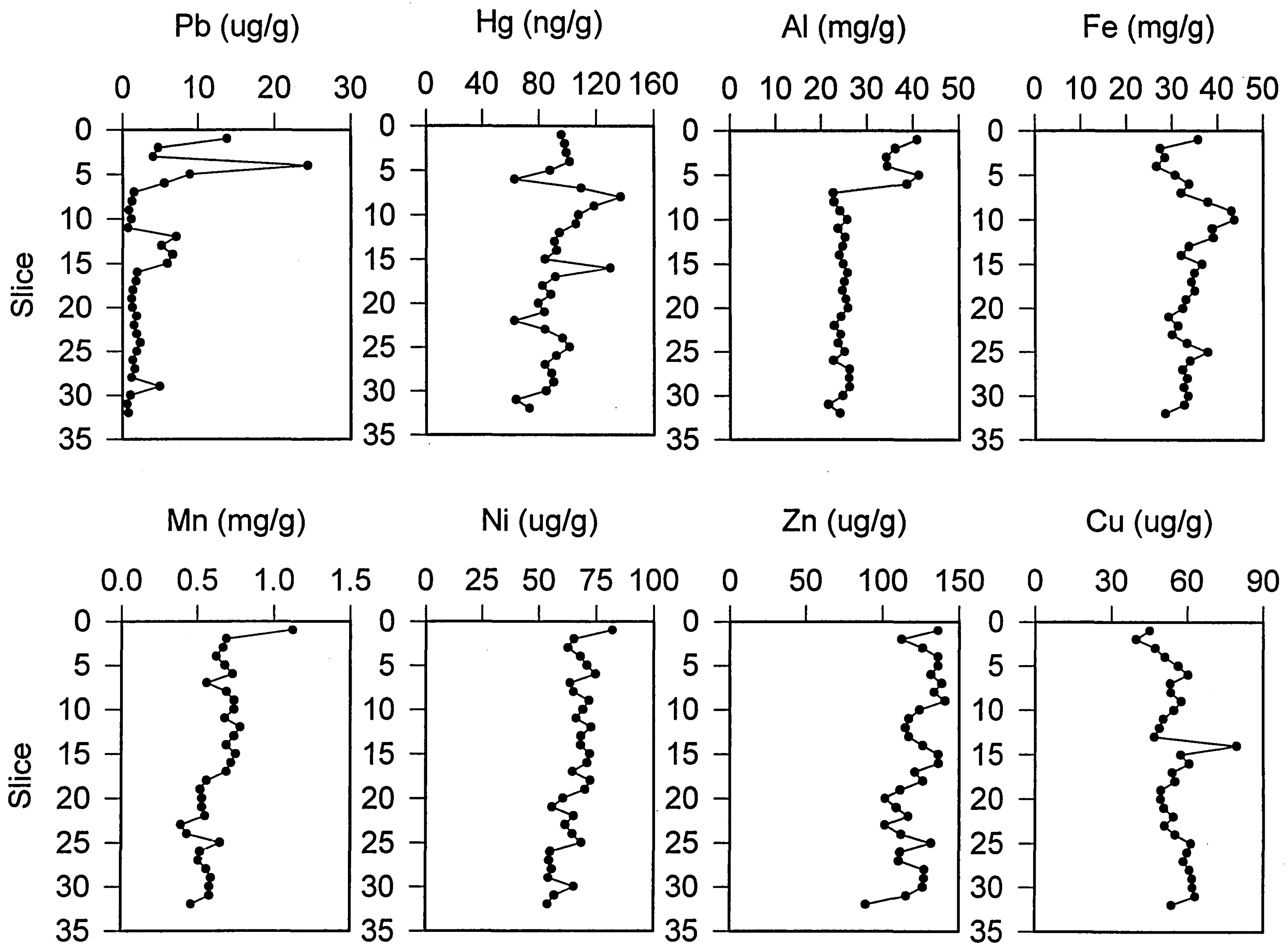

Figure 4. Fox Lake, Yukon, Core 2, February, 1993

137 (Figure 1). The lead-210 dates indicate Cs-137 peaks in both cores in the early 1960s and both also show small Cs-137 peaks in the late 1980s which probably reflect Chernobyl. Sedimentation rates were very high at 2050 and 1570 $g \cdot m^{-2} \cdot y^{-1}$, with high fluxes of Pb-210 indicating much focusing at both sites. Ten metals (Pb, Cd, Hg, Al, Ti, Fe, Mn, Ni, Zn and Cu) have been determined in core 1 and the results were strikingly uniform throughout the depth of the core. There were no indications of recent increases in any of the common contaminating metals (Pb, Cd, Hg). Similarly to Laberge, the very high sedimentation, probably with glacial flour, may have diluted and obscured any changes in lead or mercury over time.

Little Atlin

Cores 1 and 2 have been analysed for Pb-210 and Cs-137 (Figure 1). The Cs-137 peak in core 1 was broad and variable extending from the late 1950s until the mid-1970s while that in core 2 was much sharper with a peak in the early 1960s. The sedimentation rates were calculated to be 813 and 441 $mg \cdot m^{-2} \cdot y^{-1}$ for cores 1 and 2 respectively. Fluxes of lead-210 were low. Both cores have been analysed for the usual suite of 10 metals (Pb, Cd, Hg, Al, Ti, Fe, Mn, Ni, Zn, Cu). There were no consistent indications of increases in Pb, Cd or Hg in upper portions of either core.

Marsh Lake

The Pb-210 and Cs-137 profiles for core 1 are shown in Figure 1 and they were quite good. The Pb-210 dates indicated that the Cs-137 peak was in the mid-1960s with a following small peak which we interpret as Chernobyl. The ten metals have been analysed in core 1. Again with Marsh Lake, there were no indications of increases in Pb, Cd or Hg throughout the core.

PAHs

Little Atlin

Forty-one slices of core 1 have been analysed for the suite of PAHs listed below:

Naphthalene
2-methylnaphthalene
1-methylnaphthalene
Dibenzofuran
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Pyrene
Retene
Benzo(a)anthracene
Triphenylene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(e)pyrene
Benzo(a)pyrene
Indeno(1,2,3-cd)pyrene
Dibenzo(ah)anthracene
Benzo(g,h,i)perylene
Dibenzothiophene
Perylene

The down-core profiles for several of these PAHs are shown in Figure 8. The naphthalenes and their alkylated derivatives often fail to show changes with depth even in cores where the PAHs with higher molecular weights do show gradients. That is the case with Little Atlin Lake where all the PAHs except the 2-ring naphthalenes show trends towards higher levels in the upper slices. These trends indicate that the lake has been receiving increasing inputs of hydrocarbons throughout most of the history of the core. If slice 34 is taken as the basal level, then the increases appear to have started late in the 1800s. Retene has been used as a trace for smoke from the burning of coniferous trees and it has been highly variable throughout the core but with no clear trend. It appears that the other PAHs have been increasing as a result of a source other than wood smoke. Furthermore, there was no increase in lead in this core, and so the source is probably not combustion of gasoline. Even with the consistent increases over time, however, the present-day levels are still very low.

Marsh Lake

Concentrations of PAHs from Marsh Lake were quite variable; some of the less volatile components showed increases in the upper slices but the more volatile ones had peak values well down in the core. Retene, sometimes used as a trace for wood smoke, had high but variable concentrations in the upper 14 slices, dating to the early 1940s.

Organochlorines

Toxaphene

Recent findings (Miskimmin *et al.* 1995, Stern *et al.* 1996) have shown that sediment from lakes which in the past have been treated with toxaphene, yield chromatographic profiles that differ dramatically from those exposed solely to atmospheric sources and from the technical mixture itself. The number of toxaphene congeners observed in the sediment is greatly reduced with the two most prominent components corresponding to 2-*exo*,3-*endo*,6-*exo*, 8,9,10-hexachlorobornane (Hx-Sed, B6-923) and 2-*exo*,3-*endo*,5-*exo*,6-*endo*,8,9,10-heptachlorobornane (Hp-Sed, B7-1001)(Stern *et al.* 1996). This result suggests that most of the original

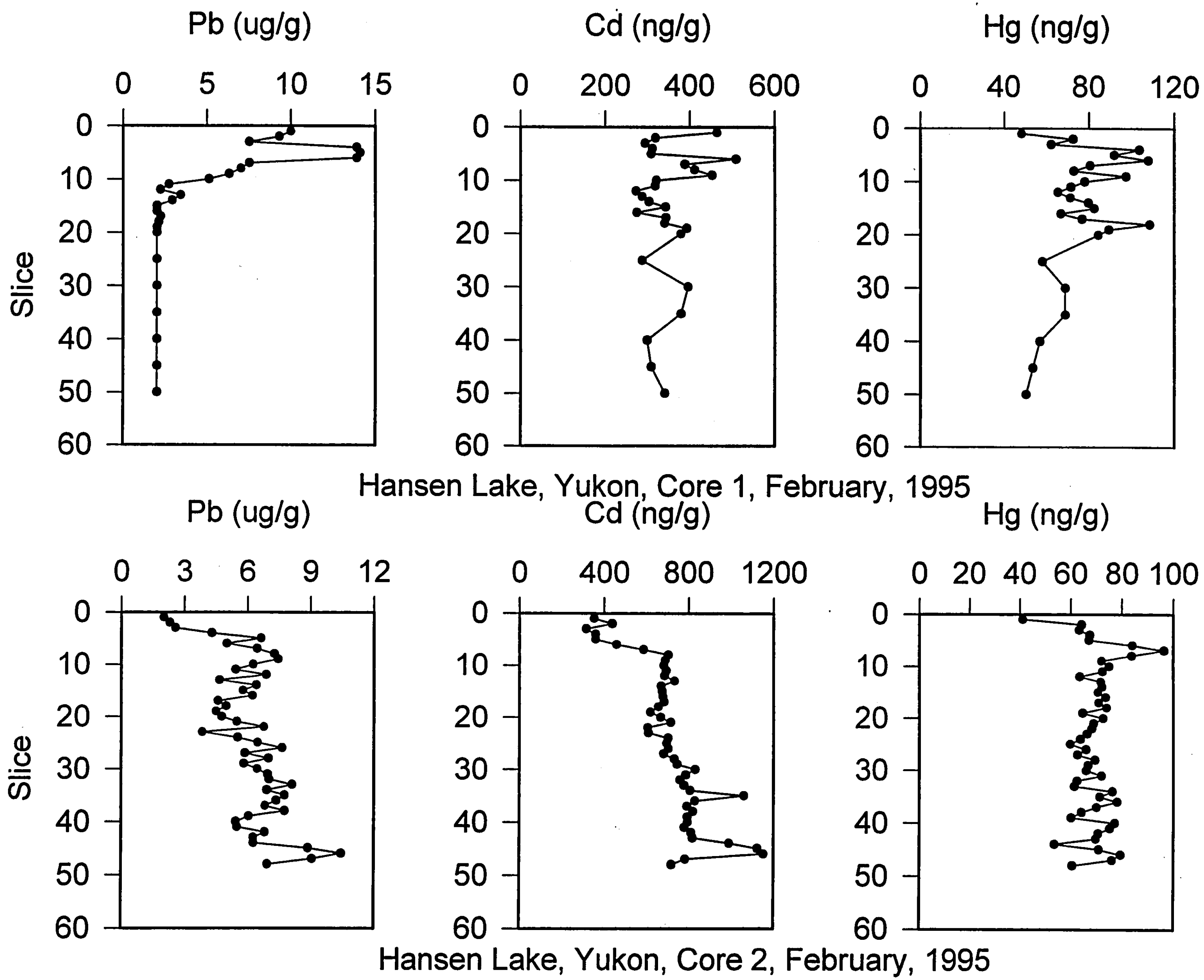

Figure 5. Hanson Lake, Yukon, Cores 1 (top and 2 (bottom), February, 1995

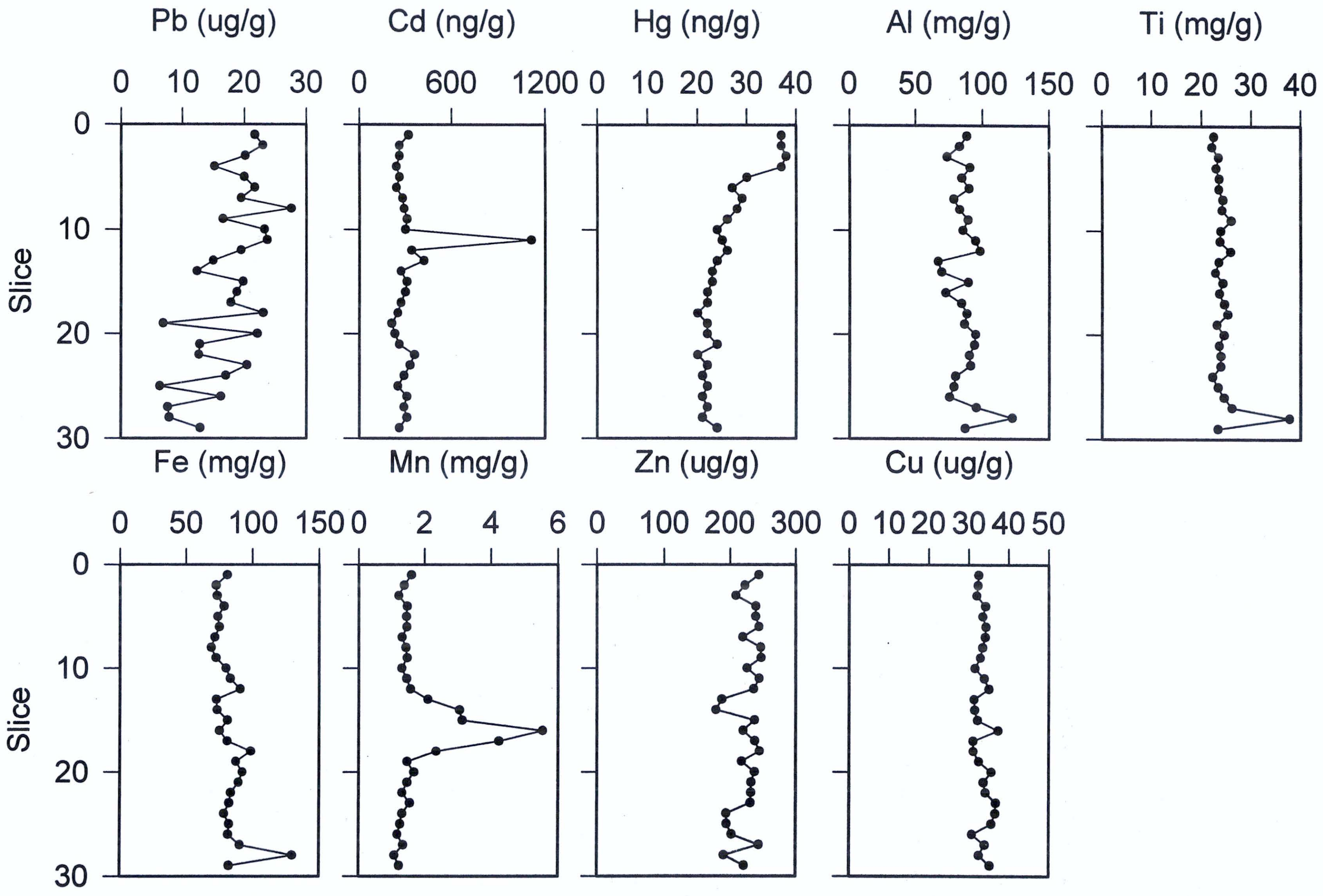

Figure 6. Kusawa Lake, Yukon, Core 1, March, 1992

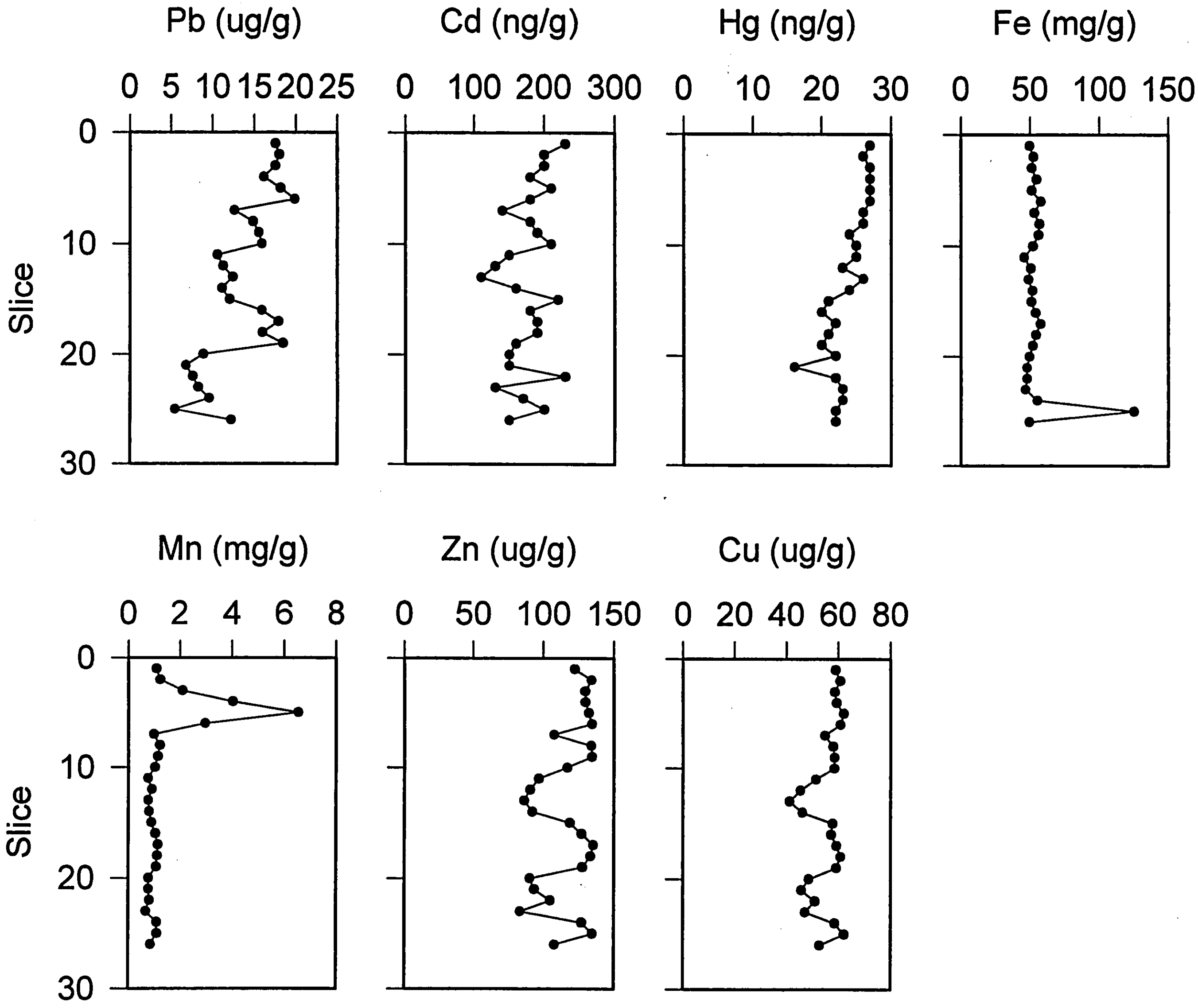

Figure 7. Lake Laberge, Yukon, Core 3, March, 1992

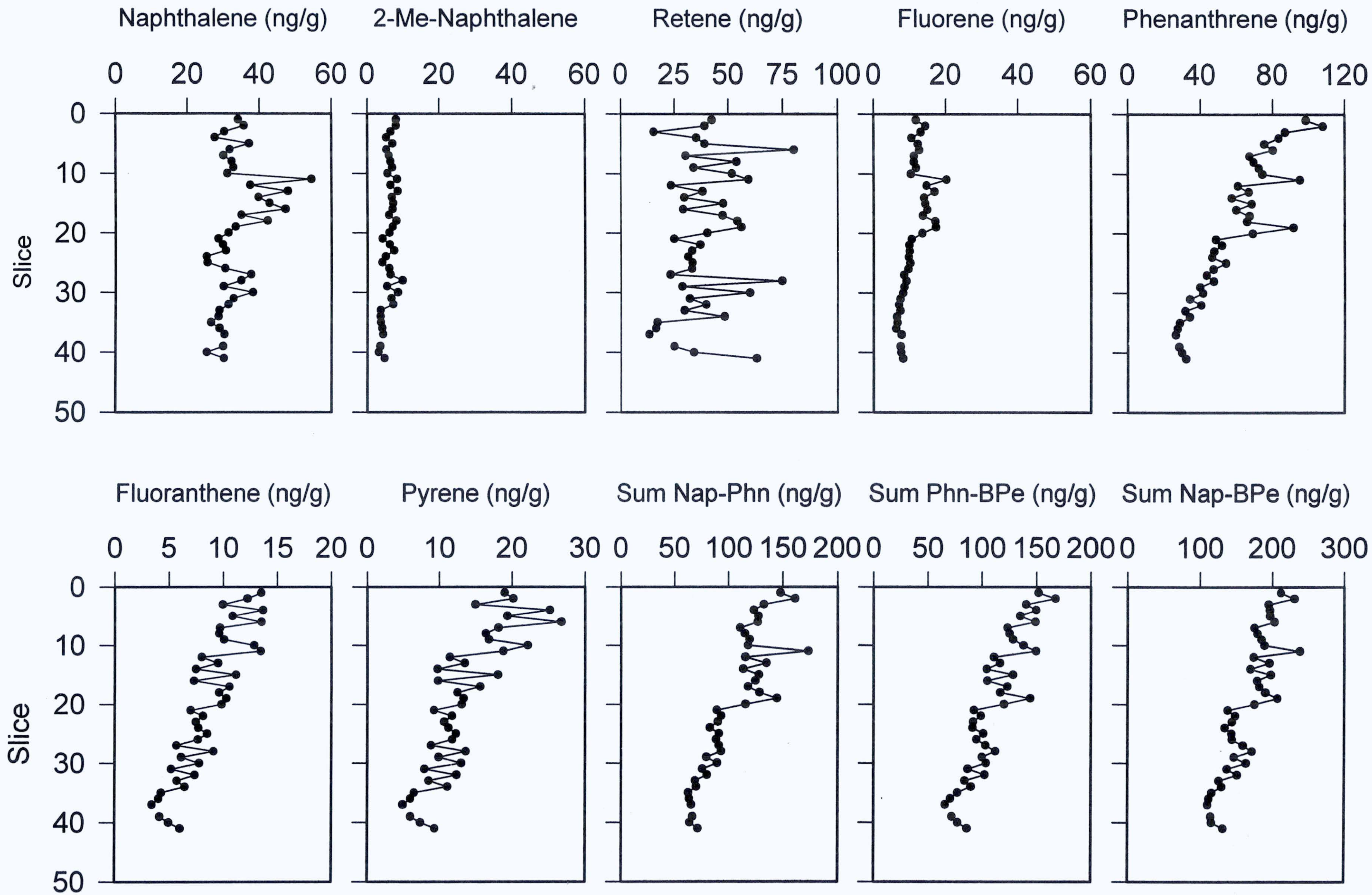

Figure 8. Down core profiles of several PAHs in Little Atlin Lake Core 1, Yukon Territory, 1995

toxaphene mixture has been dechlorinated and is redistributed through the sediment by porewater diffusion (Miskinnin *et al.* 1996).

In the interval July 11–14, 1963, Hanson Lake was treated with toxaphene to extirpate undesirable fish species (Walker *et al.* 1981). This is reflected in the concentration profile of Hanson Lake sediment core 1 (Figure 9) where the levels of toxaphene increase dramatically in 1963 and peak in the mid-1970s. As is normally seen in the sediment of toxaphene treated lakes, the two most predominant toxaphene congeners correspond to B6-923 and B7-100 and no change is observed with years since deposition (Figure 10). Toxaphene concentrations approaching 600 ppm in the surface sediment almost 30 years after its application indicate a need to analyse fish from this lake (primarily northern pike) to determine whether their levels are correspondingly high.

ΣDDT

Concentrations of ΣDDT in surface sediments of Yukon lakes are highly variable ranging from 0.4 $ng{\cdot}g^{-1}$ in Kusawa Lake to 48 $ng{\cdot}g^{-1}$ in Watson Lake. The low DDT concentrations in Lindeman and Kusawa are similar to or lower than levels found in some NWT lakes (Muir *et al.* 1995). Sources of DDT for Kusawa and Lindeman are almost certainly due to atmospheric deposition exclusively. Both lakes have very low levels of p,p'-DDD, a dechlorination product of p,p'-DDT and high proportions of p,p'-DDE. This pattern of DDT degradation products indicates that inputs to the lakes were atmospheric, where p,p'-DDE is the major DDT component. Much higher concentrations of DDT are found in lakes near the Alaska highway including Watson, Laberge, Fox and Hanson. These relatively high levels are probably due to past use of DDT within the watersheds of these lakes for control of biting insects. Historical profiles of DDT in 6 sediment cores from Yukon Lakes are shown in Figure 11. Watson, Fox and Laberge all show elevated DDT plus a high proportion of DDD in slices dated to the late 1940s and early 1950s corresponding to widespread use of DDT in the region. The results for Hanson are unusual because they show a later DDT peak corresponding to sediments dated to the 1970s. Hanson was treated with toxaphene in 1963 but the DDT peak actually occurs a few years later than that for toxaphene. Lindeman lake also has an unusual and as yet unexplained profile with highest DDT in surface slices. Results for Lindeman and Kusawa suggest continued low level inputs of DDT-related compounds to the region consistent with detection of DDT in air at Tagish (Fellin *et al.* 1996). These low level atmospheric inputs probably also explain the presence of DDT in surface slices of Laberge, Fox and Hanson lakes. Watson Lake is a special case. Levels of (DDT at the surface are much higher than other lakes possibly because of diffusion from subsurface sediments. A fresh DDT source at the surface seems unlikely because levels of p,p'-DDT, an indicator of technical DDT, are relatively low in the top 2 cm.

DISCUSSION/CONCLUSION

Yukon lakes generally showed no consistent regional influences of metals. Where individual lakes did show increased inputs of metals, these appeared attributable more to changes within the basins. Fluxes of Pb-210 were generally low and in some instances there was evidence of high degrees of sediment focusing.

Bennett Lake showed no clear indications of contamination with any of the metals often present as contaminants.

Fox Lake has been receiving increasing inputs of lead for approximately the past 40 years, but there were not corresponding increases in zinc. It has also had some changes in the type of material being eroded into the lake, reflected best in the aluminum profile for core 2, possibly as a result of road construction.

Hanson Lake sediments showed an increase in inputs of lead for about the past 50 years in one core but not in a second, undated core. Consistent with the gradual burial of the toxaphene added to the lake in 1963, levels in the sediment have been dropping since the mid 1970s. However, surface sediment concentrations are still greater than .5 ppm and may reflect correspondingly high levels in the fish which populate the lake. Relative to Lindeman and Kusawa Lakes, Hanson Lake along with Fox, Laberge and Watson Lakes have higher DDT concentrations reflecting their proximity to the Alaska highway and the past use of DDT within their watersheds for control of biting insects.

Kusawa Lake had consistent increases in mercury with highest inputs over about the last 30 years.

Lake Laberge had an erratic step-like trend towards increased inputs of lead extending over most of the 20th century but otherwise no clear trends in metals.

Lindeman, Little Atlin and Marsh lakes had no consistent indications of increasing inputs of lead, cadmium or mercury. Little Atlin Lake has had consistent but small increases in PAHs over approximately the past century but current levels are still very low in comparison with many lakes from lower latitudes.

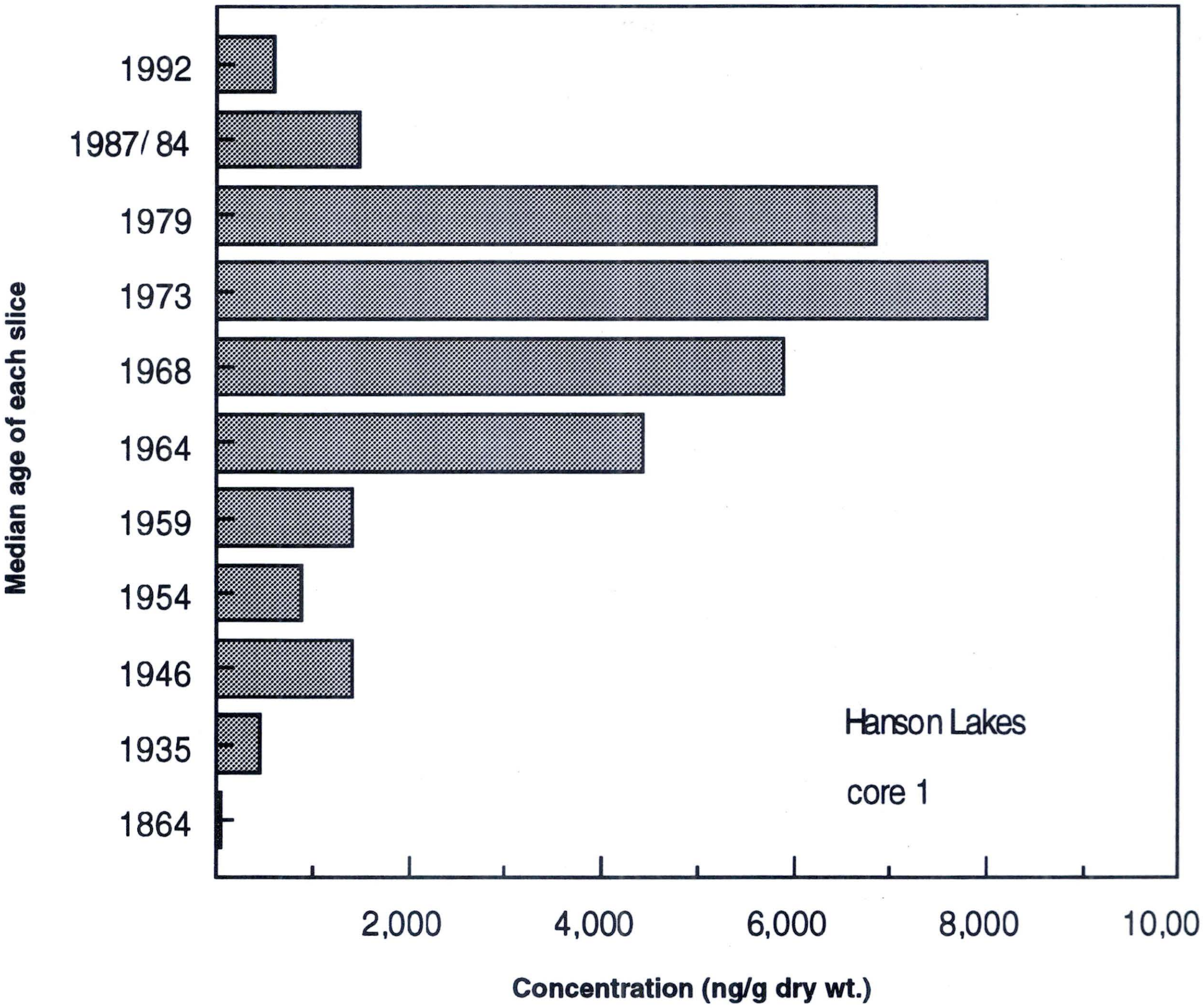

Figure 9. Toxaphene (ng/g dry wt.) in sediment slices from Hanson Lake, Yukon Territory

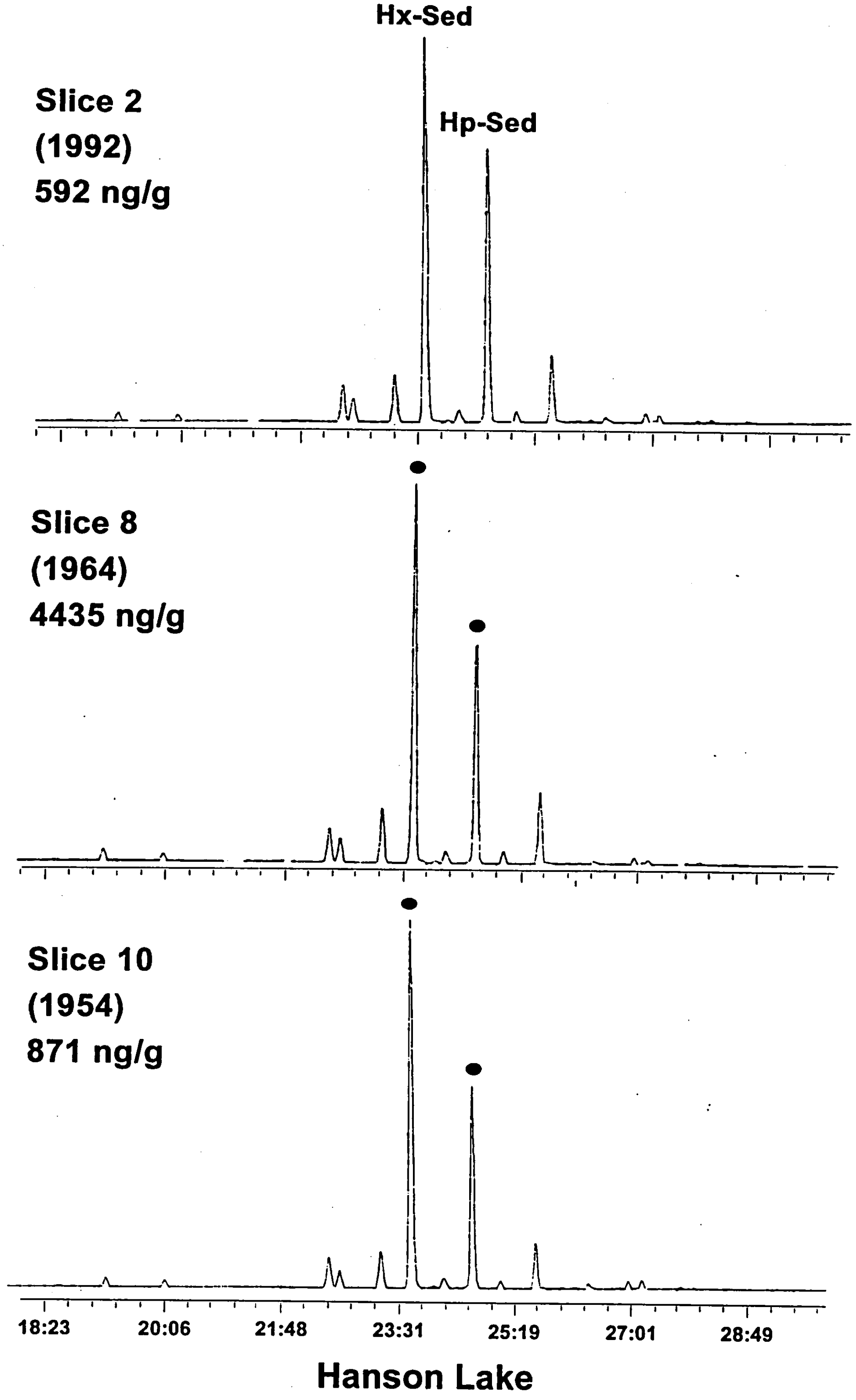

Figure 10. GC-ECNIMS selected ion chromatograom of toxaphene (sum of hexa- to nonachlorinated bornanes) in selected slices of a lake sediment from Hanson Lake.

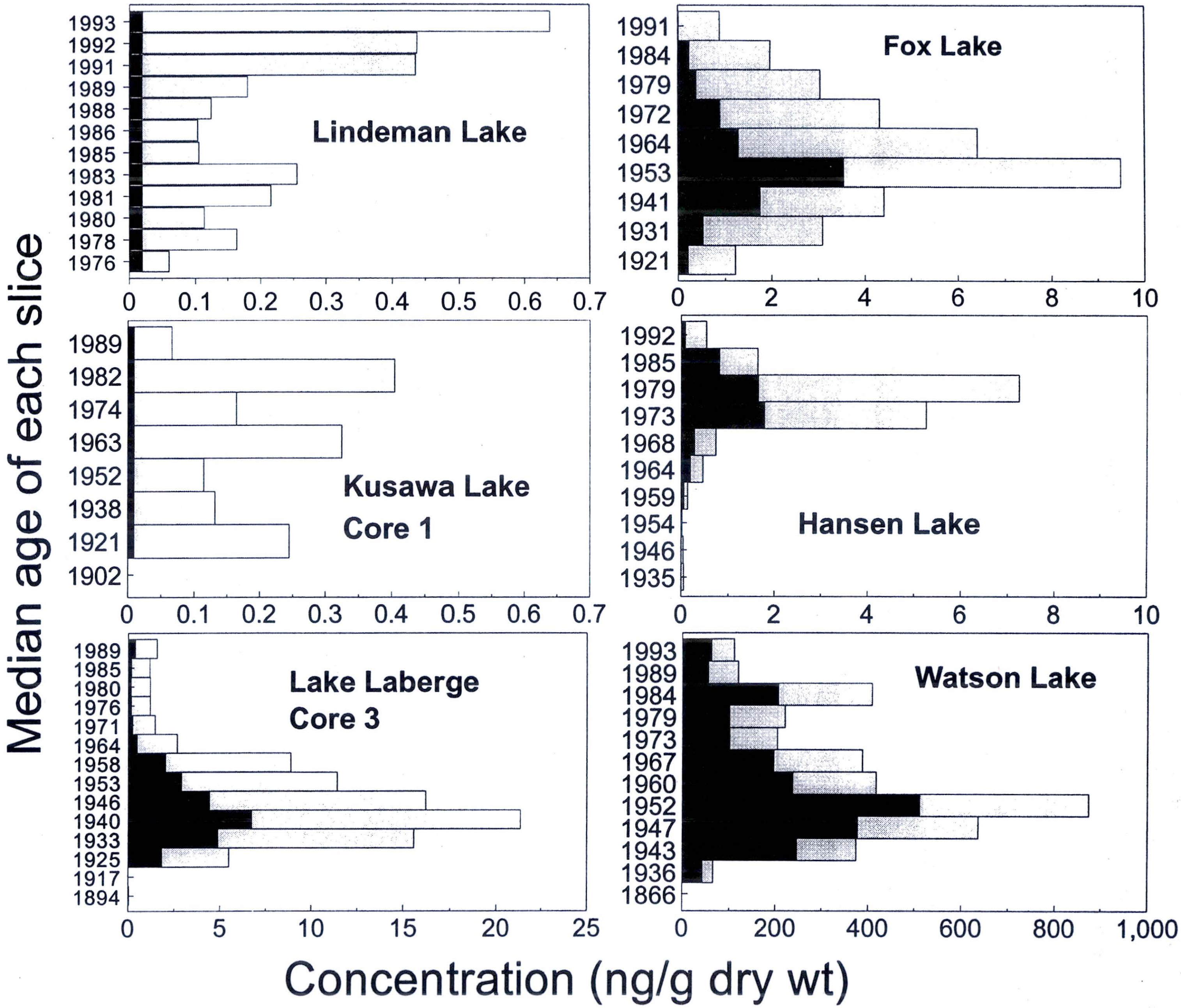

Figure 11. Concentration profiles of ΣDDT and p,p'-DDD in lake sediment cores from the Yukon. Black portions of the bar represent p,p'-DDD, which has been found to increase in proportion to ΣDDT with increasing depth due to anaerobic dechlorionation of p,p'-DDT. Entire bar represents ΣDDT concentration in each slice.

Watson lake had increased lead in upper slices but further interpretation will be possible after dating has been completed.

Expected project completion date: This project has archived several cores for which analyses have not been completed. Completion of them depends on the priority given to this type of work .

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Appendix 1. Cores taken from Yukon Lakes, Northern Contaminants Program, 1992-1995.

Lake	Core	Sample Date	Core Latitude	Core Longitude
Bennett	Ben-1	11-Mar-94	59° 56 16N	134° 55 29W
Fox	Fox-1	10-Mar-93	61° 15 21N	135° 29 14W
	Fox-2	12-Mar-93	61° 12 46N	135° 26 24W
Hanson	Han-1	27-Feb-95	64° 00.534 N	135° 20.775 W
	Han-2	27-Feb-95	64° 01.709 N	135° 21.367 W
Kusawa	Kus-1	16-Mar-92	60° 25 N	136° 10 W
	Kus-2	17-Mar-92	60° 15 N	136° 10 W
Laberge	Lab-1	10-Mar-92	61° 09 N	135° 09 W
	Lab-2	11-Mar-92	61° 09 N	135° 09 W
	Lab-3	11-Mar-92	61° 12 N	135° 11 W
	Lab-4	12-Mar-92	61° 12 N	135° 11 W
Little Atlin	Lat-1	15-Mar-93	60° 16 15 N	133° 59 29 W
	Lat-2	17-Mar-93	60° 15 18 N	133° 56 37 W
Lindeman	Lin-1	10-Mar-94	59° 47 47 N	135° 03 46 W
	Lin-2	10-Mar-94	59° 48 36 N	135° 02 01 W
Marsh	Mar-1	14-Mar-94	60° 29 08 N	134° 19 02 W
	Mar-2	15-Mar-94	60° 30 21 N	134° 20 49 W
Watson	Wat-1	23-Feb-95	60° 06.423 N	128° 46.000 W
	Wat-2	23-Feb-95	60° 06.374 N	128° 47.818 W

CONTAMINANT TRENDS IN FRESHWATER AND MARINE FISH

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Project Team: J. Gibson, K. Koczanski, B. Grift, K. Kidd, G. Stern, G. Tomy, B. Rosenberg, R. Hunt, J. DeLaronde, B. Billeck, A. MacCutcheon, and D. Tenkula

OBJECTIVES

1. To determine temporal and spatial trends in PCBs, organochlorines, PAHs and heavy metals in fish from lakes and rivers in NWT and N. Quebec.
2. To provide information on contaminants to evaluate current risks of exposure to PCBs, toxaphene, and other OCs, PAHs and mercury.

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 in arctic fish was limited while data on temporal trends was nonexistent (Lockhart *et al.* 1992, Muir *et al.* 1990). From the outset, the study focused mainly on top predators such as burbot, lake trout, inconnu, and pike because of their importance in the traditional subsistence fishery and because of interest in biomagnification in top predators. Fish feeding at lower trophic levels, such as lake and broad whitefish, which are also of dietary importance to native people in NWT and the Yukon. and Northern Quebec. 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. However, PAHs have also been determined in fish muscle and bile as part of this project and also under the Slave River Monitoring Program (Peddle *et al.* 1995). The results for research conduced between 1991 and 1994 have been summarized in previous synopsis reports (Muir and Lockhart 1993, 1994, 1996) and presented to the people of NWT and the Yukon at several workshops and public meetings. The budgets for this project in 1995/96 and 1996/97 were reduced by two-thirds from the previous two years. Thus fewer fish were analysed although an effort was made to do more with less. This report deals with results generated during 1995/96 and 1996/97.

ACTIVITIES IN 1995/96 AND 1996/97

Samples

Fish samples provided by DFO personnel from Winnipeg (J. Reist and R. Tallman), Yellowknife (Dave McKenna), and Hay River (George Lowe, DFO Fish Inspection) were used for most analyses. No new collections were made in 1996/97. We used samples provided by Steve Harbicht (DOE Yellowknife), the NWT Renewable Resource officers in Baker Lake and Arviat and Dr. Mark Hermansen (Sanikiluaq). Species analysed for OCs and Hg in 1995/96 and 1996/97 were: arctic char *(Salvelinus alpinus)*, burbot (*Lota lota*), lake trout (*Salvelinus namaycush*), lake whitefish (*Coregonus clupeaformis*), round whitefish *(Prosopium cylindraceum)*, broad whitefish (*Coregonus nasus*) and inconnu (*Coregonus leucichthys*). In addition, samples of muscle and/or bile of long nose sucker (*Catostomus catostomus)*, grayling (*Thymallus arcticus*), round whitefish, mountain whitefish *(Prosopium willamsoni)*, northern pike (*Esox lucius*) and walleye (*Stizostedion vitreum*) were analysed for PAHs over the years 1991 to 1995 and are discussed below.

Sampling locations are given in Tables 1 (OCs), 2 (Hg), and 3 (PAHs). Samples of dorsal muscle and skin were analysed with the exception of burbot, for which liver was analysed. Sex, weight and age (by using ootoliths) were determined for almost all samples. Generally larger numbers of samples were analysed for Hg than for OCs or PAHs.

Analysis

Samples of fish muscle (usually with skin) were analysed for organochlorines (PCB congeners and other OC contaminants [toxaphene, PCCs], chlordane [CHL], and the DDT group). A total of 130 individual OC compounds were determined although not all were detected. A complete list of OC analytes was given in our 1993 report on OCs in marine mammals (Muir 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 (GPC). Extracts were then chromatographed on a Florisil column to separate PCBs, p,p'–DDE and trans-nonachlor (hexane eluate) from most chlorinated bornanes (toxaphene), chlordanes and DDT-related compounds. Florisil eluates were then analysed by capillary gas chromatography with electron capture detection using a 60 m x 0.25 mm id DB–5 column with H_2 carrier gas. Confirmation of PCBs was carried out by GC-mass spectrometry using an HP5971MSD. Toxaphene in samples of mussels and zooplankton was confirmed by high resolution negative ion mass spectrometry using a Kratos Concept GC-MS.

Mercury was determined by hot block digestion followed by cold vapour atomic absorption (AA) spectrophotometry (Hendzel and Jameison 1976, Vijan and Wood 1974).

PAHs in fish muscle and bile were analysed for the EPA priority list of unsubstituted PAHs plus methylated naphthalenes, biphenyl, dibenzofuran, retene and perylene using selected ion GC-MS.

Homogenized fish tissue was Soxhlet-extracted with DCM. Deuterated internal standards were added at the extraction step. The extract was reduced to about 5 mL and lipid removed by GPC as described above. Following GPC the extracts was chromatographed on a silica column (topped with 1 cm alumina) to separate alkanes (Fraction 1; hexane) from PAHs (Fraction 2; DCM:hecane, 1:1). Extracts were analysed by capillary GC (30 m x 0.25 mm DB5MS column) using a HP 5970 MSD for detection of specific fragment ions of PAHs. A four-point calibration table, which included six deuterated internal standard PAHs, was used to quantify PAHs in the fish extracts using an internal standard isotope dilution technique.

Quality assurance

Recovery of internal standards was checked in each sample and samples with low recoveries (generally <60%) were re-extracted. Reference samples of cod liver oil (NIST 1588) were run to check lab performance. Blank and duplicate samples were run approximately every 10 samples to check contamination of reagents and glassware and reproduciblity. During 1995/96 and 1996/97 the laboratory participated in the intercomparison on PCB congeners in standards for the Northern Contaminants Program.

RESULTS

Organochlorines

Mean concentrations of major groups of persistent organochlorines in fish muscle (plus skin) samples from all lakes surveyed were relatively low—i.e. <60 ng/g ww for all major OC groups (Table 1). PCBs and toxaphene were the major OCs detected. Concentrations of PCBs and toxaphene were highest in lake trout and arctic char and lowest in lake whitefish and inconnu. Lake trout from Baker Lake had higher toxaphene levels than did lake trout from five other lakes. This may be related to higher average lipid content (13%) in those fish compared with other lakes (2.5–9.4%). As noted in previous reports, results for toxaphene are reproducible but only approximate the actual chlorobornane concentrations because the technical standard was used for quantitation. Toxaphene patterns varied between species but were generally dominated by two major peak: an octachlorobornane (T_2) and a nonachlorobornane (T_{12}). 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 21% to 75% of toxaphene levels in lake trout. Hexachlorocyclohexanes (sum of α– β– and γ–HCH isomers) and chlorobenzenes (sum of tetra, penta and hexachlorobenzene) were present at much lower concentrations (ΣHCH=1.7–4.6 ng/g ww; ΣCBz=0.3–4 ng/g) than the four major organochlorines. ΣHCH was significantly higher in inconnu from the Slave River than in the same species collected in the lower Mackenzie near Fort Good Hope. Like other coregonids, the inconnu are migratory. Those captured at Fort Good Hope probably migrate from the Mackenzie delta while those in the Slave River may migrate from Great Slave Lake (Tallman 1996). Percent lipids were higher in the Slave River inconnu muscle. Therefore, compared on a lipid weight basis concentrations of most OC groups were higher in the inconnu from Ft. Good Hope than in the Slave River (e.g. ΣPCBs = 448±315 ng/g lw, at Ft Good Hope compared with 78±11 ng/g lw for Slave River samples).

Mussels (*Mya truncata*) collected near Iqaluit were analysed for PCBs and other OCs (Table 1). Levels of all OCs in mussels were very low (<1 ng/g) except for PCBs (7.8 ng/g ww). A similar pattern of OCs was found in *Septentrion* species from Manitounuk Sound (E. Hudson Bay) in which PCBs were about 20 times higher than ΣDDT (Muir *et al.* 1995). The greater sorption of PCBs to sedimenting particles which are filtered by mussels, compared to most other OCs, especially toxaphene and HCH, may account the much higher amounts PCBs. Doidge *et al.* (1993) found low ng/g (ww) levels of PCBs and OC pesticides in blue mussels (*Mytilus edulis*) from six communities in Nunavik.

Table 1. Persistent organochlorines (ng/g ww) in fish muscle from NWT lakes (1995/96); arithmetic means ± standard deviation

	Species	N	% lipid	ΣCBz	ΣHCH	ΣCHLOR	ΣDDT	ΣPCB	Toxaphene
Baker Lake	lake trout	4	13 ± 5.9	2.6 ± 1.1	1.2 ± 0.4	9.4 ± 2.9	12 ± 3.7	42 ± 14	60 ± 28
Maguse Lake	lake trout	13	3.5 ± 1.1	2.9 ± 0.58	1.6 ± 0.29	9.1 ± 1.7	7.8 ± 1.9	27 ± 5.6	26 ± 27
Kaminak Lake	lake trout	9	2.5 ± 1.2	1.9 ± 0.79	1.3 ± 0.66	11 ± 4.0	11 ± 4.2	30 ± 8.5	24 ± 12
Cli Lake	lake trout	6	9.4 ± 3.9	1.3 ± 0.63	0.84 ± 0.32	7.4 ± 3.0	5.9 ± 3.1	24 ± 8.4	19 ± 3.5
ColvilleLake	lake trout	5	3.9 ± 2.3	1.5 ± 0.60	0.89 ± 0.60	5.5 ± 1.4	7.0 ± 3.6	19 ± 3.2	41 ± 9.2
Yaya Lake	lake trout	9	3.0 ± 1.4	2.8 ± 0.94	1.57 ± 0.5	9.1 ± 3.9	7.06 ± 3.83	27 ± 9.7	41 ± 8.5
Baker Lake	lake whitefish	3	5.8 ± 5.0	2.3 ± 0.9	0.73 ± 0.16	3.9 ± 0.54	3.3 ± 0.59	12 ± 2.1	6.7 ± 0.56
Peter Lake	round whitefish	5	6.4 ± 4.6	2.4 ± 1.92	1.36 ± 1.6	5.0 ± 3.4	10.7 ± 6.65	11 ± 7.0	14.1 ± 4.8
Sanikiluaq	arctic char	18	4.9 ± 2.3	2.8 ± 1.3	4.0 ± 2.3	10 ± 4.2	9.6 ± 4.0	30 ± 18	55 ± 30
Baker Lake	arctic char	6	8.1 ± 4.2	3.2 ± 2.1	2.4 ± 1.7	4.4 ± 3.0	5.4 ± 3.1	12 ± 6.0	14 ± 8.2
Mackenzie R., Little Chicago	inconnu	6	3.2 ± 3.2	1.7 ± 1.0	0.4 ± 0.1	5.8 ± 2.2	8.4 ± 4.0	12 ± 5.6	51 ± 40
Mackenzie R., Rampart Rapids	inconnu	5	6.4 ± 4.7	1.7 ± 1.0	0.3 ± 0.2	5.8 ± 2.3	8.3 ± 4.4	12 ± 5.3	57 ± 39
Slave River	inconnu	9	23 ± 5.9	4.6 ± 1.4	1.4 ± 0.3	11 ± 2.9	10 ± 6.0	18 ± 5.2	55 ± 18
Hudson Bay	plankton	4		26 ± 14.5	1.88 ± 0.7	2.5 ± 0.9	4.61 ± 1.0	5.6 ± 1.2	54.5 ± 15
Iqaluit	mussels *(Mya T.)*	6	1.5 ± 0.64	0.27 ± 0.09	0.49 ± 0.07	0.94 ± 0.5	0.64 ± 0.15	7.8 ± 2.2	0.72 ± 0.33

Table 2. Mercury concentrations in fish from NWT, analysed during 1995/96 and 1996/97.

Lake	Year Sampled	Species	N	Mean Hg µg/g ww ± SD
Baker Lake	1995	Lake trout	4	0.248 ± 0.055
Baker Lake	1995	Lake whitefish	3	0.077 ± 0.014
Baker Lake	1995	Arctic char	6	0.047 ± 0.013
Cli	1996	Lake whitefish	36	0.085 ± 0.029
	1996	Lake trout	49	0.876 ± 0.791
ColvilleLake	1992	Lake trout	5	0.061 ± 0.031
Great Slave Lake	1993	Lake trout	10	0.202 ± 0.069
Great Slave Lake	1993	Burbot liver	9	0.060 ± 0.039
Little Doctor	1996	Lake whitefish	18	0.130 ± 0.064
	1996	Lake trout	10	0.393 ± 0.081
	1996	Northern pike	10	0.772 ± 0.367
	1996	Sucker	6	0.195 ± 0.092
	1996	Walleye	18	0.753 ± 0.290
Manuel	1993 & 1995	Lake whitefish	24	0.144 ± 0.057
	1995	Northern pike	10	0.460 ± 0.133
Kaminak	1995	Lake trout	10	0.947 ± 0.292
Maguse	1995	Lake trout	13	0.729 ± 0.371
Peter Lake	1994	Round whitefish	5	0.168 ± 0.131
Tagatui	1996	Lake whitefish	20	0.035 ± 0.018
	1996	Northern pike	16	0.170 ± 0.121
Turton	1996	Lake whitefish	12	0.113 ± 0.030
	1996	Lake trout	55	0.600 ± 0.122
Mackenzie R., Little Chicago	1995	Broad whitefish	54	0.057 ± 0.028
	1995	Inconnu	16	0.195 ± 0.040
Mackenzie R., Ramparts	1995	Broad whitefish	82	0.057 ± 0.031
	1995	Inconnu	43	0.190 ± 0.083
Slave River	1994	Inconnu	9	0.099 ± 0.019
Yaya Lake	1995	Lake trout	9	0.430 ± 0.202

Mercury

Mercury was determined in 553 fish samples from NWT during 1995/96 and 1996/97, the majority from the Mackenzie River basin (Table 2). Mercury levels were generally low in inconnu and broad whitefish from Ramparts Rapids and Little Chicago, fishing areas near Ft. Good Hope, with mean concentrations ≤0.2 µg/g ww (the level for consumption of subsistence fish set by Health Canada). Lower concentrations of mercury were found in inconnu from the Slave River (0.1±0.02 ng/g ww). Lake trout had the highest mercury levels of fish species analysed. Highest mercury levels were found in trout from Cli, Kaminak, Maguse and Turton lakes (Table 2). Lake trout from Great Slave Lake and Baker Lake had the lowest mercury levels of all trout analysed, averaging 0.20 and 0.25 ng/g ww, respectively.

Mercury levels in fish with a given lake vary among species and with size or age of the animals especially in piscivores such as pike and lake trout (Muir and Lockhart 1996). The relationship between fish size and mercury concentration in broad whitefish and inconnu is illustrated in Figure 1. Here mercury is weakly correlated with length of broad whitefish and not correlated with length of inconnu. The lack of variation of mercury with length may be partly the result of collection of a limited range of sizes because of use of single net sizes.

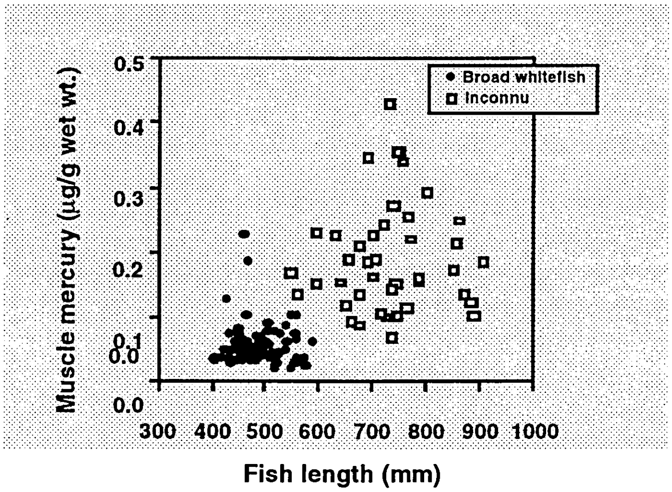

Figure 1. Relationship of mercury concentrations in muscle of broad whitefish and inconnu and fish length. Samples from Ramparts Rapids, Mackenzie River near Ft. Good Hope.

Table 3. Concentrations of polyaromatic hydrocarbons (ng/g ww) in freshwater fish from NWT (1992–95)

Location	Species	Tissue[1]	N	Naphthalene	ΣMe-naphth[2]	Acenaphthylene	Fluorene	Phenanthrene	Fluoranthene	Pyrene	Total PAH[3]
Ron Lake	Arctic grayling	M	6	2.47 ± 1.20	2.76 ± 1.28	0.09 ± 0.17	0.09 ± 0.08	0.25 ± 0.07	0.06 ± 0.05	0.07 ± 0.05	5.83 ± 2.86
Cam Lake		M	8	2.44 ± 0.72	3.28 ± 1.32	0.05 ± 0.05	0.04 ± 0.07	0.28 ± 0.05	0.02 ± 0.03	0.02 ± 0.04	6.19 ± 2.03
Lac de Gras	Lake trout	M	18	4.69 ± 2.34	1.91 ± 2.60	0.02 ± 0.05	0.09 ± 0.29	0.36 ± 0.24	0.07 ± 0.06	0.09 ± 0.07	7.26 ± 3.46
Ron Lake		M	11	1.89 ± 0.37	2.39 ± 0.50	<0.01 ± 0.00	0.04 ± 0.07	0.25 ± 0.05	0.02 ± 0.04	0.06 ± 0.07	4.70 ± 0.91
Cam Lake		M	11	2.58 ± 0.80	3.92 ± 1.47	0.07 ± 0.07	0.17 ± 0.08	0.27 ± 0.06	0.02 ± 0.03	0.02 ± 0.03	7.08 ± 2.24
Hay River	Northern pike	M	5	2.24 ± 1.24	0.27 ± 0.20	0.01 ± 0.03	<0.01	0.33 ± 0.09	0.14 ± 0.02	0.12 ± 0.06	3.27 ± 1.63
Hay River		B	3	39.4 ± 8.14	39.5 ± 11.9	<0.01	<0.01	5.35 ± 3.05	<0.01	<0.01	84.2 ± 22.7
Lac de Gras	Round whitefish	M	21	3.55 ± 1.68	2.91 ± 3.29	0.03 ± 0.04	0.03 ± 0.06	0.30 ± 0.12	0.07 ± 0.05	0.14 ± 0.08	7.34 ± 4.42
Cam Lake		M	10	2.72 ± 0.92	2.30 ± 0.67	0.02 ± 0.04	0.06 ± 0.07	0.22 ± 0.04	0.00 ± 0.02	0.03 ± 0.05	7.27 ± 2.30
Ron Lake		M	10	2.14 ± 0.69	4.19 ± 1.40	0.07 ± 0.08	0.10 ± 0.12	0.19 ± 0.03	0.05 ± 0.05	0.08 ± 0.05	4.97 ± 1.45
Hay River	Walleye	B	3	80.8 ± 57.8	78.7 ± 54.0	<0.01	4.00 ± 6.93	10.7 ± 8.23	<0.01	1.94 ± 1.84	176 ± 119

[1] M=muscle, B= bile

[2] Sum of 1- and 2-methylnaphthalene

[3] Total of 25 aromatic hydrocarbons (not including retene and perylene)

PAHs

Table 3 summarizes results for PAHs in fish muscle and bile samples mainly from the southwestern NWT waters. Low concentrations of 3- and 4-ring PAHs (naphthalene, fluorene, phenanthrene, fluoranthene) were found in muscle of all species analysed. Higher molecular weight PAH such as benzoanthracene, benzofluoranthene or benzo(a)pyrene, were not detected (<0.01 ng/g ww) in muscle of any of the five species. Similar results were found for PAHs in fish from the Slave River and control lakes (Leland Lake) in the Slave River study (Peddle *et al.* 1995). Combining these results with previous work (all by DFO Winnipeg) shows that there are no spatial trends in total PAHs concentrations, for example, between fish from the Slave River and from lakes in the region observed. Previous studies of burbot liver and muscle from the Mackenzie River also showed low ng/g of most 2- or 3-ring PAH and non-detectable concentrations of the higher molecular weight compounds (Lockhart *et al.* 1989). Low ng/g of PAHs are also found in Great Lakes fish (Lawrence and Weber 1984). Bile from long nose sucker, mountain whitefish and northern pike had much higher total PAH levels (PAH metabolites were not analysed) than muscle. This reflects the ability of fish to rapidly excrete aromatic hydrocarbons (for e.g., as glucuronide conjugates in the bile) and helps to explain the low levels in muscle.

CONCLUSIONS AND UTILIZATION OF RESULTS

As results for additional lakes and larger sample sizes of fish are obtained in this study, the picture that emerges is one of relatively low levels of persistent organochlorines in most species within NWT. Where higher levels have been observed—in Peter Lake for example (Muir and Lockhart 1996)—it is for small numbers of very old and large lake trout. The exception to this is burbot liver, which has higher levels of organochlorines than are found muscle of other piscivores such as lake trout (Evans 1996, Muir and Lockhart 1996). For mercury, on the other hand, there are relatively high levels in important subsistence fish species—that is, levels approaching or exceeding Health Canada's subsistence fish guideline of 0.2 μg/g ww in many cases.

This project has provided data on contaminants for most regions of the NWT but there are still major gaps in spatial trend information, especially for the archipelago, Northern Quebec, Northern Labrador, and to a lesser extent, the western NWT. Information is also limited on levels of organochlorines and metals in marine biota. 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 those results are reported elsewhere in this volume.

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 and G. Stephens (DIAND, Water Resources, Yellowknife).

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SPATIAL AND TEMPORAL TRENDS OF PCBS, ORGANOCHLORINE PESTICIDES AND CHLORINATED DIOXINS/FURANS IN ARCTIC MARINE MAMMALS

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OBJECTIVES

Short-term

1. To determine spatial trends in PCBs and other organochlorines in important marine mammal species including ringed seals, walrus, beluga and narwhal.
2. To provide data on contaminant levels in marine mammal tissues as part of surveys of dietary contamination and for use by the Arctic Monitoring and Assessment Program (AMAP).
3. To isolate and identify new contaminants that may be present.

Long-term

1. To document the spatial and temporal trends of bioaccumulating substances in the arctic marine ecosystem, using marine mammal tissues as bioindicators, in order to identify the magnitude, geographic extent of the problem and predict its duration.

DESCRIPTION

People in Arctic coastal communities consume marine mammals as part of their traditional diets. Information is needed to evaluate current risks of exposure to PCBs via consumption of skin, blubber and other tissues. Surveys have shown the presence of a wide range of organochlorine contaminants in Arctic marine mammals throughout the Arctic. As a result of this project (Muir 1993, 1994, 1996) and work by Addison (Addison 1992, Beck *et al.* 1994) there is a growing dataset 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. 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.

By comparison with the relatively large dataset on ortho-substituted PCBs there is much more limited information of levels of the toxic non-ortho-substituted congeners and chlorinated dioxins/furans (PCDD/Fs) in marine mammals. Co-planar PCBs are isostereomers of 2,3,7,8-TCDD and have similar mode of action; induction of hepatic mixed function oxidase (MFO) enzymes, immunotoxicity, teratogenicity and embryotoxicity (Safe 1990). Surveys of co-planar PCBs in arctic marine mammals (Ford *et al.* 1993) have indicated that planar PCBs account for most of the "TCDD equivalents" in the samples analysed. Further work is needed to fully characterize the spatial and temporal trends in coplanar PCBs and PCDD/Fs in marine mammals.

The information on levels and on spatial and temporal trends of persistent organochlorine contaminants 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.

This project combines two projects from previous years, (1) Spatial and temporal trends of organochlorines in arctic marine mammals (Muir) and (2) Planar PCBs, chlorinated dioxins/furans and related compounds in arctic marine mammals and fish (Muir). A third project "Long-term trends in organochlorines in eastern and western arctic seal blubber (Addison) is reported separately.

ACTIVITIES IN 1995/96 AND 1996/97

Samples

Beluga blubber samples were obtained from the 1995 hunt at Hendrickson Island in the Mackenzie Delta (D. Metner, DFO). Additional blubber samples were analysed from the 1994 hunts at Sanikiluaq and Lake Harbour (Southeast Baffin Island) (samples from R. Stewart DFO). Beluga blubber samples from Grise Fiord were analysed from the archive maintained at the Freshwater Institute (FWI) (R. Stewart and S. Innes). Beluga blubber samples from Cook Inlet (Alaska) provided by Paul Becker (National Institute of Standards and Technology, Charleston, SC) were analysed for comparison with Canadian arctic animals. Walrus blubber samples from Thule (Greenland) provided by Dr. Erik Born (Greenland Environmental Research Institute, Copenhagen, DK) were analysed for comparison with results from Canadian arctic animals. Ringed seal blubber samples were obtained from Quaqtaq (Nunavik) by B. Doidge (Kuujjuaq Research Centre) and from Grise Fiord (by S. Innes). Narwhal blubber samples were obtained from Pond Inlet (1994) and from archived samples (1982).

A paper on the elevated levels of PCBs and organochlorine pesticides in walrus was published in *Environmental Pollution.* A paper (in collaboration with M. Weis, University of Windsor) on the spatial trends of organochlorines in ringed seals using the data from more than 200 animals from 14 locations collected between 1986 and 1989 was published in *Environmental Pollution* in 1997.

Methods

All animals were aged by counting tooth growth layers. Samples of blubber were analysed for 90 PCB congeners (includes co-eluting congeners) and 40 other OCs 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 (ΣCHL) 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).

Non-ortho or coplanar PCBs (CB 77, 126 and 169) (nPCBs) were determined in extracts of ringed seal blubber (2 g). Separate fractions of the sample extracts had been analysed for organochlorines (Muir 1993). The methodology followed that described by Ford *et al.* (1993). In brief: Co-extractive lipids in the extracts were removed by gel permeation chromatography (GPC) on a BioBeads SX3 column. Internal standards of ^{13}C-CBs 77, 126 and 169 along with a ^{13}C-mixture of 2,3,7,8-substituted tetra- through octachlorodioxin/furans (PCDD/Fs)(Cambridge Isotope Labs, Andover MA) were added prior to the GPC step. The nPCBs and PCDD/Fs were then isolated from non-planar organochlorines using a carbon (AX21) column. The coplanar PCBs along with PCDD/Fs were reverse-eluted from the carbon column with toluene. Samples were then analysed for nPCBs by GC-low resolution mass spectrometry using a HP5971 MSD in selected ion mode. Results for the analysis of PCDD/Fs in the samples are not yet available.

Quality assurance

Internal standard recoveries (aldrin and octachloronaphthalene) 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 1995/96 and 1996/97 the laboratory participated in the intercomparison on PCB congeners and organochlorines conducted by J-P. Zhu (this volume) for the Northern Contaminants Program. A paper describing an interlab comparison of our results with those of two other leading laboratories (NIST, Gaithersburg Va; H. Ballschmiter, Univ. of Ulm, Germany) in the field of organochlorine analysis was published in Chemosphere (Schantz *et al.* 1996).

RESULTS

During 1995/96 beluga whale blubber samples were analysed from five locations, four in the Canadian Arctic. This completed the analysis of organochlorines all major beluga stocks in the Canadian Arctic during the period 1993-95 and enabled some temporal trend comparisons because the contaminant levels in same stocks were studied during the 1980s (Muir *et al.* 1990). Mean concentrations of major organochlorine (OC) groups in beluga blubber samples analysed in 1995/96 and 1996/97 are listed in Table 1. As has been found in other surveys, toxaphene was present in the highest concentrations of all the major OC in beluga tissues. Total PCBs (ΣPCB) and total DDT- related compounds (ΣDDT) were present at similar concentrations. Chlordane-related compounds (ΣCHL) are also important contaminants in beluga blubber although not present at levels as high as those of ΣDDT or ΣPCB. Male beluga from Sanikiluaq (Belcher Island area in southern Hudson Bay) had higher ΣDDT than ΣPCB. Recent results have shown that ΣDDT/ΣPCB ratios ≈ 1 in Hudson Bay and southeast Baffin belugas but are generally >2 in blubber from male beluga from other locations (Muir 1994, Table 1).

Table 1. Concentrations (ng/g ww) of major organochlorines in beluga, narwhal, ringed seal, and walrus blubber, 1995–97[1]

Species	Location	Year	Sex	N	% lipid	ΣCBz	ΣHCH	ΣCHL	ΣDDT	ΣPCB	Toxaphene	Dieldrin
Beluga	Hendrickson Is.	1995	M	19	93 ± 1	697 ± 201	363 100	1,871 ± 699	3,263 ± 1,250	4,452 ± 858	4,698 ± 1,033	321 ± 112
					88 - 95	280 - 989	205 - 547	951 - 3,195	1,043 - 5,032	2,495 - 5,753	3,009 - 6,573	186 - 516
Beluga	Cook Inlet[2]	1992	F	6	87 ± 8	164 ± 78	167 50	366 ± 160	878 ± 477	1,737 ± 784	1,790 ± 698	69 ± 28
					72 - 93	63 - 269	103 - 245	123 - 594	244 - 1,639	588 - 2,764	642 - 2,596	28 - 100
Beluga	Cook Inlet[2]	1992	M	9	88 ± 7	207 ± 85	208 62	461 ± 186	1,601 ± 905	2,596 ± 1,144	2,282 ± 959	86 ± 42
					70 - 92	66 - 365	85 - 309	165 - 817	390 - 2,953	895 - 4,727	952 - 4,316	33 - 185
Beluga	Sanikiluaq	1994	F	10	93 ± 2	254 ± 122	273 79	1,961 ± 921	3,047 ± 2,559	3,344 ± 1,838	7,185 ± 3,614	397 ± 177
					90 - 97	82 - 445	156 - 368	705 - 3,564	575 - 9,306	1,111 - 7,064	2,848 - 13,769	143 - 647
Beluga	Sanikiluaq	1994	M	8	94 ± 1	494 ± 255	439 124	4,117 ± 1,475	10,363 ± 7,984	6,557 ± 2,252	14,013 ± 6,530	916 ± 334
					93 - 96	220 - 883	308 - 699	2,362 - 6,456	2,074 - 21,660	3,521 - 9,080	8,992 - 28,906	612 - 1,639
Beluga	Lake Harbour	1994	F	5	93 ± 1	664 ± 388	522 139	2,890 ± 1,310	4,134 ± 2,150	4,643 ± 2,210	8,299 ± 3,563	786 ± 398
					91 - 95	232 - 1,241	364 - 703	932 - 4,363	1,001 - 6,229	1,403 - 7,425	2,910 - 11,824	290 - 1,239
Beluga	Lake Harbour	1994	M	6	91 ± 4	1,305 ± 781	515 163	4,236 ± 1,669	6,964 ± 3,303	6,974 ± 2,171	14,551 ± 6,361	1,447 ± 661
					86 - 96	763 - 2,804	356 - 716	3,113 - 7,533	4,264 - 11,416	4,836 - 10,554	8,696 - 26,063	899 - 2,606
Beluga	Grise Fiord	1985–87	F	3	95 ± 0	437 ± 115	375 252	2,843 ± 1,808	7,150 ± 7,876	6,377 ± 3,066	2,291 ± 1,075	8,273 ± 3,514
					94 - 95	326 - 556	92 - 572	812 - 4,275	1,394 - 16,126	2,944 - 8,845	1,274 - 3,415	4,223 - 10,525
Beluga	Grise Fiord	1985–87	M	11	93 ± 1	358 ± 151	268 189	1,870 ± 1,313	2,465 ± 1,373	5,077 ± 2,329	1,950 ± 836	6,522 ± 2,823
					90 - 95	99 - 533	35 - 599	356 - 4,451	624 - 5,171	2,455 - 9,346	846 - 3,612	2,583 - 11,044
Beluga muktuk	East Hudson	1995	M&F	14	19 ± 9	38 ± 17	31 11	220 ± 76	277 ± 111	828 ± 306	185 ± 91	31 ± 10
					3 - 34	11 - 67	11 - 46	62 - 311	90 - 437	221 - 1,254	34 - 302	16 - 45
Narwhal	Pond Inlet	1994	F	7	95 ± 2	333 ± 65	124 28	1,674 ± 532	4,753 ± 702	2,902 ± 561	4,632 ± 386	139 ± 51
					92 - 97	247 - 401	83 - 178	1,308 - 2,824	3,737 - 5,722	2,253 - 3,696	3,971 - 5,209	86 - 226
Narwhal	Pond Inlet	1994	M	7	95 ± 1	873 ± 419	213 75	3,408 ± 844	9,303 ± 502	7,542 ± 982	14,996 ± 3,846	502 ± 153
					93 - 97	639 - 1,812	153 - 363	2,762 - 5,253	8,657 - 9,901	6,673 - 9,328	11,436 - 23,035	301 - 728
Narwhal	Pond Inlet	1982	F	8	94 ± 2	378 ± 91	134 40	1,785 ± 484	4,820 ± 1,774	3,599 ± 1,114	4,977 ± 2,010	168 ± 92
					92 - 97	221 - 506	71 - 201	755 - 2,265	1,247 - 7,096	1,384 - 4,664	1,317 - 7,081	63 - 312
Narwhal	Pond Inlet	1982	M	9	93 ± 2	733 ± 432	175 88	2,855 ± 1,074	6,971 ± 2,686	5,900 ± 2,275	12,587 ± 6,111	434 ± 177
					91 - 96	211 - 1,648	55 - 330	1,119 - 4,780	2,851 - 10,945	2,237 - 8,589	3,802 - 20,961	174 - 662
Ringed seal	Quaqtaq	1994	F	7	96 ± 1	339 ± 160	109 43	1,218 ± 567	1,466 ± 804	2,887 ± 1,317	4,262 ± 2,118	150 ± 61
	(Hudson Strait)				94 - 97	74 - 384	59 - 143	562 - 1,099	468 - 1,021	1,227 - 3,532	1,658 - 2,632	42 - 132
Ringed seal	Quaqtaq	1994	M	11	95 ± 1	144 ± 79	79 20	681 ± 188	648 ± 196	1,532 ± 476	2,001 ± 377	84 ± 25
	(Hudson Strait)				93 - 97	57 - 309	58 - 117	419 - 1,036	344 - 971	842 - 2,341	1,266 - 2,365	60 - 132
Ringed seal	Grise Fiord	1995	F	4	87 ± 5	31 ± 11	66 20	168 ± 45	226 ± 120	253 ± 100	302.97 ± 109	42 ± 14
					81 - 92	17 - 42	37 - 81	114 - 224	120 - 398	179 - 401	196 - 452	29 - 58
Ringed seal	Grise Fiord	1995	M	4	86 ± 6	61 ± 5.8	66 13	466 ± 150	1,260 ± 1,021	1,083 ± 647	455 ± 193	59 ± 15
					78 - 91	55 - 68	50 - 81	270 - 633	370 - 2,717	423 - 1,916	312 - 737	38 - 71
Walrus	Thule (Greenland)	1988	F	11	86 ± 3	21 ± 4	107 20	99 ± 39	70 ± 39	244 ± 67	314 ± 41	86 ± 43
					79 - 91	14 - 29	70 - 140	57 - 175	35 - 141	161 - 355	261 - 404	36 - 152
Walrus	Thule (Greenland)	1988	M	5	87 ± 5	19 ± 6	109 29	116 ± 45	79 ± 48	301 ± 99	319 ± 39	100 ± 59
					80 - 91	12 - 26	82 - 154	58 - 169	35 - 149	164 - 423	271 - 358	30 - 168

[1] Arithmetic means +/- standard deviation with ranges

[2] Samples provided by Dr. Paul Becker, NIST, Charleston S.C. from the Alaska Marine Mammal Tissue Archival program

Spatial comparisons are best made with male beluga because they show little variation of organochlorine levels with age (Stern *et al.* 1994). The reason why male beluga show no variation of organochlorine levels with age is not known; possible explanations include inaccuracies in aging of older animals and changes in diet or feeding rate. When Cook Inlet animals are included, a distinct west-to-east spatial trend is apparent in male beluga with higher levels in the eastern stocks, especially in Hudson Bay. This trend was not apparent in previous studies (Muir *et al.* 1990) perhaps because of smaller sample sizes for the Hudson Bay stocks and lack of animals from Alaska. The Cook Inlet beluga (males), which are an isolated population inhabiting the northeast Pacific coast of Alaska, have significantly lower mean levels of ΣHCH, ΣCHL, ΣDDT, ΣPCB and toxaphene than the Beaufort Sea animals.

Beluga muktuk samples from eastern Hudson Bay animals had much lower OC levels than blubber from the same stock (not the same animals). Levels of PCBs in muktuk from Hudson Bay were higher than in muktuk from the Beaufort Sea stock on a wet weight basis. However, the Hudson Bay beluga muktuk averaged 19% fat compared to 4.3% for the Beaufort Sea samples). When compared on a lipid basis concentrations of PCBs and other OCs were similar.

Blubber samples from southern Beaufort Sea belugas collected in 1983, 1989 and 1993-94 have been analysed previously (Muir *et al.* 1990, Muir 1993, 1996). Also available were results for ΣDDT from Addison and Brodie (1973) for Mackenzie delta beluga. With the addition of the 1995 results from Hendrickson Is. there is still no evidence of changes in ΣDDT levels over a 23-year period (Figure 1). It should be noted that Addison and Brodie (1973) used different methodology for DDT determination than did this study and could have had some interferences from PCBs. If anything their DDT results were probably overestimated. The results also show few changes in ΣPCB over a 12-year period in the Beaufort Sea population. However, toxaphene levels (all by the same methodology and laboratory) appear to be declining.

Narwhal blubber samples from 1994 were compared with samples from 1982 (Table 1). In general mean concentrations of most OC groups did not differ significantly between 1982 and 1994. This result is consistent with that for the Beaufort Sea beluga.

Walrus samples from Thule in northwest Greenland were analysed for comparison with samples collected at approximately the same time in northern Quebec and Foxe basin and reported previously (Muir *et al.* 1995, Muir 1993). Unlike the results for organochlorines in beluga, toxaphene and PCBs were present at similar concentrations while ΣCHL and ΣHCH were present at higher concentrations than ΣDDT. Similar levels and relative proportions of organochlorines were found in walrus blubber from Foxe Basin (Muir *et al.* 1995). The results for the Thule animals contrast with those from Inukjuak in northern Quebec where high levels (>1000 ng/g) of most organochlorines, especially ΣPCB and toxaphene were found in walrus blubber. The high levels in these latter groups were attributed to predation on seals (Muir *et al.* 1995).

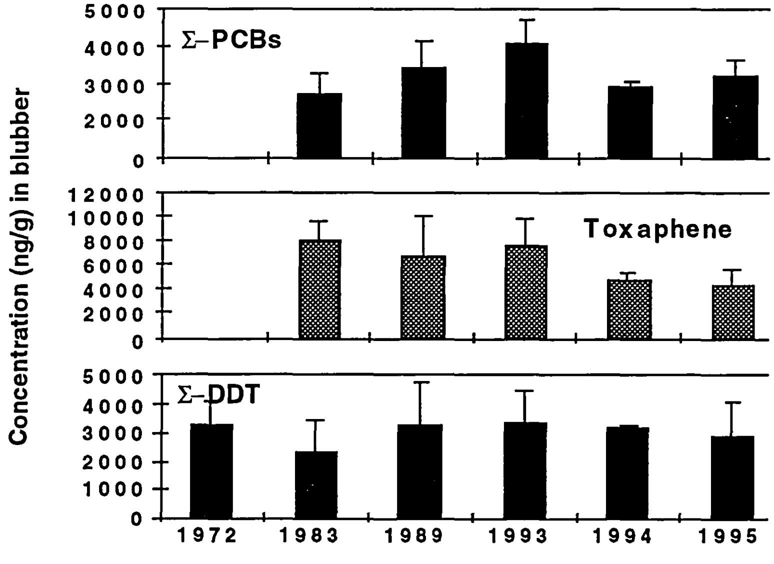

Figure 1. Temporal trends in ΣPCB, ΣDDT and toxaphene in male beluga blubber from the Mackenzie delta area. DDT data for 1972 are from Addison and Brodie 1973

Table 2. Concentrations (pg/g ww) of non-ortho and mono-ortho PCBs in ringed seal blubber.

			non-ortho PCBs				Mono-ortho PCBs				
Sex	**N**		**CB77**	**CB126**	**CB169**	**TEQs[1] nPCB**	**CB105**	**CB114**	**CB118**	**CB156**	**Total TEQs[2]**
Males	23	Mean	58	176	23	18	44600	4546	84100	14100	40
		SD	56	88	52	9	32500	3699	58600	10800	16
Females	16	Mean	56	168	21	17	29100	3133	62700	9700	33
		SD	36	104	31	11	10600	1431	22000	3500	10

[1] TEQs based on toxic equivalent factors (TEFs) from Ahlborg et al. 1994; TEFs: CB77 = 0.0005, CB126=0.1,CB169 = 0.01.

[2] TEFs for mono-ortho PCB: CB105 = 0.0001, CB114= 0.0005;CB118=0.0001; CB156=0.0005. Total TEQs = sum of TEQs for nPCBs and mono-ortho PCBs.

Ringed seal blubber samples from Quaqtaq (on Hudson Strait, Nunavik) had higher levels of most OCs than those from Grise Fiord (Table 1). An unusual finding for the Quaqtaq group was higher levels in females than males. This is being further investigated by the analysis of DNA to check the gender of the animals. The levels of PCBs and ΣDDT in the Grise Fiord animals were similar to what have been found elsewhere in the archipelago (Muir 1996), while results for Quaqtaq are among the highest levels so far observed in Canadian arctic ringed seals. It is possible that the Quaqtaq animals are feeding at a different trophic level or on a different food chain.

A total of 39 blubber samples from ringed seals collected at Arviat, NWT and previously analysed for organochlorines (Muir 1993) were re-analysed for nPCBs. Non-ortho PCBs were detected at low pg/g (wet wt) levels in blubber of all samples with CB126 predominating (Table 2). Toxic equivalents (for 2,3,7,8-tetrachlorodibenzo-p-dioxin) were calculated for nPCBs and mono-ortho PCBS using the TEFs of Ahlborg *et al.* (1994). As the result of its much higher TEF (0.1) than other planar PCBs, CB126 accounted for the major portion of total TEQs (Table 2).

TEQs due to nPCBs were significantly correlated with ethoxyresorufin-O-deethylase (EROD) activity in liver of male seals ($R^2 = 0.54$, N=23; $P<0.001$) but not in females ($P>0.1$) (Figure 2). Total TEQs (nPCBs + mono-ortho PCBs) in males were weakly correlated with EROD ($R^2=0.29$; N=23, $P<0.01$). Concentrations of CB126 were also significantly correlated with EROD activity ($R^2=0.51$, $P< 0.001$). A potentially significant confounding factor is that ΣPCBs in male seals from Arviat are significantly correlated with age ($R^2=0.79$). However, CB126, the major nPCB congener and contributor to TEQs, was not strongly correlated with age ($R^2=0.1$; $P=0.13$). Therefore the correlation of nPCB TEQs with EROD appears to be relatively unaffected by age although, for reasons yet to be explained, it is greatly influenced by the sex of the animals.

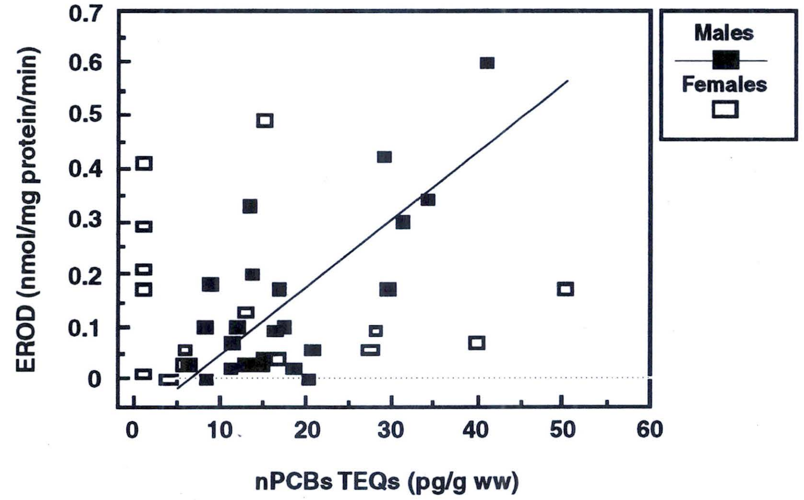

Figure 2. Correlation of EROD, a measure of mixed function oxidase activity, in ringed seal liver with nPCB TEQs in seal blubber. Samples from Arviat NWT collected in 1992. A strong correlation ($R^2=0.54$) between TEQs and EROD was found for males (indicated by the line) but there was no significant correlation for female seals.

EROD in ringed seal livers from Arviat was previously reported by Lockhart (1994). However, at that time levels of nPCBs in the blubber samples were not available.

CONCLUSIONS AND UTILIZATION OF RESULTS

Results of the project during 1995/96 and 1996/97 have added to the spatial and temporal information available on beluga and ringed seals from the Canadian Arctic and Alaska and for walrus from northwest Greenland. Levels of ΣPCB and ΣDDT do not appear to have declined significantly in male beluga from the south Beaufort Sea populations, but there may be declining levels of toxaphene. No decline of major OC groups was observed over a 12-year period in narwhal blubber. Collection and analysis of additional samples will be necessary to confirm any changes in toxaphene levels in the Beaufort Sea population.

The significant correlation of mixed function oxidase enzyme activity in male ringed seals with levels of nPCB TEQs and CB126 is in agreement with observations in beluga (White *et al.* 1994) and polar bear (Letcher *et al.* 1996). Both studies observed significant correlations of mixed function oxidase enzyme activity, as measured by CYP1A1 protein, with TEQs (primarily due to nPCBs).

Results of the work have been provided to Health Canada, presented at Northern Contaminants Program review workshops, and contributed to chapters of the *Canadian Arctic Contaminants Assessment Report* and the *Arctic Assessment Report* of the Arctic Monitoring and Assessment Program. Results have also been provided directly to northern residents in community presentations and during consultations with hunter/trapper associations.

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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CONTAMINANT TRENDS AND EFFECTS IN POLAR BEARS

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OBJECTIVES

Short-term

1. Complete publications on circumpolar geographic distribution of persistent organochlorine contaminants in the polar bear; analytical methodology for determination of methylsulphone PCB and DDE metabolites; and Cytochrome P450 protein levels, catalytic activity and correlation with organochlorine residues in polar bear liver. Communicate the findings through media releases, SOE reports/Indicator Bulletins, contributions to the NCP Assessment Report and the AMAP Report.

2. Determine chlorinated hydrocarbon contaminants in polar bear biopsy samples from the 1994 trans-polar cruise.
3. Determine temporal trends of OCs in archived samples.

4. Determine distribution of methylsulphone PCBs in polar bear tissues.

5. Determine the bioaccumulation potential of methylsulphone metabolites in the Arctic marine food chain.

6. Determine EROD- and porphyrin-inducing capability of fractionated tissue extracts in chick hepatocyte bioassay.

7. 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. 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.

2. Determine the effects, at the individual and population level, of persistent toxic organochlorine chemicals and their metabolites in the polar bear; collaborate with DFO in assessing effects on other marine mammals at the top of the arctic marine ecosystem food web.

3. Determine the potential for exposure of the human population to persistent PCB and DDT metabolites through ingestion of wild foods.

DESCRIPTION

Polar bears (Ursus maritimus) are at the highest trophic level in the arctic marine food chain. They eat primarily ringed seals, and consequently bioaccumulate relatively high concentrations of organochlorine contamination, especially PCBs and chlordane-related compounds (Norstrom and Muir 1994). The earliest extensive survey of PCB and DDT contamination in a wild mammal population was for the polar bear in the Canadian Arctic (Bowes and Jonkel 1975). Recent mean concentrations in adipose tissue are in the 4–26 mg/kg range (Norstrom and Muir 1994). Tissue samples are available from controlled hunting of polar bears in Canada and Greenland, and there are several polar bear biology research programs in which fat biopsy samples can be taken from tranquillized bears. The polar bear is therefore a good candidate for monitoring the circumpolar distribution and temporal trends of organochlorine contamination of the arctic marine ecosystem. A major hemispheric study has been completed and submitted for publication.

The polar bear is also a surrogate for human exposure to contaminants from ingestion of seal blubber. An international monitoring program provides a means of exchanging information among circumpolar countries which can lead to a stronger Canadian influence in setting the agenda for improving and protecting arctic wildlife and the people who eat them from contaminants. Polar bears have been designated as a priority species in the Arctic Monitoring and Assessment Program (AMAP).

The presence of ppm levels of persistent organochlorines may affect polar bear reproduction and endocrine systems. Because levels of organochlorines have been high throughout the period that populations sizes have been measured, it is likely that any subtle effects on reproduction would not have been noticed. Utilization of fat reserves causes relocation of these compounds from adipose tissue. During times of nutritional stress (e.g., poor hunting due to unfavourable ice conditions most of the year), organochlorine toxicity might be much more expressed than under more favourable conditions.

PCBs and DDT are the suspect compounds in the reproductive failure of 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 (MeSO2–) metabolites of these compounds, rather than the compounds themselves. Polar bear liver has been found to contain ppm levels of total MeSO2–PCBs in lipid. MeSO2–PCBs are present in other species known to be sensitive to PCB-mediated reproductive failure, such as otter. Recent evidence indicates that some 3–MeSO2–PCBs are potent inducers of liver enzymes and reduce circulating thyroid hormone levels in rats.

Hydroxy-PCBs are an important class of metabolite that may be involved in expression of PCB toxicity. The class of 3,5–chloro–4–hydroxy PCBs interfere with vitamin A and thyroid hormone transport through competitive binding with the thyroid hormone, T4, to the plasma transthyretin (TTR) carrier protein. Because of the selective binding to TTR, levels of this class of metabolite are elevated in plasma, below detection in other tissues. TTR is also the retinol (vitamin A) carrier protein, and binding of hydroxy PCBs to TTR interferes with retinol transport as well. There is therefore reason to believe that exposure of an animal to PCBs in the diet can affect the plasma transport of T4 and retinol if these animals are capable of metabolizing PCBs to hydroxy metabolites. Skaare *et al.* (1994) found a negative correlation between total plasma PCB and retinol concentrations, suggesting interference of retinol transport. Studies on the toxic effects of PCB and DDE metabolites in polar bear are therefore warranted.

Pregnant female polar bears, which experience prolonged fasts of up to six months, and cubs may be most at risk from the toxic effects of organochlorines. Mobilization of these compounds from fat to target organs occurs in the female and fetus during gestation, and to the cubs via milk during the perinatal period. Developing young exposed to PCBs are known to suffer different health effects than do adults exposed to the same chemicals which may be due, in part, to PCB metabolites. The temporal changes in pharmacokinetics of organochlorine contaminants under an annual dietary regimen of hyperphagia followed by fasting are unknown for any mammal species and must be understood to properly assess the effects of contaminants on top predators in the marine food chain. 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. It is necessary to study both the body composition and chemical levels in individuals over time.

This project addresses three of the Work Plan Objectives under the policy objectives of the Northern Contaminants Program:

1) Identification of contaminant sources and transport to the Arctic,
2) Assessing contaminant levels in fish and wildlife, and

3) Assessing the effects of contaminants on the health of northern ecosystems including human health.

ACTIVITIES IN 1995/96 AND 1996/97

(i) Complete publications

Activities in 1995/96 on geographic distribution of persistent organochlorine contaminants were mainly restricted to verifying previous data sets, and revising statistical analysis of the circumpolar studies of organochlorine contaminants in polar bear adipose tissue reported in previous years (Norstrom 1994) to include more recently obtained data on bears from the Arctic Ocean near Prince Patrick Island (M'Clure Strait) collected by Ian Stirling, and on bears from Wrangel Island in the East Siberian Sea collected by US Fish and Wildlife Scientists (Norstrom 1995). A manuscript on the hemispheric distribution of organochlorines in polar bears was completed (Norstrom *et al.* in press).

A paper describing a method for routine determination of MeSO2–PCBs and DDE in biological tissues was published (Letcher *et al.* 1995).

A paper reporting on the characterization of cytochrome P450 (CYP450) enzymes and the testosterone metabolite profile in livers of four bears from Barrow Strait was published (Bandiera *et al.* 1995a). Using hepatic microsomes from 12 to16 bears from the same area, a second study was completed demonstrating the relationships between the hepatic levels of immunoreactive 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 (Letcher *et al.* 1996a). The influence of several OCs 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 comparing immuno-quantitated CYP1A and CYP2B protein levels with OC levels of frozen (i.e., –40°C) liver homogenates from 44 individual polar bears, and archived for nine to ten years, was also published (Bandiera *et al.* 1996). The results from this study were presented at a special session on the Arctic at the DIOXIN'95 conference in Edmonton, Alberta, August, 1995 (Bandiera *et al.* 1995b).

The MeSO2–PCBs and DDE projects above and in (iv) and (v) below formed the Ph.D. research of Robert Letcher, Centre for Analytical and Environmental Chemistry, Department of Chemistry, Carleton University. Dr. Letcher successfully defended his Ph.D. in March 1996 (Letcher, 1996). This research was supported in part by a NSERC research grant to R.J. Norstrom, Carleton University.

(ii) Determine chlorinated hydrocarbon contaminants in polar bear biopsy samples from the 1994 trans-polar cruise

Biopsy samples from polar bears taken on the transpolar icebreaker cruise by Malcolm Ramsay in 1995 were analysed for OCs and PCBs.

(iii) Determine temporal trends of OCs in archived samples

Temporal trends, 1984–1990, in organochlorine concentrations in male polar bear adipose tissue samples from five areas in the Canadian Arctic: Queen Maude Gulf, Barrow Strait, north Baffin Bay and Davis Strait and north Hudson Bay were studied using archived samples from the CWS Specimen Bank. Samples from 1968 were analysed from Hudson Bay to determine long-term trends. PCDD/PCDF trends were also determined in pooled samples.

(iv) Determine distribution of methylsulphone PCBs in polar bear tissues

Several tissues from male polar bears shot by Inuit hungers from Resolute Bay in April, 1993, including lung, liver, muscle, kidney, heart, brain and testes were analysed to determine the tissue distribution of the MeSO2–PCB and –4,4'–DDE metabolites, and the relationship to the precursor PCB and 4,4'–DDE contaminants among tissues.

(v) Determine the bioaccumulation potential of methylsulphone metabolites in the Arctic marine food chain

Six adipose tissues were obtained from adult male polar bears for food chain comparison of the levels of MeSO2–PCBs and –4,4'–DDEs and their precursor PCB and 4,4'–DDE compounds. The samples were obtained from freshly killed individuals within three days of each other at the end of April, 1993 by Inuit hunters in the Resolute Bay area of the Canadian Arctic. Adult male polar bears were chosen to minimize the effect of sex and age on OC level comparisons. Blubber samples of eleven ringed seals (i.e., five males and six females) and two pools of nine arctic cod each, were also collected from the Resolute Bay area. Seal ages were unknown, except for two juvenile females and adult status for three males. A paper reporting on the bioaccumulation of the sulfone metabolites, and the relative significance of metabolite formation, accumulation from the diet, and clearance, to the observed metabolite levels in each species of the polar bear food chain is currently in preparation for Environmental Science and Technology (Letcher *et al.* in prep). The results were presented in part at a session on PCB toxicity at the DIOXIN'96 conference in Amsterdam, The Netherlands, August, 1996 (Letcher *et al.* 1996b), and at the Aquatics Toxicology Workshop in Calgary, Alberta, October, 1996 (Letcher *et al.* 1996c).

(vi) Determine EROD- and porphyrin-inducing capability of fractionated tissue extracts in chick hepatocyte bioassay

Fractionated and unfractionated OC and sulfone extracts of polar bear liver and fat were tested for porphyrinogenic and CYP1A induction in the chicken hepatocyte bioassay developed by Kennedy *et al.* (1992).

(vii) 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

Dr. I. Stirling (University of Alberta) provided 34 adipose biopsy and 12 milk samples from western Hudson Bay polar bears. These samples were analysed for MeSO2–PCB and –4,4'–DDE metabolites and their precursor PCB and 4,4'–DDE compounds to determine the degree to which these compounds from the lactating mother are biotransfered to their young via milk. The data are currently being analysed. The temporal dynamics or lactational transfer of MeSO2–PCB and –4,4'–DDE metabolites is unknown for any species. The effects of the feeding status, over a two-year period, of a single polar bear female, on several aspects of the dynamics of MeSO2–PCB and –4,4'–DDE residues in adipose and milk was studied. These results were compared to the adipose levels of one yearling (YRLG) cub and two cubs-of-the-year (COYs).

The relationships between PCB concentrations in adipose tissue biopsies and milk, body burdens, and percent body fat changes in 25 fasting females of differing reproductive classes and eight cubs near Churchill Manitoba was determined, and rate of transfer of contaminants to cubs was estimated. A paper on the preliminary results was published (Polischuk *et al.* 1995). As of August 1996, in excess of 400 plasma, milk and adipose samples for temporally sampled individuals of the same family groups have been analysed for OCs. Samples obtained temporally from the individuals of three family groups were also analysed for MeSO2–PCB and –DDE metabolites. Body composition was also measured, which will allow total body burdens to be calculated. This, in turn, will allow mass balances in multiple-sampled females to be determined over the fasting/feeding and reproductive cycle. This project forms the major portion of the Ph.D. research of Ms. S.C. Polischuk (Department of Biology, University of Saskatchewan) who is expected to complete her thesis in mid-1998.

(viii) Additional activities

The ECNI mass spectral characteristics of 24 bioaccumulating MeSO2–PCB congeners in relation to features of congener structure was studied and published (Letcher and Norstrom 1997).

The 3–MeSO2–4,4'–DDE metabolite has been shown to have an extremely high binding affinity for adrenal cortex of mice. Furthermore, it is the suspect cause of hyperadrenocorticism in Baltic seals. It is not known whether polar bears are sensitive to this effect, but this can be studied by looking at the binding affinity of radiolabelled compounds to adrenal mitochondrial fractions. Twelve adrenal samples archived at liquid nitrogen temperature were available to study the sensitivity of polar bears to this effect. A collaborative research program was initiated with Uppsala University in Sweden.

A research study was begun to develop methods of determination of hydroxy-PCB compounds in plasma, and to identify the specific compounds found in polar bear plasma. Preliminary results on identification of hydroxy-PCBs in plasma were presented at the Dioxin'96 conference in Amsterdam, The Netherlands, August, 1996 (Sandau and Norstrom 1996). Satisfactory methods of methylation have been developed. Considerable effort has been expended on developing a suitable extraction method for plasma. Several approaches have been tried, which yielded unsatisfactory recoveries of some compounds, possibly due to protein binding. Intensive efforts are ongoing to develop a suitable solid-phase extraction technique. This study is being funded largely by a $30,000 grant from the Canadian Chlorine Coordinating Committee (C4).

RESULTS

(i) Complete publications

Six papers were published in scientific journals, and one Ph.D. thesis was defended at Carleton University. The thesis was awarded a Carleton University Senate Medal for Outstanding Academic Achievement at the Doctoral

Level. See reference list for details. In addition, most of the data are summarized in the *Canadian Arctic Contaminants Assessment Report* (CACAR) and *Arctic Monitoring and Assessment Program* (AMAP) *Report*. The geographical distributions of dieldrin (DIEL), p,p'–DDE (DDE), sum of 16 polychlorinated biphenyl congeners (ΣPCB) and sum of 11 chlordane-related compounds and metabolites (ΣCHL) from Norstrom *et al.* (in press) are summarized in Figure 1. The concentrations were standardized to adult males (which have higher PCBs and lower chlordanes than females). PCBs were significantly higher (13 to 29 mg/kg lipid) in bears from Svalbard, East Greenland and near M'Clure Strait than all other areas except Southeastern Hudson Bay. Dieldrin and DDE tended to increase in a more orderly fashion from West to East, with the highest levels being found in Southeastern Hudson Bay, probably a reflection of the importance of North American sources. Chlordane was the most uniformly distributed organochlorine, although significantly lower concentrations were found in Bering and Chukchi sea bears than most of areas in the East.

(ii) Determine chlorinated hydrocarbon contaminants in polar bear biopsy samples from the 1994 trans-polar cruise.

Organochlorine contaminant concentrations in polar bear biopsy and milk samples from the Arctic Ocean proper, obtained during the 1995 Canada–USA transpolar icebreaker cruise, are given in Table 1. Samples were obtained from 7 individuals, three adults, one of which was male, one subadult female and 3 cubs. This really only represents 4 samples, since the three cubs cannot be considered separately from their mothers. Milk samples were obtained from the two

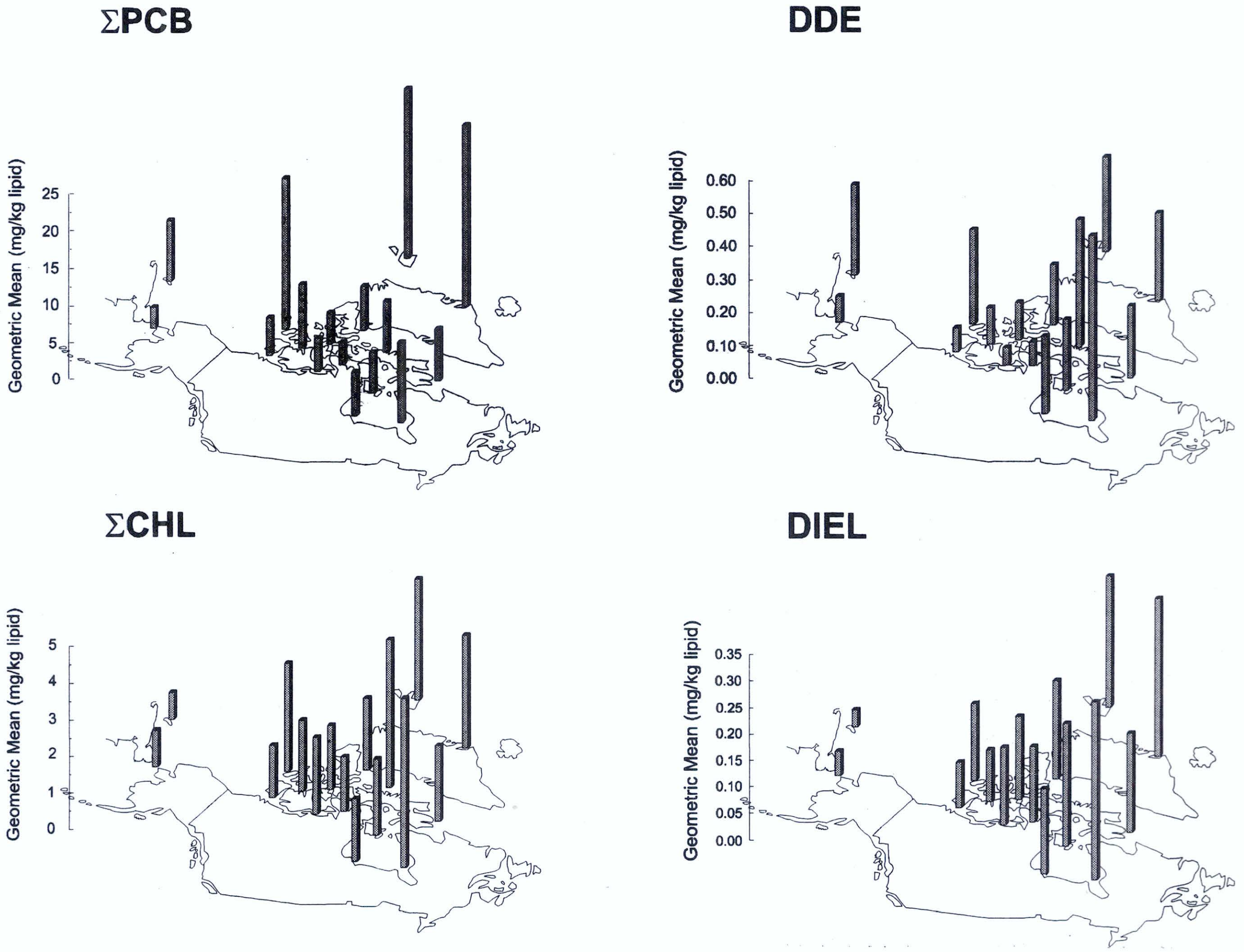

Figure 1. Geographical distribution of major organochlorine residue classes in polar bear adipose tissue. The bar heights represent geometric mean concentrations in adult bears (>5 years old) in relatively well-defined sub-populations. ΣPCB and ΣCHL concentrations in females were standardized to adult males to correct for the effect of sex. Numbers of individuals in each region ranged from 5 to 36; the average N among the 16 regions was 18. Data are taken from Norstrom et al. (in press).

Table 1. Concentrations of organochlorines in polar bear samples from the Canada-USA transpolar ice breaker cruise, 1995. Concentrations are in mg/kg (lipid weight) in biopsies or milk.

		Family Group			Family Group				
Age Class	**subadult**	**adult**	**milk**	**cub**	**adult**	**milk**	**cub**	**cub**	**adult**
Sex	**F**	**F**	**F**	**M**	**F**	**F**	**M**	**F**	**M**
%Lipid	96.9	90.0	31.6	92.1	92.8	54.4	93.0	90.5	86.0
ΣClBz	0.08	0.05	0.06	0.14	0.05	0.05	0.06	0.27	0.20
ΣHCH	0.10	0.08	0.11	0.24	0.08	0.09	0.12	0.38	0.25
ΣCHLOR	2.20	0.82	1.01	2.65	0.78	0.67	0.79	2.40	1.32
ΣDDT	0.44	0.27	0.18	0.18	0.13	0.10	0.08	0.20	0.38
ΣPCB	6.59	1.67	1.31	4.62	1.70	0.66	2.32	5.31	3.96

females. In general, concentrations of organochlorines ranked among the lowest observed in polar bears, similar to those in the Bering/Chukchi Seas and Amundsen Gulf, and significantly lower than in bears in the Arctic Ocean near M'Clure Strait (Figure 1 and Norstrom 1995). The reasons for these large differences are unknown, but will be the subject of further investigation. Contaminant concentrations in milk were similar to those in the females' adipose tissue, and concentrations in cubs were roughly twice those of the mother. These results are similar to those obtained previously (Polischuk *et al.* 1995, CWS unpublished results).

(iii) Determine temporal trends of OCs in archived samples

Temporal trends of organochlorines from re-analysis of individual archived samples are presented in Table 2, and of TCDD and PnCDD in Table 3. There were significant declines in HCHs, DDT and dieldrin in (I), significant decrease in dieldrin in (II), no changes in (III) and a significant increase in chlordanes in (IV) between 1984 and 1990. There were no significant changes in PCB concentrations. It is possible these changes are a simple reflection of a more uniform distribution of organochlorines over time. PCDDs and all PCDFs other than TCDD and PnCDD were at sub-ng/kg concentrations. Concentrations of TCDD were low and tended to be more evenly distributed in 1990 (0.8 to 3.1 ng/kg) than in 1984 (2.0 to 15 ng/kg), as was the case for the other organochlorines. Only pooled samples were analysed so the significance of the trends cannot be established. Nevertheless, concentrations of TCDD in (I) and (II) declined a factor of 4–5 between 1984 and 1990. The longer term trends in (V) indicated that only DDT consistently and significantly declined (ca. 5 fold) throughout the 1968 to 1990 period. Concentrations of all organochlorines except DDT and dieldrin were highest in 1984 (ca. a factor of 2), and were similar in 1968 and 1990, indicating that the peak of contamination in North Hudson Bay occurred much later than at mid-latitudes, and declined slowly thereafter. Dieldrin concentrations remained essentially constant throughout this period.

(iv) Determine distribution of methylsulphone PCBs in polar bear tissues

The ΣPCB distribution in several tissues of polar bear revealed that ΣPCB levels were relatively constant at 3000 to 6000 ng/g on a lipid weight basis for testes, adipose and lung, whereas brain was as much as ca. 17 times lower and liver as much as ca. 4 times higher. The 4,4'–DDE levels were highest in liver lipids (704 ng/g), whereas lipid in adipose and brain had approximately half this level and levels in testes and lung lipid were 8 to 15 times lower than in the liver.

The rank order of preference of storage for MeSO2–PCBs in tissues was similar to that for PCBs, but there was a larger disparity among tissues (Table 4). Thus, ΣMeSO2–PCB levels were highest in liver at 11% of ΣPCBs, whereas fat, testes, lung and brain had 2, 9, 13 and 60 times lower levels than liver on a lipid weight basis. The 2– and 3–MeSO2–4,4'–DDE metabolites were detected at a total level of close to 200 ng/g in liver, 126 to 337 times higher than 3–MeSO2–4,4'–DDE found in testes, adipose and lung.

The concentrations of individual MeSO2–PCB congeners expressed as a fraction of the ΣMeSO2–PCB demonstrated some tissue dependence (Figure 2). The congeners 3– and 4–MeSO2–CB87 and 3– and 4–MeSO2–CB101 dominated in all tissues with an average of ca. 50% of ΣMeSO2–PCB in brain and adipose, 45% in lung and liver and 55% in testes. The liver MeSO2–PCB congener pattern is the most dissimilar with 3– and 4–MeSO2–CB87 accounting for ca. 33% of the sum as opposed to ca. 22% for the remaining tissues. It has been shown that certain MeSO2–PCB congeners bind to proteins in lung, kidney and intestinal mucosa of rats. Such congener–specific retention may be the result of

Table 2. Temporal trends of organochlorine residues in polar bear adipose tissue from parts of the Canadian Arctic. (µg/kg lipid wt). N = 8-10. Significant differences are noted with *.

Region	Year		ΣClBz	ΣHCH	ΣCHL	ΣDDT	ΣPCB	DIEL
Queen Maud Gulf	1984	Geomean	243.6	358.4*	1459.4	98.0*	3004.3	172.3*
Larsen Sound		Range	136-423.3	166.8-474.5	860.6-2546.5	41.9-224.6	962.5-6991.5	97.7-274.4
(I)	1990	Geomean	175.3	227.7*	1284.1	29.7*	2616.3	87.6*
		Range	65.7-374.4	88.7-477.7	332.6-4193.7	12.5-150.6	717.8-6513.5	24.7-167.4
Barrow Strait	1984	Geomean	196.5	206.4*	1200.6	109.0	3376.9	148.3*
(II)		Range	111-394.2	137.1-280.7	491.9-2449.3	55.1-246	1636.8-8261.1	76.4-228.6
	1990	Geomean	128.7	294.2*	927.9	95.5	3017.8	89.3*
		Range	75-396.4	147.1-485	377.6-1372.3	31-233.4	1883.6-4621.5	40.2-139.1
North Baffin Bay	1984	Geomean	188.4	184.2	1047.6	130.8	3725.2	147.7
(III)		Range	22.6-345.3	80.2-360.5	300.9-2483	68.2-204.1	909.6-8233.1	39.8-251.3
	1990	Geomean	224.9	251.5	1746.4	139.6	4886.6	168.8
		Range	130.3-384.4	148.1-334.8	691.3-4501.4	89.2-218.2	1095.8-8492.5	80.5-409.9
North Hudson	1968	Geomean	195.7*	235.2	1085.5	884.0*	3824.1*	191.4
Bay		Range	135.3-378.2	130.2-615.5	452.7-4526.7	274.6-1851.4	1926-9466.9	114.1-482.2
(IV)	1984	Geomean	319.7**	335.4	2525.2	524.7**	7132.3**	215.0
		Range	107.3-838.7	161-647.8	1244.4-5255.4	214.2-1142	4252.2-14944.4	46.9-750
	1989	Geomean	169.4*	251.9	1382.6	148.3***	4601.6*	233.9
		Range	38.6-432.4	125.3-460.6	457.4-5838.9	20.7-587.4	1849.2-11912	81.7-565.7
Davis Strait	1984	Geomean	220.6	171.5	1293.1*	287.5	4268.1	148.7
(V)		Range	148.2-322.4	111.3-262.8	879.6-1637.4	104.5-1146.9	2201-13683.4	96.1-249.5
	1990	Geomean	185.9	181.4	1837.5*	152.4	7541.3	208.5
		Range	138.1-300.7	113.8-493.9	838.4-4999.2	78-390.1	2139.5-20215	113.5-536.3

Table 3. Temporal trends of 2,3,7,8-TCDD and 1,2,3,7,8-PnCDD concentrations in pooled polar bear adipose tissue from parts of the Canadian Arctic. Number of bears in pools in parentheses. (ng/kg lipid wt).

Region	Year	2,3,7,8-TCDD	1,2,3,7,8-PnCDD
Queen Maud Gulf	1984	11.12 (9)	2.49 (9)
(I)	1990	3.02 (10)	0.76 (10)
Barrow Strait	1984	14.82 (7)	0.97 (7)
(II)	1990	3.11 (9)	0.29 (9)
North Baffin Bay	1984	3.69 (10)	0.32 (10)
(III)	1990	2.76 (10)	0.17 (10)
Davis Strait	1984	1.95 (7)	0.24 (7)
(IV)	1990	0.81 (10)	0.39 (10)

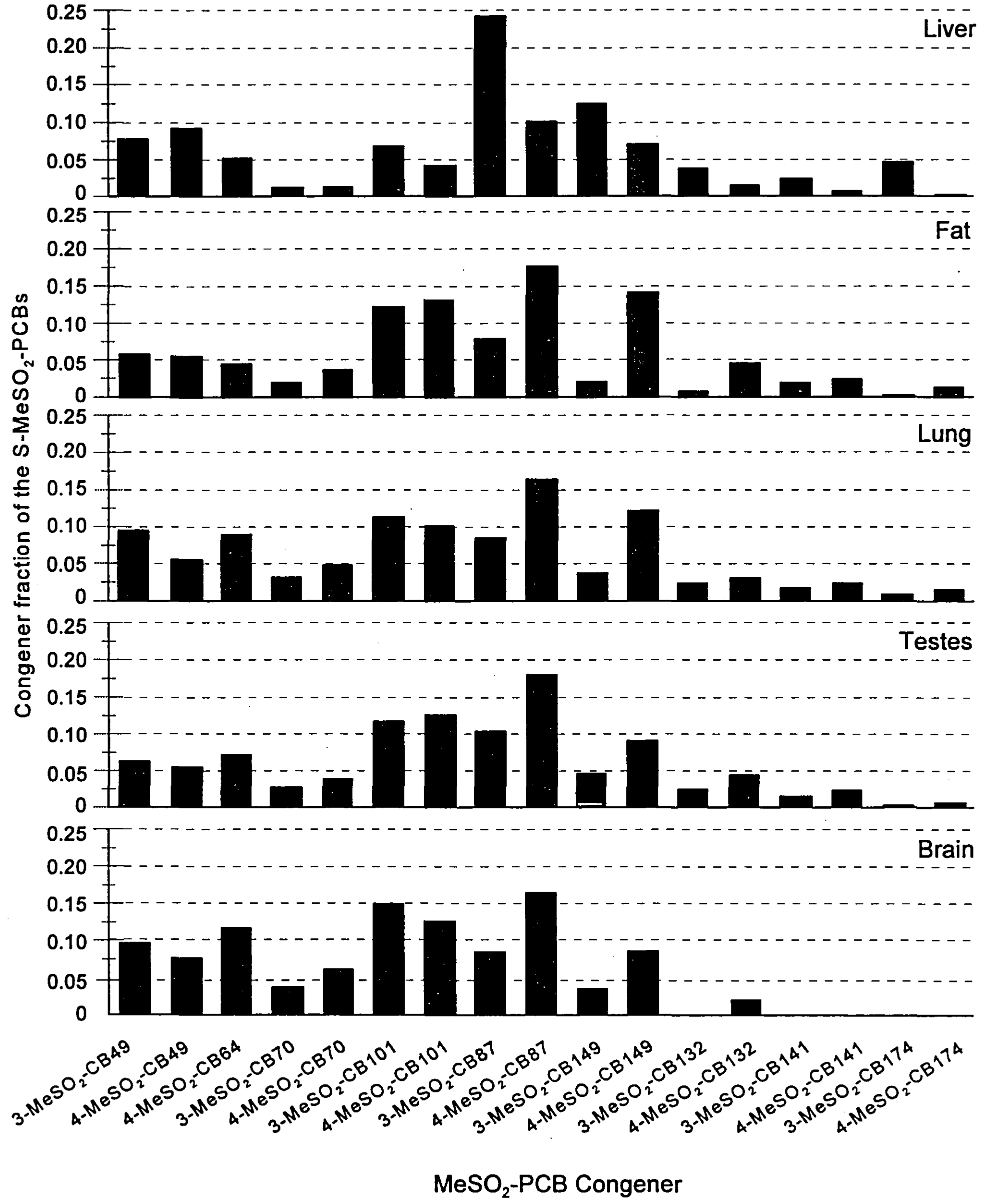

Figure 2. MeSO2-PCB congener patterns in various polar bear tissues, expressed as the congener fractions of the ΣMeSO2-PCBs. Individual congeners without bars were below the detection limite of 0.05 ng/g.

Table 4. Total MeSO2–PCB and –4,4'–DDE Levels (ng/g, lipid wt.) and ratios of the congener sums to total PCBs and 4,4'–DDE in the tissues of polar bears from the Resolute Bay Area of the Canadian High Arctic

	Liver[1]	**Fat**[1]	**Testes**[1]	**Lung**[1]	**Brain**[2]
% lipid	6.1 ± 0.5	64.5 ± 4.0	8.0 ± 8.7	2.6 ± 0.2	15.8
ΣMeSO2–PCBs	3059 ± 1290	351 ± 66	207 ± 31	143 ± 35	31
ΣPCBs	28309 ± 9268	6210 ± 948	6387 ± 1940	3263 ± 354	377
ΣMeSO2–PCB/ ΣPCB ratio	0.11 ± 0.02	0.06 ± 0.01	0.03 ± 0.01	0.04 ± 0.01	0.083
3–MeSO2–4,4'–DDE	303 ± 85[4]	2.4 ± 1.0	2.7 ± 1.4	0.9 ± 0.1	n.d.
4,4'–DDE	704 ± 100	262 ± 32	89 ± 14	48 ± 9	224
3–MeSO2–4,4'–DDE/ 4,4'–DDE ratio	0.46 ± 0.20	0.009 ± 0.004	0.03 ± 0.02	0.02 ± 0.003	N/A

[1] The mean ± SD for n = 3 liver, fat, testes and lung.

[2] Only one sample.

[3] The sum of 2– and 3–MeSO2–4,4'–DDE. The 2– to 3–MeSO2–4,4'–DDE ratio was 0.48 ± 0.18.

n.d. = not detected.

N/A = not applicable.

binding to receptor or CYP proteins. The 3–MeSO2–PCBs were found to be preferentially retained in the liver relative to adipose or muscle in Baltic grey seal and Swedish mink and otter (Bergman *et al.* 1994).

(v) Determine the bioaccumulation potential of methylsulphone metabolites in the Arctic marine food chain

The apparent biomagnification factors (BMFs) of ΣMeSO2–PCBs and 3–MeSO2–4,4'–DDE from seal to bear (Table 5) were >1 and >>1 , respectively, indicating a high bioaccumulation/formation potential for the sulfones relative to the other OC classes. Concentrations of total MeSO2–PCBs, 3–MeSO2–4,4'–DDE and their precursors in cod, seal and bear are given in Table 6. MeSO2–PCBs and 3–MeSO2–4,4'–DDE were not detectable in arctic cod (<0.05 ng/g, lipid weight). The high BMF for CB–153 from cod to seal and seal to bear was consistent with the resistance of CB–153 to metabolic degradation by either CYP1A– or CYP2B–type enzymes. Concentrations of the individual MeSO2–PCBs in ringed seal and polar bear are presented in Table 7.

Overall, there was little difference in the PCB pattern in cod relative to the Aroclor standard (1242:1254:1260, 1:1:1), however, the PCB patterns changed noticeably in seal and bear, especially PCB congeners possessing meta-para adjacent carbons (Figure 3). Meta-para unsubstituted PCBs were present in seal blubber but notably absent in polar bear (<0.05 ng/g, lipid weight). These PCBs included CB–31, CB–49, CB–52, CB–64, CB–70, CB–91, CB–95, CB–101, CB–110, CB–141, CB–132, and CB–174, all of which were present in the form of MeSO2–PCB metabolites in seal and bear (Figure 3) with the exception of 3–MeSO2–CB52 and 3– and 4–MeSO2–CB95. MeSO2–PCBs and –DDEs were not detected in arctic cod (<0.05 ng/g, lipid weight).

Because there were no detectable MeSO2–PCBs in arctic cod, all of these compounds in ringed seal were formed by the seal itself from the precursor PCBs. However, most MeSO2-forming PCB congeners with meta-para adjacent carbons were detected in seal (Table 6), and therefore only a proportion were potentially converted to 3– and 4–MeSO2–PCBs and other metabolites by the seal. The only exception was CB–132, which was below the detection limit in seal and therefore completely metabolized. Of the total meta-para-PCBs metabolized in seal, less than ca. 10% was converted to MeSO2–PCBs suggesting that sulfone formation was not the preferred metabolic route in seal.

Polar bear liver and fat tissue contained MeSO2–PCBs, but no detectable levels of precursor PCBs (<0.05 ng/g, lipid weight), with the exception of traces of CB–149. Therefore, polar bears have two potential sources of sulfones, those levels accumulated from seal and the contribution as a consequence of metabolic conversion of the precursor PCB compounds. MeSO2–PCB concentrations were converted to ratios to CB–153 in seal and bear to better observe metabolic conversion versus metabolite bioaccumulation in the polar bear food chain. Assuming that CB–153 is very slowly metabolized and therefore represents the maximum likely bio-

Table 5. Bioaccumulation Factors (BFs) for the Polar Bear Food Chain[1]

Compound	Seal blubber / cod	Bear fat / seal blubber
ΣDDT	17.1	0.6
4,4'–DDT	5.3	0.2
4,4'–DDE	38.5	0.8
ΣPCB	7.8	15.1
CB153	26.6	47.3
ΣMeSO2–PCB	n.a.	29.7 (148)[2]
3–MeSO2–4,4'–DDE	n.a.	5.4 (512)[2]

[1] Ratio of tissue concentration at one food chain level to those at the next lowest level (on a lipid weight basis).

[2] Number in parentheses is the ratio of seal blubber to polar bear liver.

Table 6. Total DDT, 4,4'-DDE, PCB and MeSO2-PCB and -4,4'-DDE levels (ng/g, lipid wt.) in the polar bear food chain from the Canadian High Arctic.[1]

Species	Tissue[2]	N	ΣDDT	4,4'–DDE	ΣPCB[3]	ΣMeSO2 -PCB	3–MeSO2-2-4,4'-DDE	ΣMeSO2 PCB/ΣPCB	3–MeSO2-4,4'-DDE/ 4,4'-DDE Ratio
Arctic cod (1993)	whole body pools[3]	2	25.9/ 34.0	9.3/ 8.1	71.8/ 33.0	<0.05/ <0.05/	<0.05/ <0.05/	n.a./ n.a.	n.a./ n.a.
Ringed seal (1993)	blubber (male)	5	542 ± 182	350 ± 130	447 ± 92	13.4 ± 6.3	0.4 ± 0.2	0.029 ± 0.0081	0.0012 ± 0.0004
	blubber (female)	6	474 ± 88	322 ± 62	387 ± 73	12.3 ± 1.8	0.4 ± 0.1	0.034 ± 0.0082	0.0011 ± 0.0003
Polar Bear (1993)	fat	6	301 ± 32	268 ± 27	6207 ± 948	458 ± 59	2.0 ± 0.7	0.061 ± 0.006	0.008 ± 0.002

[1] The concentrations are the mean ± SD. MeSO2–PCBs and –4,4'-DDEs in arctic cod were below the detection limit.

[2] The percent lipid was 6.5/7.0 % in arctic cod, 90.1 ± 6.3 % in ringed seal blubber and 65.0 ± 3.2 %.

[3] There were 2 pools, containing 9 individual cod each. Levels for both pools are shown.

[4] 72 PCB congeners were determined in arctic cod and ringed seal, and 22 PCB congeners in polar bear.

accumulation potential, the ratio of the CB–153 normalized concentrations in bear/seal can be used to estimate biomagnification potential versus formation. This ratio of ratios is presented in Figure 4. Based on the knowledge that 3– and 4–MeSO2–CB132 are not formed in bear (no precursor CB132 in seal), these congeners bioaccumulate approximately 60% as efficiently as CB–153. Therefore congeners that have a normalized ratio significantly below 0.6 are neither bioaccumulated nor formed in the bear to any extent (or are efficiently metabolized by the bear). Congeners that fall significantly above 0.6 are probably both bioaccumulated and formed. It appears that accumulation from seal to bear is more significant for the higher chlorinated MeSO2–PCBs. For congeners that have a normalized ratio significantly above 1.0, at least that portion above 1.0 must be formed, since bioaccumulation is unlikely to be higher than that of CB–153. Thus a portion of MeSO2–CB–141, CB–149, CB–91, CB–70 and possibly CB–87 are likely formed in bear, and the other appear to be bioaccumulated.

(vi) Determine EROD- and porphyrin-inducing capability of fractionated tissue extracts in chick hepatocyte bioassay

Analysis of HAH, OC and MeSO2–PCB/–DDE fractions from polar bear liver and fat tissues showed low maximal EROD activity responses in the cell cultures relative to the basal activity levels. Sub-basal activity was observed at higher dose levels. All extracts caused porphyrin accumulation in the same cell cultures. Porphyrins became elevated at the same dose levels that caused sub-basal EROD activity. It is probable that the low level of Ah-active compounds (mainly CB–156 and CB–157, Letcher *et al.* 1996a), combined with the high level of ortho-substituted PCBs caused inhibition of CYP1A.

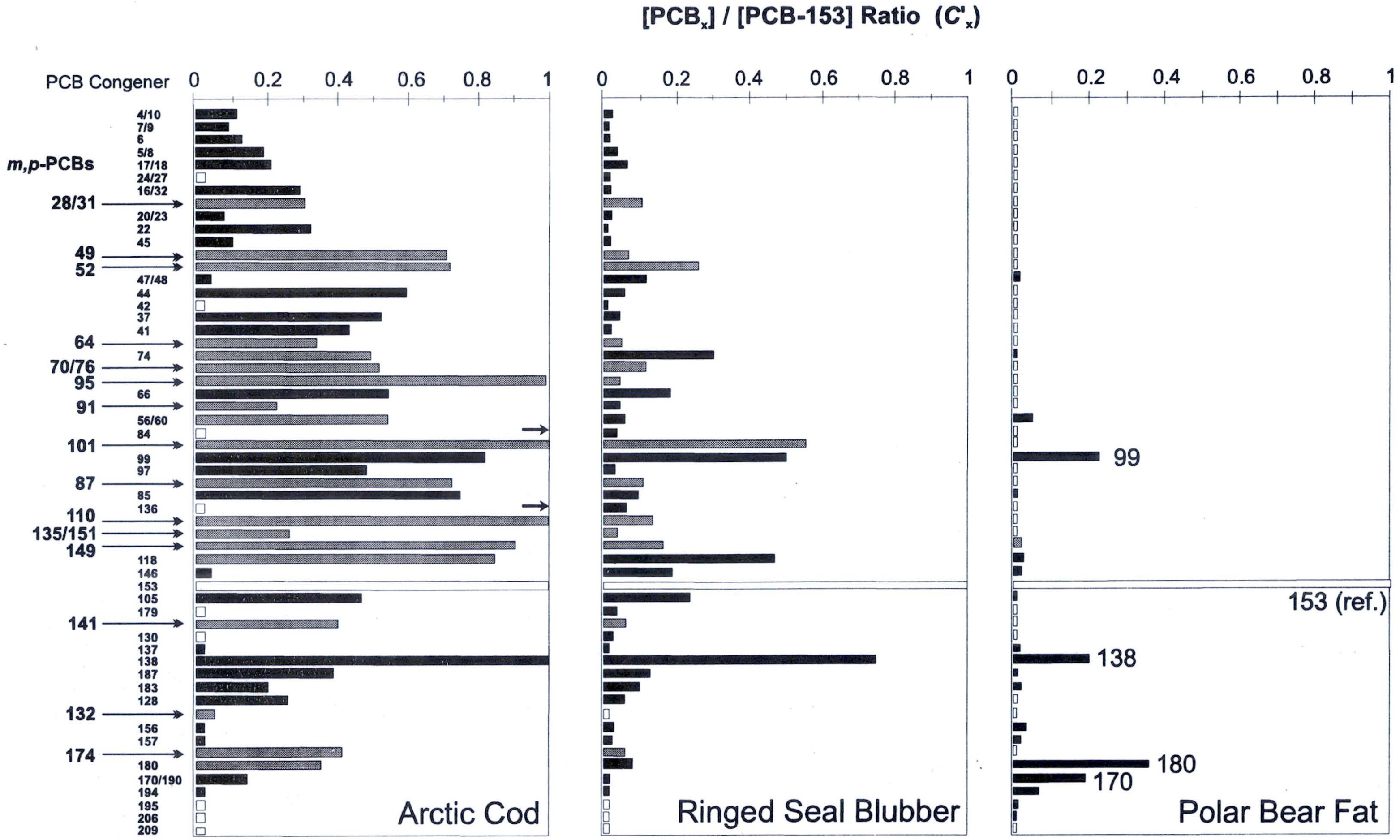

Figure 3. Ratios of PCB congener to CB 153 concentrations (C'x) in arctic cod, ringed seal blubber and polar bear fat from the Resolute Bay area of the Canadian high Arctic. The clear boxes on the baseline denote congeners that were below detection (i.e., <0.05 ng/g, lipid wt.). Shaded bars indicate PCB congeners shown to form persisten MeSO2-PCB metabolites. The major PCBs in polar bear fat are labelled. The CB153 bar is stripped for reference.

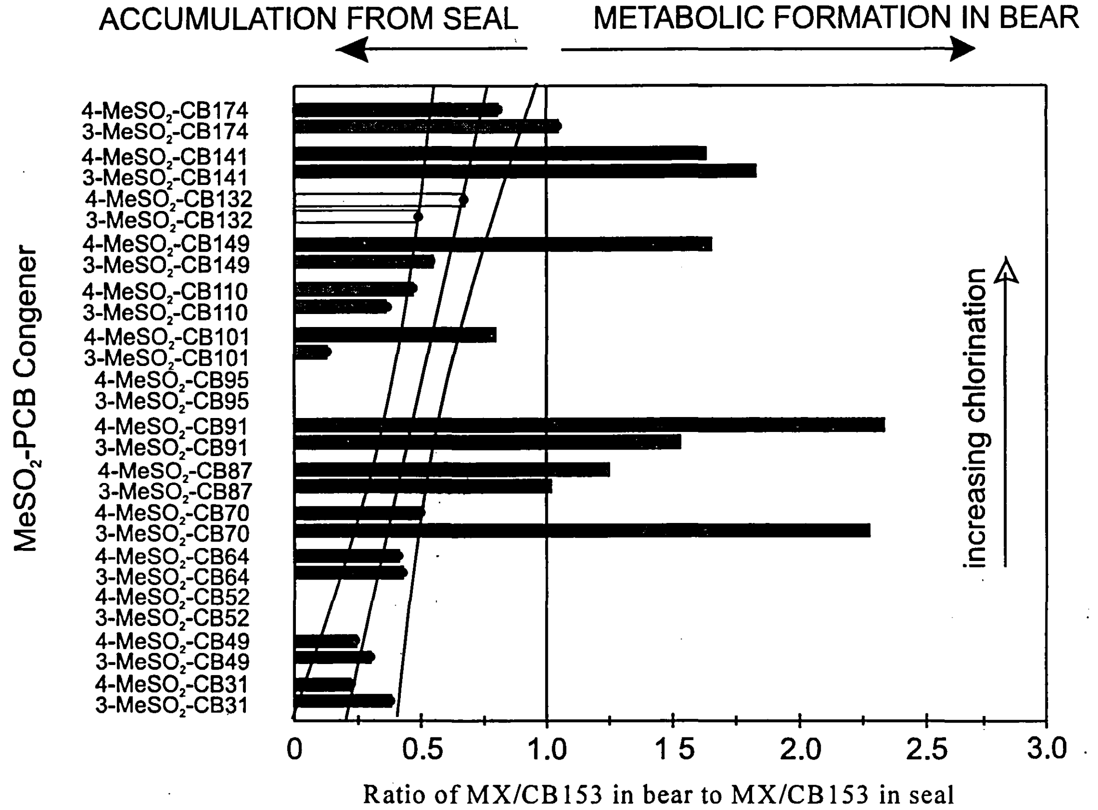

Figure 4. The bars represent the apparent bioaccumulation factor for individual MeSo2-PCB congeners in polar bear fat taken from the Resolute Bay region of the Canadian high Arctic. The middle line is defined by the equation (1) r^2 - 0.615, p <0.0002), a linear regression model for congeners falling in to Class I - bioaccumulation only (white bars with black points). The curved lines denote confidence limits for 95% significance of the correlation. The fraction above the solid line is the apparent amount of MeSo2-PCB formed in bear. The 3- and 4- MeSo2-CB132 in bear were completely accumulated from seal and thus denoted by the grey bars.

(vii) 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

The effects of the feeding status of a single polar bear female over a two-year period on several aspects of the dynamics of residues in adipose and milk were studied. These results were compared with the adipose levels of the female's yearling (YRLG) cub and two cubs-of-the-year (COYs). The results are presented in Figure 5. There was a marginal increase in ΣMeSO2–PCBs in the adipose tissue of the adult female over the two years, whereas the ratio to ΣPCB remained essentially constant. During the second fasting period of the pregnant female (i.e., Aug./93 to Mar./94), an increase in the adipose ΣMeSO2–PCB level was observed. Moreover, the ΣMeSO2–PCB to ΣPCB ratio decreased, suggesting that MeSO2–PCBs may have been transferred from adipose tissue to the fetus trans-placentally or through lactation more rapidly than PCBs as the fasting period progressed. It appeared that the opposite was true for 3–MeSO2–4,4'–DDE relative to 4,4'–DDE. This may be explained by the continuing metabolism of 4,4'–DDE to 3–MeSO2–4,4'–DDE and other metabolites and/or a low rate of excretion of 3–MeSO2–4,4'–DDE during the fasting period. The results indicated that the mobilization of MeSO2–PCBs and 3–MeSO2–4,4'–DDE from adipose tissue in polar bear was likely different from PCBs and 4,4'–DDE over the fasting period.

Regardless of feeding or reproductive status of the female, both the YRLG and the COYs had approximately three times higher ΣMeSO2–PCB levels than their mother's adipose tissue. Moreover, the ratio of ΣMeSO2–PCBs to ΣPCBs was greater for the cubs. This is further indication that transfer of MeSO2–PCBs in milk is faster than that of PCBs. It was not possible to obtain milk samples from the female when she was with the YRLG as she was not lactating.

Table 7. Mean Levels of Precursor PCBs and MeSO$_2$–PCB Metabolites (ng/g, lipid weight) in Ringed Seal Blubber and Polar Bear Fat and Liver Tissues from the Resolute Bay Area of the Canadian High Arctic[1]

parent PCB	Level in seal blubber	MeSO2-PCB[2]	Level in [3]		
			seal blubber	bear fat	bear liver
CB-28/31	10.4 ± 3.2	3–MeSO2 –CB31 (1)	0.61 ± 0.22	11 ± 1	29 ± 16
		4–MeSO2–CB31 (2)	**0.88 ± 0.33**	9 ± 2	41 ± 20
CB-49	5.4 ± 1.1	3–MeSO2–CB49 (4)	**1.40 ± 0.54**	20 ± 3	**153 ± 93**
		4–MeSO2–CB49 (6)	**1.62 ± 0.56**	20 ± 4	**172 ± 75**
CB-52	20.6 ± 7.5	3–MeSO2–CB52 (3)	0.12 ± 0.06	n.d.	n.d.
		4–MeSO2–CB52 (5)	0.01 ± 0.01	n.d.	13 ± 4
CB-64	2.4 ± 1.4	3–MeSO2–CB64 (7)	0.23 ± 0.07	5 ± 1	3 ± 4
		4–MeSO2–CB64 (9)	**0.83 ± 0.27**	16 ± 4	83 ± 30
CB-70/76	13.4 ± 4.4	3–MeSO2–CB70 (13)	0.40 ± 0.18	**43 _ 11**	8 ± 9
		4–MeSO2–CB70 (15)	0.52 ± 0.21	13 ± 2	22 ± 9
CB-87	6.5 ± 1.6	3–MeSO2–CB87 (18)	0.57 ± 0.22	28 ± 6	**398 ± 158**
		4–MeSO2–CB87 (22)	**0.90 ± 0.42**	**53 ± 10**	**148 ± 59**
CB-91	2.4 ± 1.6	3–MeSO2–CB91 (10)	0.22 ± 0.10	16 ± 4	13 ± 4
		4–MeSO2–CB91 (12)	0.35 ± 0.13	**61 ± 8**	26 ± 9
CB-95	2.8 ± 0.8	3–MeSO2–CB95 (8)	0.02 ± 0.02	n.d.	n.d.
		4–MeSO2–CB95 (11)	0.02 ± 0.01	n.d.	n.d.
CB-101	37.5 ± 9.2	3–MeSO2–CB101 (14)	**1.22 ± 0.51**	7 ± 1	**117 ± 65**
		4–MeSO2–CB101 (16)	**1.24 ± 0.50**	**46 ± 10**	66 ± 22
CB-110	7.1 ± 2.7	3–MeSO2–CB110 (19)	0.01 ± 0.00	0.13 ± 0.03	2 ± 1
		4–MeSO2–CB110 (21)	0.45 ± 0.17	9 ± 2	26 ± 10
CB-149[4]	9.1 ± 3.7	3–MeSO2–CB149 (20)	0.28 ± 0.18	7 ± 2	**180 ± 76**
		4–MeSO2–CB149 (23)	**0.72 ± 0.40**	**56 ± 3**	**113 ± 30**
CB-132	n.d.	3–MeSO2–CB132 (24)	0.11 ± 0.06	3 ± 0.4	55 _ 21
		4–MeSO2–CB132 (25)	0.52 ± 0.18	16 ± 4	36 ± 13
CB-141	3.2 ± 2.7	3–MeSO2–CB141 (26)	0.08 ± 0.04	7 ± 1	70 ± 33
		4–MeSO2–CB141 (27)	0.11 ± 0.04	8 ± 2	12 ± 4
CB-174	5.8 ± 2.1	3–MeSO2–CB174 (29)	0.02 ± 0.02	1 ± 0.2	18 ± 6
		4–MeSO2–CB174 (30)	0.12 ± 0.06	5 ± 1	9 ± 2

[1] The mean ± SD of liver and fat for *n*=6 male bears, and *n*=11 male and female seals.

[2] Numbers in parentheses refer to the peak numbers in Figures 2.2 and 4.2.

[3] The most abundant MeSO$_2$–PCB congener levels are in bold.

[4] The only precursor PCB to be detected and quantitated in polar bear liver (85 ± 55 ng/g) and polar bear fat (1.8 ± 0.4 ng/g). n.d. = not detected.

The high MeSO2–PCB levels in milk relative to female adipose tissue on a lipid weight basis, especially at the end of fasting in March 1994, explained why the ΣMeSO2–PCB levels in the cubs were higher relative to the female adipose tissue. The results suggested that the lactational transfer of MeSO2–PCBs to cubs is more significant than PCBs in polar bear.

The data on relationships between PCB concentrations in adipose tissue biopsies, blood plasma and milk, body burdens, and percent body fat changes in 138 bears are currently being analysed.

(viii) Additional activities

The ECNI mass spectral characteristics of 24 bioaccumulating MeSO2–PCB congeners were related to features of congener structure. With the assistance of multi-variate statistical analysis, the abundance of several isotopic clusters of fragment ions relative to that of the molecular ion ((M)-) was found to vary as a function of MeSO2–PCB structure (Letcher and Norstrom 1996a). For example, compared with other congeners, the relative abundance of (M–CH3)- was significantly lower for MeSO2–PCBs containing the 4–MeSO2–2,5–dichloro moiety, and the hexachloro– and heptachloro–MeSO2–PCBs had higher relative abundances of (M–Cl+H)–. Increasing the ion source temperature from 100°C to 260°C resulted in an large increase in the abundance of (M–CH3)– relative to (M)– from <20% to >100%, for all the MeSO2–PCBs studied. Decreasing the methane reagent gas pressure from 0.5 mbar to 0.05 mbar did not significantly alter the ion source temperature effect on the relative abundance of the fragment ions. However, the ECNI response sensitivity decreased by an order of magnitude.

The sensitivity of polar bear adrenal cortex cell preparations to exposure to MeSO2–DDE and other DDT-related compounds is presently being studied at Uppsala University in Sweden.

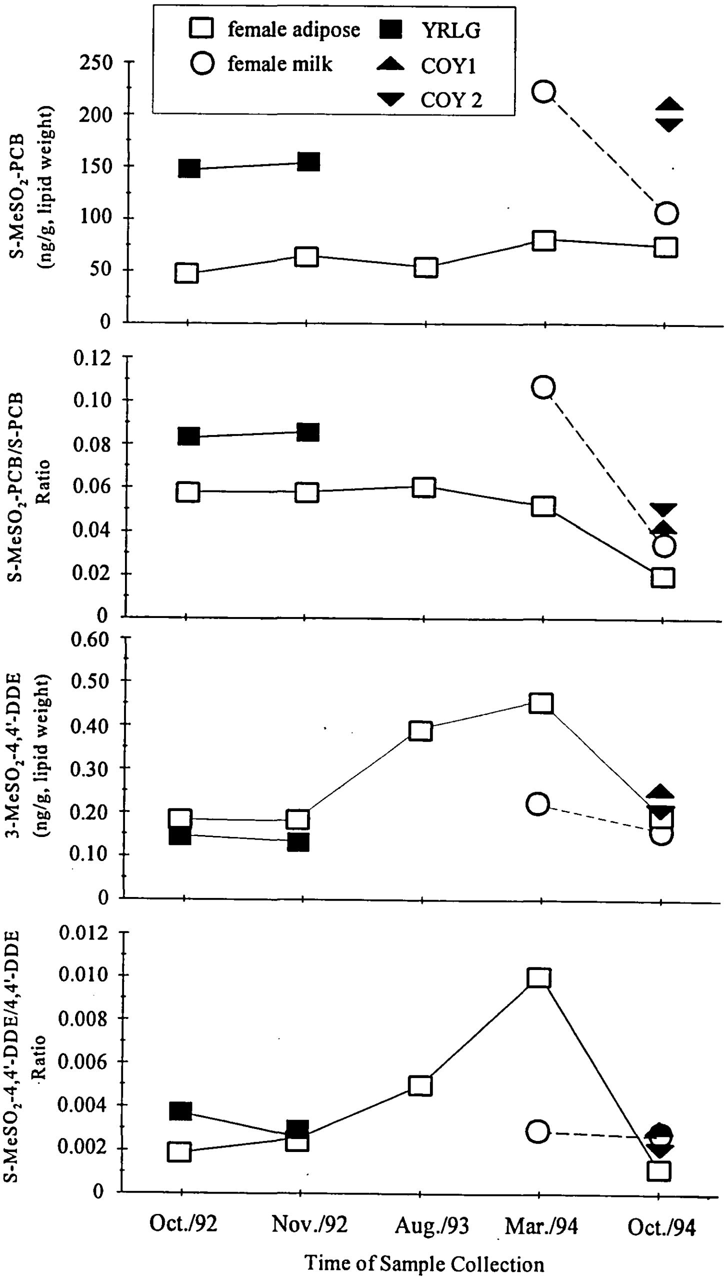

Figure 5. Total MeSO2-PCB and 3-MeSO2-4,4'-DDE levels and the ratios to the total PCBs and 4,4]-DDE for a polar bear mother and her cubs from western Hudson Bay. Top to bottom, ΣMeSO2-PCB levels, the ratio to ΣPCB, 3-MeSO2-4,4'-DDE levels and the ratio to 4,4'-DDE.

Three pools of polar bear plasma (mothers, cubs and juveniles) were prepared and analysed for HO-PCBs using the method of extraction described previously by Bergman *et al.* (1994b). The HO-PCBs were extracted and subsequently derivatized using diazomethane in hexane and analysed by both GC-ECD and GC-MSD in the SIM mode. All three pools of plasma contained the same peaks in approximately the same ratio to each other (Sandau and Norstrom 1996). It was possible to get full EI spectra of the two main peaks found in the polar bear plasma. Both of these peaks had the characteristic para methoxy fragmentation pattern. Using the available MeO-PCB standards and the distinctive hepta-chlorination pattern, the main metabolite in each of the samples was tentatively identified to be 4–MeO–2,3,5,6,2',4',5'–HpCB, based on retention time on a DB–5 column. Retention times on at least two other columns of differing properties will be necessary to confirm this identity. This is the major metabolite found in human plasma and was suggested to result from the hydroxylation of CB–187 or CB–183 (Bergman *et al.* 1994b). If CB–187 is the precursor, metabolism of the PCB would have to have proceeded via para oxygen insertion. None of the other standards in our possession exactly matched the retention time of any of the MeO-PCBs in polar bear plasma except for 4–MeO–2,3,5,6,3',4',5'–HpCB. If this indeed is the identity of the peak, it possesses the same 2,3,5,6–chloro, 4–MeO structure as the major peak. CB–193 is a minor peak in commercial PCBs, but may be present at low levels in polar bears.

The second largest peak was a hexachlorinated compound that was very close in retention time to both the 3–MeO–2,4,5,2',4',5'–HxCB and 4–MeO–2,3,5,2',4',5'–hexachlorobiphenyl standards. These are derivatives of metabolites formed from CB–153 through direct oxygen insertion and NIH shift of chlorine, respectively. Both of these compounds were identified in human plasma by Bergman *et al.* (1994b). Since the unknown hexachloro HO-PCB is found in both females and cubs, the compound or its precursor PCB must be present and persistent enough to be transferred via lactation. It is unlikely that the HO-PCB metabolites would be transferred to the cub through mother's milk and absorbed efficiently to produce the same patterns in plasma as the females. Therefore, the precursor PCB is most likely carried in the milk to the cub where it is then biotransformed to the hydroxy-metabolite.

DISCUSSION/CONCLUSIONS

Polar bears have proven to be a very useful biomonitor of circumpolar distribution of organochlorine contaminants. It is unfortunate that there are so few data from the Russian Arctic for comparison—none at all apart from Wrangel Island, which is part of the Bering/Chukchi Sea sub-population, and therefore not representative of Siberian bears. It would be useful to maintain an occasional broad scale geographical monitoring program on a more limited scale than the recent study reported in Norstrom *et al.* (in press) and in Norstrom (1995, 1994). A five-year time scale is probably adequate to determine temporal trends, and five or six areas (plus Russian areas if they could be added) would suffice to define geographical differences in trends. Sampling should be restricted to adipose tissue of adult male bears, but females could be used to supplement data where necessary, taking into account the difference in PCB and chlordane accumulation between the sexes. A minimum sample size of 10 is desirable. Analysis of 60 to 100 polar bear fat samples every five years would be a very cost-effective measure of temporal trends of organochlorines in the Arctic marine ecosystem.

Atmospheric, oceanic and ice transport, as well as ecological factors may contribute to high concentrations of PCB in some areas. The cause of the high concentrations of a number of contaminants, especially PCBs, but also mercury, in bears in the Arctic Ocean near M'Clure strait should be studied in more detail. There may be an ecological explanation. Ice algae and under-ice amphipods may be more important as the vector of contaminant flow into the food chain in these areas where there is multi-year ice. Given that most of the bears in this area were sampled on the polar ice cap, it is possible that the exaggerated concentrations of PCBs and other organochlorines 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 concentrations of cadmium in ringed seal and polar bear from the western Arctic (to Barrow Strait) have been attributed to a greater proportion of hyperiid amphipods in the ringed seal diet (Macdonald and Sprague 1986, Braune *et al.* 1991). Polar bears from M'Clure Strait also had exceptionally high concentrations of mercury in liver compared to nearby regions (Braune *et al.* 1991). If the source of mercury was biogeochemical rather than long-range transport, this finding supports the idea that polar bear or ringed seal feeding ecology in this region may differ from other areas in some respect.

There is no indication that the Arctic marine ecosystem is contaminated with PCDDs or PCDFs at concentrations that warrant further monitoring. However, further research on identification of chlordane-related contaminants is indicated. The only other study of PCDDs and PCDFS in polar bears was in milk from Svalbard bears (Oehme *et al.* 1995). Converting their concentrations to a lipid weight basis, 2,3,7,8–TCDD was lower in Svalbard bears in 1990 (mean 0.56 ± 0.42 ng/kg lipid, n = 6 individuals) than in the Canadian bears the same year (mean 2.42 ± 1.09, n = 4 pools with 39 individuals). However, OCDD was much higher in Svalbard bears, mean 45 ± 60 ng/kg, compared to 1.70 ± 0.77 ng/kg in the present study. OCDD concentrations and differences between the two studies should be viewed circumspectly, since the potential for sample contamination cannot be ruled out. One notable feature about PCDD patterns is that 1,2,3,7,8–PnCDD is consistently two to three times higher than 2,3,7,8–TCDD in ringed seals and polar bears from Svalbard, but the reverse is true for the Canadian Arctic (Norstrom *et al.* 1990, Oehme *et al.* 1995). This may indicate the importance of European sources in Svalbard, since 1,2,3,7,8–PnCDD generally tends to be higher in European than North American fish and wildlife.

Methyl sulfone formation was an important, but not the major route for most m,p–PCB and 4,4–DDE biotransformation in ringed seal or polar bear. We estimate that a maximum of ca. 10% of the metabolism of meta-para-PCBs capable of forming bioaccumulating MeSO2–PCBs proceeds by this metabolic pathway in arctic ringed seal. In polar bear, the metabolism of PCBs with meta-para adjacent carbons is complete, however, the proportion that forms MeSO2–PCB metabolites also appears to be small. At least two congeners, 3– and 4–MeSO2–CB132, are bioaccumulated entirely from ringed seal by polar bears. The bioaccumulation factor was 30, 63% of that for CB153. Therefore MeSO2–PCBs have high biomagnification potential in food chains. It is probable that a number of other congeners are also bioaccumulated mainly from ringed seal. It can also be concluded that formation and/or slow clearance of MeSO2–CB70, –CB91, –CB149 and –CB141 occurs in the bear. In no case did the actual MeSO2–PCB level exceed 63% of the maximum potential level due to bioaccumulation and metabolic formation from precursor PCBs in seals, indicating that metabolic pathways other than sulfone formation were usually favoured. The sulfone formation pathway appears more favoured for CB–70 and CB–91. Less than ca. 1% of 4,4'–DDE metabolism favoured MeSO2–metabolite formation in seal and bear. It is clear that MeSO2–PCB uptake from seal is an important source of MeSO2–PCBs in bear. Further, it appears that selective bioaccumulation, formation and retention of MeSO2–PCBs all influence the resulting MeSO2– PCBs congener levels and patterns in both seal and bear.

The present study represents the most comprehensive examination of MeSO2–PCBs and –4,4'–DDE tissue distribution in any wild animal species. In polar bear, liver was the preferred tissue of MeSO2–PCBs and –4,4'–DDE storage. Bergman *et al.* (1994a) found a similar preference for MeSO2–PCB storage in liver relative to adipose or muscle tissue in Baltic Sea grey seal and Swedish mink and otter. The ΣMeSO2–PCB to ΣPCB ratios for testes, adipose, brain and lung averaged 0.05. The liver (0.11) ratio was higher, indicating that MeSO2–PCBs are more selectively retained in liver than PCBs, relative to the other tissues. Moderately polar OCs containing oxygen, such as oxychlordane, tend to accumulate preferably in polar bear liver, possibly because of the high density of lipid-containing Stellate (Ito) cells that are specialized in retinol and retinol ester (vitamin A) storage in adults. Stellate cells are an adaptation in polar bears, due to the high levels vitamin A in ringed seal blubber, their primary dietary item.

Prior to this study, MeSO2–4,4'–DDE had not been detected in polar bear apart from the liver (Bergman *et al.* 1994b). The preferential storage of MeSO2–4,4'–DDEs in polar bear liver was emphasized by the ΣMeSO2–4,4'–DDE to 4,4'–DDE ratio of 0.46 as compared to the mean value of 0.04 for adipose, lung and testes. The highly asymmetric tissue distribution of ΣMeSO2–4,4'–DDE may be due to several factors. High levels in liver may result because this is the site of formation, or because of highly selective binding in heptatocytes or Stellate cells. Levels may be lower in other tissues because of competition with irreversible binding in specific organs. The 3–MeSO2–4,4'–DDE metabolite has been shown to irreversibly bind in the adrenal cortex of mice, Baltic grey seal, mink and birds (Jönsson *et al.* 1994).

Results from the preliminary chicken hepatocyte bioassays indicated some Ah-receptor activity was present. However, re-analysis of some of the extracts is necessary to obtain more accurate estimates of EC50s. The PCB, OC and MeSO2–PCB/-DDE fractions were not exceptionally responsive in the EROD activity portion of the assay. However, porphyrin accumulation did occur for all extracts, most notably at concentrations in the EROD dose-response curve where the activity was sub-basal. If a rough assumption is made that the MeSO2–PCBs/-DDEs were ca. 10% of the concentration of ΣPCBs in the polar bear fat and liver samples, the sulfones appeared to be approximately equipotent porphyrinogens.

The toxicological significance of the presence of MeSO2–PCBs in polar bear is difficult to assess. However, their concentration in liver lipids is ca. 2 mg/kg, and some congeners are known to be potent inducers of CYP2B enzymes (Kato *et al.* 1993), and also to inhibitory (Nagayama *et al.* 1989). The different pattern of MeSO2–PCBs in liver compared to adipose tissue indicates that there is highly selective binding occurring, possibly to CYP proteins, as has been found for other species (Bergman *et al. 1994a)*. There is therefore potential for endocrine disruption due to effects on steroid hormone metabolism. The finding that other tissues, including lung and testes, had patterns similar to adipose tissue suggests that selective binding is not occurring in these tissues. We are testing the sensitivity of polar bear adrenal cortex cells to MeSO2–DDE, which has been shown to be a potent agent causing hyperadrenocorticism in some laboratory rodents (Brandt *et al.* 1990).

Hydroxy-PCBs were shown to be present in polar bear plasma at concentrations similar to those of PCBs. Some of the congeners were the same as those reported in humans (Bergman *et al.* 1994b), but the overall pattern was somewhat different.

Expected project completion date: March 31, 1999.

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

Project Leader: Mark Palmer, Chair, Yukon Technical Committee on Contaminants in Northern Ecosystems and Native Diets

Project Team: Government of Yukon Fisheries; Dept. Fisheries and Oceans; Department of Indian Affairs and Northern Development; Canadian Wildlife Service; Council for Yukon Indians

OBJECTIVES

Short-term

1. To collect information to complement that gathered in the 1991, 1992, 1993, and 1994 seasons by sampling additional lakes.
2. To collect information to confirm that information gathered in the 1991, 1992, 1993 and 1994 seasons address concerns raised by health advisories based on existing data.
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. 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 used the fisheries resources throughout the Yukon.

The primary purpose of sampling was to assure Yukoners of the safety of fish for human consumption. For this reason, sampling was designed as a survey of fish stocks that are important primarily in aboriginal fisheries. Lake trout and whitefish were the species sampled in most lakes, as these fish are widespread and commonly eaten. Burbot livers, which are a traditional First Nations food, were sampled where possible. Arctic grayling and northern pike were sampled in Lake Laberge and at several other locations for comparison. In 1993, salmon samples were taken from important native fishing areas and from the Whitehorse fishway.

ACTIVITIES AND RESULTS

Fish were sampled from lakes and rivers throughout the Yukon from 1990 to 1996 (see map). Results of fish muscle tissue and burbot liver samples collected from 1990 to 1994 are presented in Table 1.

The sampling strategy for most lakes was to collect sufficient fish for six pooled samples of each of whitefish and lake trout. Samples were pooled on the basis of fork length, and were made up of about six fish each. Three of these pooled samples for each of whitefish and

Table 1. Organochlorines in Yukon Fish, 1990–1994. Mean concentrations (or ranges of means) for Yukon lakes

Species/ Tissue type	Location (number of lakes/rivers)	Sample Sizes[1]	Lipid[2] %	Toxaphene[2] ng/g	ΣPCB[2] ng/g	DDTs[2] ng/g	Chlordane[2] ng/g
burbot liver	Laberge	35	44	2301	1267	3433	217
	Atlin	6	33	1533	136	105	138
	other (13)	2–8	19–47	54–945	50–579	21–272	10–183
lake trout muscle	Laberge	27 P	6.1	344	448	458	30
	Watson	2 P	5.2	<12.9	38	3427	2.2
	other (24)	2–15 P	0.8–7.1	0.9–296	3.5–128	2.6–403	1.1–21
whitefish muscle	Laberge	3 P	3	33.8	61	212	8.5
	Watson	2 P	2.2	<11.7	6.9	464	2.7
	other (17)	2–5 P	0.3–3.6	0.2–52	0.1–8.3	0.1–6.6	<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
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
	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	5 P	1.8	48	90	247	14
	other(3)	3–6 P	0.2–0.6	<0.1–1.2	0.1–1.1	<0.2–2.5	<0.1–0.5

[1] Sample sets marked with a "P" are all or mainly pooled samples, usually with about 6 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, i.e. the proportion of the whole wet sample that is lipid or a certain class of organochlorines.

lake trout were submitted for analysis to Axys Analytical in Sidney, B.C., and the remaining fish were retained in case the results of the first set of analyses were not clear. Pooled sampling was used to increase the number of fish on which the average organochlorine levels for each location was based. Whitefish, being low in the food chain and low in lipid content, were consistently low in organochlorines. However, they were sampled at all locations because of their importance to the aboriginal fishery.

Duplicate samples from each fish have been kept and are archived in Whitehorse in a –80°C freezer.

DISCUSSION/CONCLUSION

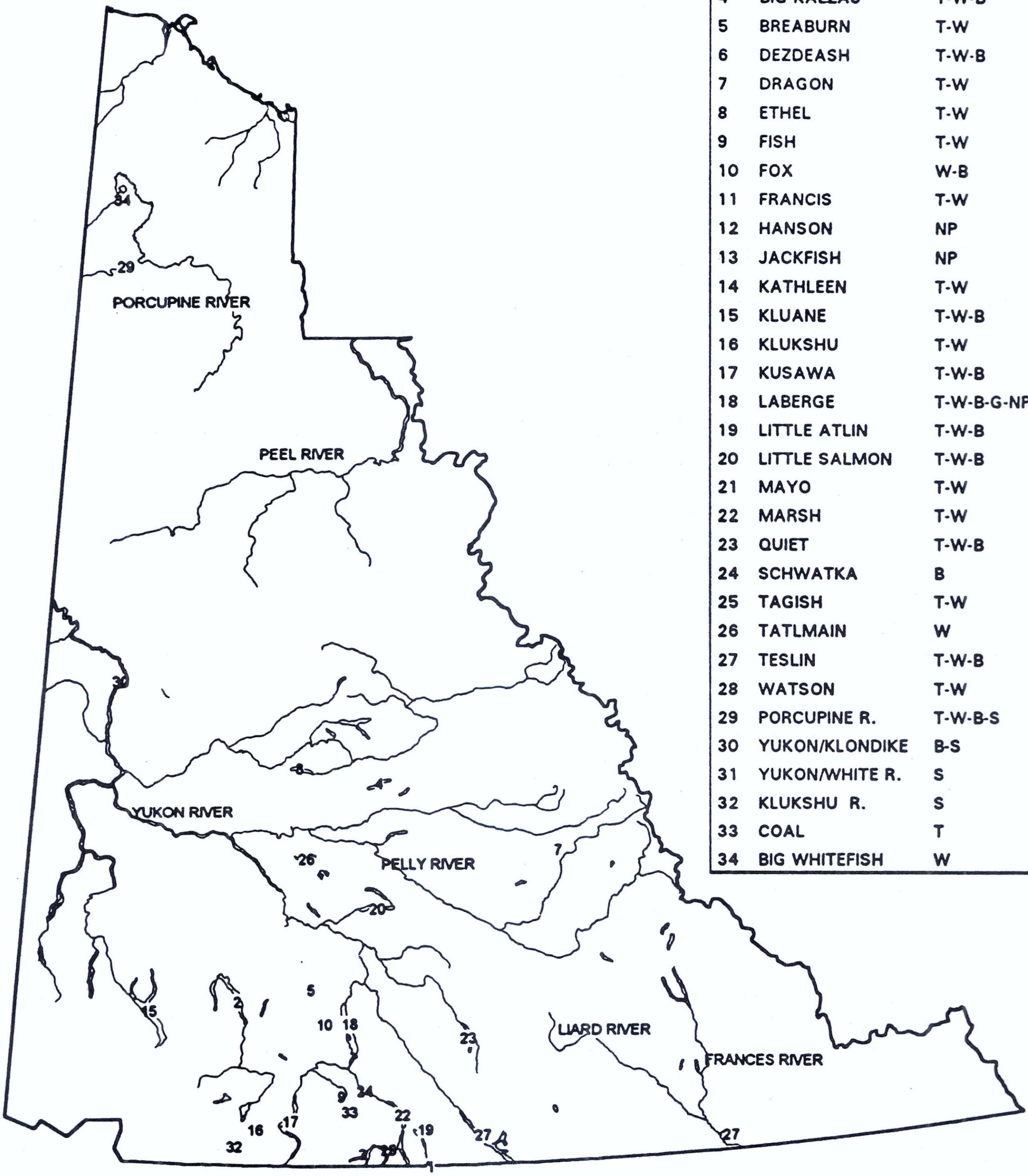
There are consistent differences in contaminant levels among species of fish from the same location. Burbot liver was consistently the highest in organochlorines of any fish tissue sampled. By contrast, the very low-lipid burbot muscle (sampled at Lake Laberge) was extremely low in organochlorines. Lake trout vary in their feeding habits and in their lipid levels, but tend to have the highest muscle-tissue contaminant levels of species sampled. Whitefish, salmon, arctic grayling and northern pike had non-detectable to low levels of organochlorines.

Some regional variations are related to past local sources. DDT is higher at Lake Laberge and Watson Lake, areas where extensive spraying of DDT for mosquito control was carried out from the 1940s to the 1960s. PCBs appear to be higher in Lake Laberge than at other locations. This is most probably related to past use or disposal of PCBs in the Whitehorse area.

Some variations may be related to location. Samples from the Old Crow and Porcupine Rivers area were all very low in organochlorines, possibly reflecting a lower rate of contaminant deposition in the northern Yukon.

YUKON FISH SAMPLING LOCATIONS

NO	WATERBODY	FISH
1	ATLIN	T-W-B
2	AISHIHIK	T-W
3	BENNETT	T-W
4	BIG KALZAS	T-W-B
5	BREABURN	T-W
6	DEZDEASH	T-W-B
7	DRAGON	T-W
8	ETHEL	T-W
9	FISH	T-W
10	FOX	W-B
11	FRANCIS	T-W
12	HANSON	NP
13	JACKFISH	NP
14	KATHLEEN	T-W
15	KLUANE	T-W-B
16	KLUKSHU	T-W
17	KUSAWA	T-W-B
18	LABERGE	T-W-B-G-NP
19	LITTLE ATLIN	T-W-B
20	LITTLE SALMON	T-W-B
21	MAYO	T-W
22	MARSH	T-W
23	QUIET	T-W-B
24	SCHWATKA	B
25	TAGISH	T-W
26	TATLMAIN	W
27	TESLIN	T-W-B
28	WATSON	T-W
29	PORCUPINE R.	T-W-B-S
30	YUKON/KLONDIKE	B-S
31	YUKON/WHITE R.	S
32	KLUKSHU R.	S
33	COAL	T
34	BIG WHITEFISH	W



Rick Seaman Jan 97

Figure 1. Yukon Fish Sampling Locations

Table 2. Levels of Selected Organochlorines in Lake Laberge Fish, 1990–1996 (mean values, wet weight basis)

Year	Lab[1]	Number of analyses	fish weight (g)	lipid (%)	ΣChlordane (ng/g)	ΣDDT (ng/g)	Toxaphene (ng/g)	ΣPCB (ng/g)
A	**Burbot Liver**							
1990	Axys, DFO	14	1672	48	227	4368	2740	1139
1991	DFO	6	2230	35	324	4109	2958	1838
1993	Axys	15	1293	45	165	2291	1629	1159
1996	Axys	8	1347	49	121	2281	2390	977
B.	**Lake Trout Muscle**							
1990	Axys	4	1597	13	27	1031	805	268
1991	DFO	6	1632	9	4	938	559	1593
1993	Axys	17	1751	4	2	154	160	87
1996	Axys	10	2205	5	1	147	173	86

[1] Axys = Axys Analytical Services, Sidney, B.C.
DFO = Freshwater Institute, Department of Fisheries and Oceans, Winnipeg, Manitoba

Old Crow whitefish had the highest lipid levels and yet had the lowest overall organochlorine levels of all whitefish sampled. Northern pike samples were collected in 1996 from the Old Crow Flats but have not yet been analyzed. Lakes with higher contaminant levels tend to be in the upper Yukon River basin, in southwest Yukon, but there are also lakes with very low levels of contaminants in fish in this region.

The three species of salmon, despite different life histories and different marine feeding areas (in the Pacific Ocean and Bering Sea), had similar levels of organochlorines. Toxaphene was the dominant organochlorine as it was in most samples from freshwater fish species.

At selected locations, lake trout and whitefish eggs, livers and stomachs, and salmon eggs were analyzed along with the muscle samples. In general, for the same fish, the organochlorine levels were found in proportion to the lipid content of the body part.

Lake Laberge Organochlorine Update

In 1996 the Yukon Government sampled lake trout and burbot from Lake Laberge as part of the Lake Recovery Program. Samples of burbot liver and trout muscle tissue were analysed for organochlorines. The results (summarized in Table 2) were similar to the 1993 sample set and confirm the downward trend for some organochlorines, especially in lake trout. During 1997/98 the Lake Laberge data (along with other data from the Yukon Southern Lakes) will be reviewed in the context of new data sets and improved understanding of the influence of lake ecology and toxaphene chemistry.

Expected project completion date: Ongoing.

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 Resources, Wildlife and Economic Development, Government of the Northwest Territories (GNWT)

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.

ACTIVITIES IN 1995/96

Data collection and laboratory analysis for this project were completed in 1994/95. During 1995/96, interpretation and analysis of the entire four years of data were started. The results of the study were released to participating communities, trappers, and wildlife personnel in the fall of 1995 using colour posters and CBC radio interviews.

RESULTS

Two hundred and seven mink were examined for organochlorine residues during the study. All groups of organochlorine compounds were detected at relatively low levels (Table 1). Among-community differences were found for all groups of organochlorine pesticide residues; however, spatial trends were evident primarily for ΣDDT, ΣChlordane and dieldrin, where, with the exception of Fort Liard mink, there was a general trend of decreasing levels with increasing latitude. No spatial pattern was apparent for ΣHCH and HCB. ΣDDT residues ranged from 1.2 $ng{\cdot}g^{-1}$ in Inuvik mink to 9.5 $ng{\cdot}g^{-1}$ in Fort Providence animals. In all but two mink, DDT was below detection limits.

Mean ΣPCB residues ranged from 7.0 $ng{\cdot}g^{-1}$ from Inuvik mink to 73.1 $ng{\cdot}g^{-1}$ from Fort Providence animals (Table 1). There was a general trend of decreasing ΣPCB levels with increasing latitude. Fort Liard mink were again the exception, having a mean ΣPCB of 10.6 $ng{\cdot}g^{-1}$. Of the more toxic non-*ortho* substituted PCB congeners,

Table 1. Arithmetic means (ng·g^{-1} wet weight (SE)) of selected organochlorine residues in livers of mink collected in the Northwest Territories, 1991/92 to 1994/95. Levels of each group of organochlorines differed among communities (ANOVA; all P < 0.0001, except dieldrin ($P = 0.004$)), calculated on lipid corrected, log$_{10}$ transformed data. Communities with similar mean levels (Duncan's multiple-range tests, $P > 0.05$) are marked by the same letter. Highest mean for each organochlorine group highlighted in bold.

Community	n	% lipid	ΣDDT[1]	ΣHCH[2]	HCB	ΣChlordane[3]	Dieldrin	ΣMirex[4]	ΣPCB[5]
Inuvik	58	5.4 (0.33)	1.19^{c} (0.25)	0.10^{b} (0.02)	0.33^{b} (0.03)	1.58^{bc} (0.16)	0.12^{b} (0.02)	0.08^{c} (0.02)	7.02^{d} (0.86)
Fort Good Hope	18	7.5 (0.88)	3.35^{b} (0.62)	0.16^{b} (0.04)	**0.67**^{ab} (0.10)	2.30^{b} (0.36)	0.45^{ab} (0.11)	0.31^{ab} (0.12)	17.17^{c} (3.25)
Fort Rae	14	5.9 0.53)	4.73^{ab} (0.91)	**0.20**^{a} (0.04)	0.48^{ab} (0.06)	2.97^{ab} (0.60)	0.22^{b} (0.09)	0.35^{a} (0.09)	24.70^{bc} (5.45)
Fort Liard	25	4.2 (0.21)	1.69^{c} (0.88)	0.05^{b} (0.01)	0.21^{c} (0.05)	0.87^{c} (0.23)	0.08^{b} (0.02)	0.17^{bc} (0.06)	10.58^{d} (3.49)
Fort Smith	26	4.5 (0.34)	3.75^{ab} (0.70)	0.11^{b} (0.05)	0.52^{a} (0.08)	**3.48**^{a} (0.80)	**0.74**^{a} (0.26)	**0.39**^{ab} (0.13)	23.51^{bc} (4.37)
Fort Providence	41	5.1 (0.36)	**9.52**^{a} (2.24)	0.09^{b} (0.02)	0.36^{b} (0.07)	2.69^{ab} (0.44)	0.23^{ab} (0.05)	0.25^{ab} (0.06)	**73.07**^{a} (13.14)
Fort Resolution	25	6.1 (0.48)	8.50^{a} (1.65)	0.03^{c} (0.00)	0.53^{ab} (0.09)	2.93^{bc} (0.96)	0.51^{ab} (0.20)	0.16^{bc} (0.04)	41.07^{ab} (7.46)

[1] ΣDDT = Sum of *p,p'*-DDT and *p,p'*-DDE and *p,p'*-DDD.

[2] ΣHCH = Sum of α–HCH, β–HCH and γ–HCH.

[3] ΣChlordane = Sum of *oxy*-, *cis*-, *trans*-chlordane, heptachlor epoxide and *cis*-, *trans*-nonachlor.

[4] ΣMirex = Sum of photomirex and mirex.

[5] ΣPCB = Sum of individual congeners.

Table 2. Arithmetic means (μg·g^{-1} (SE)) of metals from mink collected from the Northwest Territories, 1991/92 to 1994/95. All metals given in dry weight in kidneys, except for total mercury (Hg) given in wet weight in livers. Levels of each metal differed among communities (ANOVA; all $P < 0.0001$, except Cu ($P = 0.007$), and Fe ($P = 0.015$)), calculated on log$_{10}$ transformed data. Communities with similar mean levels (Duncan's multiple-range tests, $P > 0.05$) are marked by the same letter. Highest mean for each metal highlighted in bold.

Community	*n*	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Hg
Inuvik	53	5.63^{bc} (0.76)	0.59^{bc} 0.12)	**0.77**^{a} (0.08)	18.28^{b} (1.70)	818.9^{b} (30.5)	2.88^{c} (0.22)	0.71^{b} (0.12)	0.52^{b} (0.17)	76.97^{bc} (3.04)	1.45^{b} (0.11)
Fort Good Hope	20	8.41^{a} (0.75)	0.90^{a} (0.19)	0.45^{a} (0.03)	19.89^{a} (1.04)	964.6^{a} (53.4)	**11.18**^{a} (2.96)	**1.89**^{a} (0.33)	0.27^{b} (0.11)	67.91^{c} (6.00)	2.17^{ab} (0.29)
Fort Rae	16	**9.49**^{a} (1.47)	**1.12**^{ab} (0.45)	0.44^{a} (0.05)	**20.82**^{a} (1.27)	957.9^{a} (45.8)	4.95^{a} (0.30)	1.32^{a} (0.22)	**0.99**^{a} (0.18)	104.37^{a} (5.34)	**3.30**^{a} (0.65)
Fort Liard	26	8.63^{b} (2.42)	0.85^{ab} (0.23)	0.32^{b} (0.08)	16.89^{ab} (0.80)	808.3^{b} (43.5)	3.18^{bc} (0.19)	0.29^{c} (0.03)	0.22^{b} (0.01)	78.77^{b} (5.14)	1.00^{cd} (0.16)
Fort Smith	16	7.64^{cd} (2.35)	0.16^{d} (0.03)	0.60^{a} (0.13)	14.29^{b} (0.83)	818.6^{ab} (51.2)	2.43^{bc} (0.20)	0.32^{c} (0.04)	0.10^{c} (0.02)	81.74^{b} (4.48)	1.30^{bc} (0.28)
Fort Providence	30	5.87^{bcd} (1.02)	0.35^{cd} (0.08)	0.20^{b} (0.04)	19.56^{ab} (1.37)	968.0^{b} (51.4)	2.94^{a} 2.94^{a} (0.13)	0.19^{c} (0.01)	0.22^{b} (0.01)	85.34^{b} (3.55)	1.02^{d} (0.21)
Fort Resolution	24	2.34^{d} (0.50)	0.86^{a} (0.13)	0.15^{b} (0.03)	20.70^{a} (1.20)	**992.2**^{ab} (60.2)	3.20^{ab} (0.20)	0.20^{c} (0.01)	0.27^{b} (0.03)	**108.16**^{a} (4.20)	0.91^{e} (0.32)

PCB77 was detected in no samples, PCB126 was found in three samples (two from Fort Good Hope and one from Fort Smith), and only one mink from Fort Smith had residues of PCB169.

Mink from all communities were pooled to examine differences in organochlorine burdens between sexes and with age. Only two groups of compounds showed significant differences between sexes; ΣHCH and HCB levels were higher in females than males. No differences were detected between mink <2 years old and mink $\geq$2 years old for any groups of compounds. Between-community differences in levels may have masked true differences among these variables.

PCDDs and PCDFs were not detected in any of the five pooled mink liver samples. Total toxaphene ranged from 1.4–8.3 $ng \cdot g^{-1}$ in 10 pooled liver samples. There was no apparent spatial pattern to the levels of toxaphene observed.

Levels of heavy metal burdens were found to be relatively low (Table 2). Significant among-community differences were detected in all of the metals. There was no obvious geographic trend to the pattern of concentrations; however, mink from Fort Rae had the highest levels of five of the metals.

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.

Expected project completion date: No further funding from NCP/AES requested after March 31, 1996. The first two years of data have been published (Poole *et al.* 1995). The complete data set will be submitted for publication during 1996/97.

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

Project Leader: R. Wagemann, Freshwater Institute, Winnipeg, Man.

Project Team: R. Wagemann, G. Boila, E. Trebacz (contractor), and W. L. Lockhart.

OBJECTIVES

1. To determine spatial and temporal trends of toxic metals (lead, cadmium, mercury) and methylmercury in tissues of ringed seals and arctic whales.
2. To provide a data base of methylmercury and toxic metals for estimating dietary contamination in arctic marine mammals.
3. To provide a data base of the average fraction of methylmercury in groups of arctic mammals and fish.

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, for deducing temporal trends by comparison with past and future data, and for providing a basis for dietary calculations. Past information on methylmercury especially, has been very sparse for most tissues of arctic marine mammals, and nonexistent for contaminants in muktuk. Methylmercury (MeHg) is of interest because of its toxicity to biota, including man, and the role it plays in environmental pollution. This report deals largely with the determination of the average percentage of methylmercury and organic mercury in marine mammals from across the Arctic and in fish.

A variety of methods have been developed in the past to determine MeHg in various types of biological and environmental samples. They differ in the procedure used to release and extract MeHg from tissues and in the separation and detection of MeHg. The most specific method for measuring MeHg is mass spectrometry (MS). It is unpopular, however, because of mercury's tenacious adherence to surfaces causing protracted "contamination" of the instrument. A commonly used method is gas-liquid chromatography (GC) using the electron-capture detector (ECD) which is fairly specific for methylmercuric halides and has been used frequently for such determinations with packed columns and more recently with capillary columns. This was the method used by this project to measure methylmercury.

Some studies have reported "organic" mercury in tissues (Filippelli 1987, Shum *et al.* 1979, Schintu 1992, Sanpera *et al.* 1993) using cold-vapour spectroscopic analyses (CVAAS) and equated this with methylmercury. It is unclear whether or not the "organic" mercury is equivalent to MeHg in all types of tissue. There is only scant comparative information to show whether or not this is or is not the case (Thibaud and Cossa 1989).

This study had two objectives. One was to investigate whether or not the organic mercury determined by CVAAS, using an appropriate organic solvent to extract the tissues, was substantially MeHg in both muscle and liver of different animals. The CVAAS method is simpler, less time consuming, and less costly than any GC method, and for these reasons would be more attractive if found valid. The other was to determine, using a number of different approaches, the average percentage of MeHg and organic mercury in groups of animals and to demonstrate their validity or lack of it.

ACTIVITIES IN 1995/96

Samples

Analyses for methylmercury, organic mercury and total mercury in tissue were performed on samples from belugas and ringed seals already in hand, and on fish tissues of Walleye (*Stizostedion vitreum vitreum*) from Lac Ste Therese obtained through Dr. J. Klaverkamp's program at the Freshwater Institute (FWI). Some analyses for mercury in blubber on samples in hand (narwhal, belugas) have already been performed and the results will be included in the next report, pending completion of the present comparative work. The highest priority will now be given to additional methylmercury and total mercury analyses in blubber and other tissues and to body fluids to complete the production of a substantial data set for methylmercury in marine mammal tissues from across the Arctic. Samples already in hand will be analysed for methylmercury preferentially, except when requested by Government agencies or outside interests to analyse new samples on an urgent basis. New samples will only be analysed when necessary to fill a gap in the sampling grid or when provided by Native people in conjunction with Native hunts. In the next two years, time and effort will be directed largely toward the production of an overview of methylmercury levels in marine mammals from across the Arctic and sub-Arctic in different types of tissues and body fluids and the speciation of mercury in tissues.

Methods

Muscle and liver tissues of beluga whales *(Delphinapterus leucas)*, narwhal (*Monodon monoceros*), ringed seals (*Phoca hispida*) and fish (walleye, *Stizostedion vitreum vitreum*) were analysed for MeHg, organic Hg and total Hg. The release of MeHg and organic mercury from the tissues was achieved by the commonly used procedure of Uthe *et al.* (1972) using acidic sodium bromide and cupric sulfate.

Total Mercury

A quantity of tissue (ca 0.2 g) was digested with a mixture of nitric and sulfuric acids (1:4 v/v) and total mercury was determined by cold-vapour atomic absorption spectroscopy (CVAAS), using the air-segmented, flow-injection method (Armstrong and Uthe 1971). A TM 3200 (TSP Thermo Separation Products) mercury monitor was used. Data were recorded with a "Chrom Jet Integrator" (TSP Thermo Separation Products). Aqueous working standards (1-10 µg/L) were prepared daily from a "Baker instra-analysed" 1000 µg/ml Hg stock solution. The detection limit for Hg by the CVAAS method under the operating conditions employed was 5 ng/g wet wt.

Total Selenium Determination

Essentially the semi-automatic borohydride method of Vijan and Wood (1976) was used. Tissue samples were digested with nitric, perchloric and sulfuric acids (4:1:0.5 v/v), and the resulting digest was diluted with hydrochloric acid and water to 30% hydrochloric acid. The diluted digest and reductant (2% borohydride solution) were combined at flow rates of 4 and 1 mL/min respectively, using a Technicon pump, Model III, coupled to a Varian programmable Model 55 sampler. The hydride was decomposed in a heated quartz tube and the selenium was analysed at a wavelength of 196.1 nm using a Varian Spectra AA-20 Absorption Spectrometer.

Organic Mercury

Toluene was used as the initial extraction solvent in the determination of organic mercury. Since toluene did not lend itself to mineralization or evaporation with HNO_3/H_2SO_4, it was back-extracted with aqueous thiosulfate and the latter was analysed for mercury by CVAA as described for total mercury. The detection limit for organic mercury by this method was 10 ng/g wet wt.

Methylmercury

The procedure of Uthe *et al.* (1972) was largely followed. The acidic, aqueous tissue homogenate, was extracted with toluene. A fraction of the toluene was withdrawn and extracted with aqueous thiosulfate. To the separated thiosulfate solution (1–2 ml), KI was added and this solution was then back-extracted with toluene. The separated toluene extract was dried over anhydrous sodium sulfate and injected (1 µL) into the GC column for MeHg analysis.

A Varian model 3400 gas chromatograph with a ^{63}Ni electron capture detector (ECD), temperature programmable injector (SPI), and a 5 m, SPB-5 mega-bore column (0.53 mm ID) with a bonded film (5 m) of polysiloxane (94% dimethyl, 5% diphenyl, 1% vinyl) was used. The carrier gas was helium (12 ml/min), the make-up gas nitrogen (28 ml/min). The temperature of the column and injector was maintained at 50°C for 1 min, programmed to increase to 240°C (at 20°C/min), and maintained at this temperature for 15 min before the cycle was repeated. The detector was maintained at 300°C at all times.

Working MeHg standards (5–100 ng /ml Hg in toluene) for GC analysis were prepared daily from a toluene/MeHg stock solution (1 µg/ml Hg). Within the concentration range of these working standards, the ECD response was linear. The absolute detection limit for CH_3HgCl by GC-ECD was 2 pg (based on 3 x sd of blank analyses), or 10–80 ng/g Hg wet wt (depending on dilution factor) in terms of the procedure used.

Quality Assurance

Marine mammal liver tissue with relatively high organic mercury and MeHg content was used to test recovery and successive extraction efficiencies of MeHg. Tests to determine the accuracy of MeHg determinations were carried out using standard MeHg solutions, certified reference materials Dorm–1 and Dorm–2, (NRC, Ottawa) and spiked liver samples. Recoveries for the two procedures (CVAAS and GC-ECD) were on average the same for MeHg and organic Hg, 92%, with one extraction.

RESULTS

The calculation of the average percentage of MeHg and organic mercury relative to total mercury involves multiplication (or division) of two variables namely, the MeHg or organic mercury concentration (M_i), and the total mercury concentration (T_i). The average ratio of the two variables can be calculated by averaging the two variables individually and then obtaining the ratio (using both, arithmetic and geometric averages of the two variables), or by taking the ratio of the two variables first M_i/T_i (=f_i) for each set of data and then averaging these fractions (n= sample size) as shown above to the left. The corresponding geometric averages were calculated as shown above to the right.

For geometric averages, the two calculation methods for mean ratios are in effect the same.

$$\frac{\Sigma M_i}{\Sigma T_i} \qquad \frac{\Sigma f_i}{n} \qquad \frac{\sqrt[n]{\Pi_i M_i}}{\sqrt[n]{\Pi_i T_i}} \leftrightarrows \sqrt[n]{\Pi f_i}$$

Based on the algebra of expectations (E) the equation E(MT) = E(M)E(T) (Winkler and Hays 1975) is true only if M and T are independent, random variables. The left-hand side of the "expectations" equation represents the average of the combined variables (in this case the average ratio or percent) and the right-hand side the averaged individual variables algebraically combined to obtain the average ratio. However, the variables in question were found not to be independent but linearly related in the groups of animals we investigated. The average ratio could then also be obtained by linear regression of the two variables (i.e. using the regression slope as the average ratio). The results obtained by the different calculating approaches were different (Table 1). Under conditions of non-compliance with the "expectations" equation the results obtained by regression analysis were deemed to be the most acceptable (column A, Table 1). Robust, linear regression analysis, Andrews' sine algorithm (Andrews 1974) was used, which minimizes regression errors by reiterative calculation and weights data points accordingly, minimizing or removing the influence of extreme values.

For all samples investigated MeHg, organic mercury, and total mercury were linearly related in muscle and liver. The regression slopes of organic mercury and MeHg on total mercury in muscle of narwhal, beluga, ringed seals, and fish (mixed sample) were 1.10 (Figure 1a) and 1.04, respectively (Figure 1b), indicating that on average all mercury in muscle was organic mercury and also that the organic mercury consisted entirely of MeHg in this type of tissue.

The regression slopes of organic mercury and MeHg on total mercury in liver of the mixed sample were 0.145 (Figure 1c) and 0.058 (Figure 1d), respectively, indicating that on average 14.5% of the total mercury in the liver was organic mercury, and 5.9% of the total mercury was MeHg (Table 1). When calculated by first averaging the MeHg, organic mercury and total mercury, and using these averages to obtain the respective average percentages, higher values were obtained than by regression analysis. It also mattered whether arithmetic or geometric means were used in this procedure. For geometric means, because the two calculation methods (Table 1, columns B and C) reduce to the same formula, identical percentages were, of course, obtained, but the two calculation methods are not equivalent for arithmetic means. The mean percentages were higher when calculated from separately averaged variables, irrespective of the type of average, than when obtained by regression analysis (Table 1).

The regression slope of MeHg on organic mercury in liver of marine mammals (mixed sample) was 0.377 (Figure 1a), indicating that only 37.7% of the mercury in the organic phase was MeHg (Table 1). The remaining 62% of mercury in the organic phase was some other form of non-halogenated mercury, but aside from eliminating some candidates, no attempt was made to identify this mercury species. The solubility of HgSe was investigated (HgSe is present in liver, (Martoja and Berry 1980) under conditions employed to extract MeHg from tissues i.e. aqueous acidic NaBr and $CuSO_4$. It was found to be <35 ng/ml at room temperature. This compound could therefore not have formed a significant part of the organic phase. Similarly, Hg-glutathione and Hg-cysteine were not sufficiently soluble in the organic solvent to be organic mercury candidates. The possibility of ethylmercuric chloride being part of this phase was considered but it was not detected in any of the tissues analysed.

DISCUSSION

In muscle tissue, all of the mercury was essentially organic mercury (Figure 1a), in agreement with results reported for narwhal, beluga (Dietz *et al.* 1990) and fish (Lansens *et al.* 1991, Sum *et al.* 1979, Fukui *et al.* 1972, May *et al.* 1987, Ahmed *et al.* 1988). However, lower values in muscle tissue have also been reported: 83% in ringed seals (Dietz *et al.* 1990), and 80% and 62% in fin whales and polar bears, respectively (Dietz *et al.* 1990, Sanpera *et al.* 1993).

The organic mercury in muscle of belugas, narwhal, ringed seals and some fish consisted on average of 100% MeHg which means that determining either organic mercury or total mercury by CVAAS would suffice to obtain a measure of the average MeHg

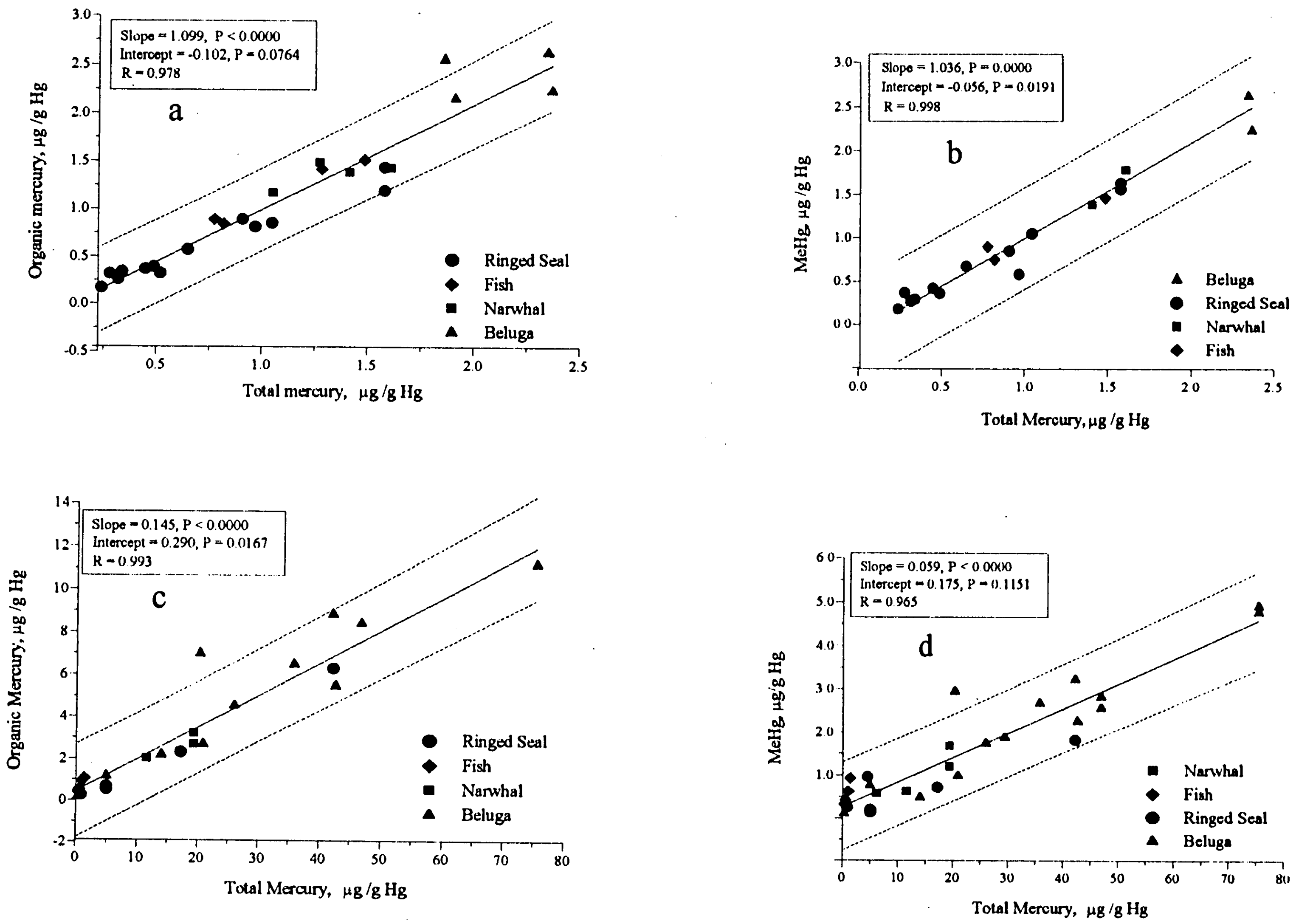

Figure 1. Robust linear regression of organic and methylmercury on total mercury in muscle and liver of maring mammals and fish: a) organic mercury vs. total in muscle; b) methylmercury vs. total mercury in muscle; c) organic mercury vs. total mercury in liver; d) methylmercury vs. total mercury in liver.

Table 1. Percent (%) MeHg and organic mecury of total mercury, and MeHg of organic mercury in liver of a (mixed) sample of marine mammals and fish (28 animals), and of belugas only (67 animals), calculated from the slope of robust, linear regression (column A), the arithmetic mean and [geometric mean] concentrations of organic mercury, MeHg, and total mercury (column B), and by arithmetic and [geometric] averaging of the individual ratios of the corresponding variables (column C).

	Regression Parameters Slope	**From Regression** **A**	$\frac{\Sigma M^{\dagger}}{\Sigma T_i}$ **B**	$\frac{\Sigma f_i^{\ddagger}}{n}$ **C**	
		%			
MeHg TotHg	$\beta^{\P}=0.0593$, $P<0.0001$ $a^{\S}=0.175$, $P=0.115$ $R^2=0.931$	5.93	6.81 [10.81]$^{\&}$	18.8 {10.81]$^{\&}$	Mixed
MeHg TotHg	$\beta=0.0563$, $P=<0.0001$ $a=0.760$, $P=<0.0001$ $R^2=0.792$	5.63	12.2 [14.7]	16.9 [14.7]	Belugas
OrgHg TotHg	$\beta=0.1446$, $P=<0.0001$ $a=0.290$, $P=0.167$ $R^2=0.986$	14.5	17.2 [23.1]	30.7 [23.1]	Mixed
OrgHg TotHg	$\beta=0.1472$, $P<0.0001$ $a=0.894$, $P<0.0001$ $R^2=0.843$	14.7	23.0 [25.8]	28.9 [25.8]	Belugas
MeHg TotHg	$\beta=0.3766$, $P<0.0001$ $a=0.079$, $P=0.218$ $R^2=0.964$	37.7	39.7 [43.8]	47.7 [43.8]	Mixed
MeHg TotHg	$\beta=0.3550$, $P<0.0001$ $a=0.505$, $P<0.0001$ $R^2=0.905$	35.5	52.8 [56.7]	59.2 [56.7]	Belugas

[†] M_i is the MeHg or organic mercury concentration and T_i the total mercury concentration.

[‡] $f_i=M_i/T_i$; [¶] = regression coefficient; [§] = intercept

[&] The fractions in columns B and C derived from the geometric means are equal by definition.

concentration in this type of tissue, although, among individual animals significant variations in percent MeHg occurred. Other workers also found MeHg to be equivalent to total mercury in muscle of fish and mussels (Drabaek and Carlsen 1984, Thibaud and Cossa 1989, Horvat 1990), and in some arctic fish, while in some invertebrates it was much less than the total mercury (Lasorsa and Allen-gil 1995).

In liver tissue, the average fraction of organic mercury to total mercury was approximately 15% by regression (Figure 1c) for this group of animals, and that of methylmercury to total mercury approximate 6% by regression (Figure 1b). A wide range of MeHg percentages have been reported for fish liver and liver of other organisms (Drabaek and Carlsen 1984, Dietz *et al.* 1990, Palmisano *et al.* 1993, Sanpera *et al.* 1993) and in lower-trophic-level organisms (Drabaek and Carlsen 1984). In liver tissue, where the ratio of MeHg/Organic Hg is clearly <1, the CVAAS method obviously could not be applied to estimating MeHg in liver tissue, as it can be applied to muscle tissue, since it would then greatly overestimate the MeHg concentration in this tissue.

Significant variation occurred in the percentage of methyl and organic mercury among individuals, which dictates the use of some form of averaging. The different methods of calculating the average percentage produced different estimates (Table 1), 17 to 31%, compared with 15% by regression analysis for organic mercury. A similar range was obtained for percent MeHg using the different calculation modes. The variables of interest were found to be interdependent. To further exemplify the differences that can be obtained by the different modes of calculation when the variables are not independent, the average MeHg and organic mercury percentages were determined in 75 belugas (regression not shown) Table 1. These results were similar to those for the mixed sample when obtained by regression analysis, but as for the mixed sample, showed an upward bias when calculated from separately averaged variables (Table 1).

The average percentage of organic mercury in the liver of marine mammals reported in the literature varies: 40% in Atlantic fin whales (Sanpera *et al.* 1993), 33% in pilot whales (Schintu *et al.* 1992), 9% in ringed seals (Dietz *et al.* 1990), and 22% in belugas (Dietz *et al.* 1990). The latter percentage was significantly higher than the value we obtained by regression analysis (15%) for belugas. These differences may be largely species related but the calculation methods employed may introduce a bias. The comparison of such average percentages can be problematic if the statistical properties of the samples and the mode of calculation are unknown.

It is evident from Figure 2, that not all the organic mercury extracted from liver tissue was MeHg. In the mixed sample, on average, 38% (in belugas alone 36%) of the mercury in the organic phase was MeHg. (This represented approximately 6% of the total mercury in the liver.) The remaining 62–64% of mercury in the organic phase was in a form other than MeHg, probably a non-halogenated organic mercury species and thus not detectable by ECD. Other investigators have reported finding inorganic "protein-bound Hg^{++} " in aqueous liver extracts of dolphins by HPLC chromatography (Palmisano *et al.* 1993). The unidentified mercury fraction in the organic solvent was probably not inorganic mercury considering the low solubility of such compounds in toluene. However, no attempt was made to identify it, except to eliminate some obvious candidates. Mercuric selenide (HgSe) is known to be present in the liver of marine mammals (Martoja and Berry 1980), but it was sufficiently insoluble and therefore could be excluded as a candidate. For similar reasons Hg-glutathione and to a lesser extent Hg-cysteine were unlikely candidates, and ethylmercuric halide was not detected in any of the tissues analysed.

When the variables in question are significantly correlated, as was the case for our samples, the higher average percentages calculated from the average methyl or organic mercury and the average total mercury concentration, are upwardly biased. The average percentage obtained by regression analysis should then be used (Table 1). Published average percentages are difficult to interpret and to assess in the absence of any knowledge of how they were calculated and the statistical properties of the underlying data.

Expected project completion date: March 31 1998.

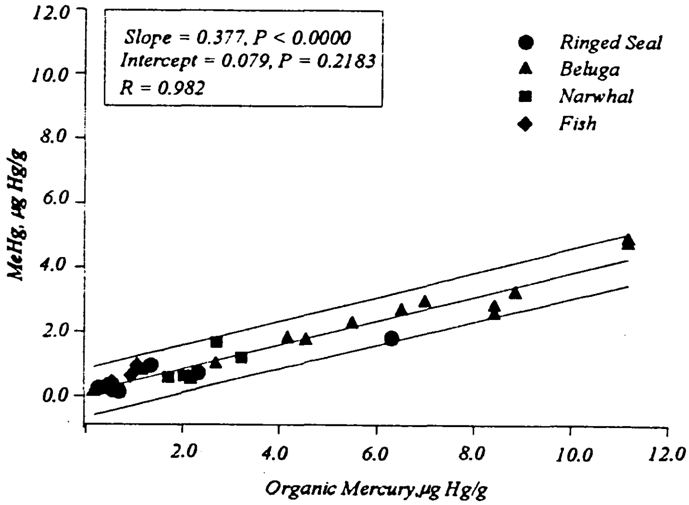

Figure 2. Robust linear regression of methyl on organic mercury inliver of marine mammals and fish.

PARTNERS

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1996/97 ADDENDUM

The first part of this report focused on experimental and calculation methodologies. This part of the report focuses on MeHg results from surveys conducted subsequently. Total mercury concentrations in tissues of arctic marine mammals are now available from across the Canadian and parts of the European Arctic and Alaska (Wagemann and Muir 1984, Zeisler *et al.* 1993, Skaare *et al.* 1994, Becker *et al.* 1995, Mackey *et al.* 1995, Dietz *et al.* 1996, Wagemann *et al.* 1996). In many instances the total mercury concentration significantly exceeds the Canadian Federal Consumption Guideline for humans for mercury in fish (0.50 g/g wet weight). Considering that in coastal arctic communities the diet of Indigenous people consists partly of marine mammal tissues, and that methylmercury (MeHg) is more toxic than most inorganic mercury compounds, the importance of measuring MeHg in marine mammal tissues is obvious. Some MeHg data (Julshamn *et al.* 1987, Wagemann 1994, Donais *et al.* 1996) and "organic" mercury data are currently available for arctic marine mammals (Dietz *et al.* 1990), pilot whales (Julshamn *et al.* 1987, Schintu *et al.* 1992) and Atlantic fin whales (Sanpera *et al.* 1993). This information, although valuable is not extensive geographically or temporally. This part of the report focuses on MeHg in marine mammals with the objective of determining whether or not a spatial trend also exists for MeHg in marine mammals as it does for total mercury (Wagemann *et al.* 1996), of providing a sufficiently broad MeHg data base for use in estimating risk from dietary intake of MeHg via the consumption of beluga (*Delphinapterus leucas*), ringed seal (*Phoca hispida*) and narwhal (*Monodon monoceros*) tissues, and of testing circumstantially the hypothesis that an end-product of demethylation of MeHg may be mercuric selenide.

Statistics

Means were compared (at α=0.05) using Scheffe's multiple means comparison test (Scheffe 1959). This test is fairly robust toward non-normal distribution of the population and does not require equal sample size. To determine the association between age of animals and MeHg, total mercury and percent MeHg, robust, linear regression (Andrews' sine) was used (Andrews 1974) which minimizes regression errors by reiterative analysis and weights data points accordingly, thus minimizing or eliminating the influence of extreme values. Regression slopes were tested for parallelism (at α=0.05) using the large-number z-test (Kleinbaum and Kupper 1978). Regressions of MeHg on total Hg were forced through the origin since a positive intercept on the MeHg axis at zero total Hg concentration did not make physical sense. It was ascertained through repeated chemical analyses using certified reference materials that these relatively small intercepts did not represent an instrumental or analytical bias. If this had been the case, then a non-forced regression would have been appropriate. Closer examination revealed that the intercepts were in essence an artifact produced by the non-linear relationship of the two variables close to the origin i.e. at low total Hg and MeHg concentrations. However, a non-linear fit (power curve) did not improve the overall fit relative to a linear fit, and a linear fit forced through the origin was chosen. Curve fits were performed with the computer program Table Curve™, Vers. 4, Jandel Scientific, 2591 Kerner Blvd. San Rafael, CA 94901, USA. Statistical analyses were performed with the computer program NCSS (Number Cruncher Statistical Systems) Ver. 6.0, Kaysville, Utah, USA.

RESULTS

Beluga tissue samples were collected (1993/94) at different sites in the western and eastern Arctic at locations to the west and east of longitude 105°W, respectively. No significant differences were found in the mean MeHg concentrations between sampling sites neither in the western nor the eastern Arctic. However, the overall MeHg mean was significantly higher for the western than the eastern Arctic (Table 2), for liver, muscle and skin. The regression slopes of MeHg on age were significantly different for the western and eastern Arctic for muscle and skin. The mean MeHg concentration in the liver of ringed seals was also significantly higher (α =0.05) in the western (1.03 µg/g) than the eastern (0.61 µg/g) Arctic. There was no significant difference in the mean ages of the two groups of ringed seals and age was not a factor in the comparison. The spatial trend for MeHg followed that for total mercury (Wagemann *et al.* 1996) of being higher in the western than the eastern Arctic. Since an accurate and efficient method for determining the age of narwhal is still lacking MeHg concentrations in the different narwhal tissues were regressed on length of animals. A significant correlation between MeHg and length was found for muscle and skin.

In beluga muscle, on average, 97% and 93% of the total mercury was MeHg in the western and eastern Arctic, respectively. In the skin (muktuk), 91% and 89%, and in the liver 6% and 12%, respectively was MeHg. In narwhal the mean percentages were 96 in muscle, 92 in the skin and 9 in the liver. Narwhal are not found in the western Arctic and a west-east comparison for these animals was obviously not possible. In ringed seals from the western Arctic, the mean percentages were 94% and 2.7% in the muscle and liver, respectively, and 92% and 2.7% in muscle and liver, respectively, from the eastern

Table 2. Means ±SD (arithmetic), n, ranges of methylmercury (MeHg) and total mercury concentrations (&g/g Hg wet weight) and percentages of MeHg to total mercury in tissues of belugas, narwhal and ringed seals from the western and eastern Canadian Arctic.

			Liver		Skin		Blubber
Area/Species/Year of Sampling	**MeHg µg /g Hg**	**Hg total µg /g Hg**	**MeHg µg /g Hg**	**Hg total µg /g Hg**	**MeHg (91 %)**	**Hg total µg /g Hg**	**Hg total µg /g Hg**
Western Arctic	(97 %)		(5.9 %)				
Belugas, 1993–1994							
Mean±sd	1.32±0.66	1.33±0.66	1.87±1.15	27.06±24.67	0.69±0.37	0.78±0.41	0.103±0.005
n	75	75	77	77	63	65	60
Range	0.35–3.16	0.41–3.44	0.11–6.13	0.31–116.55	0.14–1.71	0.19–1.93	0.19 – 0.02
Eastern Arctic	(93 %)		(11.7 %)		(89 %)		
Belugas 1993–1994							
Mean±sd	0.96±0.39	1.04±0.43	1.39±0.54	10.19±8.00	0.53±0.19	0.59±0.22	0.07±0.05
n	74	74	73	73	45	45	62
Range	0.44–2.36	0.44–2.77	0.44–3.06	1.24–38.56	0.31–1.07	0.32–1.37	0.19 – 0.01
Eastern Arctic	(96 %)		(9.0 %)		(92 %)		
Narwhal, 1992–1994							
Mean±sd	0.97±0.33	1.03±0.37	1.03±0.42	10.77±8.02	0.54±0.19	0.59±0.04	0.04±0.03
n	56	56	55	55	48	48	45
Range	0.39–1.66	0.41–1.94	0.20–2.43	0.32–37.21	0.15–1.19	0.16–1.27	0.13–0.003
Western Arctic	(94 %)		(2.7 %)				
Ringed S., 1987–1994							
Mean±sd	0.37±0.31	0.41±0.37	1.03±0.88	28.64±29.31	n/a	n/a	n/a
n	39	39	66	66			
Range	0.11–1.49	0.1–1.58	0.19–4.08	0.54–137.17			
Eastern Arctic	(92 %)		(2.7 %)				
Ringed S., 1992–1994							
Mean±sd	0.43±0.31	0.46±0.33	0.61±0.54	18.99±26.32	n/a	n/a	n/a
n	100	100	146	144			
Range	0.05–1.80	0.05–1.93	0.04–4.02	0.09–149.5			

* n/a = not analysed

Arctic. Since MeHg and total mercury concentrations were strongly correlated in each case, regression analysis of MeHg on total Hg was used to obtain the average percentages (Wagemann *et al.* 1997). The different mean percentages of MeHg, obtained by regression analysis, by taking the ratio of the average MeHg over the average total Hg, and by averaging the individual ratios are indicated in Figure 3, by arrows above each frequency distribution curve. The mean obtained by averaging the individual ratios was consistently farthest from the mode.

Linear regression of total selenium on total mercury in livers of belugas, narwhal and ringed seals was significant and gave, in terms of g-atom concentrations, a regression slope of approximately 1 in each case (Figure 4), indicating that the two elements are stoichiometrically associated in this tissue in a 1:1 ratio as they are in HgSe. A hypothetical diagram (Figure 5) shows HgSe as an end-product of demethylation.

DISCUSSION

A spatial trend of higher mean total mercury concentrations in marine mammal tissues in the western than the eastern Arctic was first reported by Wagemann *et al.* (1995). Mean MeHg concentrations were also significantly higher in the western Arctic than the eastern Arctic, in muscle, liver and skin of belugas and in the liver of ringed seals. It should be pointed out that liver tissue may be a poor choice for determining spatial or temporal trends of MeHg because of the continuous demethylation of this compound in the liver. Factors such as geological background and the level of food contamination in the particular area could be responsible for the trend. The geology in the western Arctic is such that generally higher environmental background concentrations of mercury appear to be present there in comparison with the eastern Arctic (Wagemann *et al.* 1995) and this may be reflected in the food chain leading up to marine mammals. In all tissues examined of belugas and ringed seals (except in muscle of ringed seals from the eastern Arctic) MeHg was significantly, positively correlated with age which may indicate decreased demethylation or increased uptake with age. The regression slopes (MeHg vs age) were significantly different between the western and eastern Arctic for muscle and skin of belugas, indicating the existence of a spatial trend notwithstanding any age differences. Ringed seals from the eastern and western Arctic were not confounded by significant age differences and the mean MeHg concentrations in liver were indicative of a spatial trend.

Mostly MeHg is taken up by marine mammals, predominantly from muscle tissue of fish (muscle tissue makes up most of the mass of the fish), but only a small fraction of the total mercury in the liver was MeHg. The results presented here and those of others (Palmisano *et al.* 1995, Dietz *et al.* 1990) show that the mean MeHg concentration in liver of marine mammals is usually not much higher than in muscle, seldom exceeding 2.0 μg/g (Table 2) despite the fact that the total mercury concentration in the liver was several factors higher than in muscle. In contrast to muscle and skin where the percentage of MeHg to total mercury was between 89% and 97%, in the liver it ranged from 3% to 12%. Demethylation in the liver leads, we hypothesize, to the formation of inorganic mercury (Hg^{++}) and the detoxification of the latter by reaction with selenium to form mercuric selenide (HgSe), Figure 5. This compound has been identified in the liver of marine mammals and humans (Martoja and Berry 1980, Hansen *et al.* 1989, Pelletier 1985) as amorphous, highly insoluble, inert particles. In support of the existence of this compound (HgSe) we have found, as have others (Koeman *et al.* 1973, Nielsen *et al.* 1990, Skaare *et al.* 1994, Wagemann and Stewart 1994), that total selenium and total mercury in the liver are significantly, positively correlated with a regression slope of 1 in terms of g-atom concentrations (Figure 4) indicating that these two elements are associated in a ratio of 1:1 as they are in HgSe. The relatively high concentration (Table 2) and long half-life of total mercury in the liver (10 years in humans, Friberg *et al.* 1979), the positive, high correlation between total mercury and age of animals (Wagemann *et al.* 1996), the strong, positive correlation between mercury and selenium with a regression slope of approximately 1, and the relatively short half-life of MeHg (20–500 days in ringed seals, Tillander *et al.* 1972) are consistent with a progressive accumulation of mercuric selenide (HgSe) with age, and HgSe being an end-product of demethylation as generally depicted in Figure 5. The process of demethylation of MeHg and transformation into an inert form of mercury would obviously be an effective mechanism for counteracting the potentially damaging action of MeHg.

Only in muscle of ringed seals and blubber of whales was the concentration of MeHg (and total mercury) below the Federal Consumption Guideline for fish. It is noteworthy that the mean total mercury concentration in narwhal blubber sampled from 1992 to 1994 (0.04 μg/g), had not changed significantly in this tissue from the value (0.03 μg/g) found in 1978/79 (Wagemann *et al.* 1983) but did change over this time span in liver (Wagemann *et al.* 1996) where mercury preferentially

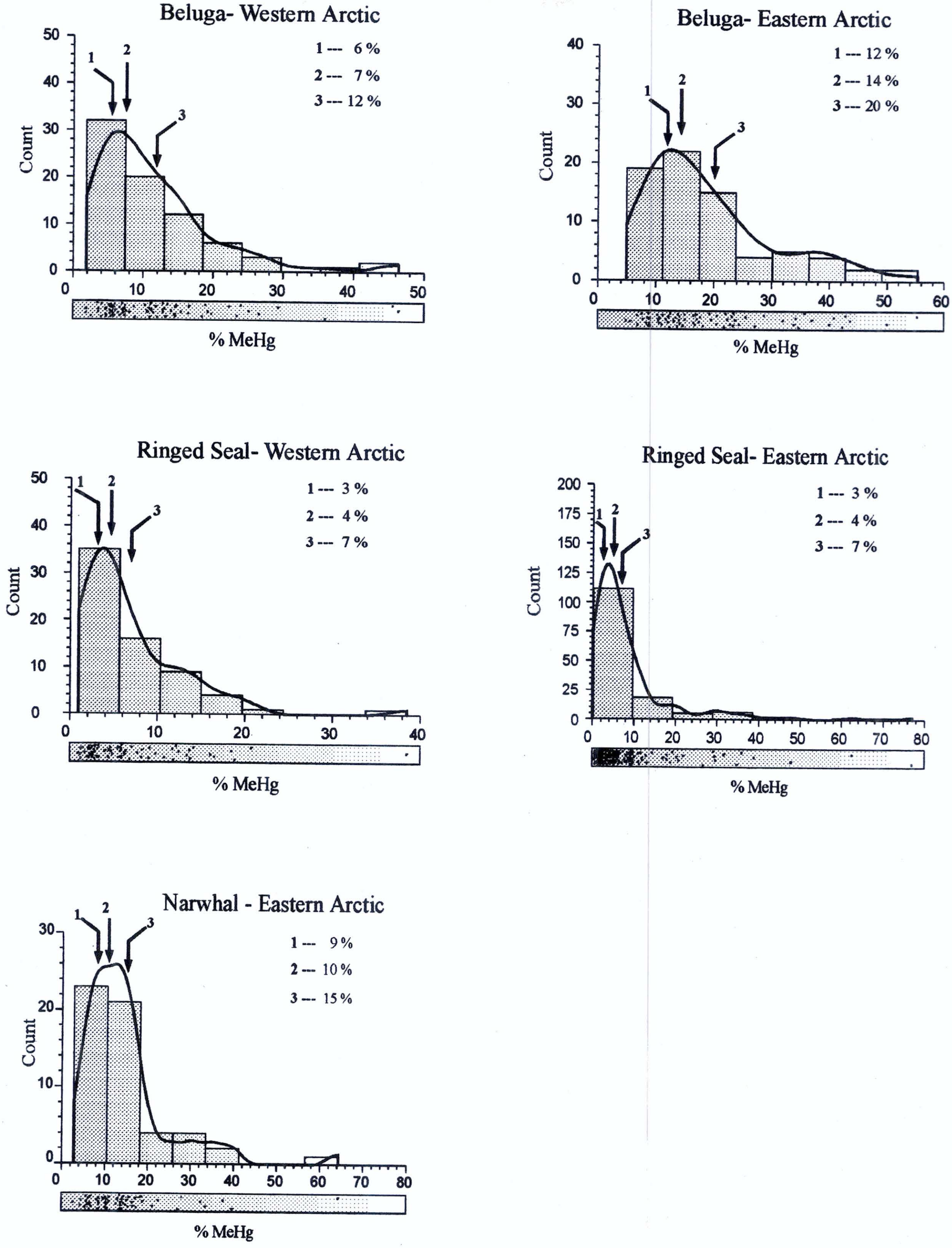

Figure 3. Frequency distribution of percentrage of MeHg in liver of marine mammals from the Canadian Arctic. The arrows above each distribution graph indicate the position of the different percentage means: 1 = by regression; 2 = the ratio of the mean MeHg over the total HG; 3 = the average of the individual MeHg/total Hg ratios.

accumulates. In most other tissues analysed the MeHg concentration exceeded the Canadian Federal Consumption Guideline for mercury in fish.

These findings, combined with the great differences in toxicity among organic and inorganic mercury compounds and the fact that some mercury species can be transferred from mother to fetus (Julshamn *et al.* 1987, Wagemann *et al.* 1988, Smith and Smith 1975) reveal the importance of differentiating mercury species in tissues used as food sources. Determination of the levels of various mercury species such as MeHg and HgSe and not just total mercury will allow a more accurate assessment of the health risk to animals and to humans from the consumption of contaminated animal tissues.

SUMMARY

Concentrations of methylmercury, total mercury and selenium in marine mammal tissues were determined in liver, muscle, skin (muktuk) and blubber of belugas, ringed seals and narwhal. With few exceptions mean MeHg concentrations in the tissues analysed exceeded the Canadian Federal Consumption Guideline for mercury in fish (0.5 µg/g wet weight). A spatial trend of higher MeHg levels in western compared with eastern Arctic in belugas and ringed seals was found which followed a similar trend observed for total mercury. Robust linear regression of MeHg on total Hg and MeHg on age of animals was performed and a strong correlation between the two variables was found in each

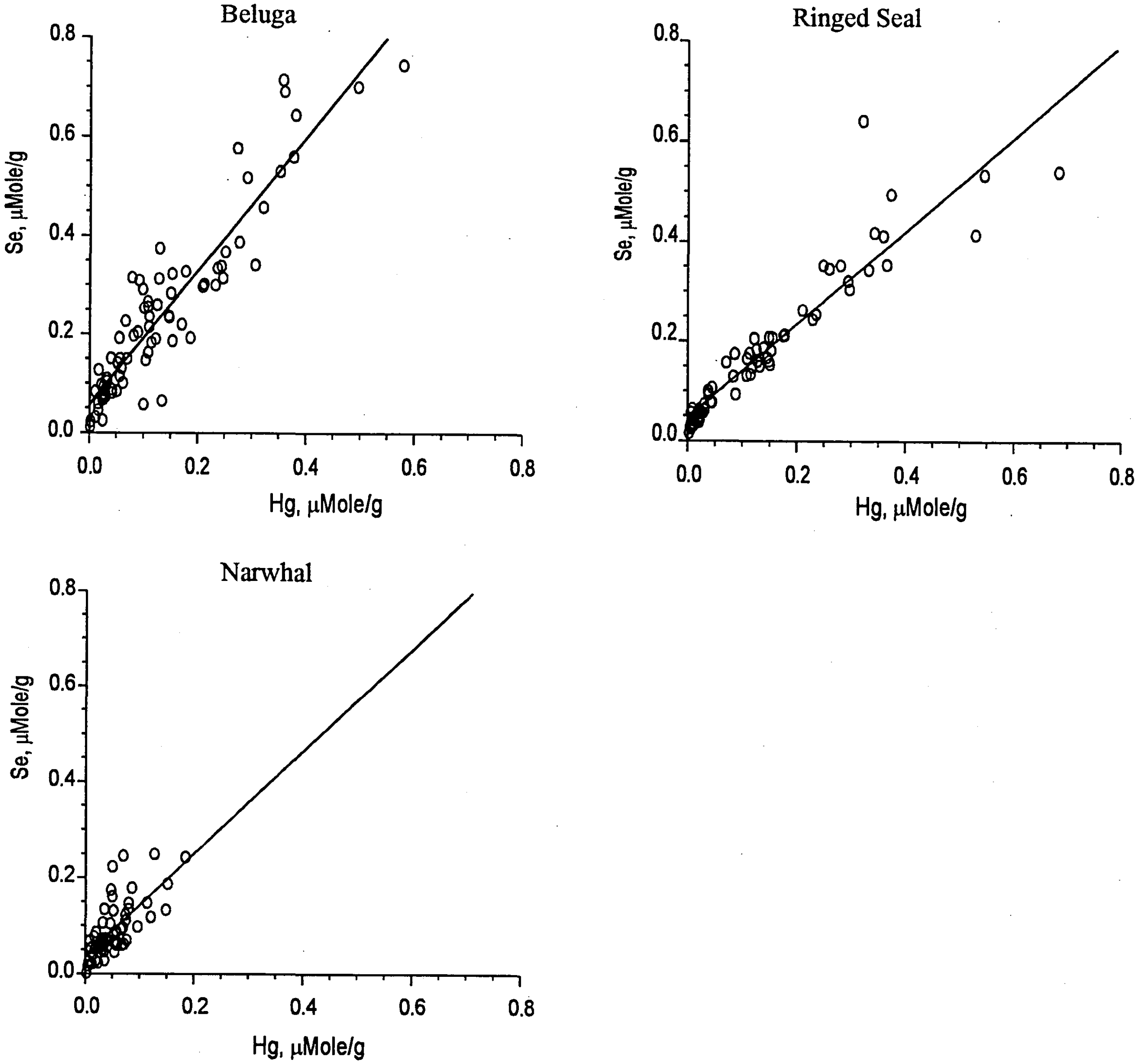

Figure 4. Robust linear regression of total Se on total Hg (g-atom concentrations) inliver of belugas, narwhal and ringed seals from the Canadian Arctic.

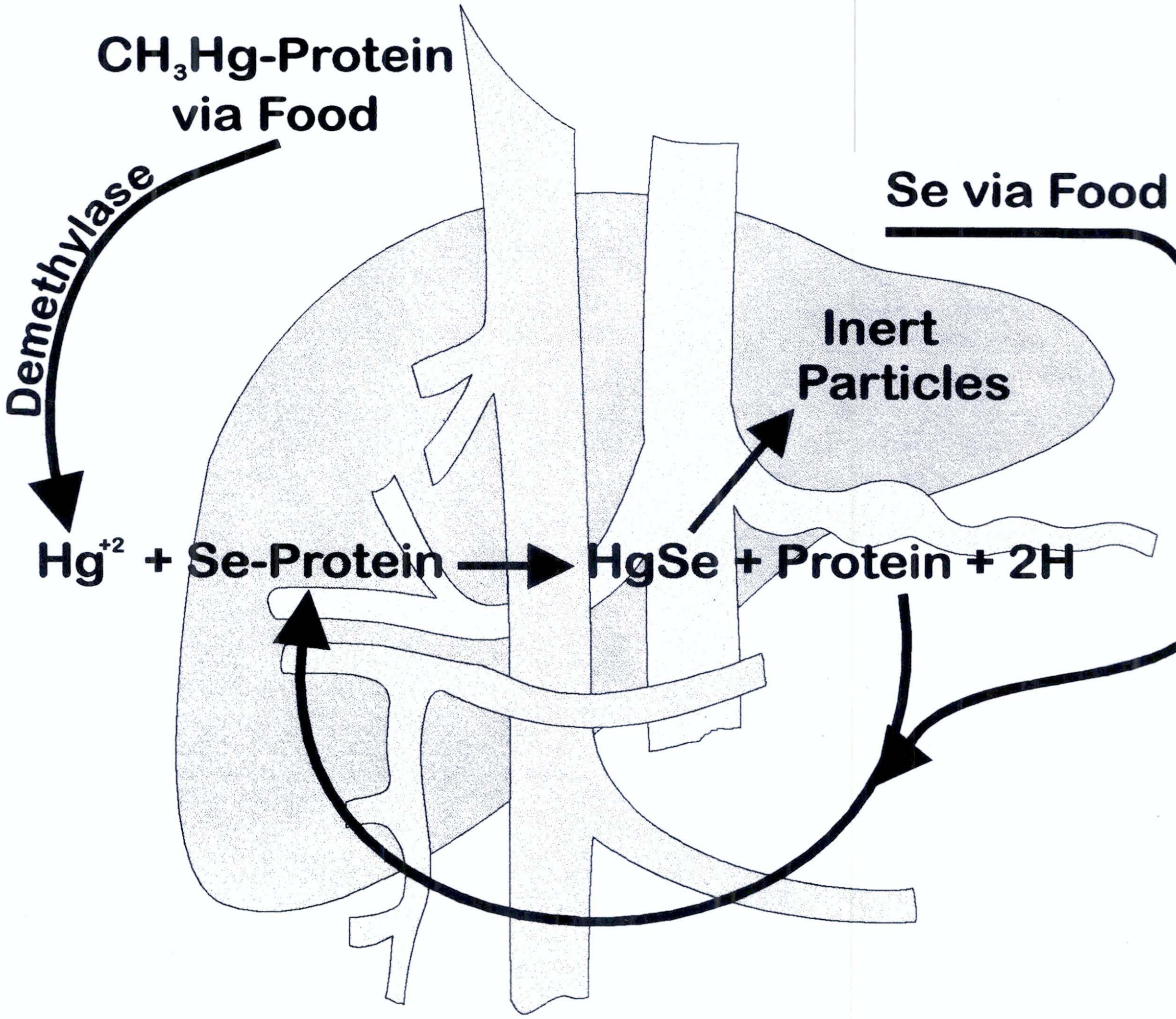

Figure 5. Hypothetical demethylation scheme with consequent formation of inert mercuric selenide particles in the liver.

case. The ratio of MeHg to total mercury was close to one, for muscle and skin (muktuk), while for liver it was <<1. The mean percentage of MeHg in the liver of marine mammals was 3% to 12%, depending on species and geographic area, and 92% to 97% in muscle. It is postulated that the formation and deposition of mercuric selenide in the liver is part of the demethylation process in this tissue, based on the relatively low fraction of MeHg in the liver not withstanding the fact that the predominant form of mercury taken up via food is MeHg. The long half-life for total mercury and the relatively short half-life for MeHg in this organ are in accord with this postulate as is the 1:1 stoichiometric relationship between mercury and selenium in the liver.

ACKNOWLEDGMENTS

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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, Yukon Hunters

OBJECTIVES

1. To determine the presence and quantity of organic and inorganic contaminants in country foods used in the Yukon.
2. To identify potential health risks to First Nations and others consuming country foods.
3. To identify potential health problems in wildlife populations as a result of contaminant loading.
4. 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. High levels of cadmium found in the livers and kidneys of arctic caribou (Gamberg and Scheuhammer 1994, Gamberg 1993, Crete *et al.* 1989, Froslie *et al.* 1986) have caused concern among First Nations and others using caribou as a food source, and raised the issue of contaminants in other food sources. This project was designed to work with the individual First Nations to address these concerns.

In 1993/94, a survey on contaminants in plants used as traditional foods and medicines was conducted by the Kaska First Nation in the Southeastern Yukon. At the same time, a pilot study measured contaminants in mammals used as country foods in the same area. In 1994/95 the pilot project was expanded to cover the entire Territory, and to include plants and birds as well as mammals. In all cases, sampling lists were devised in consultation with local First Nations to ensure that results and conclusions would be locally relevant. Sampling was designed to take place over a calendar year so that each food could be sampled at the time of traditional harvest. Sampling for this part of the project began in December, 1994.

In addition to sampling by First Nations, all Yukon hunters were requested to submit liver, kidney and muscle samples from moose and caribou hunted during the 1994 hunting season. A tooth or incisor bar was also requested for aging purposes. Livers and kidneys were obtained from grouse and ptarmigan collected in the Yukon in 1994/95 as part of a Canadian Wildlife Service study of contaminants in birds.

Liver or fat tissues from selected animals were pooled by species and area, and analysed by Axys Analytical Ltd. (Sidney, B.C.) for organic contaminants including pesticides, PCBs (total and as Aroclors), dioxins and furans. Vegetation, liver, kidney and muscle samples were analysed for a suite of metals by the Analytical Services Ltd. (Vancouver, B.C., 1993/94) or Elemental Research, (Vancouver, B.C., 1994–96).

Where possible, animals were aged to year by tooth eruption, or by the tooth cementum technique (Matson's Laboratory, Milltown, Montana). Where this was not feasible, gross morphology, pelage or feather characteristics or epiphyseal closure was used to classify the animal as juvenile or adult.

ACTIVITIES IN 1995/96 AND 1996/97

Sampling for the ongoing survey of contaminants in country foods was completed by Yukon First Nations in November of 1995. Most samples were analysed for a suite of inorganic contaminants, and six vegetation pools from the pipeline region of the Champagne Aishihik traditional area were also analysed for organic contaminants by Axys Analytical Ltd. Moose and caribou tissue samples submitted by Yukon hunters and Yukon Territorial Government (YTG) biologists during the 1995 and 1996 hunting seasons were analysed by Elemental

Research for inorganic contaminants only. Due to budgetary constraints, only kidney samples were analysed in 1996, and the liver and muscle tissue from these submissions have been archived. Animals were aged as described above. A summary of bird and mammal species and tissues sampled is presented in Table 1.

RESULTS

Vegetation

Dioxins, furans, PCBs and most pesticides were not detectable in any vegetation samples from the Champagne Aishihik traditional area. Two of the branch pools had detectable levels of α–HCH (0.3 and 0.35 ng/g wet wt.) and one berry pool had 0.39 ng/g DDE.

Inorganic vegetation data from the Kaska traditional foods and medicines study, and the Yukon country foods study are presented here together. Most plants analysed contained element levels considered normal for vegetation, although some concentrations ranged into the high or low end of the normal range. Aluminum was high in some individuals, barium was high in general, while with few exceptions, cadmium and lead were found at low concentrations (Table 2). Mercury was below detection levels in all vegetation samples analysed with the exception of mushrooms, where it ranged from <0.05–0.57 ppm dry wt., and tree twigs where it ranged from <0.05–0.0877 ppm dry wt.

Birds and Mammals

Levels of organic contaminants in the birds and mammals tested were usually below detection limits.

Table 1. Country foods sample collections

Common name	Species	Kidney	N Liver	Muscle
BIRDS				
Waterfowl				
American Wigeon	*Anas americana*	0	4	4
Green-winged Teal	*Anas crecca*	0	17	17
Mallard	*Anas platyrhynchos*	2	12	10
Northern Pintail	*Anas acuta*	0	3	3
Scaup	*Aythya* sp.	1	1	1
Gallinaceous Birds				
Grouse, Blue	*Dendragapus obscurus*	3	3	0
Grouse, Ruffed	*Bonasa umbellus*	7	7	0
Grouse, Spruce	*Dendragapus canadensis*	38	28	7
Ptarmigan	*Lagopus* sp.	6	6	0
Ptarmigan, Rock	*Lagopus mutus*	4	4	0
Ptarmigan, White-tailed	*Lagopus leucurus*	2	2	0
Ptarmigan, Willow	*Lagopus lagopus*	9	9	0
MAMMALS				
Small Game				
Beaver	*Castor canadensis*	14	13	14
Hoary Marmot	*Marmota caligata*	1	3	0
Lynx	*Lynx canadensis*	1	2	2
Muskrat	*Ondatra zibethicus*	13	12	13
Porcupine	*Erethizon dorsatum*	6	6	6
Snowshoe Hare	*Lepus americanus*	28	27	28
Squirrel, Ground	*Spermophilus parryii*	20	20	20
Squirrel, Red	*Tamiasciurus hudsonicus*	26	23	27
Large Game				
Bear	*Ursus americanus*	2	2	0
Caribou	*Rangifer tarandus*	214	252	106
Dall Sheep	*Ovis dalli*	4	5	5
Elk	*Cervus elaphus*	1	1	0
Moose	*Alces alces*	112	159	100
Mountain Goat	*Oreamnos americanus*	4	4	3
Mule Deer	*Odocoileus hemionus*	1	1	0

One pool of porcupine fat had detectable levels of dioxins and furans. These data were presented in the 1994/95 synopsis of research for this project.

Metal levels appeared normal in most cases, although for some species there was little or no existing data with which to compare them. Mercury was relatively high in kidneys of some species, and measurable in some livers and kidneys (Figure 1). Cadmium was also high in kidneys and livers of many species (Figures 2 and 3), but was uniformly low in muscle tissue, averaging 0.095 ppm dry wt., and ranging from <0.21 ppm to 0.82 ppm (in porcupine muscle). Cadmium was positively correlated with age in moose and caribou livers and kidneys, and concentrations in tissues of the Finlayson and Tay caribou herds were significantly higher than those of the Bonnet Plume and Porcupine herds (Figures 4 and 5). Data from other caribou herds were not included in these analyses because sample sizes were small. However, cadmium levels in the Pelly, Klaza, Nahanni, Wolf Lake, Redstone, Hart River and Forty-Mile herds fell either between the two groups or closer to the Porcupine and Bonnet Plume herds. Cadmium concentrations were not significantly affected by sex of the animal or year of collection. The opportunistic nature of the sampling yielded highly variable numbers of samples from each community, making analysis of the data by geographical location impossible in most cases.

The data collected prior to 1996 were evaluated by Health Canada for potential hazards to human consumers. The resulting advisory from Yukon Health is presented in Table 3.

DISCUSSION/CONCLUSIONS

Vegetation

Organic contaminants in plants were not detectable for the most part, and the few detectable levels are close to background levels. This suggests that contamination of vegetation along the pipeline corridor by organic pesticides is not a problem. However, sample sizes analysed were low, and not all areas were represented. A local point source of contamination could be missed using these opportunistic methods of sampling.

Al was high in some individual samples, but there was high variability in Al within a species for the same plant part. Ba was very high in most plants relative to commercial livestock diets. It should be noted however, that although Ba toxicity is possible, it is dependent on the form of the chemical in the plant. The toxic Ba ion is never found free in nature, but occurs mainly as sulphate which is virtually insoluble and nontoxic, or as carbonate, which has a low toxicity (Puls 1994). The vegetation in this study was analysed for total Ba, so the chemical form in not known. Cd and Pb were low in most plants analysed. One exception was a puffball mushroom from Ross River, which contained 13.3 ppm Cd and 8.72 ppm Pb (dry wt.). A sample of the same species from Watson Lake contained <0.1 ppm Cd and <0.50 ppm Pb (dry wt.). The mushroom sample from Ross River also contained high levels of Al, Cr, Co, Cu, Fe, Ni, Se, V and Zn, whereas the sample from Watson Lake contained high levels of Cu and Zn only. The element levels in these mushrooms appear to reflect the mineral composition of the substrate, and would be expected to be highly variable among locations. Cadmium was also relatively high in willow and balsam poplar twigs, and in willow bark.

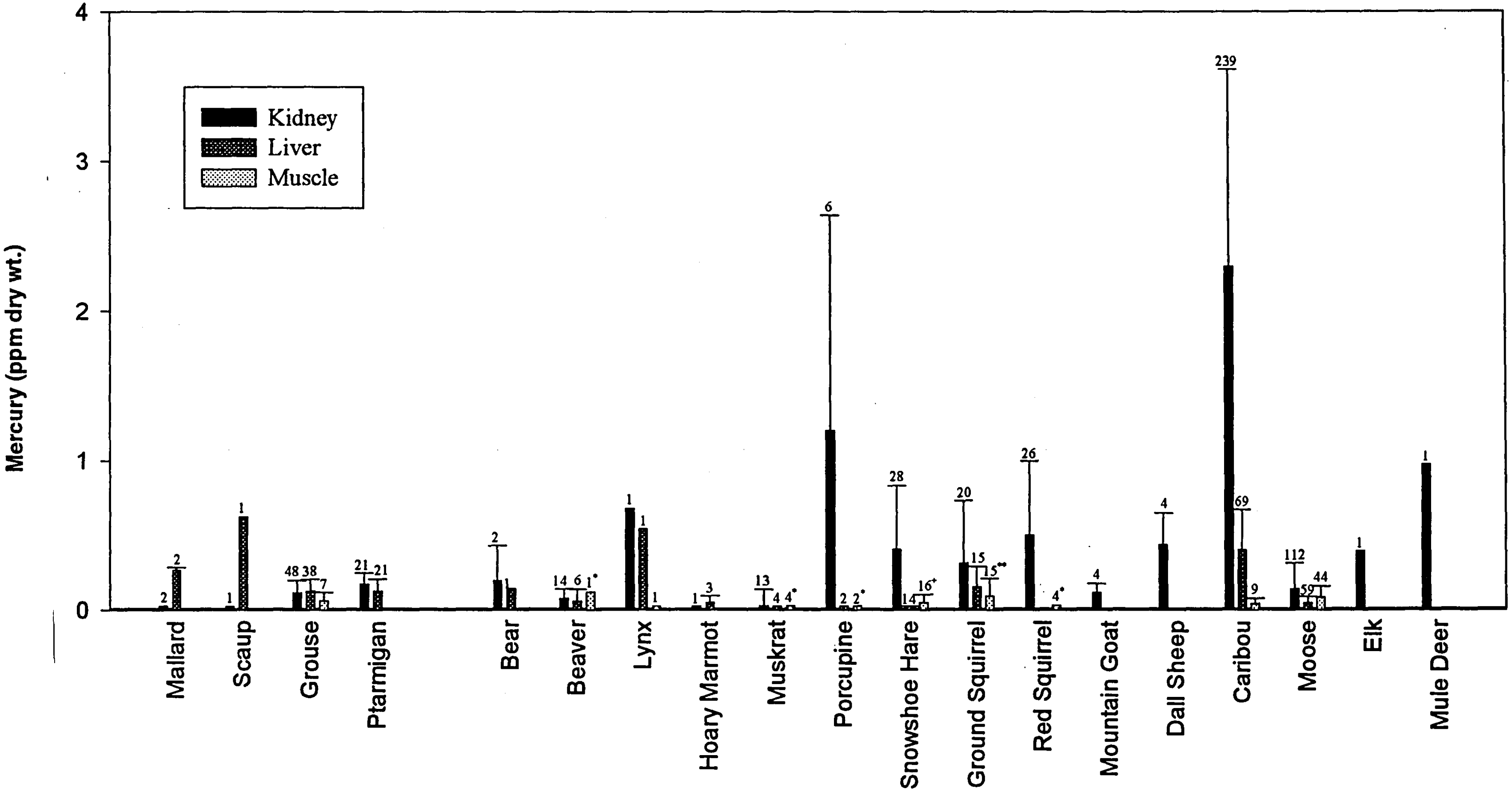
Metal uptake in plants is species-specific and metal-specific, and can be affected by soil pH, organic content, calcium content, cation exchange capacity, oxides of iron and manganese and the presence of ligands in the soil (Crowder 1991). Terrestrial plants generally have highest concentrations in roots, but this is not consistent. Bear root plants in this study had higher levels of some elements, such as aluminum, copper and iron, in their roots than in foliage and stems, but both plant parts had similar levels of other elements such as calcium, lead and zinc. Some metals are taken up mostly from the soil, whereas some, such as Pb, accumulate primarily from the atmosphere. In these cases high concentrations may accumulate in bark of trees. The only measurable levels of Pb in tree bark in this study were still very low, indicating low levels of airborne Pb in this area. Cd ranged from 0.2 ppm to 4.0 ppm in bark samples, reflecting slightly higher airborne levels of this contaminant.

No unusually high concentrations of any elements were found in the plants analysed in this study. However, it should be noted that element concentrations in vegetation tend to be extremely variable depending on plant species, plant organ and local soil conditions.

Mammals and birds

Levels of organic contaminants were generally low and not of concern. Only one porcupine had dioxins and furans at levels above background, and these were below levels that would cause concern for the animal or for human consumers.

Although mercury was elevated in the tissues of some species, previous work with the Finlayson caribou indicated that all mercury present was in the inorganic form, and therefore of little concern (Gamberg 1993). While methylmecury has not been measured in tissue from other species, it is likely that levels are also low, and the detectable Hg is in the inorganic form.



* Analyzed in 1 pool
** Analyzed in 3 pools
\+ 6 individual samples, and 10 samples analyzed in 2 pools

Figure 1. Mercury concentrations in Yukon wildlife (N above standard error bars)

Table 2. Element concentrations in Yukon vegetation (ppm dry wt.)

Plant Part	Common Name	Species	N	Al		Ba		Cd		Pb	
				X	SD	X	SD	X	SD	X	SD
Bark	Alpine fir	*Abies lasiocarpa*	1	275.0		184.0		1.0		0.6	
	Balsam Poplar	*Populus balsamifera*	1	102.0		135.0		0.2		<0.4	
	Tamarack	*Larix laricina*	1	263.0		147.0		0.8		<0.5	
	Willow	*Salix* sp.	1	23.7		54.9		4.0		0.2	
Berry	Bearberry+	*Arctostaphylos uva-ursi*	2	8.5	± 1.2	16.9	± 2.0	<0.2	± 0.0	<0.8	± 0.1
	Black Currant	*Ribes hundonianium*	3	17.9	± 23.6	8.7	± 5.8	<0.3	± 0.2	<1.4	± 0.3
	Blueberry	*Vaccinium uliginosum*	10	67.0	± 168.5	29.1	± 39.7	<0.4	± 0.1	<2.2	± 0.4
	Cloudberry	*Rubus chamaemorus*	1	22.4	–	1.6	–	0.9	–	<1.5	–
	Cranberry, Highbush+*	*Viburnum edule*	12	9.0	± 12.4	8.3	± 3.0	<0.4	± 0.1	<2.0	± 0.4
	Cranberry, Lowbush	*Vaccinium vitis-ideae*	10	15.1	± 9.1	13.9	± 4.1	<0.4	± 0.1	<2.0	± 0.4
	Crowberry	*Empetrum nigrum*	12	19.4	± 26.0	6.1	± 1.4	<0.5	± 0.1	<2.7	± 0.4
	Gooseberry+*	*Ribes oxyacanthoides*	2	4.4	± 1.6	24.1	± 8.7	<0.3	± 0.0	<1.7	± 0.1
	Juniper	*Juniperus communis*	1	13.9	–	18.9	–	0.1	–	0.1	–
	Nagoon berry	*Rubus arcticus*	1	18.3	–	17.3		<0.3		<1.4	
	Raspberry+*	*Rubus ideaus*	8	59.8	± 150.0	16.8	± 16.2	<0.3	± 0.1	<1.4	± 0.3
	Red Currant	*Ribes triste*	2	23.0	± 10.7	12.3	± 5.4	<0.3	± 0.0	<1.5	± 0.1
	Rose+*	*Rosa acicularis*	11	8.0	± 6.9	19.3	± 19.6	<0.2	± 0.0	<0.9	± 0.2
	Saskatoon	*Amelanchier alnifolia*	2	2.7	± 2.0	8.5	± 5.7	0.01	± 0.0	0.0	± 0.0
	Silverberry	*Elaeagnus commutata*	1	9.6	–	0.8	–	<0.01	–	0.1	–
	Soapberry+*	*Sheperdia canadensis*	7	13.4	± 4.2	1.3	± 0.9	<0.2	± 0.1	<1.2	± 0.2
	Strawberry*	*Fragaria virginiana*	2	71.0	± 19.7	119.2	± 14.1	<0.3	± 0.0	<1.3	± 0.0
Branch	Alder	*Alnus incana*	5	53.6	± 23.2	68.0	± 83.7	<0.1	± 0.0	<0.5	± 0.0
	Bear Root	*Hedysarum alpinum*	1	341.0	–	85.0	–	<0.1	–	<0.7	–
	Caribou Leaves	*Artemesia tilesii*	7	250.4	± 235.0	189.4	± 384.5	0.7	± 0.5	<0.1	± 0.4
	Dandelion	*Taraxacum officinale*	5	425.0	± 242.2	54.5	± 49.0	0.2	± 0.1	1.1	± 0.9
	Dogwood	*Cornus stolonifera*	2	10.8	± 6.2	56.3	± 16.0	<0.1	± 0.0	<0.5	± 0.0
	Juniper	*Juniperus communis*	4	158.3	± 214.2	29.8	± 15.9	<0.1	± 0.0	<0.5	± 0.0
	Labrador Tea	*Ledum groenlandicum*	4	138.6	± 56.4	120.5	± 27.8	<0.1	± 0.0	<0.5	± 0.0
	Lodgepole Pine	*Pinus contorta*	1	306.0	–	14.1	–	0.3	–	0.3	–
	Rhubarb	*Polygonum alaskanum*	5	127.5	± 259.2	82.2	± 103.9	<0.2	± 0.0	1.4	± 2.0
	Sage	*Artemisia frigida*	4	364.4	± 303.5	29.9	± 24.3	0.5	± 0.4	<1.0	± 0.4
	Shrubby Cinquefoil	*Potentilla fruticosa*	5	156.0	± 162.1	73.4	± 33.8	<0.1	± 0.0	<0.5	± 0.3
	Soapberry	*Sheperdia canadensis*	5	28.7	± 18.8	5.4	± 3.4	<0.1	± 0.0	<0.5	± 0.0
	Spruce	*Picea mariana*	2	87.5	± 26.1	229.7	± 235.2	<0.01	± 0.0	0.5	± 0.6
	Tamarack	*Larix laricina*	1	92.7	–	42.7	–	0.1	–	<0.5	–
	Yarrow	*Achillea millefolium*	7	172.9	± 128.5	42.2	± 62.4	0.4	± 0.4	<1.0	± 0.5

+ Branches from Champagne Aishihik traditional area analysed for organic contaminants

* Berries from Champagne Aishihik traditional area analysed for organic contaminants

Table 2. cont'd....

Plant Part	Common Name	Species	N	Al X	Al SD	Ba X	Ba SD	Cd X	Cd SD	Pb X	Pb SD
Cone	Spruce	*Picea mariana*	1	7.6	–	0.6	–	<0.1	–	<0.3	–
Flower	Labrador Tea	*Ledum groenlandicum*	1	87.2	–	130.0	–	<0.5	–	<2.3	–
Root	Bear Root	*Hedysarum alpinum*	2	1497.0	± 739.6	260.2	± 234.5	<0.2	± 0.0	3.7	± 3.9
Thallus	Caribou Horn	*Cornicularia aculeatum*	3	499.3	± 406.7	175.8	± 262.7	<0.1	± 0.0	2.6	± 1.3
	Caribou Moss	*Cladina* sp.	25	647.9	± 634.8	58.0	± 65.7	<0.3	± 0.1	1.7	± 1.5
	Mushroom	*Boletus* sp.	1	369.0	–	9.1	–	0.1	–	0.5	–
	Mushroom	*Agaricus* sp.	1	231.0	–	4.5	–	2.9	–	1.9	–
	Puffball Mushroom	*Lycoperdon calvatia*	2	842.5	± 1173.3	60.6	± 75.6	6.8	± 9.2	4.5	± 6.0
Twig	Aspen	*Populus tremuloides*	6	32.7	± 25.6	61.7	± 56.4	2.8	± 2.2	0.2	± 0.2
	Balsam Poplar⁺	*Populus balsamifera*	2	2.1	± 2.9	18.9	± 0.5	6.5	± 8.8	<0.01	± 0.0
	Birch	*Betula papyrifera*	5	68.2	± 127.7	91.5	± 112.5	0.7	± 0.5	0.1	± 0.2
	Dogwood	*Cornus stolonifera*	2	3.1	± 3.3	23.8	± 2.5	0.02	± 0.0	0.0	± 0.0
	Larch	*Larix laricina*	1	16.1	–	61.4	–	0.01	–	0.0	–
	Willow⁺	*Salix* sp.	14	13.9	± 26.7	35.3	± 32.7	4.1	± 5.8	<0.5	± 0.1

⁺ Branches from Champagne Aishihik traditional area analysed for organic contaminants

* Berries from Champagne Aishihik traditional area analysed for organic contaminants

Cadmium levels in muscle tissue of all animals were consistently low but levels in kidneys and livers ranged from very low in muskrats, to very high in moose and some grouse (Figures 2–5). Moose liver and kidneys had higher cadmium levels than reported in moose from Manitoba (Wotton and McEachern 1988), Quebec (Crete *et al.* 1987), Newfoundland (Brazil and Ferguson 1989), Norway (Froslie *et al.* 1986; Scanlon *et al.* 1986) and Sweden (Frank 1986). However, moose from some areas of Ontario (Glooschenko *et al.* 1988) and New Brunswick (Redmond *et al.* 1988) had similar levels of cadmium to those found in Yukon moose. The Bonnet Plume and Porcupine caribou herds had cadmium levels similar to other arctic caribou (Gamberg and Scheuhammer 1994, Crete *et al.* 1989, Froslie *et al.* 1986), but concentrations in the Finlayson and Tay herds were considerably higher (Gamberg 1993). Beaver from the Yukon had higher levels of cadmium than beaver from the Sudbury mining area of Ontario, which were considered to have elevated levels (Hills and Parker 1993). Cadmium concentrations in Yukon grouse and ptarmigan were 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, had uniformly low levels of cadmium.

The accumulation of cadmium in wildlife varies widely among species and individuals. This may be the result of geographical variability, but low sample sizes in this study did not allow statistical analysis of differences among locations. However, there did not appear to be high levels of cadmium particularly associated with industry (mining) or populated areas. Frequently, animals taken from the Ross River and Watson Lake areas (north of the Tintina Trench) had high levels of cadmium as compared with animals from the rest of the territory. This was not, however, a consistent trend. Higher than average cadmium concentrations were also seen in individuals taken from Whitehorse, Dawson and Teslin, while some taken from north of the Trench had cadmium levels below average. 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 accumulating in some plants (such as willow), and in this way being passed on to certain herbivores, depending on their dietary habits. Heavy consumers of willow, such as moose and ptarmigan reflect the highest accumulations of cadmium.

The health advisory issued by Yukon Health and Social Services is presented as the number of organs from each species that should be consumed by an average person in a year. This simplified version of the Health Canada assessment has been found to be effective when communicating results and advisories to the Yukon public. Most of the limits set are quite high and will not affect most Yukoners. However, the limit for moose liver and kidney is one of each per year. One moose liver weighs approximately 5 kg, so limiting consumption to one/year will not affect most people. A moose kidney weighs approximately 500g, and is considered to be a choice part of the animal by some Yukoners, particularly by those living on the land. Limiting consumption to one kidney/year may change the dietary habits of some of these people.

Table 3. Yukon Health and Social Services Health Advisory (1996)

Animal	**Recommended**	**Maximum # of Kidneys per year Recommended for Consumption***	**Maximum # of Livers per year for Consumption***
Caribou			
	Bonnet Plume	32	16
	Nahanni	28	13
	Porcupine	25	12
	Forty-mile	20	12
	Wolf Lake	15	8
	Finlayson	8	5
	Tay	7	4
Moose	1	1	
Sheep	178	no limit	
Goat	382	26	
Beaver	15	46	
Porcupine		13	17
Snowshoe Hare		485	no limit

* There are no limitations on the amount of muscle (meat) than can be consumed from any animal.

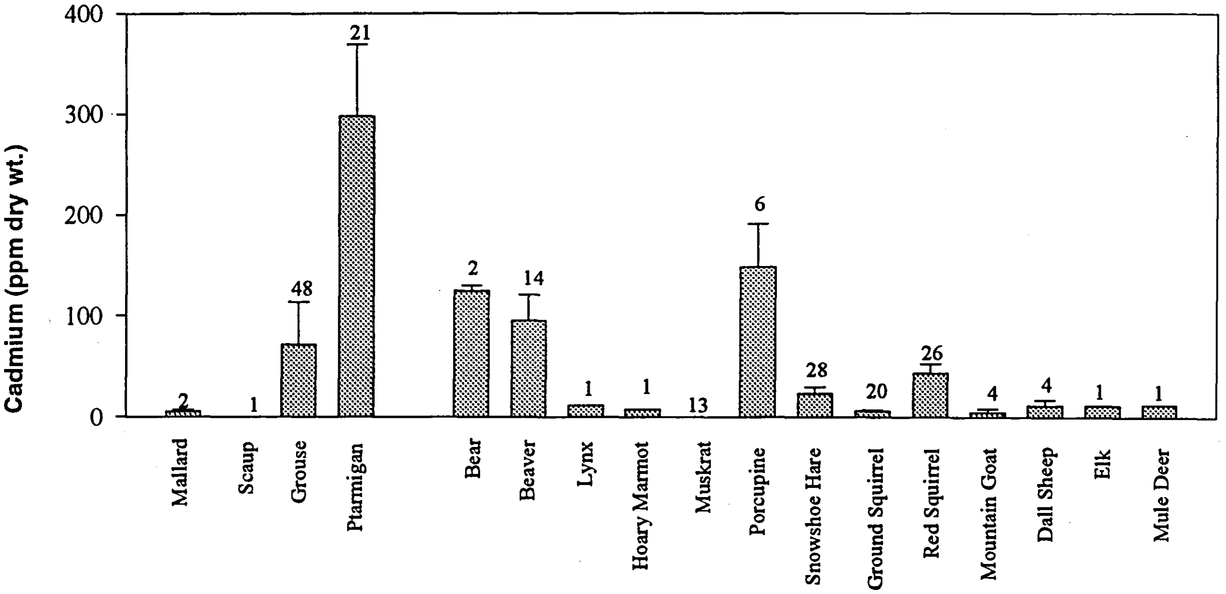


Figure 2. Kidney cadmium concentrations in Yukon wildlife (N above standard error bars)

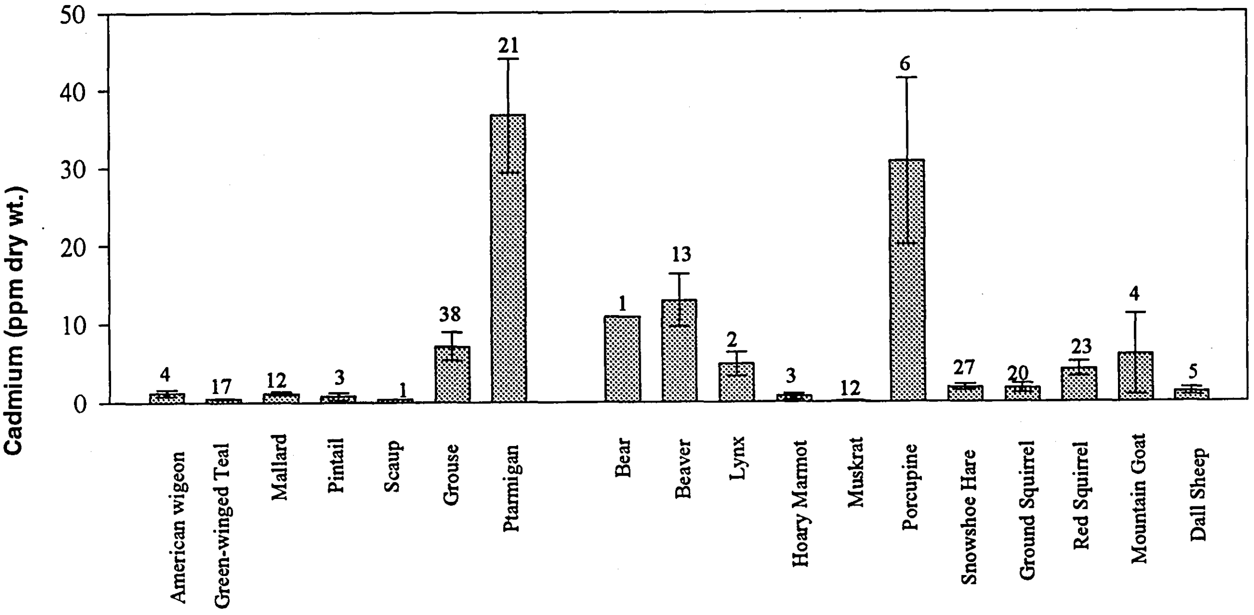


Figure 3. Liver cadmium concentrations in Yukon wildlife (N above standard error bars)

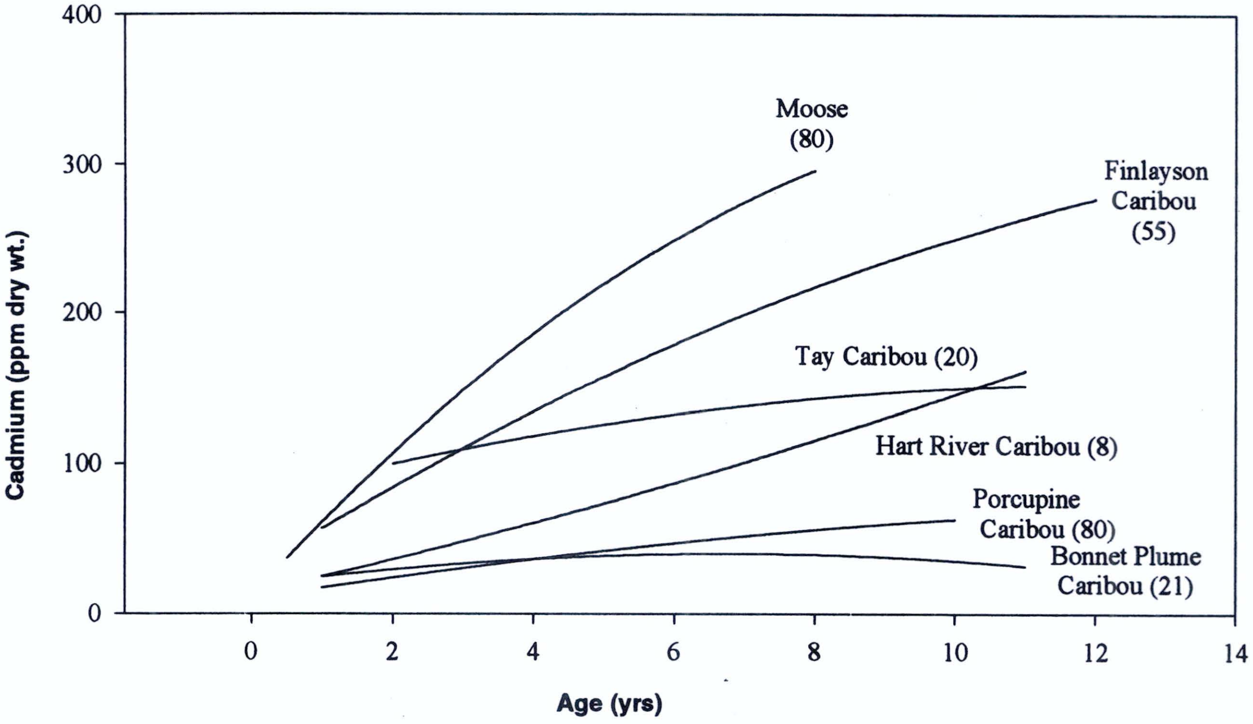


Figure 4. Kidney cadmium concentrations in Yukon moose and caribou (N)

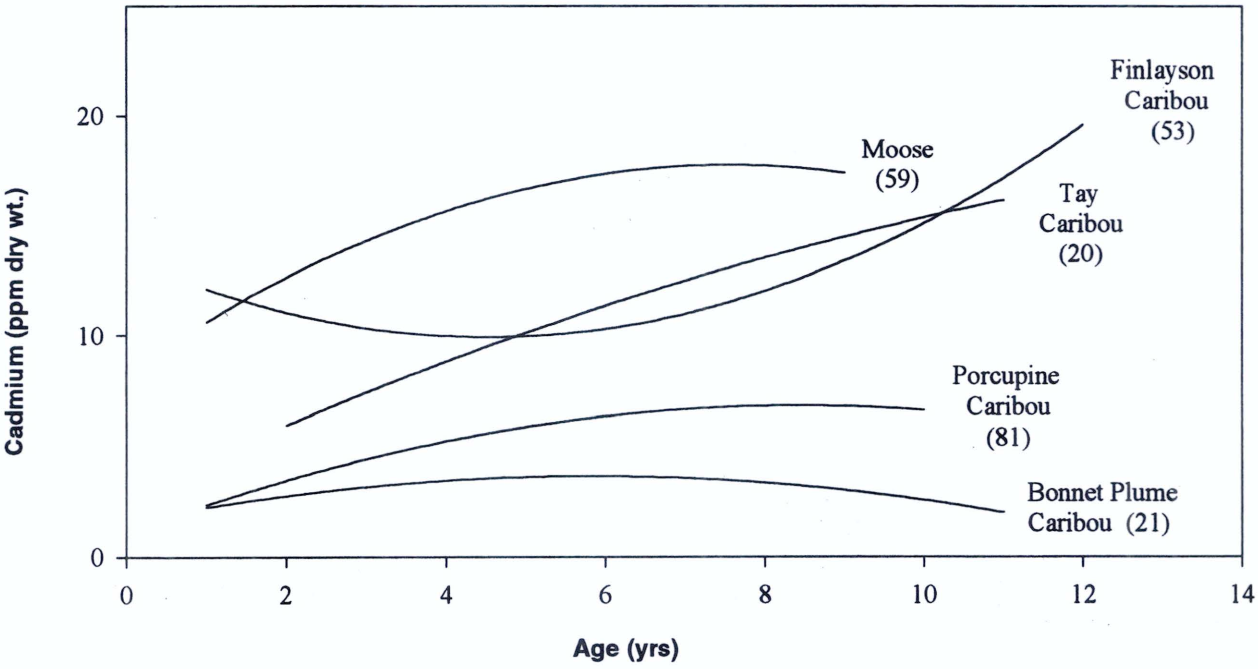


Figure 3. Liver cadmium concentrations in Yukon moose and caribou (N)

This project is continuing in 1997/98 only to the extent of collecting liver, kidney and muscle submissions from hunters and analysing them for inorganic contaminants. This will enable some trend monitoring, and increase the sample size so that potential geographical variations may be explored.

Expected project completion date: March 1998

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III HUMAN HEALTH

ASSESSMENT OF EFFECTS OF PREPARATION ON LEVELS OF ORGANIC CONTAMINANTS IN INUIT TRADITIONAL FOOD

Project Leader: Centre for Indigenous Peoples' Nutrition and Environment (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 in the 1980s showed considerable variations/differences in levels of PCBs and toxaphene in raw versus prepared (e.g. boiling or aging) samples (Kinloch *et al.* 1992). Further sampling was decided because of the small number of replicates in these studies. If certain food preparation methods can alter the levels of contaminants significantly, it may be possible to lower the intake levels of organic contaminants from consumption of traditional food by recommending adaptation of cooking methods.

After community consultation, it was decided to study walrus blubber, seal meat and blubber, narwhal meat, and mattak and blubber. They were chosen because of their high fat content and the relative importance in the traditional diet. Two local research assistant, Ms. Mary Killiktee and Ms Ooleepeeka Audlakiak, collected and prepared the samples.

ACTIVITIES IN 1995/1996

Sample collection was completed. Total fat contents for the samples were determined using an automatic soxhlet system. Organochlorines were measured as described in Chan *et al.* (1996). Fatty acid analysis were performed as described in Kuhnlein (1996). 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 were presented to the Hamlet Council on the 12th of September, 1996.

RESULTS

A list of samples analysed are presented in Table 1. Due to logistic reasons, sample sizes were less than five in some cases. PCB and other organochlorine pesticides were found in all food samples; the highest levels were found in narwhal blubber (Figure 1).

Frying and boiling decreased the PCB and pesticide concentrations in ringed seal meat by more than 80%. The contaminants leached out in the frying oil and the broth. Drying did not change the contaminant levels (Figure 2). Frying and boiling did not change the contaminant concentrations in ringed seal blubber (Figure 3).

For walrus blubber, frying had no effect. Boiling decreased the levels by 20% and aging increased the levels by 40% (Figure 4).

Drying did not change the levels in narwhal meat (Figure 5). Both the dip and aged dip of narwhal blubber contained about 60% to 70% of the contaminants in the raw samples. Both boiling and aging had little effect on contaminant level (Figure 6). Frying the narwhal mattak increased both the PCB and pesticide concentrations by about 50% because of the increase of fat. Boiling and aging had little effect. Aged dip had six times the levels of raw samples. The levels were similar to those found in narwhal blubber (Figure 7).

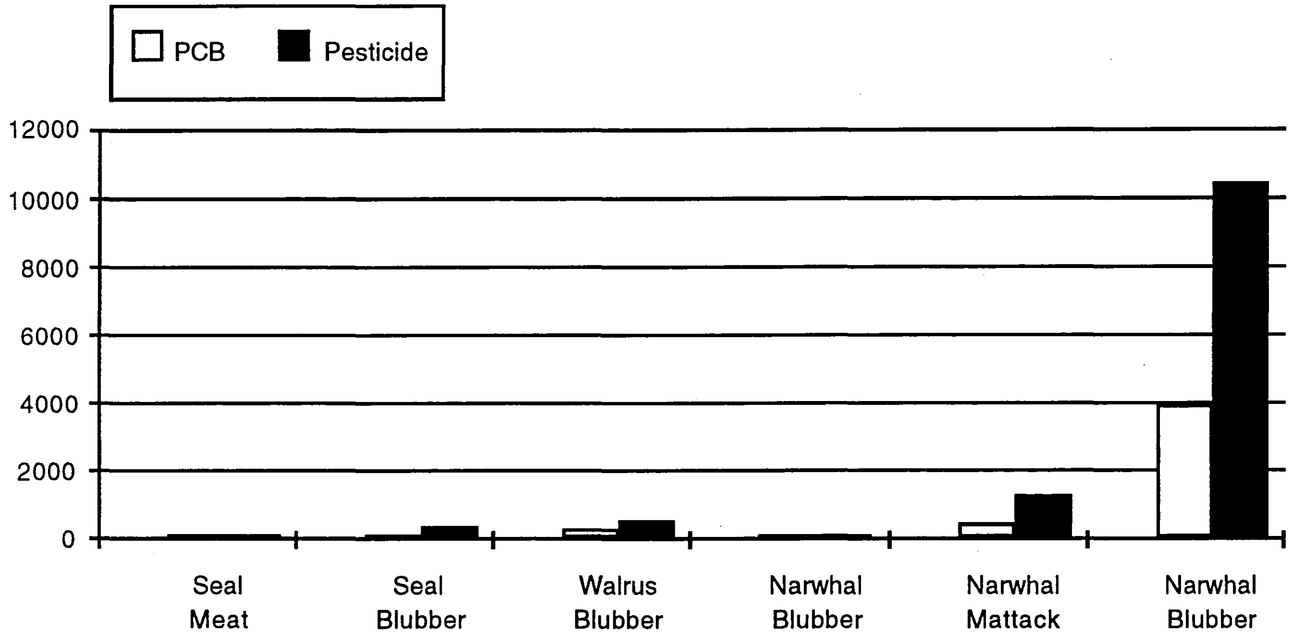

Figure 1. PCB and pesticide in raw food (ppb)

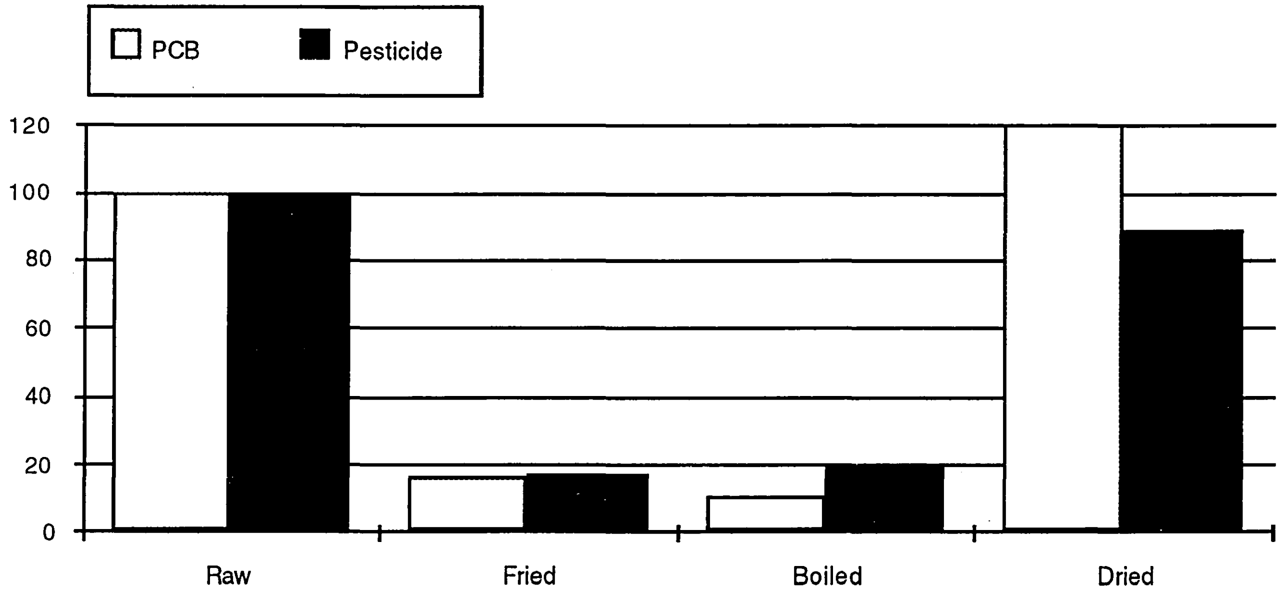

Figure 2. PCB and pesticide in seal meat (%)

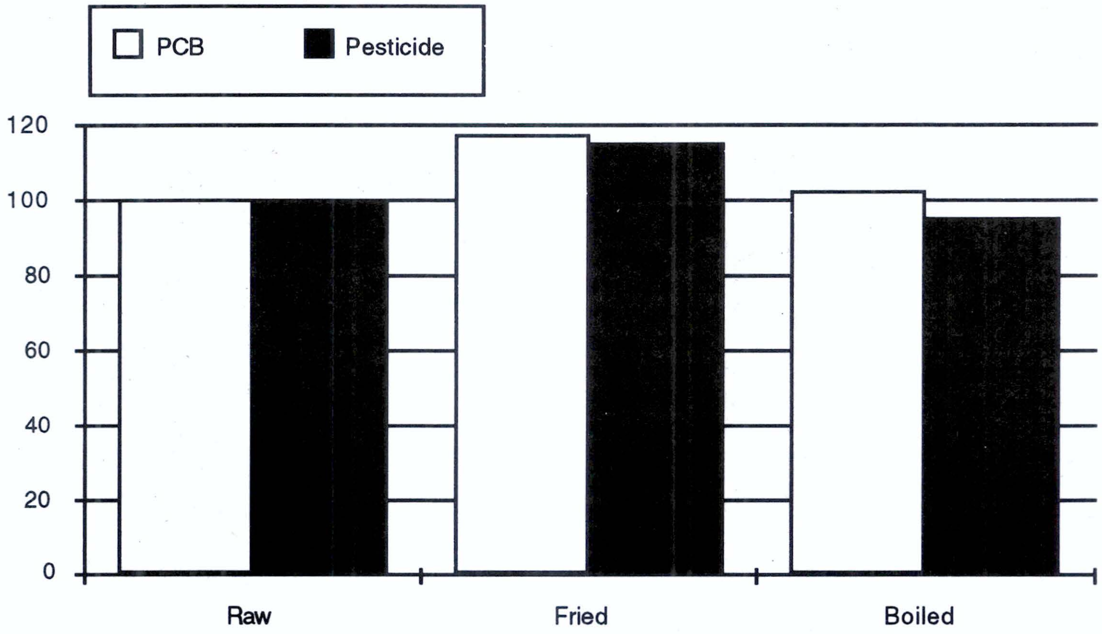

Figure 3. PCB and pesticide in seal blubber (%)

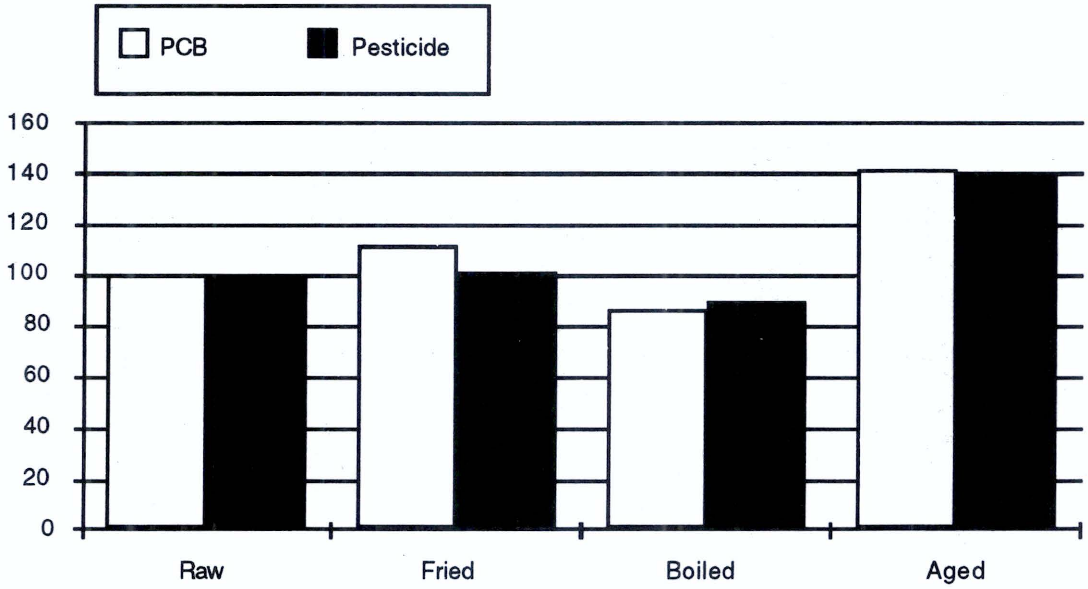

Figure 4. PCB and pesticide in walrus blubber (%)

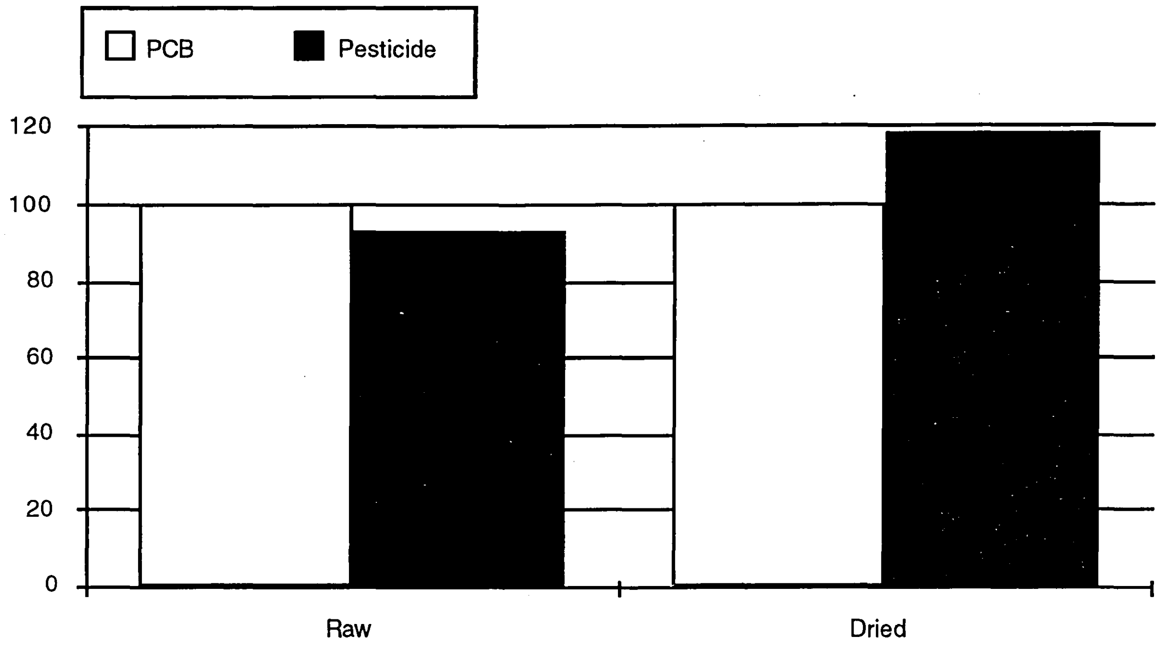

Figure 5. PCB and pesticide in narwhal meat (%)

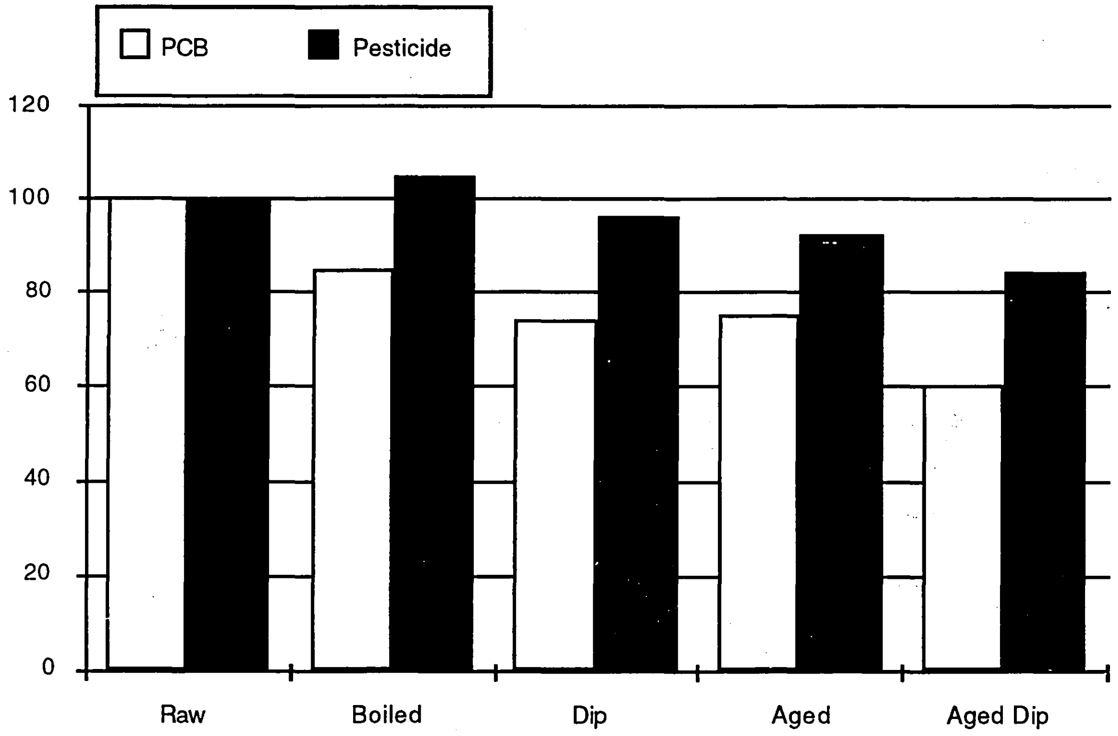

Figure 6. PCB and pesticide in narwhal blubber (%)

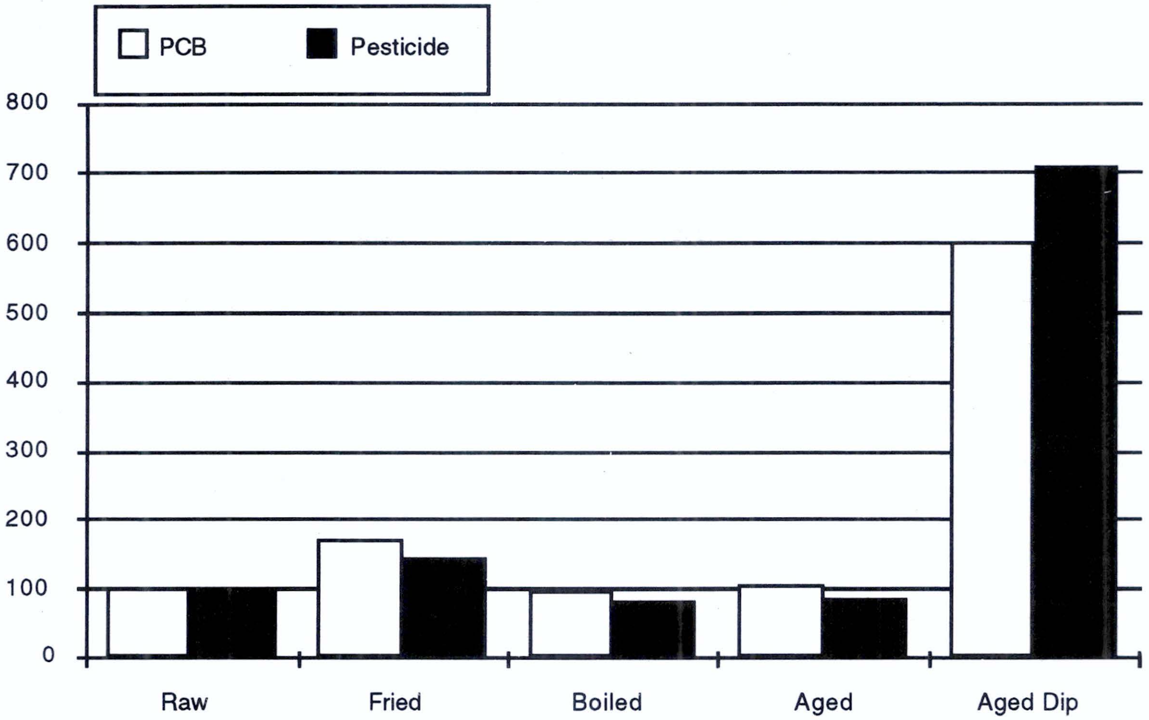

Figure 7. PCB and pesticide in narwhal mattak (%)

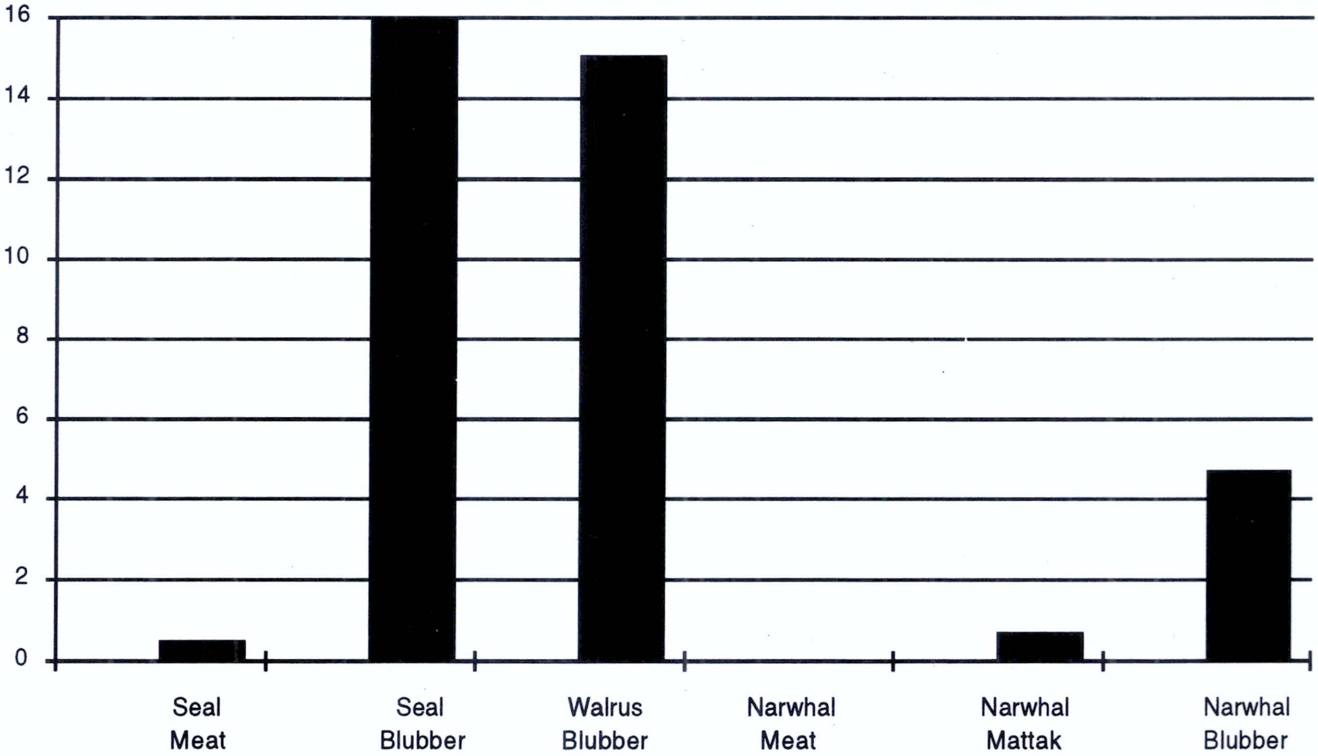

Figure 8. Omega-3 fatty acids concentrations (g/100)

Table 1. Sample size (N) of food items analysed

Animal Parts	Preparation Methods Raw	Fried	Boiled	Dried	Frying Oil	Dip	Aged	Aged Dip
Ringed Seal Meat	4	4	4	4	4	N/A	N/A	N/A
Ringed Seal Blubber	4	4	4	N/A	4	N/A	N/A	N/A
Narwhal Meat	3	N/A	N/A	3	N/A	N/A	N/A	N/A
Narwhal Blubber	3	3	3	N/A	N/A	3	3	3
Narwhal Mattak	3	3	3	N/A	N/A	3	3	3
Walrus Blubber	5	5	5	N/A	5	N/A	N/A	N/A

Ringed seal blubber and walrus blubber had the highest omega-3 fatty acid contents (Figure 8). Food preparation had little effect on omega-3 fatty acid concentrations.

DISCUSSION/CONCLUSIONS

Those preparation methods that decreased the lipid contents also decreased the organochlorine contents in the samples. The total polyunsaturated fatty acids or omega-3 fatty acid contents, however, remained unchanged. To decrease contaminant intake, one might fry and/or boil the seal meat and drain away the frying oil and broth. If blubber is preferred, one should eat more seal blubber than walrus and narwhal. Seal blubber has about half of the contaminants compared with walrus and more than thirty times less compared with narwhal. Less walrus blubber, particularly from aged walrus, should be consumed. Boiled walrus blubber (no broth) had less contaminants. Narwhal blubber and aged narwhal mattak dip had highest level of organochlorines. Susceptible persons such as women of child bearing age might want to decrease the consumption of these items.

Expected project completion date: Completed.

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VARIANCE IN FOOD USE IN DENE/MÉTIS COMMUNITIES

Project Leader: Centre for Indigenous Peoples' Nutrition and Environment (CINE), McGill University.

Project Team: H.V. Kuhnlein, B. Erasmus, B. Masuzumi, C. Mills, W. Carpenter, O. Receveur, H.M. Chan, M. Boulay.

OBJECTIVES

1. To define the levels of consumption of traditional food by maximum users in Dene/Métis communities.
2. To understand the extent of traditional food use in order to define contaminant and nutrient intake so that timely advice regarding benefits and risks of food consumption can be made.

DESCRIPTION

This study, initiated by the Dene Nation and the Métis Nation of the Northwest Territories, builds on the experiences and food use data completed in Fort Good Hope/Colville Lake (Kuhnlein 1991) and aims at providing the information necessary to evaluate the benefits/risks of consuming various types and quantities of traditional and market foods in Dene/Métis communities (NWT).

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 (1994/95). Each interview includes:

(1) frequency of traditional food use,
(2) 24 hour diet recall, and
(3) sociocultural questionnaire. In addition a price list for market food and a traditional food harvest calendar were completed in each community.

A total of 1012 individual interviews were collected in random samples of adult males and females during two time periods: March–April and October–November 1994. Participating communities included: Aklavik, Tssigehtchic (Arctic Red River), Teetl'it Zheh (Fort McPherson), K'ahbamitúé (Colville Lake), Radeli Ko (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 was converted to electronic form and one person per community was instructed on the use of Epi-Info to access the files.

ACTIVITIES IN 1995/96

This last phase of the study was aimed at data interpretation. Interpretation of the results included visits to the communities with formal presentations to Aboriginal organizations and discussion of preliminary results in the following meetings:

June–August 1995:
Progress reports presented to the community councils of Tsiigehtchic, Fort McPherson, Lutzel K'e and the Deninu Koe Environment Committee in Fort Resolution. Presentations at the Gwich'in/Inuvialuit Contaminants Workshop (Inuvik), the Métis Nation General Assembly (Hay River) and the Dene General Assembly (Fort Providence).

October 18-20, 1995:
Workshop on interpretation of research results (Edzo).

March 5-7, 1996:
Poster presentation at the "Dene Environment Gathering", (Yellowknife).

March 13, 1996:
Presentation at the Sahtu Caregivers Conference (Norman Wells).

July 6, 1996:
Presentation to the Métis Nation (NWT) General Assembly (Inuvik)

In October 1996, the final report was completed (Receveur *et al.* 1996). Multiple copies of the final report together with posters and leaflets summarizing study results were sent to each participating community together with an electronic version of community specific dataset. The complete dataset was archived at the offices of the Dene Nation, the Métis Nation of the Northwest Territories and at CINE.

RESULTS

Preliminary results of interest relating to overall diet adequacy and the particular role of traditional food in the food system have been previously summarized (CINE 1996). Peer reviewed articles are being submitted for publication.

Analyses focused on benefits and risks of current intakes of traditional food (food that comes from the local natural environment). Significant dietary contributions of market food (food purchased at a store) were also considered, but risks associated with market food consumption, particularly in light of the relationships between market food intake and increase in chronic diseases such as diabetes, high blood pressure or heart disease were not analysed in this report. Finally, results of a preliminary evaluation of exposure to contaminants through traditional food intake were presented.

In summary, traditional food is widely consumed throughout the territories with great variation in type and amount consumed in different communities. Variation in food intake across communities is important to consider when assessing benefits as well as risks associated with current food intakes. Within each community, younger people eat significant amounts of traditional food but less than older age groups.

Dene/Métis people are generally well aware of the many benefits of traditional food: nutritional, sociocultural and economic.

Traditional food is the main contributor of iron, zinc and protein in all communities. These nutrients are essential to health. Current levels of intake in these communities are higher than those for the rest of Canada and known to provide good protection against anemia, infectious diseases, as well as promote wound healing. Traditional food is also lower in fat than market food, and the types of fat present in traditional food are more conducive to health. Traditional food could also contribute significantly to vitamin A and calcium intakes, but at present, rich sources of these nutrients do not appear to be consumed in sufficient quantities to assure adequate intake.

Although the particulars of a nutrition programme were not discussed, it was recommended that the overall diet, considering contributions of both traditional and market foods across communities, could be improved by addressing the following factors:

1) Vitamin A intakes are consistently low across all regions and rarely meeting 50% of the Recommended Nutrient Intakes.
2) Calcium intakes are also often below requirements although to a lesser extent than vitamin A.
3) Fat often represents more than 35% of energy intake, with higher intakes observed in younger age groups, and more fat derived from market food.
4) Fibre intakes are extremely low in all age groups.
5) Sucrose intake ranges between 10% to 15% of energy intake, which is not excessively high, but a trend towards higher intakes in the younger age group may need to be addressed.

Traditional food has important socioeconomic and cultural functions. Market food is expensive and in each community a large proportion of the population reported that they were unable to afford to purchase all the food needed from the store. Apart from its economic value, harvest and consumption of traditional food is further associated with sharing of the harvest within the community, quality of the time spent on the land, opportunity to practice spirituality and encourage children to discover the natural environment. In general, harvest and consumption of traditional food may also benefit health by providing people with a chance to command the events that affect their lives—to do what they need to do to and live as they wish to live.

Exposure to contaminants through traditional food intake was assessed based on the assumption that contaminant levels in all communities would be similar to those measured in Fort Good Hope and Colville Lake (Kuhnlein 1991) and Deninu Kue (Kim *et al.* in press). This assumption is obviously in need of verification and unlikely to hold true in all cases. This exercise was encouraging nevertheless since in no instance was the average contaminant intake above the reference guidelines (Table 1). It is generally assumed that levels of contaminant intakes below these limits are most unlikely to cause observable health effects. The facts that any contaminant at all is present in the traditional food supply, and that occasional significant levels of exposure can be reached through consumption of particular traditional foods, are cause for concern and warrant further monitoring.

Because of concern that people may already limit their traditional food intake as a result of fear of contamination,

Table 1. Estimated intake (mean ± SE[1]) of organochlorines[2] and heavy metals[3] on days when traditional food is consumed (late winter and fall combined)

	Females		Males		
	Age 20-40 (n=138)	Age 41+ (n=188)	Age 20-40 (n=146)	Age 41+ (n=190)	TDI[4]
			µg/day		
PCB	1.5 ± 0.1	3.1 ± 0.4	2.2 ± 0.2	3.0 ± 0.2	60
TOX	0.3 ± 0.1	1.3 ± 0.5	0.6 ± 0.1	0.8 ± 0.2	12
CBZ	0.4 ± 0.03	0.7 ± 0.1	0.6 ± 0.1	0.8 ± 0.2	16
HCH	0.3 ± 0.03	0.7 ± 0.1	0.6 ± 0.1	0.7 ± 0.1	18
CHL	0.2 ± 0.04	0.6 ± 0.1	0.4 ± 0.1	0.5 ± 0.1	3
DDT	0.2 ± 0.02	0.6 ± 0.3	0.3 ± 0.03	0.4 ± 0.04	1200
DIE	0.02 ± 0.005	0.1 ± 0.04	0.04 ± 0.01	0.06 ± 0.01	6
Cd	7.3 ± 1.3	26.8 ± 10.8	9.8 ± 1.2	11.9 ± 4.0	60
As	10.4 ± 5.4	58.6 ± 21.4	10.8 ± 6.1	13.8 ± 6.5	120
Pb	36.2 ± 2.3	48.9 ± 2.9	48.2 ± 2.4	65.6 ± 12.2	214
Hg	2.2 ± 0.4	4.2 ± 0.7	3.6 ± 0.5	4.6 ± 0.6	43

[1] Means and standard errors are calculated based on equal weight for each season.

[2] Polychlorinated biphenyls (PCB), toxaphenes (TOX), chlorobenzene (CBZ), hexachlorexanes (HCH), chlordane (CHL), dichlorodiphenyltrichloroethane (DDT), dieldrin (DIE)

[3] Cadmium (Cd), arsenic (As), lead (Pb), mercury (Hg)

[4] For an adult of 60 kg

participants were asked what significant health risks they associated with traditional food consumption. Between 10% and 32% of the respondents avoided a traditional food because of a perceived health risk. High fat content, spoilage, the fact that some animals eat garbage or carry disease were the reasons most frequently cited. Some animals, in particular bear and beaver, are also often avoided because of spiritual relationships. Allergies were reported to dall sheep (Gwich'in and Sahtù), pickerel (Sahtù), unspecified fish species (Deh-Cho and South-Slave), porcupine (Deh-Cho) and beaver (South-Slave). The level of contaminants in traditional food was perceived as a risk associated specifically with fish consumption in Gwich'in, Sahtù, Deh-Cho and South-Slave regions.

When participants were also asked whether they had observed any changes in the quality of animal or plant traditional foods, 14% to 24% of participants reported that they had. Changes were generally negative although some participants reported that caribou were healthier now (Gwich'in), fish was fatter (Dogrib), and that fire in the South-Slave area may have benefitted some animals. In all regions, however, participants reported the increased presence of parasites in fish. Fish with soft flesh were reported in Gwich'in, Deh-Cho and South-Slave areas; abnormal loche liver in Gwich'in, Sahtù and Deh-Cho. Numerous animal and plant species were reported to be less plentiful.

DISCUSSION/CONCLUSIONS

The creation of this data set was made possible through a partnership between Indigenous organizations and academic researchers—a partnership promoted within the Northern Contaminants Program. The use of this data set will depend in large measure on the extent of further discussion it will generate at the community level. It can be used to develop interventions aimed at improving nutritional status and monitoring exposure to contaminants. It also represents a baseline dietary survey against which future assessments can be compared, in particular as they relate to change in dietary practices and corresponding changes in patterns of disease. It can be expected that these chronic conditions will increase more rapidly in communities with lower traditional food intake. This hypothesis, when confirmed, would support further allocation and targeting of resources towards prevention of "the diseases of deculturation".

Additional assessment of exposure to contaminants must be performed based on more geographically specific contaminant values. The analysis presented to date suggests that traditional food, as consumed by Dene/Métis, does not present significant health hazards. Nevertheless, regular monitoring seems appropriate since daily diets can occasionally contain levels of contaminants above reference guidelines. The data in this report can be used to logically prioritize which particular traditional food could be monitored in specific locations.

The multiple concerns expressed in all communities regarding physical and ecological changes in fish and other animal species beg to be addressed further. These concerns may be perceived as significant for community members and less so for scientists accustomed to more critical end-points. Although it was not a direct objective of this project to probe the depth and validity of traditional ecological knowledge, this study of the traditional food system suggests that subtle changes may have widespread consequences. Indigenous Peoples have been previously recognized as the best stewards of some of the most sensitive environments in the world (Johns *et al.* 1994) and following up on concerns expressed by Dene/Métis community members may lead to significant improvement in our understanding of ecosystem and human health.

Completion date: October 1996

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YUKON FIRST NATIONS ASSESSMENT OF DIETARY BENEFIT/RISK

Project Leader: Centre for Indigenous Peoples' Nutrition and Environment (CINE), McGill University

Project Team: H.V. Kuhnlein, O. Receveur, H.M. Chan, M. Boulay (CINE); N. Kassi (CYFN); M. Palmer (YCC)

OBJECTIVES

1. To derive quantitative estimates of traditional and market food intake among adults from Yukon First Nations.
2. To investigate benefits of traditional food in terms of nutritional, socioeconomic and cultural significance.
3. To incorporate existing data on organochlorines and heavy metals content of traditional food with quantitative estimates of food intake.

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 also expressed concerns as to the consequences of a shift toward increase consumption of market food, a shift that may be accelerated by the reported presence of contaminants in traditional food.

The present study included administering a set of interviews (24-hr diet recall, traditional food frequency and socioeconomic questionnaire) to a representative sample of adults in participating communities during late winter and fall 1995. In addition, food samples were collected for nutrient analyses to complete the traditional food composition database, or for contaminant analyses if requested by the community.

The data collected in this study were merged with existing contaminants databases to estimate benefits and risks of diets as consumed by Yukon First Nations.

ACTIVITIES IN 1995/96

Data collection proceeded between February and April 1995, and again between October and December 1995 in the same 10 communities: Dawson, Mayo, Carmacks, Ross River, Watson Lake, Lower Post, Beaver Creek, Burwash Landing, Carcross and Atlin. The final data set includes 802 individual interviews.

In addition 409 food samples were collected and analysed for nutrient and/or contaminant contents.

RESULTS

Since the participation rate was excellent, the sample was random, and reported energy intakes are within the expected range, the food records appear to be of the required quality to generate valid estimates of nutrient intakes as well as contaminant exposure.

Analyses to date have focused on documenting the nutritional, sociocultural and economic benefits of the traditional food system.

Table 1 shows the relative importance of traditional food species used by Yukon First Nations. Seasonal variation in traditional food use is further illustrated in Figure 1. Over the entire year, traditional food was consumed on average every other day. Figure 2 shows seasonal variation in the contribution of traditional food to selected nutrients. Traditional food is a major contributor to required levels of protein, iron and zinc. The use of traditional food also affects diet quality through changes in the macronutrient profile: on days with traditional food, fat intake represents 30.2 % of total energy; on days when market food only is consumed, this percentage is 40.0%.

Table 1. Traditional food species consumed in Yukon communities, ranked by the percentage of population consuming each species (Food Frequency Questionnaire)

WINTER (n=373)	% population	SUMMER (n=429)	% population
LAND ANIMALS			
Moose	90.6	Moose	97.9
Caribou Woodland	38.5	Caribou Woodland	48.0
Caribou Barrenland	26.2	Sheep	29.2
Rabbit	25.1	Rabbit	27.4
Sheep	9.9	Arctic ground squirrel	21.3
Beaver	8.3	Caribou Barrenland	18.8
Arctic ground squirrel	4.5	Porcupine	16.9
Deer	3.7	Beaver	16.0
Porcupine	3.2	Hoary marmot	8.6
Mountain goat	3.2	Muskrat	5.6
Hoary marmot	2.9	Deer	4.6
Lynx	1.6	Mountain goat	3.0
Muskrat	1.3	Bear	0.9
Bison	1.1	Lynx	0.2
Bear	0.5	Bison	0
FISH			
Chinook salmon	47.9	Chinook salmon	65.7
Trout	37.7	Grayling	56.8
Lake whitefish	28.1	Trout	49.4
Sockeye salmon	20.9	Lake whitefish	45.2
Grayling	19.5	Sockeye salmon	33.9
Jackfish	11.0	Jackfish	22.3
Coho salmon	10.2	Coho salmon	17.9
Halibut	8.8	Dolly varden	15.5
Chum salmon	8.3	Rainbow trout	15.1
Broad whitefish	6.4	Chum salmon	14.6
Loche	5.1	Halibut	13.9
Rainbow trout	5.1	Eulachon	11.4
Eulachon	4.0	Broad whitefish	9.0
Dolly varden	3.7	Round whitefish	8.4
Round whitefish	2.9	Connie	7.7
Arctic char	2.4	Cisco	6.0
Longnose sucker	1.6	Longnose sucker	4.9
Connie	1.3	Loche	4.9
Brown trout	1.1	Arctic char	1.6
Cisco	0.8	Brown trout	0.9
BIRDS			
Spruce grouse	27.3	Spruce grouse	61.7
Ducks	10.2	Ducks	25.1
Ptarmigan	6.1	Blue grouse	17.9
Blue grouse	5.9	Ptarmigan	11.1
Canada goose	2.1	Canada goose	8.6
Sea gull eggs	0.5	Swan	1.4
White fronted goose	0.3	White fronted goose	0.9
Swan	0.3	Sea gull eggs	0.5
Blue goose	0	Arctic tern	0.2
Arctic tern	0	Cranes	0.2
Cranes	0	Brant goose	0.2
Snow goose	0	Snow goose	0
Brant goose	0	Blue goose	0

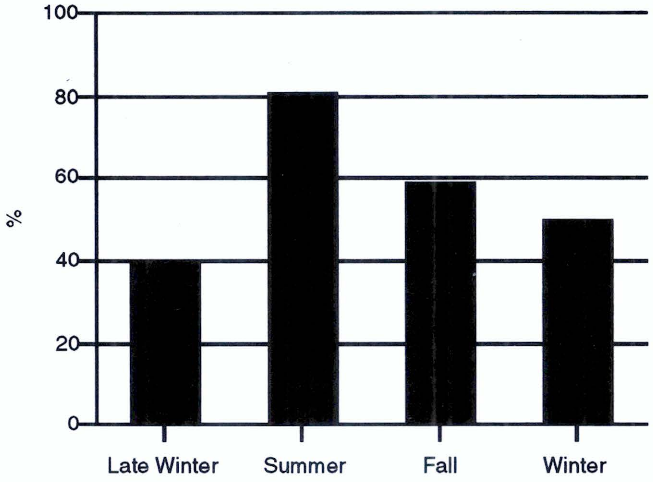

Figure 1. Percentage of days with traditional food consumption, by season.

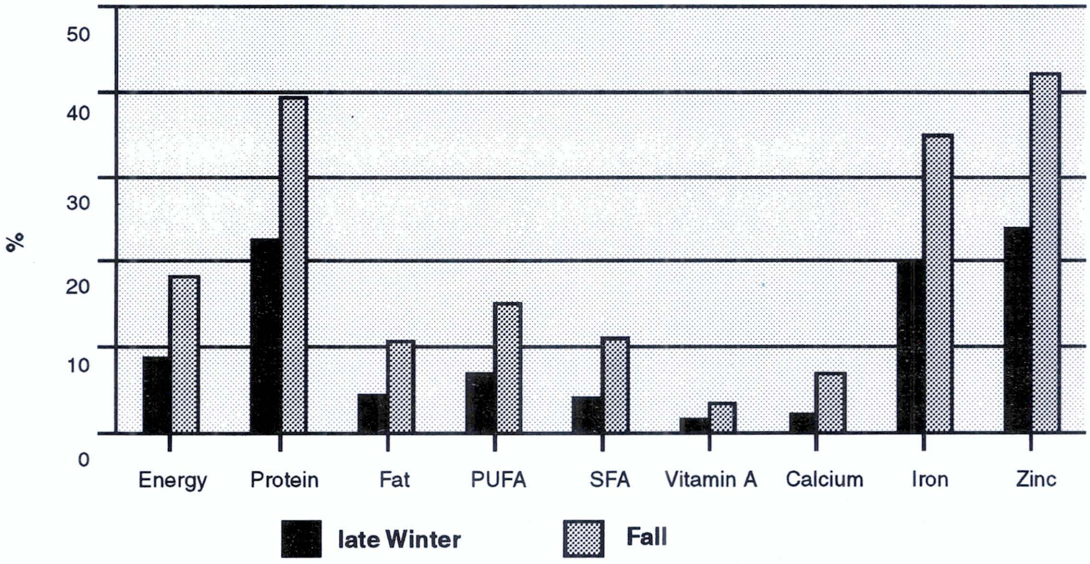

Figure 2. Mean proportion of energy andnutrients contributed by traditional food, by season.

Table 1. ...cont'd)

WINTER (n=373)	% population	SUMMER (n=429)	% population
PLANTS			
Blueberries	34.5	Blueberries	74.5
Low bush cranberries	28.6	Wild raspberries	51.3
High bush cranberries	17.9	Low bush cranberries	48.0
Balsam fir	17.1	Wild strawberries	39.4
Wild raspberries	15.2	High bush cranberries	32.0
Labrador tea	11.8	Soapberries	25.3
Soapberries	9.6	Crowberries (blackberries)	23.7
Crowberries (blackberries)	9.1	Labrador tea	23.4
Caribou weed	7.5	Mushrooms	20.9
Caribou moss	6.7	Balsam fir	19.0
Wild strawberries	6.1	Wild rhubarb	16.2
Wild rhubarb	6.1	Rosehips	11.6
Black spruce	5.6	Caribou moss	7.2
Rosehips	5.3	Sage	7.0
Mushrooms	4.5	Caribou weed	6.5
Sage	3.2	Bear root	6.3
Bear root	2.9	Wild chives (wild onions)	6.3
Birch	2.9	Rosebuds	6.0
Bog cranberries	2.4	Black currants	5.8
Salmonberries	2.4	Saskatoon berries	5.8
Dandelion	2.4	Willow	5.3
Black currants	2.4	Black spruce	5.3
Saskatoon berries	2.1	Birch	4.4
Lodgepole pine	1.9	Red currants	4.2
Red currants	1.9	Bog cranberries	3.9
Wild chives (wild onions)	1.9	Salmonberries	3.9
Rosebuds	1.9	Juniper	3.9
Poplar	1.6	Gooseberries	3.7
Bearberries (kinnikinick)	1.6	Poplar	3.5
Juniper	1.6	Cloudberries	2.8
Yarrow (stink flower)	1.3	Yarrow (stink flower)	1.9
Gooseberries	1.3	Rat root (wild ginger)	1.9
Willow	1.1	Bearberries (kinnikinick)	1.9
Mint	1.1	Honeysuckle	1.6
Fireweed	0.8	Dandelion	1.4
Honeysuckle	0.8	Lodgepole pine	1.2
Rice root (Indian rice)	0.8	Mint	1.2
Cloudberries	0.5	Fireweed	0.7
Rat root (wild ginger)	0.3	Bristly black currants	0.7
Bristly black currants	0.3	Arctic dock	0.2
Arctic dock	0.3	Rice root (Indian rice)	0

Sociocultural benefits of traditional food are many. When respondents were asked whether they agree, disagree or had no opinion on a list of statements regarding potential benefits of traditional food, more than 95% agreed on the following attributes of traditional food:

Harvesting and using traditional food by the family:

- contributes to physical fitness and good health
- provides people with healthy food
- keeps people in tune with nature
- saves money
- is an essential part of the culture
- provides education on the natural environment
- contributes to children's education
- provides skills in survival
- provides skills in food preparation at home
- offers an opportunity to learn patience and develop other personality qualities

The traditional food economic role needs to be further emphasized since 38% of the participants reported that they could not afford to buy all the food they need from the store. Compared with Edmonton, the average cost of the Northern Food Basket was approximately 50% higher in participating communities.

DISCUSSION/CONCLUSION

The close collaboration between CINE and the Yukon Contaminants Committee made the development of this project possible, and thanks to the guidance of Council of the Yukon First Nations (CYFN), the negotiation of the research agreements and the actual administration of this project were successfully completed.

This project provides Yukon First Nations with valid estimates of dietary intake among the adult population, documents the benefits of traditional food, and will integrate the nutritional and contaminant information relevant to the consumption of various types and amount of traditional and market food.

After discussion of study results with Community Health Representatives and community delegates at the Yukon College in December 1996, results will be presented to each Community Council before being summarized in a final report in Fall 1997.

Expected completion date: December 1997

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EVALUATION OF PRENATAL EXPOSURE TO ORGANOCHLORINES AND HEAVY METALS IN NUNAVIK NEWBORNS 1993-1996

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OBJECTIVES

The general objective of this project is to monitor prenatal exposure to heavy metals, organochlorines and nutrients in order to properly assess the risks and benefits of the Inuit diet.

SPECIFIC OBJECTIVES

1. To measure lead, mercury and organochlorines in the cord blood of all Inuit newborns from Nunavik over a five-year period, ending in 1999.
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 acids content in plasma phospholipids) variables.
3. To study the relationship between of omega-3 fatty acids levels in plasma 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 complete the AMAP-Health sub-program for Canada.
5. To lay out, in collaboration with the Public Health Department of the Nunavik Regional Board of Health and Social Services, the background of a risk management strategy.

DESCRIPTION

For cultural and economic reasons, the Inuit from the eastern Arctic rely heavily on marine food for their subsistence. Their large consumption rate of sea mammal fat (in particular from ringed seal and beluga) leads to body burdens of various organochlorines exceeding those of southern Québec populations by factors varying between 2 and 10 (Dewailly *et al.* 1989, 1992, 1993;). However, while contaminants found in country food may pose health risks, these foods also constitute an important source of several key nutrients.

Health risk characterizations and assessments of human exposure to environmental contaminants have been ongoing in the eastern Arctic for more than 10 years. To date, research has narrowed down to focus on two main groups of chemicals: namely heavy metals and organochlorines. As regards heavy metals, only mercury and lead are still part of the environmental health priorities in Nunavik because exposure to other metals is very low in the region and cadmium has been shown to be linked essentially to smoking (Benedetti et al, 1993). Most epidemiological and experimental studies on health effects related to lead, mercury and PCB exposure suggest that prenatal life is the most sensitive period for the induction of adverse neurodevelopmental effects.

The effects of prenatal exposure to background levels of PCBs from environmental sources have been studied in four major cohort studies: Michigan, North Carolina, Netherlands and New York. In the Michigan study, Fein and collaborators (1984) showed that high concentrations of PCBs in the cord blood were associated with lower birth weights. Furthermore, Jacobson and collaborators (1990a, 1990b) reported that, by the age of four years, deficits in body size persisted and indicators of poorer cognitive performances continued to be present and associated with *in utero* exposure as measured by cord blood PCBs. Furthermore, newborn's behavioural function deficits have been observed in the Michigan, North Carolina and New York studies. The consumption of PCB-contaminated fish was associated with an increase in abnormal reflexes and a decrease in reactions to external stimulation (Jacobson *et al.* 1985, Lonky *et al.* 1995). In the Netherlands, prenatal and postnatal exposure to PCBs were significantly associated with hypothonia and a decreased neurologic optimum at two weeks post-partum (Huisman *et al.* 1995). The North Carolina study indicated that the dose-response analysis showed deficits in psychomotor development at 6, 12 and 24 months of age in highly exposed children (Rogan and Gladen 1991. Gladen *et al.* 1988). Finally, the more exposed children of the Michigan study clearly showed poorer visual information processing abilities, which indicate a deficit in visual memory and attention (Jacobson *et al.* 1985, 1990a, 1992). This association was not confirmed in the Netherlands study but was recently confirmed in a study where infants were born to Taiwanese (Yu-Cheng) exposed mothers (Ko *et al.* 1994).

In contrast, high exposure to omega-3 fatty acids during the prenatal period improves birth weight and the 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.* 1992), showed that a diet rich in fish and marine mammals results in high levels of omega-3 fatty acids in the plasma of adults. These substances transmitted to the fetus during pregnancy, have a direct effect on the weight of the newborn and on the gestation period by extending it. Selenium is another essential nutrient found in sea products. This element is anti-carcinogenic and can antagonize mercury-induced toxicity.

ACTIVITIES IN 1995/1996

Each 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 participants signed the consent form, cord blood was collected at birth. In 1996, a total of 131 mothers agreed to participate in this study. Since 1993, 491 participating mothers were recruited and 444 were retained in the present study. A total of 47 mothers/babies couples were excluded because either the questionnaire was not filled out or contaminants cord blood sampling was not done properly. Nevertheless, since 475 analyses of metals and organochlorines and 432 analyses of phospholipids were performed and the results are presented in Appendix 1.

The present synopsis will focus on descriptive results and univariate analysis. A final and more complete report is in preparation and will be available in the fall of 1997.

Study population

The population under study comprises all children born at the Tullatavik Health Centre of Ungava (Kuujjuaq) and the Inuulitsivik Health Centre (Puvirnituq) between November 1993 and December 1996.

Collection of information

When arriving at the Health Centre, women were asked to participate in the present study and a consent form was signed by each one (Appendix 2). Blood samples were collected by a midwife or a doctor and an identification form was filled in at that time. All samples were sent to and analysed by the Centre de toxicologie du Québec.

Questionnaire

Information on the health status of the baby at birth and on pregnancies issues were collected using a questionnaire presented in Appendix 3. The following information was obtained:

BABY

- Name, village of residence
- Birth date
- Sex
- Weight
- Height
- Cranial circumference
- Intrauterine growth retardation
- Medical problems at birth
- APGAR

MOTHER

- Birth date
- Height
- Usual Weight
- Weight before delivery
- Length of gestation
- Date of last menses
- Total number of pregnancies
- Total number of live births
- Use of medication and vitamins
- Medical problems during pregnancy
- Blood pressure during labour
- Smoking habits

Toxicological and biochemical analyses

The following organochlorines (PCBs and pesticides) were measured in the plasma by high resolution gas chromatography and electron-capture detectors: No. IUPAC: 28, 52, 99, 101, 105, 118, 128, 138, 153, 156, 170, 180, 183, 187, aldrine, α-chlordane, γ-chlordane, cis-nonachlor, p,p'-DDE, p,p'-DDT, hexachlorobenzene, mirex, oxychlordane, trans-nonachlor, β-HCH. The detection limit, based on three times the average standard deviation of noise is 0.02 µg/L for PCB congeners and chlorinated pesticides, except for heptachlor-epoxide and dieldrin for which the detection limit is 0.1 µg/L. Mercury blood levels were measured by cold vapour atomic absorption spectrometry and lead and selenium blood levels by graphite furnace atomic absorption with Zeeman background correction. Detection limits are respectively of 5 nmol/L, 0.1 µmol/L and 0.5 µmol/L. Detailed analytical protocols are available upon request.

To facilitate the interpretation of the present study, only a few organochlorines were retained or regrouped. The following variables were retained: Aroclor 1260, Σ of 14 congeners, Σ of chlordanes, p,p'–DDE + p,p'–DDT ; hexachlorobenzene, mercury, lead, selenium.

Lipid analysis were performed by the Centre de recherche sur les maladies lipidiques of the Laval University Hospital Centre (CHUL) and the Omega-3 fatty acids analysis was performed by the Nutritional Science laboratory, at Guelph University, Ontario. This report present results for the following fatty acids: c20:5n3 (EPA), c22:6n3 (DHA), the sum of EPA and DHA and the sum of all Omega 3s.

Finally, the analysis of the thyroid hormones (TSH, T_3, T_4 and TBG) have been performed respectively by the Département de génétique humaine (CHUL) and the Laboratoire du centre de toxicologie du Québec (CHUL).

RESULTS

Table 1 shows that 52.1% of participating mothers came from the Hudson Bay area and 47.9% came from the Ungava Bay area.

Blood and plasma concentrations for the different contaminants are presented in Appendix 1. Some of the contaminants were detected for all samples: congeners 138 and 153; p,p'- DDE and hexachlorobenzene. Congeners # 118, 180 and 187 were detected in more than 95% of contaminants samples. Nevertheless, some contaminants were detected in less than 10% of the samples: congeners # 28 and 128 and the following pesticides: aldrin, cis-chlordane and trans-chlordane.

Figures 1 and 2 show the profile of PCB congeners and chlorinated pesticides in the cord blood plasma. All concentrations are expressed on a fat basis.

Contaminants and Omega-3 fatty acids concentrations by region of residency

On a lipid basis, the mean concentration of PCB, expressed as Aroclor 1260, measured in Inuit newborns is 830.7 µg/kg (geometric mean [CI 95% = 779–886]). This concentration is 2 times higher than that found in lower North Shore newborns (572.0 µg/kg; IC 95%: 503.8–649.5). The arithmetic mean of 1072.6 µg/kg is more than 3 times greater than that found in southern Quebec (300µg/kg) and less than half the mean concentration measured in milk fat (2900 µg/Kg) of Inuit mothers during 1990/1991. In Nunavik, 10% of Inuit newborns had blood concentrations above the intervention level of 2000 µg/L.

Of all contaminants studied, only hexachlorobenzene and lead concentrations are not statistically different between the two regions (Table 2). All other contaminant concentrations are significantly higher in the Hudson Bay region.

Table 1. Number of newborns according to mother's region of residency

Ungava Bay region	**Number of newborns**	**%**
Kuujjuaq	92	20.7
Tasiujaq	13	2.9
Kangirsuk	27	6.9
Kangirsujuaq	23	5.2
Kangirsualujjuaq	40	9.0
Aupaluk	9	2.0
Quaqtaq	21	4.7
Sub-total Ungava	**225**	**50.7**
Hudson Bay region	**Number of newborns**	**%**
Kuujjuarapik	16	3.6
Umiujaq	12	2.7
Inukjuak	49	11.0
Puvirnituq	73	16.4
Akulivik	22	5.0
Ivujivik	16	3.6
Salluit	31	7.0
Sub-total Hudson	**219**	**49.3**
TOTAL	**444**	**100.0**

Table 2. Organochlorines (lipid basis), mercury, and lead concentrations by the mothers region of residency

	Region of résidency	N	Geometric mean	Confidence interval (95%)	Range
Mercury (nmol/L)	Hudson	244	92.8	84.5 - 101.8	5 - 520
	Ungava	231	53.5	48.3 - 59.2	9 - 443
	Total	**475**	**71.0**	**65.9- 76.3**	**5 - 520**
Lead (µmo/L)	Hudson	244	0.204	0.187 - 0.222	0.01 - 1.31
	Ungava	231	0.180	0.166 - 0.196	0.05 - 1.28
	Total	**475**	**0.191**	**0.180 - 0.203**	**0.04 - 1.01**
Aroclor 1260 (µg/kg)	Hudson	243	922.6	837.0 - 1017.0	81.9 - 8855.0
	Ungava	232	744.3	685.7 - 808.0	138.8 - 3553.3
	Total	**475**	**830.7**	**778.8 - 886.2**	**81.9 - 8855.0**
p,p'-DDE + p,p'-DDT (µg/kg)	Hudson	243	431.5	391.7 - 475.3	56.3 - 3612.9
	Ungava	232	364.1	335.5 - 395.2	62.1 - 2071.2
	Total	**475**	**397.2**	**372.5 - 423.4**	**56.3 - 3612.9**
Σ of 14 PCB congeners (µg/kg)	Hudson	243	355.4	325.6 - 387.7	62.7 - 3209.6
	Ungava	232	291.4	271.4 - 312.9	74.5 - 1196.1
	Total	**475**	**322.6**	**304.7 - 341.5**	**62.7 - 3209.6**
Σ of chlordanes (µg/kg)	Hudson	243	116.1	106.0 - 127.1	19.3 - 652.4
	Ungava	232	95.2	88.4 - 104.8	20.3 - 514.3
	Total	**475**	**105.9**	**99.5 - 112.8**	**19.3 - 652.4**
Hexachlorobenzene (µg/kg)	Hudson	243	57.1	52.0 - 62.8	6.8 - 417.7
	Ungava	232	56.7	52.3 - 61.6	6.8 - 282.0
	Total	**475**	**56.9**	**53.5 - 60.7**	**6.8 - 417.7**

The mean concentration (geometric mean) of lead in Nunavik samples is 0.19 µmol/L. By comparison, the average concentration found is in the 954 southern Quebec samples in 1994 is 0.08 µmol/L (CI 95%: 0.07–0.08). In Nunavik, 7% of Inuit newborns had a blood concentration above the intervention level of 0.50 µmol/L.

The mean concentration of total mercury was 71.0 nmol/L. This concentration is approximately 1.5 times the level of 40 nmol/L found during the Santé Quebec Inuit Health Survey among women aged 18 to 25 years. In cord blood samples recently collected from 954 southern Quebec newborns and 213 lower North Shore newborns, the mean mercury concentrations were respectively 4.3 nmol/L (CI 95%: 4.1–4.6) and 10.9 nmol/L (CI 95%:9.9–12.0). Even though the levels measured in Nunavik newborns were 16 times greater than those measured in southern Quebec newborns and 6 times higher than Lower North Shore newborns, the mean level found in Inuit newborns is still below the intervention level set a 150 nmol/L. However, 3% of Inuit newborns had mercury concentrations above this safe biological level.

Plasma analysis performed on 432 Inuit cord blood samples indicated a mean (arithmetic) concentration of eicosapentanoic acid (EPA: C20:5n3) of 0.41% (% of total phospholipid content, weight basis) compared with 0.20% in 30 southern controls ($p < 0.001$).

The proportion of the sum of omega-3 fatty acids measured in cord blood phospholipids of Nunavik newborns (4.5%) is higher than the one observed in Southern Quebec (2.0%), but lower than the one observed on the Lower North Shore (6.5%). In the Santé Québec Health Survey, the mean omega-3 concentration (arithmetic) for the 18 to 24 year age group (men and women) was 6.9%. The difference with the present result (4.5%) could be explained by the fact that the EPA mildly crossed the placental barrier.

Fatty acids concentrations in phospholipids are presented in Appendix 1. Meanwhile, Table 3 shows that there is no significant difference between the two regions under study.

Temporal variations of contaminants and omega-3 fatty acids concentrations

Tables 4 and 5 look at temporal variations of concentrations by year of birth. Table 4 shows that between 1994 and 1996 concentration levels increased slightly but this variation is not significant. Inversely, one can observe a significant decrease in the proportion of EPA + DHA (Table 4), between 1994 and 1996.

Associations between Contaminants, Selenium, and Phospholipids Concentrations

An examination of Pearson correlation coefficients shows (Table 6) that selenium is significantly associated ($p < 0.05$) with organochlorines and mercury. In general, organochlorines strongly correlate between each other. Finally, one can observe that the correlation between organochlorines and heavy metals is moderate.

Table 7 shows that except for selenium, all organochlorines and heavy metals concentrations are moderately associated (positive correlation) with omega-3 fatty acids concentrations.

CONCLUSION

This cord blood monitoring was carried out throughout Nunavik during the last three years. Since January 1, 1997 monitoring has continued in the Hudson Bay area only (encompassed in the cohort study on neurobehavioural effects).

Among the 475 participating newborns, only 10% had PCB concentrations in their cord blood lipids above the tolerable level of 2 mg/kg. These concentrations are still three times higher than in levels southern newborns. For mercury, only 3% of newborns had concentrations above 150 nmol/L (30 µg/L) but these were 20 times those of southern babies. Lead was 2.5 times higher than in infants from southern latitudes, and 7% of newborns are above 0.48 µmol/L (10µg/dl). Although Inuit newborns from Nunavik are the most exposed human group to organochlorines in Canada (even compared with other northern communities) we don't think that major interventions are required. Considering the current status of knowledge on health effects associated with low doses of methylmercury and PCBs it would be too early to modify drastically the diet of women in age of procreation.

The observed decrease of omega-3 fatty acids in cord blood phospholipids could be related to a decrease inseafood consumption over the past three years; this will have to be confirmed. To counteract this decrease, less contaminated traditional foods (especially seafood) will have to be promoted to increase pregnant womens' consumption. For example, in many Nunavik communities, Arctic char is already available for pregnant women, free of charge.

For lead we will have to find the major sources of exposure. Lead shots appear to be the most plausible. If this is confirmed, this exposure will be relatively easy to avoid by implementing non-toxic pellets in Nunavik.

For all of these contaminants Hudson Bay residents show higher exposure levels than those in the Ungava Bay. This is due to the difference in sea mammal consumption.

During the past three years, we have not observed any decrease in exposure of pregnant women in Nunavik. This temporal trend will be monitored in the forthcoming years, in the Hudson Bay region.

Table 3. Omega-3 fatty acids plasma concentrations by the mother's residency of region

Fatty acids (% of phospholipids)	Region of residency	N	Median	Arithmetic mean	Confidence interval (95%)	Range	Kruskall-Wallis test p*
EPA (c20: 5n3)	Hudson	211	0.30	0.41	0.36–0.46	0.0–2.9	
	Ungava	221	0.27	0.37	0.32–0.41	0.0–2.3	0.16
	Total	**432**	**0.28**	**0.39**	**0.36- 0.42**	**0.0–2.9**	
DHA (c22: 6n3)	Hudson	211	3.6	3.6	3.5–3.8	1.1–7.3	
	Ungava	221	3.5	3.7	3.5–3.8	1.2–7.7	0.97
	Total	**432**	**3.6**	**3.6**	**3.5–3.7**	**1.2–7.7**	
Σ of oméga-3	Hudson	211	4.3	4.5	4.3–4.7	1.2–10.3	
	Ungava	221	4.3	4.5	4.3–4.7	1.3–9.4	0.96
	Total	**432**	**4.3**	**4.5**	**4.3–4.7**	**1.2–10.3**	
EPA + DHA	Hudson	211	3.9	4.0	3.9–4.2	1.2–9.1	
	Ungava	221	3.9	4.0	3.8._4.2	1.2–8.2	0.81
	Total	**432**	**3.9**	**4.0**	**3.9–4.2**	**1.2–9.1**	

* non- parametric variance analysis

Table 4. Temporal variations of organochlorines and mercury concentrations

	Year	N	geometric mean	Confidence interval (95%)
Aroclor 1260	1994	166	777.9	696.7–868.4
	1995	136	759.0	675.5–852.8
	1996	131	906.3	804.9–1020.9
Mercury (nmol/L)	1994	159	70.7	62.3–80.2
	1995	139	71.8	63.0–82.0
	1996	131	74.9	64.7–86.8

Table 5. Proportion of EPA + DHA in phospholipids by year of birth

	Year	N	Median	Arithmetic Mean	Confidence Interval 95%	Range	Kruskall-Wallis Test p*
EPA + DHA (%)	1994	130	4.2	4.4	4.2–4.6	1.4–8.1	
	1995	129	3.8	4.0	3.7–4.2	1.2–9.1	0.001
	1996	131	3.5	3.8	3.5–4.0	1.2–8.2	

* non- parametric variance analysis

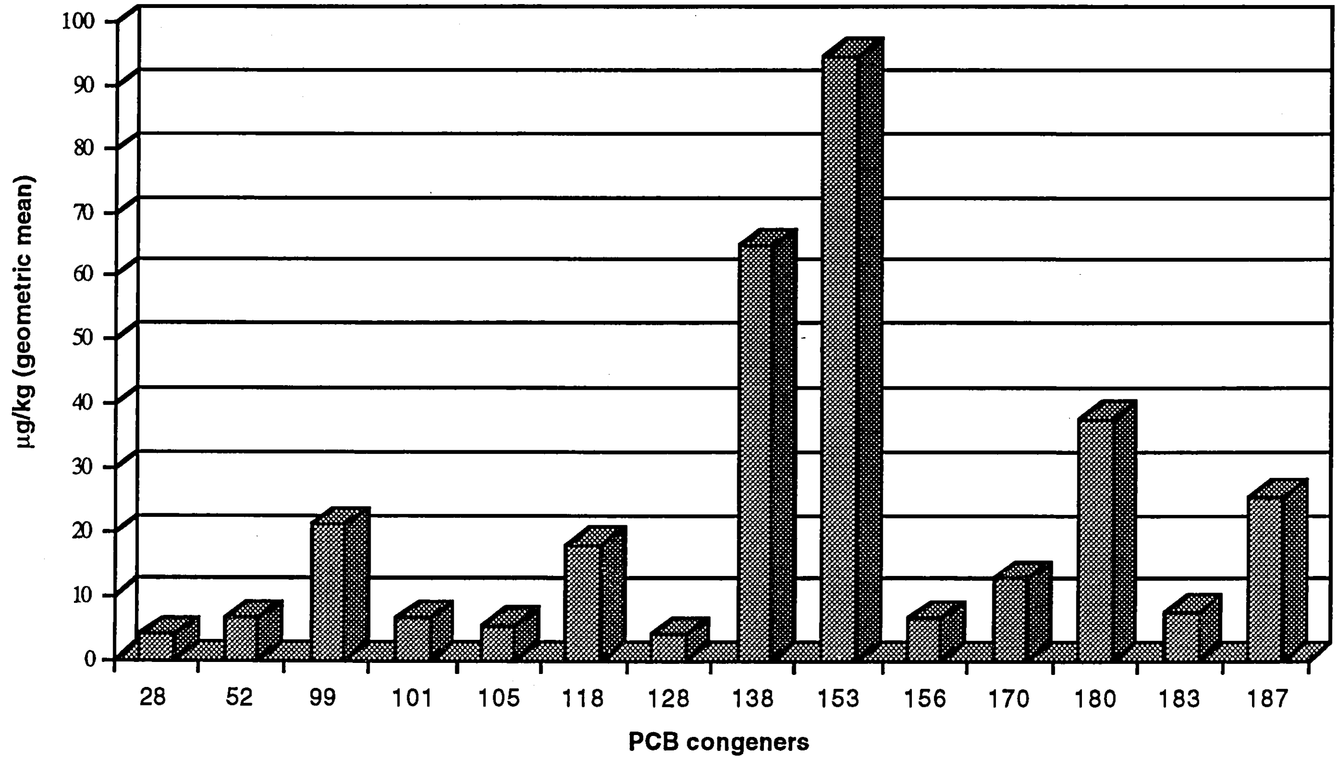

Figure 1. Profile of PCB congener concentrations measured in cord blood plasma of Inuit newborns

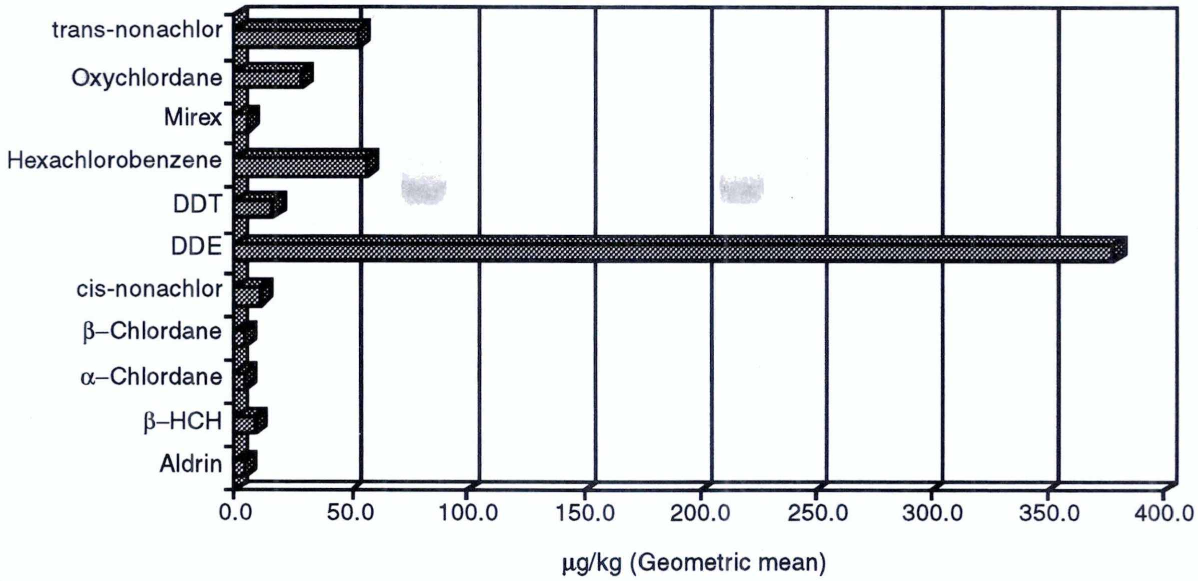

Figure 2. Concentrations of chlorinated pesticides in the cord blood plasma of Inuit newborns

Table 6. Correlation coefficients between contaminants and between selenium and contaminants ($p < 0.05$)

	Sum of 14 congeners	p,p'–DDE + p,p'–DDT	Σ chlordane	Hexachloro-benzene	Mercury	Lead	Selenium
Aroclor 1260	0.99 n = 428	0.91 n = 428	0.87 n = 428	0.78 n = 428	0.39 n = 414	0.33 n = 414	0.16 n = 248
Σ congeners	1	0.90 n = 428	0.87 n = 428	0.78 n = 428	0.39 n = 414	0.35 n = 414	0.17 n = 248
p,p'–DDE + p,p'–DDT		1	0.88 n = 428	0.82 n = 428	0.36 n = 414	0.28 n = 414	0.18 n = 248
Σ chlordane			1	0.89 n = 428	0.49 n = 414	0.31 n = 414	0.34 n = 248
Hexachlorobenzene				1	0.40 n = 414	0.33 n = 414	0.22 n = 248
Mercury					1	0.29 n = 429	0.46 n = 260
Lead						1	N.S.

Table 7. Correlation coefficients between contaminants concentrations and phospholipids concentrations ($p < 0.05$)

	Σ oméga-3 n = 386	EPA (c20: 5n3) n = 377	DHA (c22: 6n3) n = 386	EPA + DHA n = 386
Aroclor 1260	0.13	0.16	0.11	0.13
Σ 14 congeners	0.16	0.19	0.14	0.15
p,p'–DDE + p,p'–DDT	0.15	0.14	0.15	0.15
Σ chlordanes	0.25	0.24	0.23	0.24
Hexachlorobenzene	0.29	0.28	0.28	0.29
Mercury	0.24	0.33	0.21	0.24
Lead	0.16	0.23	0.13	0.16
Selenium	N.S.	0.14 n=209	N.S.	N.S.

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APPENDIX 1

PROJET : SANG AU CORDON, KATIVIK
Concentrations sanguines des contaminants
(métaux lourds, BPC et pesticides)

Contamin	Nombre d'échantillons	MOY_ ARI	IC95% Borne inférieure	IC95% Borne supérieure	MOY_ Géo	IC95% Borne inférieure	IC95% Borne supérieure	Min.	Max.	Proportion de détectés
ARO_FAT	475	1072.556	993.162	1151.950	830.742	778.761	886.192	81.911	8854.962	99.789
c_28_f	475	4.401	4.215	4.586	4.209	4.110	4.311	1.004	40.000	0.842
c_52_f	475	8.160	7.635	8.685	6.759	6.414	7.122	2.518	41.109	50.105
c_99_f	475	26.939	25.046	28.831	21.147	19.848	22.530	2.793	169.323	95.158
c_101_f	475	7.686	7.232	8.140	6.510	6.197	6.840	2.735	34.722	49.263
c_105_f	475	6.544	6.148	6.939	5.643	5.394	5.903	2.562	33.915	33.474
c_118_f	475	23.030	21.484	24.575	18.210	17.113	19.378	2.793	120.968	94.526
c_128_f	475	4.291	4.188	4.393	4.168	4.080	4.258	1.004	15.204	0.421
c_138_f	475	82.748	76.859	88.636	64.871	60.885	69.117	6.826	630.725	99.789
c_153_f	475	123.509	114.084	132.934	94.677	88.660	101.101	9.693	1072.519	99.789
c_156_f	475	8.154	7.490	8.818	6.575	6.231	6.937	2.562	94.943	44.842
c_170_f	475	18.285	16.596	19.975	12.916	12.000	13.902	2.793	229.962	79.158
c_180_f	475	51.360	46.905	55.814	38.008	35.491	40.705	3.413	591.603	98.947
c_183_f	465	7.628	7.073	8.183	6.387	6.078	6.713	2.562	79.676	46.667
c_187_f	475	25.678	23.867	27.490	20.668	19.491	21.915	3.380	238.550	97.263
ALDRINf	475	4.384	4.250	4.519	4.219	4.121	4.320	1.004	18.692	1.895
BHC_f	475	9.669	9.150	10.188	8.498	8.141	8.872	2.389	41.156	33.474
A_CHLOf	475	4.516	4.146	4.887	4.198	4.090	4.309	1.004	73.046	0.211
Y_CHLOf	473	4.292	4.154	4.430	4.152	4.063	4.243	1.004	28.964	0.634
CIS_NOf	475	15.401	14.222	16.579	11.400	10.636	12.220	2.931	77.535	74.105
DDE_f	475	488.446	452.782	524.111	378.060	354.381	403.321	51.195	3421.511	100.000
DDT_f	475	22.509	20.605	24.413	16.825	15.738	17.986	4.031	191.438	75.579
HEXACHf	475	71.981	67.243	76.718	56.915	53.448	60.608	6.768	417.682	99.579
MIREXf	474	6.769	6.147	7.392	5.519	5.255	5.795	2.562	90.649	27.426
OXYCHLf	475	40.674	37.270	44.078	28.612	26.485	30.910	2.793	333.665	94.737
TRANSNf	475	70.845	65.695	75.995	53.459	49.900	57.273	4.710	393.317	99.368
SE	282	4.151	3.926	4.376	3.799	3.622	3.984	1.420	14.100	–
HG	475	96.640	89.468	103.812	70.957	65.948	76.346	5.000	520.000	–
PB	475	0.238	0.222	0.254	0.192	0.181	0.204	0.010	1.310	–
vitam_a	134	147.672	137.234	158.109	137.495	129.012	146.536	52.000	547.000	–

PROJET : SANG AU CORDON, KATIVIK
Concentrations sanguines des contaminants selon l'hôpital (métaux lourds, BPC-Totaux et lipides)

VARIABLE = aro1260

Hôpital d'où provient la mère	Nombre d'échangillons	MOY-ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
	480	2.617	2.430	2.805	2.027	1.901	2.162	0.240	18.560
Hudson	246	3.024	2.717	3.332	2.295	2.087	2.523	0.240	18.560
Ungava	234	2.190	1.994	2.386	1.779	1.636	1.934	0.270	8.538

……

VARIABLE = aro_fat

Hôpital d'où provient la mère	Nombre d'échangillons	MOY-ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
	475	1072.556	993.162	1151.950	830.742	778.761	886.192	81.911	8854.962
Hudson	243	1231.159	1098.004	1364.313	922.594	836.968	1016.979	81.911	8854.962
Ungava	232	906.433	828.141	984.724	744.324	685.667	807.999	138.748	3553.283

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VARIABLE = c20_5n3

Hôpital d'où provient la mère	Nombre d'échangillons	MOY-ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
	432	0.390	0.357	0.423	0.297	0.276	0.319	0.000	2.886
Hudson	211	0.414	0.364	0.464	0.313	0.281	0.348	0.000	2.886
Ungava	221	0.367	0.323	0.410	0.282	0.255	0.312	0.000	2.319

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VARIABLE = c22_6n3

Hôpital d'où provient la mère	Nombre d'échangillons	MOY-ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
	432	3.648	3.535	3.761	3.447	3.336	3.561	1.120	7.733
Hudson	211	3.632	3.474	3.791	3.433	3.276	3.598	1.120	7.262
Ungava	221	3.663	3.502	3.824	3.460	3.306	3.621	1.156	7.733

……

VARIABLE = epa_aa

Hôpital d'où provient la mère	Nombre d'échangillons	MOY-ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
	432	0.041	0.037	0.044	0.030	0.028	0.033	0.000	0.280
Hudson	211	0.046	0.041	0.052	0.035	0.031	0.039	0.000	0.280
Ungava	221	0.036	0.031	0.040	0.027	0.024	0.030	0.000	0.209

……

VARIABLE = epa_dha

Hôpital d'où provient la mère	Nombre d'échangillons	MOY-ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
	432	4.038	3.903	4.173	3.787	3.659	3.920	1.171	9.106
Hudson	211	4.046	3.853	4.240	3.790	3.604	3.985	1.171	9.106
Ungava	221	4.029	3.841	4.218	3.784	3.609	3.968	1.220	8.214

……

VARIABLE = ft4

Hôpital d'où provient la mère	Nombre d'échangillons	MOY-ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
	466	16.635	16.357	16.912	16.364	16.097	16.636	7.700	29.400
Hudson	248	16.579	16.206	16.952	16.318	15.961	16.684	9.600	29.000
Ungava	218	16.699	16.284	17.113	16.417	16.018	16.826	7.700	29.400

VARIABLE =hexachf

Hôpital d'où provient la mère	Nombre d'échangillons	MOY–ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
	475	71.981	67.243	76.718	56.915	53.448	60.608	6.768	417.682
Hudson	243	75.122	67.636	82.608	57.097	51.917	62.793	6.826	417.682
Ungava	232	68.690	62.995	74.385	56.726	52.275	61.555	6.768	281.989

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VARIABLE =hg

Hôpital d'où provient la mère	Nombre d'échangillons	MOY–ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
	475	96.640	89.468	103.812	70.957	65.948	76.346	5.000	520.000
Hudson	244	118.488	108.001	128.975	92.759	84.498	101.828	5.000	520.000
Ungava	231	73.563	64.736	82.390	53.466	48.284	59.205	9.000	443.000

……

VARIABLE = n3_tous

Hôpital d'où provient la mère	Nombre d'échangillons	MOY–ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
	432	4.511	4.361	4.661	4.236	4.094	4.383	1.181	10.251
Hudson	211	4.494	4.281	4.706	4.220	4.018	4.432	1.181	10.251
Ungava	221	4.527	4.315	4739	4.251	4.054	4.458	1.299	9.437

……

VARIABLE = n6_tous

Hôpital d'où provient la mère	Nombre d'échangillons	MOY–ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
	432	26.609.	26.323	26.895	26.433	26.145	26.724	16.889	35.166
Hudson	211	26.002	25.628	26.376	25.852	25.477	26.233	17.513	33.717
Ungava	221	27.189	26.771	27.606	27.000	26.578	27.428	16.889	35.166

……

VARIABLE = pb

Hôpital d'où provient la mère	Nombre d'échangillons	MOY–ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
	475	0.238	0.222	0.254	0.192	0.181	0.204	0.010	1.310
Hudson	244	0.255	0.230	0.279	0.204	0.187	0.222	0.010	1.310
Ungava	231	0.220	0.200	0.240	0.180	0.166	0.196	0.040	1.010

……

VARIABLE = rat_dd

Hôpital d'où provient la mère	Nombre d'échangillons	MOY–ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
	480	26.837	25.038	28.637	22.591	21.508	23.728	4.390	174.000
Hudson	246	28.061	25.401	30.720	23.369	21.776	25.080	4.390	146.667
Ungava	234	25.551	23.146	27.957	21.801	20.369	23.333	6.632	174.000

……

VARIABLE = s_chlof

Hôpital d'où provient la mère	Nombre d'échangillons	MOY–ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
	475	135.711	126.210	145.211	105.919	99.463	112.795	19.317	652.390
Hudson	243	150.654	135.774	165.534	116.069	105.979	127.120	19.317	652.390
Ungava	232	120.058	108.733	131.384	96.239	88.386	104.789	20.305	514.262

VARIABLE = som_14f

Hôpital d'où provient la mère	Nombre d'échangillons	MOY-ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
475	398.250	370.848	425.653	322.560	304.657	341.514	62.696	3209.590	
Hudson	243	453.259	407.148	499.371	355.376	325.788	387.651	62.696	3209.590
Ungava	232	340.633	313.919	367.347	291.432	271.399	312.943	74.450	1196.135

……

VARIABLE = som_ddf

Hôpital d'où provient la mère	Hôpital d'où Nombre d'échangillons	MOY-ARI	INFA	SUPA	Moyenne Géométrique	Borne inférieure	IC95% Borne supérieure	IC95% Minimum	Maximum
475	510.955	473.912	547.999	397.174	372.539	423.439	56.314	3612.948	
Hudson	243	573.375	512.702	634.049	431.504	391.722	475.325	56.314	3612.948
Ungava	232	445.576	405.744	485.408	364.141	335.491	395.239	62.112	2071.211

……

VARIABLE = t3

Hôpital d'où provient la mère	Nombre d'échangillons	MOY-ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
466	0.578	0.558	0.598	0.537	0.517	0.557	0.030	2.000	
Hudson	248	0.551	0.523	0.580	0.511	0.487	0.536	0.180	2.000
Ungava	218	0.608	0.581	0.635	0.567	0.537	0.599	0.030	1.230

……

VARIABLE = tbg

Hôpital d'où provient la mère	Nombre d'échangillons	MOY-ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
463	890.997	872.278	909.715	868.955	851.955	886.794	457.000	2082.000	
Hudson	245	861.288	840.293	882.283	844.782	823.921	866.172	457.000	1462.000
Ungava	218	924.384	892.920	955.849	896.947	868.436	926.395	478.900	2082.000

……

VARIABLE = tsh

Hôpital d'où provient la mère	Nombre d'échangillons	MOY-ARI	INFA	SUPA	Moyenne Géométrique	IC95% Borne inférieure	IC95% Borne supérieure	Minimum	Maximum
466	6.702	6.326	7.078	5.879	5.624	6.145	1.330	39.810	

APPENDIX 2

CORD BLOOD SAMPLING STUDY
CONSENT FORM

The authorities of the Tulattavik and Inuulitsivik Health Centres have accepted to collaborate with the Environmental Health Service of the Public Health Centre of Québec to set up a bank of cord blood and placenta. Blood sampling of the newborns' umbilical cord and placenta could help to learn more about certain health problems, including infectious disease. This monitoring will also allow us to characterize more precisely the prenatal exposure to contaminants like PCB and mercury.

Participation in this monitoring will not affect the baby in any way, because the blood from the cord and the placenta is taken after the birth, before it is discarded. The results of the laboratory tests will not be communicated to you unless they are abnormal. In that event, appropriate recommendations will be made to you regarding the baby.

I understand that blood will be sampled from the umbilical cord after birth and that the placenta will be used to conduct tests.

I accept that certain information will be collected from my medical file as well as from that of my child (name, date of birth, village of residence, baby's weight, height, head circumference, APGAR, pregnancy duration). I understand that this information will be kept strictly confidential.

I am free to accept or to refuse to participate in this study without any further need for justification and without prejudice as regards to the quality of medical services that both my child and myself are entitled to receive.

I understand the project and its usefulness, and agree to participate in this study.

Date:

______________________	______________________
Mother's name	Signature
______________________	______________________
Witness' name	Signature

CORD BLOOD SAMPLING STUDY
NUNAVIK PROJECT

IDENTIFICATION CHART

ID. #

1. Date of birth: **Month** ______ **Day** ______ **Year** _____

2. Sex of newborn **Boy** ___ **Girl** ____

3. Mother's name: ______________________________

4. Residence:

Kuujjuaq	___	**Kangiqsualujjuaq**	___
Tasiujaq	___	**Aupaluk**	___
Kangirsuk	___	**Quaqtaq**	___
Kangiqsujuaq	___		

5. Baby's name:____________________________

6. Is the baby given in adoption? **Yes**___ **No**___ (If yes, go to Question 8)

7. Will the baby live in the same village as the mother?

Yes___ **No**___ **Dnk**___ (if no, go to Question 8)

8. In which community will be baby inhabit?________________________

NB: **Please do not forget to insert this information chart in the "Ziploc" bag and send it along with the samples to the laboratory. THANKYOU!**

BLOOD SAMPLING STUDY
NUNAVIK PROJECT

IDENTIFICATION CHART

Cord Blood ID. # ____________________

1. Date of birth___ **(y)** ___ **(m)** ___ **(d)**

2. Sex of newborn **M** ___ **F** ___

3. Mother's name: ______________________________

4. Residence:

Kuujjuarapik	___	**Akulivik**	___
Umiujaq	___	**Ivujivik**	___
Inukjuaq	___	**Salluit**	___
Povungnituk	___		

5. Baby's name:____________________________

6. Is the baby given in adoption? **Y**___ (go to Q.7) **N**___

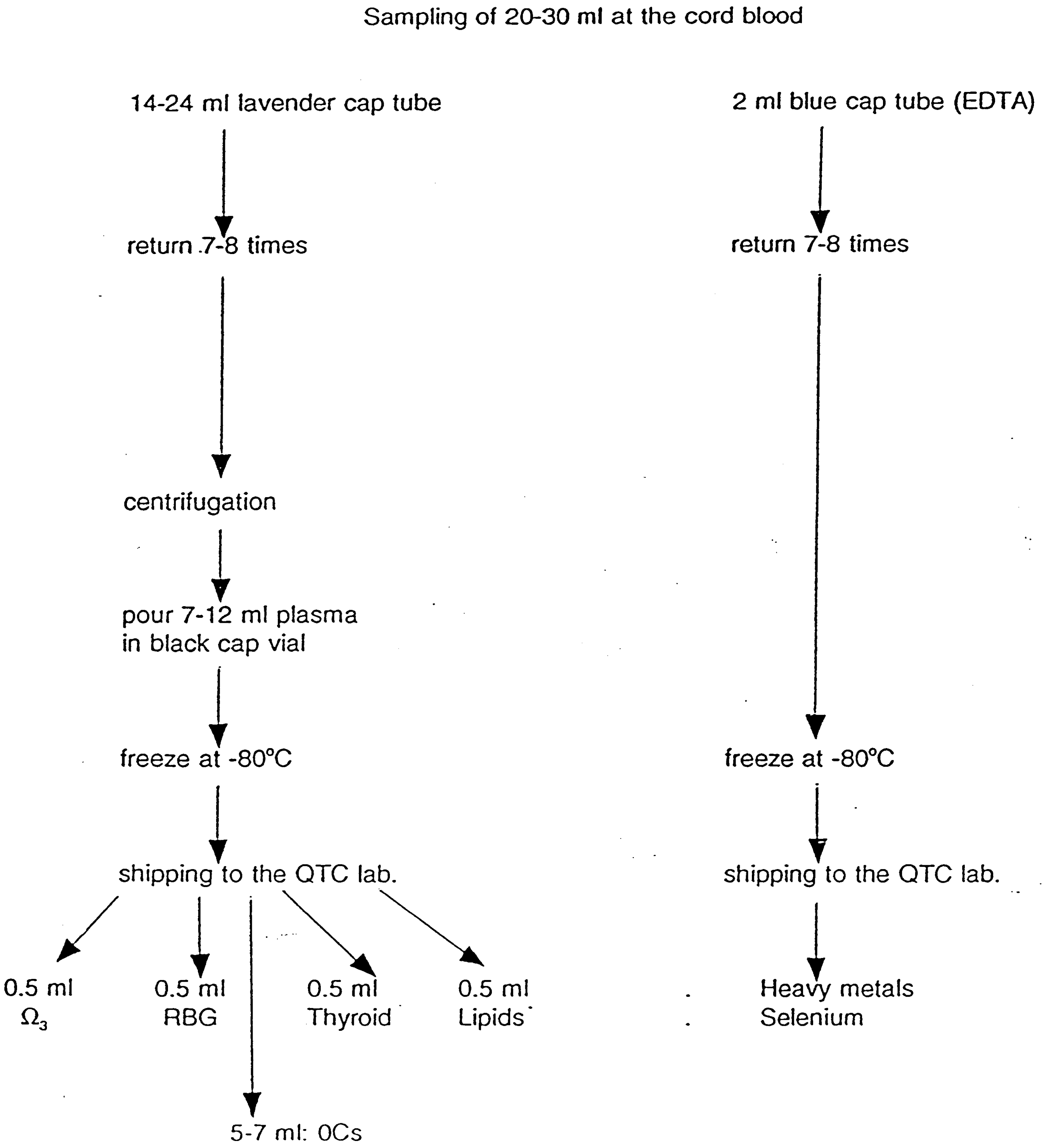
7. Will the baby live in the same village as the mother?

   Y ___ **N** ___ (go to Q.8) **DKN**___

8. In which community will be baby inhabit?_________________________

NB: Please insert this information chart in the "Ziploc" bag and send it along with the samples to the laboratory. THANKYOU!

BLOOD CORD STUDY
SAMPLING AND LABORATORY PROCEDURES



APPENDIX 2

SURVEILLANCE PROGRAM ON PRENATAL EXPOSURE TO LEAD, MERCURY AND ORGANOCHLORINES

HOSPITAL

___TULATTAVIK ___ INUULITSIVIK

INFORMATION FOUND IN PATIENT'S FILE

INFORMATION ON THE CHILDREN

1. Hospital file #: __________
2. Project identification #: _____________
3. Twin pregnancy: ___ Yes ___ No
4. Date of birth: _______/_______/_________
   day /month / year
5. Gender: ___ M ___ F
6. Weight:________________________ grams (at birth)
7. Height:________________________ cm
8. Cranial circumference: ________________ cm
9. Thoracic circumference: ______________ cm
10. APGAR at 5 minutes: / 10
11. Intra uterine growth retardation: __ Yes __ No __ Unknown

    if yes, specify:
12. Cardiac problems: __ Yes __ No __ Unknown

    if yes, specify:
13. Note any other medical problem seen at birth (e.g.: congenital anomalies, assisted ventilation):

    ____

    ____

    ____

INFORMATION ON THE MOTHER

14. Hospital file #: ____________________

15. Date of birth: ________/________/________
day /month / year

16. Height: ___ feet ____ inches or 1.___meter __ Unknown

17. Usual weight (before pregnancy):______ pounds __ Unknown
or kg

18. Weight before delivery: ______ pounds __ Unknown
or kg

19. Ultra sound exam performed: __Yes __ No __ Unknown (if no, go to Q.22)

20. Date: ______/______/______
day /month / year

21. If yes, how many weeks of gestational age based on ultra sound exam: ________ Weeks ________ Days

22. How many weeks of gestational ages based on date of last menses: ________ Weeks ________ Days

23. Total number of pregnancies: __ Unknown

24. Total number of live births: __ Unknown

25. Use of medication or vitamin during the pregnancy: __Yes __ No __ Unknown

If yes, specify the name of medication or vitamin taken the does and frequency:

____

26. Gestational diabetes: __Yes __ No __ Unknown

27 Note any other medial problem during pregnancy:

28. All blood pressure during labour (s/d mm Hg)

______/______/______/______/______/______/______/______/
1st /2nd /3rd /4th /5th / / / /

______/______/______/______/______/______/______/______/
/ / / / / / / /

________/______/______/______/______/______/______/______/
/ / / / / / / /

29. Did the mother smoke before her pregnancy? __ Yes __ No __ Unknown

If yes, how many cigarettes per day: ____________

30. Did the mother smoke during her pregnancy? __ Yes __ No __ Unknown

If yes, how many cigarettes per day: ____________

31. If the mother has stopped smoking before or during the pregnancy, can you specify the date?

_____/________/______
year/ month /day

32. What is your ethnic origin?

__ Caucasian __ Inuit __ Others (specify): ________________

HEALTH RISK ASSESSMENT AND ELABORATION OF PUBLIC HEALTH ADVICE CONCERNING FOOD CONTAMINANTS IN NUNAVIK

Project Leader: Éric Dewailly, MD, Ph.D., Public Health Centre of Quebec
Project Team: Pierre Ayotte, Department of Social and Preventive Medicine, Laval University; Carole Blanchet, Public Health Centre of Quebec; Suzanne Bruneau, Public Health Centre of Quebec; Gaétan Carrier, University of Sherbrooke; Bruce Holub, Department of Nutrition Sciences, University of Guelph

OBJECTIVES

1. To assess the health risks associated with the presence of contaminants in traditional foods (organochlorines and heavy metals) and to propose, if needed, public health recommendations aimed at reducing exposure to these chemicals while ensuring that major nutritional benefits are maintained.

2. To assess the health risks associated with the presence of contaminants in imported foods in to elaborate on sound public health advice regarding food contaminants in Nunavik.

3. To propose scenarios (resulting in the desired risk reduction while maximizing the dietary benefits) to the local public health authorities and Native groups so that they can be submitted to a social, economic and cultural acceptability and feasibility evaluation.

DESCRIPTION

The contamination of the arctic aquatic food chain has been brought to light throughout the last decade (Dewailly 1993a). Contaminants are carried to the Arctic by ocean and air currents from industrialized areas of the planet. The two main groups of contaminants that may affect human health are heavy metals (e.g. mercury, lead) and the organochlorines (e.g. polychlorinated biphenyls or PCBs, and chlorinated pesticides). Contaminants diffuse into the environment and find their way into the food chain on land and in the sea. Inuit are more exposed to these food chain contaminants than populations living in meridional regions, because their diet comprises large amounts of fatty tissues from marine mammal species (Dewailly 1994).

Since 1986, we have conducted various studies and programs in Nunavik to assess which contaminants are potentially harmful to human health, the levels of exposure of Inuit people (breast-fed babies, fetuses and adults) and which effects could be linked to this exposure (breast-fed infants and forthcoming, fetuses) (Dewailly 1989, Dewailly 1991, Dewailly 1992, Dewailly, 1993a, Dewailly 1993b, Dewailly, 1994–1996). More recently, pilot studies were conducted regarding the early effects of prenatal exposure to food chain contaminants at the biological and the clinical levels (Ayotte 1994, Muckle 1994). We also started risk characterization by comparing the exposure with safety levels recommended by various health organizations (Ayotte 1995, 1996). In reviewing the literature regarding the possible health effects induced by low-level environmental exposure to the major food chain contaminants (mercury, lead, PCBs and DDE), adverse effects on reproduction and development were identified as the main public health concerns. Therefore, our evaluation of the health risks associated with food chain contaminants in Inuit from Nunavik was focused mainly on these possible health issues.

In addition to being a source of contaminants, foods from the aquatic food chain provide nutrients of utmost importance. To provide a balanced view of potential health risks related to traditional foods, their benefits must also be taken into account, particularly with regard to protection against ischaemic diseases such as heart attacks among adults (Dewailly 1994). Numerous studies reported that fish consumption protects against cardiovascular diseases. Indeed, a diet rich in fish and marine mammals has been linked to a lower incidence of thrombotic disease in Greenland and in Japan (Bang 1972, Bang 1976, Dyerberg 1975, Dyerberg 1978, Yamori 1985). Death owing to ischaemic illnesses is a rare event in Inuit living along the shores of Hudson Bay (Dewailly 1994). This beneficial effect can be attributed to the high omega-3 fatty acid intake obtained from seafood consumption. Recent studies indicated that omega-3 type fatty acids constitute an essential factor for child development (Nettleton 1993, Olsen 1992). Lastly, omega-3 type fatty acids may also afford protection against other illnesses such as high blood pressure, diabetes, rheumatoid arthritis and some types of cancers (breast, colon) (Beilin 1993, Frolich 1992, Kremer 1987). Inuit traditional foods are also important sources of proteins, vitamins A & D, iron, selenium and other nutrients that are essential to good health.

Phase I of this project was designed to estimate the health risks and the benefits associated with the consumption of traditional foods by Nunavik Inuit and to propose dietary advice, if needed, to reduce exposure to contaminants while maintaining nutritional benefits. Phase II of the project focused on the contaminant load and nutritional value of imported foods.

Methodology

Biological measurements were obtained from the Santé Québec Health Survey conducted among the Inuit of Nunavik (Santé Québec 1994). Analyses of mercury, lead and organochlorines were undertaken among 492 Inuit adults (210 men and 282 women) (Dewailly 1994). Food contamination data were drawn from Hydro-Québec's extensive surveys in the Great Whale and Nottaway-Broadback-Rupert areas, covering species of both freshwater and marine fish, marine mammals, and edible waterfowl (Somer Inc. 1993, Somer Inc. 1994). The following contaminants measured in the species were included in the risk assessment of traditional foods: lead, mercury, p,p'–DDE and PCB congeners. Imported food contamination data were obtained from Health Canada's Total Diet Program. Information for imported foods was available only for lead and PCBs (sum of 31 congeners). Methylmercury, which is found mainly in fish, was extensively studied during the Phase 1 and it was therefore not included in Phase II. Indeed, since contaminant level data of imported foods were obtained for the period between 1985 and 1991 and therefore, present levels could be substantially different, results concerning imported food contamination will not figure in this report.

Nutritive values were determined in archived samples (11 species of fish, 3 species of marine mammal and 8 species of edible waterfowl). The following nutrients were included in Phase I: omega-3 fatty acids (C20:5 n-3 or EPA and C22:6 n-3 or DHA), proteins, vitamins A (retinol) and D, iron, calcium, selenium, zinc, magnesium and phosphorus. Animals and tissues most often eaten by the Inuit population were selected for nutrient analysis; constraint was imposed on the number of nutrients to be analysed because of the small amounts of archived samples available. Nutritive values of imported foods were drawn from the *Fichier Canadien sur les Éléments Nutritifs.* Selenium, EPA and DHA were not under study during Phase II because they were not found in the nutritive value database; α–linolenic acid was the only omega-3 fatty acid studied during Phase II. Food consumption data were obtained using two dietary questionnaires administered during the Santé Québec Inuit Health Survey (24-hour dietary recall and food frequency) (Santé Québec 1994).

To determine the percentage of the population at risk, concentrations of contaminants in blood or plasma (mercury, lead, p,p',–DDE and total PCB) were compared with biological indices of public health concern. These were based on data available from epidemiological and experimental studies as well as from guidelines published by various public health authorities (WHO, CDC). A statistical analysis of biological data was conducted to estimate the proportion of men and women (divided in two age-groups) exposed above critical levels. To determine benefits of traditional and imported foods, daily nutrient intakes were compared with recommended nutrient intakes (RNI). These were based on nutrition recommendations issued by the Scientific Review Committee (Health and Welfare Canada 1990). Daily nutrient and contaminant intakes were calculated by multiplying the daily food intake in grams by the corresponding concentration of the substance (wet weight basis). Percentages of recommended nutrient intakes (RNI) were calculated by dividing the daily intake of each nutrient by the corresponding recommended daily intake.

When exposure exceeded the level of action defined for a given contaminant in a significant proportion of individuals belonging to specific subgroups, scenarios of risk abatement were generated, considering the contribution of each food item to the total dose and their nutritional value. Scenarios were generated in which the intakes of the most contaminated food items were reduced one at a time, or simultaneously, to achieve the required reduction in exposure. Toxicokinetic models allowed for the estimation of the proper dietary dose reduction to achieve the required diminution in blood levels. These models were also used to estimate to time required to reach the acceptable blood concentration. Optimal scenarios were those that resulted in the desired reduction of exposure to contaminants, while maintaining the proper intake of nutrients.

RESULTS

According to the WHO (1990), the blood mercury concentration in the general population must not exceed 1000 nmol/L, a concentration which was not reached in Inuit adults. Table 1 shows average mercury concentrations, which are well under this limit for all age groups. We have considered a critical blood concentration of 300 nmol/L for women of reproductive age (18–39 years). Only 1.7% of women aged between 18 and 39 years had mercury concentrations above this critical level, all concentrations being inferior to 360 nmol/L. A 0.5 µmol/L critical exposure limit was selected for lead. Blood concentrations in Inuit adults from Nunavik increased with age but remained, overall, quite low (5.3% over 1 µmol/L)(Table 1). In women of reproductive age (18–39 years) however, 24% exceeded the 0.5–µmol/L limit. A 2–ppm critical concentration in lipids has been applied to our PCB data. This should correspond to a 12 µg/L blood concentration in Inuit women aged 18 to 39 years, since the mean total blood lipid concentration for this group was 6.0 g/L (Santé Québec 1994). Thirty-three percent of women between the ages of 18 and 39 years had PCB levels above the critical level. As regards p,p'–DDE, the major primary metabolite of DDT, a 65–µg/L critical plasma concentration was proposed (Kelce 1995). Table 1 shows that average concentrations in Inuit adults are well below this level. Only two women and three men more than 40 years of age showed concentrations above 65 µg/L (Table 1).

Table 1. Average blood concentrations of contaminants among Inuit adults

Sex - Age /	Women		Men	
Contaminant	18-39	40-75	18-39	40-75
Mercury (nmol/L)	75.8	162	80.1	149
Lead (umol/L)	0.48	0.61	0.40	0.58
Aroclor 1260 (ug/L)	18.8	54.2	12.6	49.0
"p,p'-DDE (ug/L)"	7.32	21.5	5.42	21.4

The daily frequency of traditional food consumption on an annual basis is set out in Table 2. The traditional foods consumed in largest quantities by Inuit the year before the survey were, in decreasing order: Red Charr, Canada Goose, Willow Ptarmigan, White Whale (Beluga) skin and Lake Trout. Fish is consumed very frequently. Inuit men, particularly older men, consumed on average 122 grams of fish per day compared with 20 grams for the general Canadian population. Table 3 shows average portion sizes of imported foods consumed by Inuit adults on the day prior to the survey. Average portion sizes varied according to sex and age. For some foods, quantities are quite variable due to the small number of individuals who ate these foods on the day before the survey.

Samples analysed for contaminant levels were collected in 1990–1991 and therefore, present levels could differ somewhat (Table 4). Among fish, the Northern Pike, the Lake Trout and the Walleye showed the highest mercury levels (greater than 0.7 mg/kg). Among fish-eating birds species, the Herring Gull and the Common Loon displayed the highest mercury concentrations. Marine mammal liver contained the greatest mercury concentration of all country foods. Lead levels among fish and marine mammals were generally low. The Northern Pintail, the Green-winged Teal, and the American Black Duck contained relatively elevated concentrations of lead (~0.3 mg/kg). The Atlantic Salmon showed the highest p,p'-DDE and PCB concentrations of all fish. Among wildfowl, the Herring Gull and the Common Loon had the greatest levels of p,p'-DDE and PCB, followed by the American Black Duck. As expected, fatty tissues from marine mammals, especially the White Whale, contained the largest organochlorine concentration of all country foods. Contamination data regarding imported foods will be available during fall 1996.

Table 2. Daily frequency of traditional food consumption by Inuit adults (in grams, on an annual basis).

Sex - Age /	Women		Men	
Traditional food	18-39	40-75	18-39	40-75
White Whale: meat	6.23	7.31	6.61	6.55
White Whale: skin	12.2	12.9	7.82	19.9
White Whale: fat	1.89	2.37	2.21	2.28
White Whale: liver	0.04	0.04	0.14	0.14
Ringed Seal: meat	4.98	7.03	5.67	4.55
Ringed Seal: liver	1.51	1.84	3.30	3.05
Ringed Seal: fat	1.67	1.29	3.13	2.09
Canada Goose	24.0	20.3	20.8	21.8
Willow Ptarmigan	16.7	13.0	10.8	11.4
Common Loon	0.17	0.15	0.12	0.13
Red Charr	32.5	37.8	57.4	67.0
Atlantic Salmon	1.52	0.76	2.15	7.92
Lake Trout	9.14	11.6	11.2	15.8
Arctic Cod	2.29	2.89	2.79	3.95
Lake Whitefish	5.17	7.23	6.97	9.87
Brook Trout	6.09	7.71	7.44	10.5
Fourthorn Sculpin	4.95	6.27	6.04	7.86

Table 5 shows daily contaminant intakes of Inuit adults. Daily mercury intake increases with age and is higher among men than women. White Whale meat, Ringed Seal liver, White Whale skin and Lake Trout provide the major part of the daily mercury intake among men and women. Atlantic Salmon contributes for 15% of the daily intake among men aged 40 years and over. Wildfowl (Canada Goose and Willow Ptarmigan), followed by White Whale liver are the main sources of lead among women. White Whale meat, Red Charr and Atlantic Salmon consumption represents also a non negligible part of the daily lead intake among men. Daily p,p'–DDE and PCB intakes increase with age and are higher among men than women. Close to 80% of p,p'–DDE and PCB intakes (men and women) originates from the consumption of White Whale skin and fat and Ringed Seal fat. Red Charr, Atlantic Salmon and Lake Trout contribute for at least 13% of the daily PCB intake.

Table 3. Mean portion size (grams) of imported foods consumed by Inuit adults on the day prior to the survey (from the 24-hour food recall).

	Women				Men			
Imported food groups	**18–39**	**(n)**	**40–75**	**(n)**	**18-39**	**(n)**	**40–75**	**(n)**
Milks (whole, 2%, powdered)	117	(66)	75.6	(40)	297	(52)	93.7	(29)
Creams		(0)	15.3	(1)		(0)		(0)
Frozen dairy products	129	(3)	50.8	(2)	168	(3)		(0)
Yogourts	150	(3)		(0)	38.5	(2)		(0)
Cheeses	34.6	(21)	32.4	(4)	56.2	(18)	89.4	(6)
Beef	144	(27)	129	(13)	147	(27)	186	(4)
Pork	224	(18)	234	(9)	226	(19)	280	(10)
Chicken &Turkey	189	(27)	148	(17)	277	(28)	232	(9)
Eggs	70.7	(40)	51.0	(24)	85.6	(38)	68.2	(15)
Sausages & delicatessen	43.5	(23)	65.0	(11)	80.9	(21)	189	(13)
Canned fish		(0)		(0)		(0)	213	(1)
Shellfish	330	(4)	121	(7)		(0)	271	(1)
Soups	35.4	(9)	58.2	(6)	43.1	(15)	47.1	(11)
White Breads	72.3	73)	51.9	(27)	102	(62)	85.5	(22)
Whole wheat Breads	42.8	(6)	48.0	(2)	108	(2)	63.8	(2)
Crackers	21.4	(9)	29.7	(7)	30.6	(6)	43.9	(3)
Pasta &rice	137	(33)	138	(24)	142	(33)	226	(10)
Cakes & cookies	51.1	(10)	34.6	(9)	44.7	(13)	35.9	(4)
Breakfast cereals	63.1	(8)	227	(5)	201	(3)	19.5	(1)
Vegetables	81.1	(58)	80.3	(29)	91.4	(46)	143	(21)
Potatoes	164	(29)	155	(16)	154	(30)	189	(9)
Potatoes, fried & chips	72.7	(51)	40.3	(11)	111	(36)	32.0	(5)
Beans (canned)		(0)		(0)	213	(1)	111	(1)
Fruits	191	(22)	143	(11)	99.8	(14)	116	(10)
Fruit juices	263	(12)	341	(6)	456	(14)	299	(6)
Margarine	8.38	(43)	7.01	(20)	8.83	(33)	8.93	(15)
Butter	9.22	(54)	1.4	(30)	19.2	(42)	12.9	(23)
Vegetable oils	4.24	(28)	14.1	(16)	5.92	(28)	17.4	(11)
Nuts, Seeds & Peanut butter	9.91	(7)	5.85	(2)	32.9	(5)	15.5	(4)
Sugars & Preserves	29.9	(112)	33.4	(72)	32.4	(87)	54.7	(67)
Confectionary-sugar & chocolate	34.6	(10)	16.7	(2)	64.7	(11)	50.0	(1)
Pudding	85.4	(5)	3.49	(1)	66.2	(5)	57.2	(2)
Tea., Coffee & Water	996	(123)	1223	(98)	890	(107)	1498	(80)
Gaseous water	53.3	(19)	56.0	(8)	77.2	(26)	1.84	(4)

* to express portion size on a weight basis, volumes were ultiplied by food-specific densities.

Mean nutritive values of animal tissues are presented in Table 6. Inuit country foods are important sources of protein, vitamin D, iron, selenium and phosphorus as well as the largest source of omega-3 fatty acids (EPA and DHA). Vitamin D, a fat-soluble vitamin, was analysed in fish and marine mammals only. Fish, seal fat and seal liver are very good sources of vitamin D. As expected, marine mammal fat shows very high concentrations of omega-3 fatty acids. Fish (especially Red Charr) and White Whale skin are also important sources of omega-3 fatty acids. Indeed, although it was believed that freshwater fish are a negligible source of these fatty acids, our results show that freshwater fish as well as marine fish represent a good sources of omega-3 fatty acids. Ringed Seal liver is the greatest source of retino! (vitamin A), another fat-soluble vitamin, followed by marine mammal fat. Moreover, marine mammal meat and liver and wildfowl are important sources of iron and zinc. White Whale liver followed by Ringed Seal liver and White Whale skin are the major sources of selenium. Finally, country foods in general represent a moderate source of phosphorus and zinc and a weak source of calcium and magnesium.

Table 7 shows daily nutrient intakes of Inuit adults. Recommended daily intake (RDI) for vitamin D and selenium are fully reached by Inuit adults. Red Charr and Lake Trout are the main sources of vitamin D. White Whale skin is the main source of selenium. The RDI for vitamin A was reached, even though beta-carotene was not measured in animal tissues. Ringed Seal liver is the greatest source of vitamin A, followed by Ringed Seal fat and White Whale fat. Fish and wildfowl are generally low in vitamin A (retinol) but they may contribute to the daily intake of this vitamin due to their high beta-carotene concentration. More then 67% of the RDI for proteins is afforded by country foods consumption among women (all age groups), and men aged 40 years and over. Fish

Table 4. Mean concentrations of heavy metals and organochlorines in animal tissues (per kg, wet weight).

Contaminant / Animal species		Mercury (mg)	Lead (mg)	p.p'-DDE (μg)	PCB[1] (μg)
FISH:					
Lake Whitefish *(Coregonus clupeaformis)*		0.15	0.01	0.85	2.46
Arctic Cod *(Gadus ogac)*		0.06	< 0.10	0.80	5.53
Fourhon Sculpin *(Myoxocephalus quadricornis)*		0.21	<0.10	0.46	2.70
Brook Trout *(Salvelinus fontinalis)*		0.12	<0.10	1.05	3.02
Lake Trout *(Salvelinus namaycush)*		0.74	<0.10	19.5	52.4
Red Charr *(Salvelinus salvelinus)*		0.04	0.01	2.17	30.4
Atlantic Salmon *(Salmo Salar)*		0.68	0.08	36.0	188
WILDFOWL:					
Canada Goose *(Branta canadensis)*		0.05	0.06	5.33	1.67
Common Loon *(Gavia immer)*		0.70	0.03	199	841
Willow Ptarmigan *(Lagopus lagopus)*		0.03	0.06	< 1.00	2.70
MARINE MAMMALS:					
White Whale	meat	2.60	0.05	53.1	46.7
(Delphinapterus leucas)	fat	0.07	na	8440	2507
	liver	20.3	0.02	58.8	141
	skin	0.56	na	362	336
Ringed Seal:	meat	0.32	< 0.10	22.1	31.6
(Phoca hispida)	fat	0.05	0.09	1533	1318
	liver	5.12	< 0.10	10.2	163

[1] PCB concentrations are expressed as Aroclor 1254:1260 (1:1) except for fishes (Aroclor 1260).

is the main source of protein in the Inuit diet, followed by wildfowl and marine mammals. With regard to iron intake, wildfowl and marine mammals meat are the main sources and contribute more than 58% to the RDI among women aged over 40 years and men (all age groups). RDI of phosphorus are partially reached (35–48%). Red Charr and wildfowl, especially Canada Goose, are the main sources of this nutrient. For zinc intake, White Whale skin, Canada Goose, Red Charr and marine mammal meat are the main dietary sources, representing 20% of the RDI among men and women. Traditional foods are however poor sources of dietary calcium and magnesium, contributing less than 5% and 16% respectively to the RDI. Finally, Red Charr is the food item with the highest consumption rate of all traditional food items and therefore constitutes the greatest source of EPA and DHA. White Whale fat and Ringed Seal fat are also major sources of omega-3 fatty acids.

Table 8 shows that among Inuit adults, daily nutrient intakes from imported food consumption generally decreased with age, whereas traditional food consumption increased. On the day prior to the survey (24-hour dietary recall), imported foods were significant sources of proteins, iron, magnesium, phosphorus, zinc and α–linolenic acid. However, intakes of vitamin A, vitamin D and calcium were low, particularly among older men and women.

Table 5. Daily contaminant intakes of Inuit adults (annual basis).

Sex - Age / Contaminant	Women 18-39	Women 40-75	Men 18-39	Men 40-75
Mercury (μg)	47.7	54.4	57.6	81.0
Lead (μg)	4.05	4.07	3.00	4.45
p,p'-DDE (mg)	23.7	28.2	28.3	31.1
Aroclor 5460 (mg)	13.8	15.0	16.3	22.1

Table 6. Mean nutritive values of animal tissues (per 100 grams, wet weight)

Nutrient / Animal species	Proteins (g)	Vitamin A (U.I.)	Vitamin D[1] (U.I.)	Iron (mg)	Calcium (mg)	Magnesium (mg)	Phosphorus (mg)	Selenium (mg)	Zinc (mg)	EPA[2] (mg)	DHA[3] (mg)
FISH:											
Lake Whitefish *(Coregonus clupeaformis)*	23.3	4.88	445	0.32	25.7	17.2	237	0.05	0.38	59.1	251
Arctic Cod *(Gadus ogac)*	24.8	2.49	198	0.59	20.2	18.1	194	0.07	0.47	165	329
Fourhon Sculpin *(Myoxocephalus quadricornis)*	20.6	15.3	356	2.50	96.5	18.5	460	0.05	0.79	198	324
Brook Trout *(Salvelinus fontinalis)*	23.5	2.40	335	0.30	9.30	21.0	230	0.04	0.46	112	322
Lake Trout *(Salvelinus namaycush)*	20.9	3.94	890	0.25	6.11	20.8	209	0.08	0.38	72.7	232
Red Charr *(Salvelinus salvelinus)*	20.2	2.40	335	0.70	7.20	21.0	257	0.04	0.60	780	690
Atlantic Salmon *(Salmo Salar)*	19.8	40.0	335	0.80	12.0	29.0	200	0.04	0.64	300	900
WILDFOWL:											
Canada Goose *(Branta canadensis)*	23.9	36.5	na	5.63	8.07	13.3	250	0.02	1.33	12.9	27.9
Common Loon *(Gravia immer)*	24.1	8.70	na	7.35	5.8	19.5	260	0.06	2.40	76.8	32.0
Willow Ptarmigan *(Lagopus lagopus)*	25.6	14.8	na	5.03	8.04	18.2	252	0.01	0.67	17.8	28.8
MARINE MAMMALS:											
White Whale 79.4	meat	24.2	na	na	16.1	4.30	13.0	180	0.17	3.00	80.1
(Delphinateus Leucas) 340	skin	24.2	na	na	0.18	10.0	14.0	140	0.55	3.00	326
4974	fat	0	1556	372	0.28	3.30	0.10	14.0	na	0.20	4303
	liver	na	na	na	na	na	na	na	2.11	3.22	na na
Ringed Seal 118	meat	29.3	3.20	36.2	26.3	3.4	22.5	205	0.05	2.54	88.3
(Phoca Hispida) 12285	fat	0	2221	3012	2.10	2.10	1.90	25.0	na	0.30	6277
140	liver	25.1	160661	938	15.5	15.5	15.0	275	0.61	4.12	189

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[1] Vitamin D could not be determined in all species due to the small amount of tissue available.

[2] EPA = Eicosapentanoic acid: C20:5n3.

[3] DHA = Docosahexanoic acid: C22:6n3.

na= data not available.

Table 7. Daily nutrient intakes of Inuit adults from traditional foods (annual basis).

Sex - Age / Nutrient	Women 18-39	Women 40-75	Men 18-39	Men 40-75
Proteins (g)	29.5	32.2	33.2	44.5
Vitamin A (U.I.)	2296	3043	5423	4969
Vitamin D (U.I.)	337	384	517	644
Iron (mg)	4.91	5.71	6.26	5.33
Calcium (mg)	16.0	17.1	18.5	26.5
Magnesium (mg)	23.7	26.3	28.8	40.1
Phosphorus (mg)	308	337	356	477
Selenium (mg)	0.14	0.14	0.14	0.22
Zinc (mg)	1.44	2.05	1.58	2.20
EPA (mg)	551	603	885	940
DHA (mg)	639	720	1052	1075

Table 8. Daily nutrient intakes of Inuit adults from imported foods (24-hour dietary recall).

Sex - Age / Nutrient	Women 18-39	Women 40-75	Men 18-39	Men 40-75
Proteins (g)	37.5	27.5	46.9	30.9
Vitamin A (U.I.)	744	303	1009	422
Vitamin D (U.I.)	47.4	16.4	44.5	20.1
Iron (mg)	6.76	5.59	8.69	7.33
Calcium (mg)	312	239	321	290
Magnesium (mg)	141	107	154	125
Phosphorus (mg)	601	425	734	516
Zinc (mg)	4.38	2.82	5.91	3.11
Linolenic acid (mg)	740	700	921	928

Risk abatement

Comparison of blood contaminant levels with acceptable concentrations revealed that PCB exposure in about one third of women aged 18–39 years may represent a risk of impaired fetal neurodevelopment. Hence, risk abatement scenarios were elaborated to reduce this potential risk. To evaluate the impact of various dietary restrictions on the frequency distribution of PCB concentrations, additional simulations were effected with the arithmetic mean reduced by 33%, 50% and 66%, while assuming a constant coefficient of variation (SD/mean x 100 = 93%). A 33% reduction in the mean concentration reduced to 18% the percentage of women who would show a plasma concentration exceeding the 12–µg/L limit. When the mean concentration was reduced by 50%, 10% of women are expected to exceed the guideline. Finally, when a 66% reduction of the mean concentration is assumed, only 3% of women would show a PCB concentration exceeding 12 µg/L. For the purpose of this exercise, a 65% reduction of PCB intake was selected as the target.

Ringed Seal fat, White Whale skin and White Whale fat contribute among women aged between 18–39 years respectively 16%, 29% and 34% of the total daily PCB intake. In generating risk abatement scenarios, food items that are excluded from the diet must ideally be replaced by others with lower organochlorine content but similar (or better) nutritional value. In the first scenario, we calculated the contaminant and nutrient intakes when White Whale fat was replaced by Ringed Seal fat, which contains about 50% less PCBs than White Whale fat but constitutes a better source of omega-3 fatty acids. White Whale skin was also excluded but not replaced because of the uniqueness of this food item. Results of this dietary modification are shown in Table 9 for contaminant intakes and Table 10 for nutrient intakes. The mean daily PCB intake would be lowered to 7.5 µg, corresponding to a 46-% reduction. Ringed Seal fat would then represent 63% of the total PCB intake. This dietary modification would also decrease DDE intake by 74%, but would be without effect on lead and mercury intakes. Regarding nutrient intakes, omega-3 fatty acids (EPA and DHA) as well as vitamins A and D intakes would be augmented if White Whale fat was to be replaced by Ringed Seal fat. Among major nutrients, only protein intake would be marginally decreased (10%).

A second scenario would involve eliminating White Whale skin and fat, without replacing these food items by other country foods. This scenario would lower the PCB intake by 65% and DDE by 86%, thereby reducing to 3% the proportion of women aged 18 to 39 years showing a PCB concentration exceeding 12 µg/L (Table 9). However, in doing so, EPA and DHA intakes would also be reduced by 19% (Table 10). Other nutrient intakes would not be substantially modified, except for protein intake, as previously stated.

Finally, a third scenario would imply eliminating White Whale skin and fat as well as Ringed Seal fat. This extreme scenario would lower the PCB intake by 86% (Table 9). In doing so however, the nutritional value of the diet would be substantially modified. EPA and DHA intakes would be reduced by 36% and 47% respectively (Table 10). Furthermore, vitamin D intake would be diminished by 17%.

Table 9. Daily contaminant intakes of women aged 18-39 years according to scenarios.

Scenario/Contaminant	Current intake	Scenario 1	Scenario 2	Scenario 3
Mercury (µg)	47.7	40.8	40.7	40.7
Lead (µg)	4.05	4.21	4.05	3.91
p,p'-DDE (µg)	23.7	6.24	3.34	0.78
Aroclor 5460 (µg)	13.8	7.47	4.78	2.58

Table 10. Daily nutrient intakes of women aged 18-39 years according to scenarios of dietary advice.

Scenario/Nutrient	Current intake	Scenario 1	Scenario 2	Scenario 3
Proteins (g)	29.5	26.5	26.5	26.5
Vitamin A (U.I.)	2296	2314	2272	2239
Vitamin D (U.I.)	337	386	329	279
Iron (mg)	4.91	4.93	4.89	4.86
Calcium (mg)	16.0	14.7	14.7	14.7
Magnesium (mg)	23.7	22.0	22.0	21.9
Phosphorus (mg)	308	291	291	290
Selenium (mg)	0.14	0.07	0.07	0.07
Zinc (mg)	1.44	1.07	1.07	1.06
EPA (mg)	551	563	445	352
DHA (mg)	639	752	520	339

ACTIVITIES IN 1995/96

During 1995/96, extensive data analysis of Phase I of the project was carried out. Risk abatement scenarios were also elaborated. Contaminant and nutrient data for imported foods were detained and data analysis was performed (Phase II). Further statistical analyses regarding the contribution of imported foods as sources of contaminants are in progress. Finally, results of Phase I of the project were presented in January 1996 to the local public health authorities and Native groups (Nunavik Nutrition and Health Committee).

SUMMARY AND CONCLUSIONS

Traditional foods from the marine food web are an important source of nutrients but also contain relatively high concentrations of organochlorines and heavy metals. Scenarios of risk abatement were elaborated to reduce PCB exposure in women aged 18 to 39 years. A 46-% reduction in PCB exposure would lower from 33% to 10% the percentage of women of reproductive age displaying a PCB concentration greater than 12 µg/L (the critical exposure limit). This would be achieved by eliminating White Whale skin and fat from the diet, which would also result in a 25% decrease in omega-3 fatty acid intake. The elimination of Ringed seal fat from the diet, in addition to White whale tissues, would further reduce the proportion of women at risk below 3%, with a concomitant decrease of more than 40% in omega-3 fatty acid intake. Hence, the reduction of PCB-associated health risks would be effected at the expense of nutritional benefits, which may adversely affect the cardiovascular health of Inuit and also the development of the newborn. Since the scientific community cannot at the present time reliably assess the health impacts of PCB exposure on the Inuit population, and because nothing can be done to eliminate this potential health hazard without creating new problems, it is concluded that dietary advice is not warranted at the present time. Moreover, this assessment was based on data obtained during 1992, and there is some evidence to suggest that exposure of women of reproductive age to organochlorines (as well as dietary omega-3 fatty acid intake) has declined over the recent years. Upon review of the scientific evidence, the decision whether or not to propose dietary advice lies with the Inuit population.

In addition to the undesirable effects of these dietary modifications on nutrient intake, one may also question the pertinence of this dietary advice from a socio-cultural point of view. Nutrition is the juncture of values, economic practices, health-related behaviour and knowledge systems that contribute to the relationship of Inuit to their environment and resources. Consequently, dietary advice may have far-reaching consequences on the general well-being of the Inuit population, which cannot be predicted at present. The risk scenarios developed for risk reduction will be submitted to a social, economic and cultural acceptability and feasibility evaluation.

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THE INFLUENCE OF EXPERTS' KNOWLEDGE ON THE SOCIAL REPRESENTATION OF RISKS AND ON THE MODIFICATION OF HEALTH-RELATED BEHAVIOUR: A PILOT PROJECT

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OBJECTIVES

General

1. To determine if the communication of expert knowledge is influencing the social representations of risks and benefits linked to food chain contamination, and health related behaviours.

Specific

1. To assess to what extent risk data is interpreted and adapted among participants of the Infant and Health Development Study (Dr. Gina Muckle).

DESCRIPTION

The accumulation and biomagnification of potentially toxic substances in the fauna and the physical environment of the eastern Canadian Arctic, including Nunavik, has been clearly demonstrated during the last decades (Barrie *et al.* 1992, Lockhart *et al.* 1992). Since 1987, the studies undertaken in Nunavik (risk identification, external dose assessment, biological exposure, health impact evaluation) have all clearly stated that unusual quantities of contaminants are present in the food chain and that there is potential health risks as regards contaminants intake.

Paradoxically, these studies also showed that there are very important benefits from eating relatively large quantities of marine mammals and fish (Dewailly *et al.* 1989, 1992, 1994). Hence, confusing messages (potential risks vs. real benefits) are transmitted to the populations under study. In this context, it has been observed that community residents tend to generate their own information and explanations through a process of "contaminants gossip" (Usher *et al.* 1994). It is well recognized in the literature that individuals who do not have the technical expertise needed to interpret scientific data will counteract this situation by putting in place a set of heuristic rules that can create a dissonance between perceived risk and real risk identified by scientists (Grondin and Larue 1995). For many authors lay knowledge derives from what people experience and is of great value (Brown 1993, Stacey 1994, Phillimore and Moffat 1994). For Stacey, lay knowledge can be quite complex. It is the essence of people's experience and it can be modified and passed on, mostly by word of mouth. Its crucial characteristics are that it is informal, experiential, and mostly unwritten.

It has been observed that in the eastern Arctic, communication activities related to environmental topics have induced a great variety of social effects. The notification of the population about PCB contamination in Broughton Island and the Northwest Territories (Allen 1991), or mercury contamination in Salluit (Wheatley and Wheatley 1981), are good examples of psychosocial repercussions linked to environmental contamination. Furthermore, the Santé Québec Inuit Health Survey (1992) showed that risk communication on PCBs in Nunavik seems to affect perceptions of food quality and life habits (imported food is better for your health, decrease in consumption of marine mammals and fish during breast-feeding) (Dewailly *et al.* 1993). However, these repercussions have not been adequately characterized and one can ask how do the Nunavimiut perceive, interpret, and adapt the risks to which they are exposed?

It seems that the range of induced behaviours can vary according to the type of environmental stress experienced, the personality of each individual, the availability of a natural support network and the community context (Elliott *et al.* 1993). Meanwhile it is quite surprising to observe that few studies raise the question of modification of behaviour adopted to cope with perceived environmental risks.

ACTIVITIES IN 1996/97

The budget initially requested for the realization of this study was $44,500 and the amount granted by the Northern Contaminants Program was $19,500. Since no co-funding was found, this grant allowed the main researcher to work part-time (1.5 days/week) on the realization of the preliminary phase of the study. The main activities consisted of a literature review and the observation of the ongoing process of the Infant Health and Development study.

Proposed methodology

For the purpose of the pilot project, a sub-sample of 7 women in prenatal period and 7 women at twelve months' post-partum will be solicited to participate in semi-structured interviews. These interviews will include questionnaires and directed open-ended questions. With the authorization of all participants, the semi-structured interviews will be recorded.

For the final phase of the study, 50 participants will be recruited from the Infant Health and Development Study, which consists of all women who gave birth in Kuujuarapik, Inukjuak and Puvirnituq and agreed to participate.

The Infant Health and Development Study

Observations on the implementation and the ongoing process of the study have indicated that an important dimension has been taken into account in the 1996/97 project: information has been disseminated on a community basis as well as at the individual level. For example, at the first interview with a participating mother, background information, objectives of the study and future steps are discussed with the scientific team members. Meanwhile, the main researcher and members of the Nunavik Nutrition and Health Committee have done some phone-in shows during which listeners raised questions on this particular project, as well as questions on contamination of the food chain and interpretation of other study results. These communication activities are creating a situation where the study participants, as well as all members of the community are aware of the Infant Health and Development study and have formed their own opinions about it and about the overall context of risk and benefits linked with the food chain contamination. This context is outlining the fact that a social dynamic of risk communication exists and that it is essential to take it into account. One can ask how will the participants of the study adapt and interpret scientific data? Will the participants be influenced by "contaminants gossip"? Can it have an impact on their health related behaviour?

Finally, the Infant Health and Development study procedures include samples of hair from the participants (when first interviewed), blood (just before delivery), milk, babies cord blood (at delivery) and first meconium. When the baby is 6.5, 9.5, and 12 months of age, its neurobehavioural and cognitive development, as well as its neuromotor and neurological functions, are assessed in the presence of the mother. A blood sample is also taken from the baby at 6.5 months.

Given this information we realized that a medical framework (interventions such as hair, milk and blood samples) is used to clarify the question of *in utero* exposure to contaminants creating a situation of medical control. Could the fact of medicalizing a situation that has not yet been declared a medical problem have an impact on health related behaviours of the participants? This indeed, adds a new dimension to our study and has to be documented.

CONCLUSION

It has been decided to broaden the objectives of the study to propose a conceptual framework that is more appropriate to include this new preoccupation: the social representation of risks. The social representation framework includes a society's values, ideas, beliefs and practices as rules systems structuring social life and as codes facilitating communications (Moscovici 1990). This field of study gives great importance to social interactions and cognitive processes. It is now recognized that social representations are governing our relations with the world and with others and are orienting and organizing social conducts and communications (Moscovici 1989, Jodelet 1989).

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TOXAPHENE AND CHLORDANE INDUCED LIVER TOXICITY AMONG INUIT

Project Leader: Éric Dewailly

Project Team: Éric Dewailly , Pierre Ayotte, Quebec Public Health Center, Quebec, Canada; Gert Mulvad, Primary Heath Care Unit, Nuuk, Greenland; William P. Newman, Louisiana State University Medical Center, Louisiana, USA; Jens P.H. Hansen, University of Copenhagen, Copenhagen, Denmark; Jean-Philippe Weber, Quebec Toxicology Centre, Quebec, Canada; Henning S. Pedersen, Primary Health Care Unit, Nuuk, Greenland; Alain Demers, Quebec Public Health Center, Quebec, Canada; Jens C. Hansen, University of Aurhus, Denmark

OBJECTIVES

1. To measure chlordane and toxaphene concentrations in omental fat of Greenlanders.
2. To describe specific histopathological lesions of the liver and kidneys.
3. To study possible associations between exposure and the presence of these specific histological abnormalities.

DESCRIPTION

In December, 1995, Health Canada reviewed Fisheries and Oceans' data on contaminants in fish and marine mammals collected from 1982 to 1994. Recommended maximum weekly intakes (RMWI) were proposed for beluga muktuk and blubber (<10 g week), mainly because of chlordane and toxaphene contamination. Tolerable daily intake (TDI) for toxaphene and chlordane are respectively 0.05 and 0.2 mg/Kg/day. Because of the lack of data on long-term toxicity of chlordane and toxaphene, animal studies were used to set these TDIs.

Chlordane and toxaphene have been shown to induce liver damage when administered to laboratory animals. Toxaphene was reported to cause enzyme induction, histochemical and histomorphological changes, jaundice, liver dysfunction, and liver hypertrophy. Toxaphene-induced generalized hydropic degenerative changes, cytoplasmic vacuolization, centrilobular cell hypertrophy, peripheral migration of basophilic cytoplasmic granules and/or presence of lipospheres, increased liver weight, increase microsomal activity, vesiculation, focal necrosis, hepatomegaly, and eosinophilic inclusions. Although many of these changes occurred when animals were highly exposed, increased liver weight, jaundice, or mild histopathologic changes appeared at low doses.

Both toxaphene and chlordane were identified in the milk of nursing Inuit women of northern Quebec (Dewailly 1992, 1993, 1994, Stern 1992, Zhu 1995, Ayotte 1995). Stern (1992) reported concentrations of T_2 (congener 26) and T_{12} (congener 50) of 70 and 150 mg/Kg (lipid basis), respectively. Recently we analysed these two congeners in plasma lipids of eight Inuit adults from Nunavik. T_2 and T_{12} concentrations were 50 and 73 mg/kg respectively, with considerable variation between subjects (range of 5 to 350). A more extensive assessment has recently been conducted on 56 adult Inuit. Total chlordane averaged 8 mg/Kg (lipid basis). Little is still known about human exposure consequences to these compounds.

The study presented here evaluates the presence of histological abnormalities in liver tissue in relation to the body burden of Inuit Greenlanders to chlordane and toxaphene.

ACTIVITIES IN 1995/1996

Phase One: Contaminant Assessment

This project is nested in a large autopsy study of native Greenlanders. Chlordane related compounds (CRCs) and toxaphene congeners were measured in 40 omental fat and 4 liver samples (out of the 42 omental fat samples and 27 liver samples available). Autopsies were carried out between November 1992 and mid-October 1994 at the Queen Ingrid's Hospital in Nuuk (Greenland). Autopsied persons came from the area of Nuuk and some other areas in Greenland. Only individuals over 18 years of age and born in Greenland were included. The mean age of the population was 60 years (Table 1). The causes of death were cancer (n = 11), cardio-vascular diseases (n = 7), chronic bronchitis (n = 2), violent death (n = 8), others (n = 13). The age structure of the population is described in Table 1.

Chlordane-related compounds (α-chlordane, γ-chlordane, cis-nonachlor, trans-nonachlor, oxychlordane, nonachlor III, and photoheptachlor) were quantified by electron capture gas chromatography, using a Hewlett-Packard 5890 Series II chromatograph equipped with two electron capture detectors. Toxaphene congeners (parlar no 26 (T_2), 32, 50 (T_{12}), 62 (T_{20}), and 69) were quantified using a gas chromatograph negative ion chemical ionization mass spectrometer (GC-NICI MS) in selected ion mode. Experimental conditions and quantification method for total toxaphene were those of Swackhamer (Swackhamer, 1987). Detection limits in omental fat were, for chlordane, 0.4 to 1.1 µg/kg (lipid basis) and for toxaphene 0.1 to 0.3 µg/kg (lipid basis).

Table 1. Age structure of the population

	Age[a]
Total	60 (3, 40)
Female	61 (4, 22)
Male	58 (3, 18)
0 - 54	44 (2, 16)
55 - 69	61 (1, 11)
70 - +	77 (1, 13)

[a] mean (standard deviation, number of individuals)

Phase Two: Histological Assessment (ongoing)
Liver and kidney histology was conducted by Dr. William Newman from Louisiana State University, in collaboration with Dr. Jens Peter Hart Hansen from Copenhagen University. Results are in preparation.

RESULTS

The mean age of the population was 60 years old; men and women had similar mean ages (Table 1). α-Chlordane and toxaphene parlar no 32 and 69 were detected in less than 25% of omental fat samples. α-Chlordane and toxaphene parlar no 32, 62 and 69 were not detected in liver samples (Table 2). Non-detected pesticides were not included in the calculation of Σ Chlordane and Σ Toxaphene (Table 3).

The three most abundant CRCs were trans-nonachlor, oxychlordane, and nonachlor III. In omental fat and liver, they accounted for 89% of Σ Chlordane. Most (96%) of the total toxaphene concentration in fat and liver was attributable to parlar no 26 and 50 (T_2 and T_{12}).

CRCs concentrations were similar in liver and omental fat (Figure 1), whereas toxaphene parlar no 26 and 50 (T_2 and T_{12}) appeared to accumulate more in liver. Toxaphene parlar no 69 (T_{20}) was not detected in liver.Omental fat concentrations of Σ chlordane and Σ toxaphene of women appeared lower than in men, although differences were not statistically significant (α = 0.05, Table 4). Statistically significant differences were observed between age groups for Σ chlordane and Σ toxaphene in omental fat. The number of liver samples was too small to allow for additional statistic analysis.

Table 2. Detection percentage of chlordane and toxaphene in autopsy tissues from Greenlanders

Pesticides	Omental fat	Liver
Chlordane		
α-Chlordane	24	0
γ-Chlordane	90	100
Oxychlordane	100	100
Cis-nonachlor	100	100
Trans-nonachlor	100	100
Nonachlor III	100	100
Photoheptachlor	100	100
Toxaphene		
Parlar no 26 (T_2)	100	100
Parlar no 32	2	0
Parlar no 50 (T_{12})	100	100
Parlar no 62 (T_{20})	100	0
Parlar no 69	0	0

DISCUSSION

Individuals included in this study are representative of the Greenland population but their provenance may reflect different life habits, especially if they come from the eastern or the northern part of the country. The population is spread along the coast in 16 towns and 60 minor settlements. Every town is very isolated, and in some of them people eat mostly sea mammals, whereas in others they eat mostly fish. The biggest town is the capital, Nuuk. It has a more predominant western lifestyle than elsewhere in Greenland.

Most previous studies conducted to evaluate CRCs body burden were breast milk surveys. We chose to compare our results with those obtained in other autopsies in which adipose tissue samples were analysed. Even though they are not exactly the same tissues (i.e., omental fat and adipose), because their fat contents are close, their organochlorine concentrations should be similar (Dewailly, personal communication). CRCs body burden in Greenlanders is high in comparison to other populations. Compared with the general Canadian population (Mes *et al.* 1990), Greenlanders show approximately the same concentration of α-chlordane, 5 times more γ-chlordane, and 23 times more oxychlordane. A smaller difference (approximately 10 times) was observed between Greenlanders and a population

Table 3. Mean Chlordane and Toxaphene concentrations in autopsy tissues from Greenlanders (mg/kg, fat basis)

	Omental fat (n = 40)				Liver (n = 4)			
	Mean[a]	Std[b]	Min	Max	Mean	Std	Min	Max
Chlordane								
α-Chlordane	1	1.4	0.2	7.5	7.8	10.1	1.3	48.5
γ-Chlordane	11	8	0.3	36.7	33	33	1.1	138.9
Oxychlordane	881	612	130	3080	1311	886	268.4	3830
Cis-nonachlor	317	172	66.8	795	372	228	91	910.9
Trans-nonachlor	1485	862	260	3455	1750	1018	430.9	3880
Nonachlor III	750	502	110	2130	980	457	560	1460
Photoheptachlor	50	28	7.2	110	112	43	56	160
Toxaphene								
Parlar no 26 (T_2)	279	172	30	680	595	338	250	950
Parlar no 32	nd[c]	—	—	—	nd	Ñ	—	—
Parlar no 50 (T_{12})	375	214	60	1100	725	439	310	1180
Parlar no 62 (T_{20})	24	17	1.7	74	nd	—	—	—
Parlar no 69	nd	—	—	—	nd	—	—	—

[a] arithmetic mean

[b] standard deviation

[c] not detected

Table 4. Mean concentrations of the sum of CRCs and the sum of toxaphene congeners in autopsy tissues from Greenlandic Inuit according to sex and age (mg/kg, fat basis)

OCs		Omental fat			
		Mean[a] (n)	Std[b]	min	Max
Σ Chlordane[c]		3494 (40)	2074	611.3	8407
Σ Toxaphene[d]		677 (40)	390	91.7	1817
Σ Chlordane	F	3072 (22)	1928	611	7862
	M	4010 (18)	2182	1094.8	8407
Σ Toxaphene	F	583 (22)	303	175.6	1434
	M	792 (18)	459	91.7	1817
Σ Chlordane	0 - 54	3521 (16)	2361	611.3	8407
	55 - 69	2974 (11)	1989	1094.8	7862
	70 - +	3902 (13)	1812	1452.5	7510.6
Σ Toxaphene	0 - 54	677 (16)	334	175.6	1219
	55 - 69	561 (11)	468	91.7	1817
	70 - +	775 (13)	388	355	1552

[a] arithmetic mean

[b] standard deviation

[c] Σ chlordane = γ-chlordane + cis-nonachlor + trans-nonachlor + oxychlordane + nonachlor III + photoheptachlor

[d] Σ Toxaphene = $T_2 + T_{12} + T_{20}$

in Texas (USA) for oxychlordane (Adeshina 1990). Much less information is available on toxaphene. Mussalo-Rauhamaa (1984) estimated, in Finland, similar toxaphene and Σ chlordane concentrations in the population (i.e. 7.8 µg/kg, lipid basis). However these results cannot be compared with those obtained in our study because the the method used by Mussalo-Rauhamaa (1984) to measure toxaphene had technical limitations.

It will be interesting to see if the relatively high concentrations of CRCs and toxaphene observed in our population samples from Greenland are correlated to liver and kidney changes.

Expected project completion date: December 1997

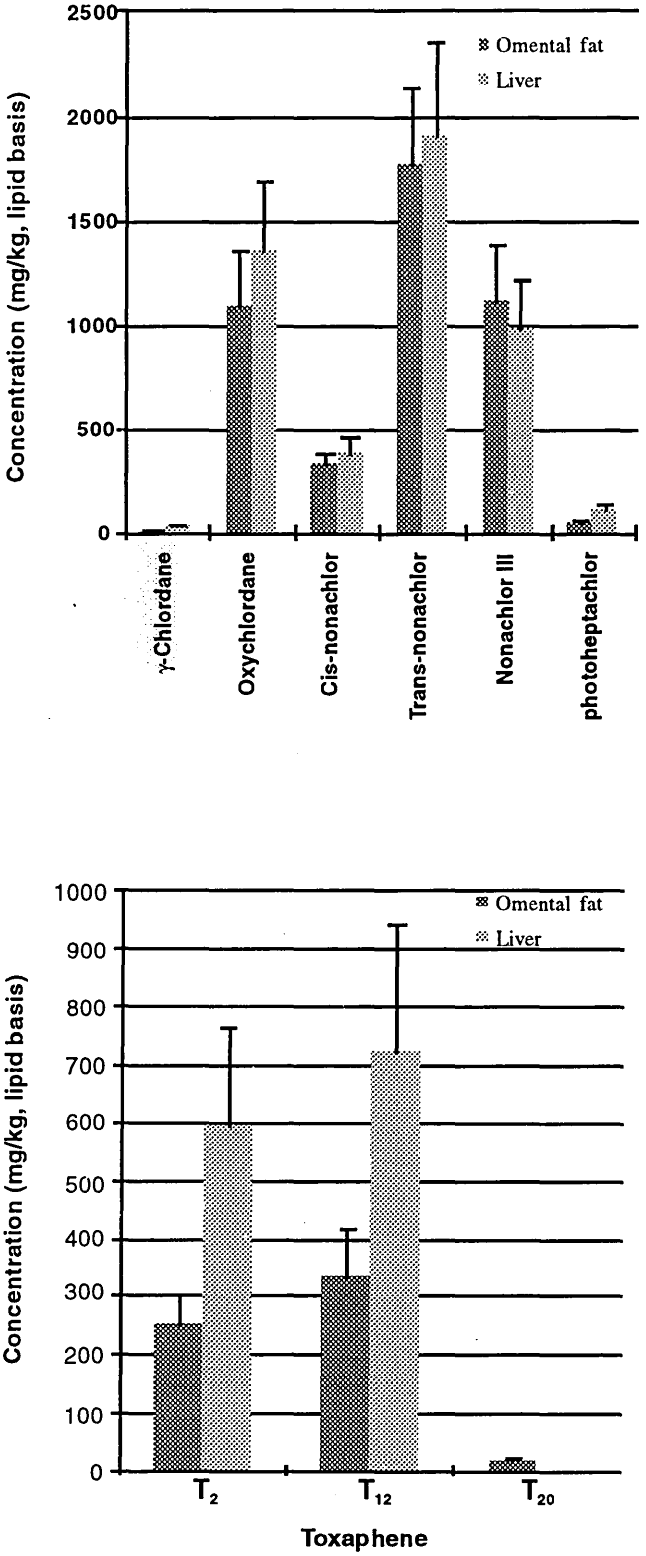

Figure 1. Chlordane and toxaphene concentrations in omental fat and liver of the four individuals for whom levels in both tissues were available (mean ± std).

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HUMAN CONTAMINANT TRENDS IN ARCTIC CANADA

Project Leader: GNWT Health and Social Services, Baffin Regional Health Board,
Keewatin Regional Health Board

DESCRIPTION

Activities that began in 1995/96 in the Baffin and Keewatin Regions were continued into the next fiscal year for the development and implementation of their contaminants blood monitoring programs. The results of these programs will be combined with those from other regions to establish a baseline of exposure of organochlorine and metal contaminants in maternal and umbilical cord blood of women who volunteered to participate.

BAFFIN REGIONAL HEALTH BOARD

In the Baffin, the coordinator of the Baffin Regional Health Board's Environment and Lifestyle Assessment Project was guided by the Contaminants Core Committee (BRHB, Qikiqtani Inuit Association, Department of Health and Social Services (DHSS) representatives) and the Baffin Region Working Group (Community Health Representatives (CHRs), nurses and Health Centre clerk-interpreters). An Inuktitut-speaking Research Assistant played an important role in the development of education and information materials and in their subsequent communication, and in administering the Participant Survey to most of the participants. Experts from Health Canada, Laval University, CINE, and representatives from other health boards in the NWT also contributed to the project.

Bilingual (English and Inuktitut) contaminants resource materials and information were developed and distributed to communities in the Baffin Region through Health Centres, Health Board Trustees and Education Councils. They were also distributed to the regional offices of other agencies.

Health workers directly and indirectly involved in the project were updated regularly, and they also made valuable contributions in several ways. These workers included Baffin Regional Health Board community and hospital nursing staff, various departments in the Hospital (Laboratory, Nursing, Health Records, Hospital Ward), the BRHB Medical Advisory Committee, and the Board of Trustees.

In December 1996, a Results Communication Workshop was held for Working Group members. This Workshop covered Contaminants education and issues related to pre- natal recruitment, community interests and concerns, evaluation of resource materials and information, and results interpretation.

The recruitment of participants took place for one calendar year, from mid-December 1995 to mid-December 1996. There were a total of 99 women recruited into the program; 83 participants completed surveys, and blood samples were collected from 67 babies (umbilical cord) and 35 mothers.

These blood samples were analysed between March 1996 and January 1997. Results were received by the end of March 1997.

KEEWATIN REGIONAL HEALTH BOARD

In the Keewatin, the regional coordinators of the Keewatin Regional Health Board's (KRHB) Keewatin Environmental Health Project: Contaminants and People were guided in the development and implementation by the Keewatin Project Team, and the KRHB. Community health workers were key at all stages of development and implementation.

Resource materials that were developed collaboratively and produced in English and Inuktitut were distributed to communities and to other agencies by the Project Team and community health workers.

There were four birthing locations participating in the program—Rankin Birthing Centre, Churchill Health Centre, Stanton Regional Hospital, and the Baffin Regional Hospital. Health workers at these locations guided the development of information materials and sample handling protocol, and were regularly updated about program progress.

A Results Communication Workshop for Working Group members was held in January, 1997 in Arviat. Discussions at this workshop included ongoing contaminants education, evaluating resource materials and information, and various aspects of results communications.

Participants were recruited from women delivering between August 1996 and the end of February, 1997.

Altogether, 38 women volunteered to participate in the blood sampling program, and a total of 17 maternal and 16 cord blood samples were taken.

To ensure that the results communications phases of both the Baffin and Keewatin projects received sufficient time for full consultation before they were implemented, they were scheduled to be completed in fiscal year 1997/98.

TERRITORIAL EXPOSURE BASELINE

Once individual results have been communicated to participants, and regional program results have been communicated to the board and the communities, the data from the regional programs will be merged to produce the Territorial baseline. This work will be completed during 1997/98.

TRANSPLACENTAL EXPOSURE TO PCBS AND INFANT DEVELOPMENT STUDY: POWER ANALYSIS AND PRELIMINARY RESULTS ON EXPOSURE

Project Leaders: G. Muckle, É. Dewailly, P. Ayotte, Quebec Public Health Centre; J.L. Jacobson, S.W. Jacobson, Wayne State University.

Project Team: C. Bouffard, L. Fortin, E. Lachance, S. Bruneau, Québec Public Health Center.

OBJECTIVES

1. To examine the consequences of *in utero* and lactational exposure to PCBs on Inuit infants, from birth to 12 months of age. Of particular interest is the impact of exposure on newborn's thyroid hormones and physical growth, on infant's overall health, mental, psychomotor and neurobehavioural development, and on visual and spatial information processing abilities.

DESCRIPTION

Results from several surveys have indicated that Inuit newborns are exposed to doses of organochlorines which exceed acceptable exposure for several health endpoints. Dewailly *et al.* (1992) reported that the mean concentration of PCBs (Aroclor 1260) in breast milk fat was 2.9 (n=107) and 0.52 mg/kg (n=536) respectively for Inuit women and women from Southern Québec. This level among Inuit is 5.6 times greater than that of Southern women and is higher than 1.43 mg/kg, the lipid concentration corresponding to the maximal acceptable concentration in breast milk (50 µg/L) established by Health Canada (1978).

The effects of prenatal exposure to background levels of PCBs from environmental sources have been studied in four major cohort studies: Michigan, North Carolina, Netherlands and New York. The effects of PCB/PCDF poisoning were also studied in Taiwanese children. In Michigan, higher cord serum PCBs concentrations were associated with lower birthweight (Fein *et al.* 1984, Jacobson *et al.* 1990b). This exposure also appeared to be associated with less optimal newborn behavioural function (ex. reflexes, tonicity and activity levels) in all three studies that administered the Neonatal Behavioral Assessment Scale (Jacobson *et al.* 1984, Lonkey *et al.* 1995, Rogan *et al.* 1986). The main conclusion of the Netherlands study was that elevated levels of PCBs can alter the thyroid hormone status in early infancy: higher TSH, and lower FT_4 and TT_4 levels were found to be significantly correlated to PCBs measured in human milk (Koopman-Esseboom *et al.* 1994). In North Carolina, dose-response analysis indicated deficits in psychomotor development at 6, 12 and 24 months in highly exposed children: those whose mothers' milk PCB levels exceeded 1.75 mg/kg (Gladen *et al.* 1988, Rogan and Gladen 1991). At higher levels of PCB/PCDF exposure in Taiwan, deficits were seen in mental and psychomotor development (Yu *et al.* 1991). The principal finding in Michigan was an association with poorer visual information processing ability, which indicated a deficit in visual memory or attention (Jacobson *et al.* 1985, 1990a, 1992). This deficit was not confirmed in the Netherlands study.

ACTIVITIES IN 1996/97

The activities carried out in 1996/97 related to data collection. Two research professionals were trained to ensure comparability when they perform the maternal interviews and the infant testing procedures. New hospital and nursing station nurses, midwives and laboratory technicians directly involved in the data collection process were presented with the objectives of the research and the research procedures. Meetings were also held with all medical professionals to identify emerging problems and difficulties in the data collection, and to find ways to facilitate their work and to ensure the quality of the data collected. Phone-in radio programs were held on local stations in Puvirnituq, Inukjuaq and Kuujjuaraapik to update the population on the research activities.

RESULTS AND DISCUSSION

Overview of the Research Protocol

The prospective cohort study involves approximately 300 Inuit newborns, 200 from Nunavik, and 100 from Greenland. The pregnant mothers are recruited during pregnancy, at their first or second prenatal medical exam. Mothers are met during the second trimester of their pregnancy and one month after their delivery. Infants are assessed at 6.5 and 12 months of age. At these infant testing sessions, an interview with the mothers is also carried out. Concentrations of PCBs, chlorinated pesticides and heavy metals are obtained at birth through cord and maternal serum analyses, and postnatally through breast-milk analysis. Thyroid hormone levels and anthropometric characteristics are measured in newborns. At 6.5 and 12 months, numerous domains of infant neurobehavioural and cognitive development are assessed as well as physical growth and overall health status.

Five groups of potentially confounding variables are measured: 1) exposure to other toxic substances, 2) dietary fat composition, 3) perinatal medical complications, 4) sociodemographic status, and 5) psychosocial risk. Exposure to other toxic substances and nutritional effects is evaluated through cord serum analyses. Substances of interest include DDE and other organochlorine pesticides, dioxins/furans and lead. The effects of dietary fat composition is controlled through an assessment of omega-3 fatty acids and a lipodogram. Prenatal exposures to alcohol, drugs, and nicotine are measured during pregnancy and after delivery through a structured maternal interview; fetal exposure to illicit drugs is also documented through meconium analysis. Perinatal information is obtained from medical records, and sociodemographic status from maternal reports. Perinatal data include APGAR, gestational age, information about delivery and medical complications of the neonate. Sociodemographic data include maternal age and education, employment and marital status, gravidity, literacy, and the number of children in the family. Psychosocial variables that were consistently found to be related to infant development (the quality of intellectual stimulation provided by the mother, maternal depression and intelligence, and family violence) are measured at 6.5 and 12 months postpartum.

Revised Power Analysis

Our previous power analysis focused on determining the sample size needed to detect a small effect ($r = 0.16$) without regard to the exposure level in the population. We re-evaluated power in terms of the number of infants exposed above the thresholds for effects found in the Michigan study. During infancy, the lower threshold for the effect of prenatal PCB exposure on the Fagan Test of Infant Intelligence was 1.0 µg/g in maternal milk (Tilson *et al.* 1990). Due to differences in the analytic methodologies used by the Michigan and Toxicology Center of Québec (TCQ) laboratories to evaluate Aroclor 1260, Dewailly and Ayotte (1996) recommended that the Michigan values be multiplied by a factor of 2 to make them comparable to those reported by TCQ. Using this approach, the threshold expressed in terms of milk PCB concentration analysed by the TCQ methodology would be 2.0 µg/g. An examination of data for the first 19 infants with both cord blood and maternal milk samples in this study indicates that, although the lipid-adjusted PCB concentrations in cord blood and mothers' milk reported by TCQ are highly correlated ($\underline{r} = 0.93$), the milk concentrations are 50% higher on the average than the cord blood. This discrepancy appears to be due to differences in assessing lipid contents—in milk samples, lipids are weighted; in blood samples, they are estimated biochemically. Given this discrepancy, we estimate the Fagan test threshold expressed in terms of cord blood concentration on a fat basis for the TCQ data to be 1.33 µg/g.

An examination of cord blood data collected during the 1994-96 Cord Blood Monitoring Program showed a markedly lower incidence of exposure above this threshold in Kuujjuaq (9.7%) than in the Hudson Bay communities (26.1%). This difference appears to be largely a function of diet: Ungava Bay Inuit traditionally eat more lean caribou meat and less marine mammals fat than the Hudson Bay Inuit. Originally, we planned to recruit all pregnant women from Puvirnituq, Inukjuaq and Kuujjuaq—the three most important communities in Nunavik as far as the number of births per year. To be able to perform powerful dose-response analysis, more highly exposed infants have to be over-represented in the sample. Based on the differences between communities in regard to exposure levels, we decided to discontinue data collection in Kuujjuaq and to substitute a third Hudson Bay community, Kuujjuaraapik. With this modification, the proportion of infants exposed above the 1.33 µg/g threshold of effects was 23%. Using Cohen's (1988) test for between-group differences in proportions, statistical power was estimated. With alpha set at $\underline{p} < .05$, two-tail, assuming a 23% rate of exposure above threshold, the power to detect a difference of this magnitude in a sample of 218 infants is 0.74.

Cord blood PCB concentrations in Greenland averaged 1.7 µg/g (Report of the Arctic Monitoring Assessment Program, in preparation), compared with 1.1 µg/g in Hudson Bay, and 0.2 µg/g in Southern Québec. Moreover, 50.6% of the Greenlandic samples were above the 1.33 µg/g TCQ threshold for deficient performance on the Fagan Test of Infant Intelligence. Based on the Greenlandic cord blood samples analysed by the TCQ, an additional sample of 100 infants from Greenland is expected to almost double the number of infants exposed above the 1.33 µg/g threshold—from 57 in Nunavik alone to 108 in the two sites combined. With alpha set at $\underline{p} < .05$, two-tailed, the addition of these 100 infants from Greenland will increase the power to detect the Fagan test deficit found in the Michigan cohort from 0.74 to 0.92. Since other effects associated with prenatal PCB exposure are likely to be more subtle than the effects measured by the Fagan test, this added power will maximize the opportunity to detect the full range of relevant deficits.

Participation and Retention Rates in Hudson Bay

To date, 110 mothers have completed the prenatal assessment; 55, the postnatal assessment; and 27 infants have been assessed at 6.5 months, four, at 12 months (Table 1). The initial participation rate is higher than the 80% we had projected, and only one mother has refused to continue in the study after completing the prenatal interview. Attrition due to perinatal mortality or congenital malformations (n=2) has been markedly lower than the 16.1% we had projected. However, postnatal attrition has been somewhat higher than projected due to difficulties associated with reaching mothers without telephones or mothers moving to other villages where, given the high cost of travel, we will not be able to assess their infants. Based on the data in Table 1, we are now projecting an 85% initial participation rate, 8% perinatal loss, 20% attrition prior to the postnatal interview, and an additional 15% attrition through the 12-month assessment.

Table 1. Participation and Attrition Rates

First 127 declared pregnancies		
Interviewed prenatally	110	86.6%
Refused	16	12.6%
Unable to contact	1	0.8%
Eligible for postnatal interview (n=66)		
Interviewed postnatally	55	83.3%
Refused	1	1.5%
Unable to contact	5	7.6%
Moved to another village	3	4.5%
No biological sample	1	1.5%
Died	1	1.5%
Eligible for 6.5 month assessment (n =31)		
Tested at 6.5 months	27	87.1%
Refused	0	—
Unable to contact	3	9.7%
Moved to another village	1	3.2%
Died	0	—

Given the number of births projected for the three Hudson Bay communities over the 50-month period planned for data collection, we now project a final sample size of 218 infants (Table 2).

Table 2. Projected Participation and Attrition in the 3 Hudson Bay Communities

Births projected over 50 months	**410**
Participation in prenatal interview (85%)	349
Perinatal mortality and congenital malformations (-8%)	321
Postnatal attrition (-20%)	257
Attrition through 12 month assessment (-15%)	218

Preliminary Findings—Prenatal Exposure

The first 31 cord blood samples collected in this study have been assessed for PCBs, mercury, selenium and lead. (No data are yet available on organochlorine pesticides or polyunsaturated fatty acids.) The mean cord PCB, lead and selenium concentrations are virtually identical to those reported by Dewailly and collaborators (1995); mercury concentrations are somewhat higher (Table 3). Because the correlations of PCB concentrations with the other environmental pollutants assessed in cord blood are, as expected, in the low-moderate range (Table 3), it should be feasible to control for their effects by means of multivariate analysis.

CONCLUSIONS

The National Institute of Environmental Health in the United States, Indian and Northern Affairs (NCP program) and Hydro-Québec in Canada, and the Danish Agency for Environmental Protection in Denmark are co-financing this prospective, longitudinal study of 300 Inuit newborns followed until 12 months of age. The high initial participation rate probably reflects the interest of the Inuit women regarding the possible effects of the environmental contaminants on their infant's development. Moreover, the low number of withdrawals after enrollment should reflect that the Inuit women felt at ease with the procedures used at every step of the data collection process. Finally, becuase the associations of PCB concentrations with the other environmental pollutants assessed in cord blood are in the low–moderate range, it should be feasible to control for their effects in multivariate analysis.

Expected project completion date: December, 2001.

Table 3. Cord Blood Concentrations of Contaminants in Nunavik

	94-95 Survey		Current Study		Correlations with PCBs
	N	Mean	N	Mean	*r*
PCBs (Aroclor 1260) (µg/g)	216	994.6	31	1044.8	—
Mercury (nmol/L)	238	93.51	31	139.23	.27
Selenium (µmol/L)	228	4.02	28	4.13	.12
Lead (µmol/L)	238	0.24	31	0.26	.54

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IV EDUCATION AND COMMUNICATIONS

CONTAMINANTS CURRICULUM PHASE IIIA, IV, AND V, A PROGRAM OF INTEGRATED CURRICULUM DEVELOPMENT FOR NORTHERN EDUCATION/COMMUNICATION

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OBJECTIVES

Short-term

1. To give Northerners a better understanding of all issues relating to the Northern Contaminants Program (NCP) under the Arctic Environmental Strategy (AES).

Long- term

1. To provide Northerners with some of the necessary information and tools to make informed decisions regarding health risks from person-made 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. The program materials are cross-referenced to the relevant curricula and to existing Dene, Kede and Inuuqatigiit documents that explore the school curricula from the Dene and Inuit perspectives, to ensure that the traditional point of view is reflected whenever possible.

Research projects funded by the AES: Northern Contaminants Program (NCP) have been the main source of information for the development of this education program. During the planning stages, the NCP categories of Sources, Pathways and Fate; Ecosystem Uptake; Human Health and Education/Communications were cross-referenced to the existing curricula. This exercise ensured proper representation of the scope of the NCP through the lesson plans.

ACTIVITIES IN 1995/96 AND 1996/97

The Métis Nation continues to maintain a client partnership arrangement for this project. Initially, policy was formulated by a Steering Committee made up of, but not restricted to the following agencies: Science Institute of the NWT, Canadian Polar Commission, GNWT Department Resources, Wildlife and Economic Development (RWED) Conservation Education Division, Environment and Renewable Resources of the Department of Indian and Northern Affairs (DIAND), Yellowknife Education District No. 1, GNWT ECE, Arctic/Aurora College and Department of Health (GNWT).

Database

The project database that was established during Phase II was updated to include data from the Synopsis of Research Conducted under the 1993/94 and 1994/95 Northern Contaminants Program. The search parameters have also been expanded to include details of all NCP projects, community profile data, and some health risk assessments.

The database capability allows cross-referencing of NCP information with: community profile data, school boards, schools, Arctic/Aurora College, and Community Learning Centres. This capability allows a better understanding of the target audience at both regional or community levels. 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 our ongoing program development process and we hope to make it available online to educators via the GNWT ECE, 'North of 60 Bulletin Board' or the Internet.

In 1996/97 fiscal year Water Resources DIAND funded data entry of AES water research for 1992/93, 1993/94 and 1994/95 projects into the database.

Table 1. Search Parameters Métis Nation NCP Data Base

NCP Data:

- Author
- Journal
- Contaminants
- NCP category
- Animal group
- Plant group
- School Board District
- Location
- Abstract
- Title
- Contaminant group
- Funding
- Ecosystem
- Animal species
- Plant species
- Community
- Ocean Region
- Medium

Health Risk Assessment Data:

- Region
- Researcher
- Sample data
- Species and tissue
- Location
- Contaminant
- Comments
- Assessment completed

NWT Community Data:

- Local co-ordinates
- Traditional names
- Population by ethnic group
- Land claim areas
- Schools
- Community learning Centres
- Names, official/unofficial
- Meaning of traditional names
- GNWT administrative regions
- School boards
- Colleges
- Language/Dialect

Junior High Program

Lesson plans have been produced for the NWT school science curriculum for grade 7 to 9. These lesson plans have been cross-referenced to NCP research and have been designed to fit a particular unit within the curriculum. In the books, teachers are introduced to the Arctic Environmental Strategy, Northern Contaminants Program and are then guided to the appropriate curriculum unit. An overall view of lesson plans and sequence are provided to aid teachers in scheduling and preparation.

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 and consequently some testing extended into the 1995/96 school year. Teacher in-service workshops were held in Iqaluit in January 1997.

Publication of Lesson Plans

This program has published the following books for Junior High School:

- Contaminants in Northern Canada. Information for Science Teachers of Grades 7, 8 and 9
- Contaminants in Northern Canada. Lesson Plans For Grade 7 Science
- Contaminants in Northern Canada. Lesson Plans For Grade 8 Science

Distribution of Junior High Materials

Distribution of the Junior High Program has been accomplished, through the assistance of GNWT, ECE. The distribution plan is shown in Table 2. The school populations vary and in some cases, it was necessary to send more than three copies to some schools. As schools were given priority, it meant that there was a reduction in the number of inspection copies available to AES partner agencies.

Table 2. Distribution of Junior High Books

Destination	No. of copies
10 Regional Education Resource Centres	
Library copy	
Science Co-ordinator copy	
10 x 2 copies	20
67 NWT schools offering grades 7–9	
Library copy	
Science teachers 2 copies	
66 x 3 copies	201
GNWT Education Headquarters	
Library copy	
Science curriculum specialist	4
Métis Nation and other AES partner agencies, inspection copies	25
Total number of copies produced	**250**

Table 3. NWT Regional Education Centres

- Baffin District Education Council
- Beaufort Delta District Education Council
- Deh Cho District Education Council
- Dogrib District Education Council
- Keewatin District Education Council
- Kitikmeot District Education Council
- Sahtu District Education Council
- South Slave District Education Council
- Yellowknife Education District #1
- Yellowknife Education District #2

Table 4. Distribution of Junior High Books by School Board/Agency

Destination	**No. of copies**
Baffin Region schools*	41
Beaufort Delta schools*	23
Deh Cho schools*	26
Dogrib schools*	20
Keewatin schools*	29
Kitikmeot schools*	20
Sahtu schools*	17
South Slave schools*	20
Yellowknife #1 schools*	14
Yellowknife #2 schools*	11
GNWT Education Headquarters	4
Métis Nation and other AES partner agencies, inspection copies	25
Total number of copies produced	**250**

*includes Regional Resource Centre.

Figure 1. Map Showing District Education Councils in the Northwest Territories

High School Program

Lesson plans have been developed for use at the Grade 10 and 11 levels. The lesson plans have been designed for use with the relatively new NWT Science 15–25 Courses. It is the policy of GNWT, ECE, to publish curriculum documents and other materials in a CD-ROM or on-line format. After teacher workshops during Sivumut 97, the Baffin Region Teachers Converence, held in Iqaluit in January, 1997, it became clear that despite GNWT ECE policy to provide curriculum materials in electronic format, not all schools and/or teachers were in a position to make use of documents in that format. The format of preference was printed hard copy. In the interests of making our produce "user friendly" at a reasonable cost, a hard copy layout was produced "in-house" at the Métis Nation, using Microsoft Word. The resulting Teachers' Manual for NWT Science 15–25 was then "Quick Printed" on three-hold punch paper. Section dividers were custom-printed for the manual. Recipients were asked to put the materials into their own three-ring binders. This kep the print and production costs to a minumum.

The program files were then converted into Adobe Acrobat PDF (portable document format) and HTML (hyptertext markup language) formats to produce a master CD (compact disc). PDF format enables users of the CD to view the documents in a page-for-page layout that is identical to the original hard copy. Teachers who have the appropriate hardware and ability to use this format are able to rpint out all or individual pages to suit their particular classroom needs. HTML format is included on the CD to allow users to browse the material using the convenience of "hot links" which, when activated with the click of a mouse, automatically jump to related information.

Table 5 illustrates precisely where the lesson plans, developed from NCP materials, may be used for NWT Science 15–25.

Table 5. Lesson Plans for NWT Science 15–25. Bold italicized text indicates where NCP materials may be used.

MAJOR CONCEPTS	**KNOWLEDGE** **Students should be able to demonstrate an understanding that:**	**SKILLS** **Students should be able to demonstrate the skills and thinking processes associated with the practice of science , by:**	**STS CONNECTIONS** **Students should be able to demonstrate the interrelationships among science, technology and society, by:**
NWT Science 15 Unit 4 Investigating Matter and Energy in the Environment.			
I. N/A	•	•	•
2. The cycling of matter through living systems perpetuates the biosphere's steady state equilibrium.	Matter is cycled through the biosphere along characteristic pathways that involve living systems by: • ***describing the hydrologic cycle*** • ***describing how carbon, oxygen and nitrogen are cycled through the biosphere*** • explaining the role of living systems in the cycling of matter in the biosphere	• ***diagramming how water moves throughout the biosphere along characteristic pathways*** • describing the biogeochemical cycles of carbon, nitrogen or oxygen and communicating this information in clearly labelled charts, models or diagrams • ***researching the influence of a specific living organism on the cycling of matter through the biosphere; e.g. Nitrogen bacteria, sulphur bacteria, sea birds, molluscs and communicating information in the form of a clearly written report*** • designing and performing experiments to determine the biodegradability of various forms of organic matter and communicating information in the form of charts, graphs or tables • demonstrating invertebrates ecycling of matter using annelid worms.	***Understanding how matter cycles characteristic pathways and explaining the role of living systems in these processes; and by describing and diagramming matter cycles, and designing experiments to determine biodegradability or organic matter, within the context of:*** • assessing technological developments that produce materials the ecosystem cannot recycle; e.g. Plastics OR • discussing how biodegradable materials reduce the impact of human-made products on the environment OR • evaluating the role of saprophytes in the cycling of matter and biosphere equilibrium OR • comparing the recycling of matter through ecosystems OR • assessing impact of modern agricultural technology on the carbon cycle OR • ***any other relevant context.***

Table 5. ...cont'd.

MAJOR CONCEPTS	**KNOWLEDGE** **Students should be able to demonstrate an understanding that:**	**SKILLS** **Students should be able to demonstrate the skills and thinking processes associated with the practice of science , by:**	**STS CONNECTIONS** **Students should be able to demonstrate the interrelationships among science, technology and society, by:**
3. ***The biosphere is composed of a variety of ecosystems each with distinctive biotic and abiotic factors demonstrating that their structure is determined by the nature of their matter and energy exchange.***	Ecosystems are defined in terms of their biotic and the abiotic components, by: • describing how energy and matter exchange contribute to the biosphere's major biomes • describing how various abiotic factors influence ecosystem structure; e.g., climate, substrate temperature, elevation,topography • ***explaining how the biotic relationships can be explained in terms of the movement of matter and energy using food chains, webs and pyramids*** • ***explaining the various factors that influence the growth of populations and describing how the interactions between organisms limits populations.***	• performing a field study on an aquatic or terrestrial ecosystem and measuring, quantitatively, appropriate abiotic data; e.g. Temperature, humidity, precipitation, light intensity, pH, hardness, oxygen content • performing a field study on an aquatic or terrestrial ecosystem and measuring, quantitatively, appropriate data on the abundance species, that describes in, general terms, the biotic component of the ecosystem • analysing the biotic and abiotic data collected on the ecosystem studied and presenting this information in a written format, graphic format or oral presentation to the peers of the student or students involved • ***collecting quantitative data using micro-organisms that demonstrate how closed populations of organisms change over time and presenting their data in tables, graphs or charts; e.g. Hay infusions, pond water samples, fruit flies*** • ***modelling the movement of matter and energy of the ecosystem chosen using food chains, webs or pyramids and communicating this information in the form of a graphic illustration.***	Understanding how the nature of energy and matter exchange determines ecosystem structure, defining major biomes, describing and explaining abiotic and biotic ecosystem components and the factors that influence population growth; by performing a field study on an ecosystem including collecting, analysing and modelling relevant data, and demonstrating closed population change over time, within the context of: • evaluating the relationship between human population density and the production of wastes that exceed the environment's capacity to recycle OR • evaluating the relationship between land use practices and endangered ecosystems; e.g. Swamp drainage, slash and burn forest agriculture OR • ***tracing a scientific and technological development that creates or intensifies problems in the biosphere; e.g. Hydroelectric power generation*** OR • compare and contrast growth of human populations and specific natural populations of organisms; e.g. Salmon, mosquitoes, wolves, elk OR • debating the concept of extinction as a natural phenomenon OR

(cont'd next page)

Table 5. ...cont'd.

MAJOR CONCEPTS	**KNOWLEDGE** **Students should be able to demonstrate an understanding that:**	**SKILLS** **Students should be able to demonstrate the skills and thinking processes associated with the practice of science , by:**	**STS CONNECTIONS** **Students should be able to demonstrate the interrelationships among science, technology and society, by:**
			• assessing the impact of theintroduction of an exotic species ona specific ecosystem or biome; e.g. English sparrows in North America, rabbits in Australia OR • ***any other relevant context.***
NWT Science 25 Unit 1 Environmental Disruptions to Living Systems			
1. ***Internal homeostasis of the human organism, as a system, can be disrupted by various environmental influences.***	Various environmental factors can affect the equilibrium of the human organism, by: • describing how human disorders may result from an interaction of variables; e.g. Poor nutrition, stress, environmental toxins.	• ***investigating a specific environmental toxin that manifests itself as a characteristic disease of human beings,e.g. Mercury, lead,or arsenic, and communicating the information and data collected in a flow chart that models ecosystem trophic structure.***	Understanding how the interaction of various environmental factors including stress, nutrition or toxins can affect the equilibrium of the human organism; and by investigating and communicating how a specific environmental toxin can manifest itself as a characteristic disease, within the context of: • evaluating the connection between political instability and non-pathogen related human diseases; e.g. Heavy metal poisoning, malnutrition, compromised immune systems, cancer OR • any other relevant context.
2. N/A		•	

Table 5. ...cont'd.

MAJOR CONCEPTS	KNOWLEDGE **Students should be able to demonstrate an understanding that:**	SKILLS **Students should be able to demonstrate the skills and thinking processes associated with the practice of science , by:**	STS CONNECTIONS **Students should be able to demonstrate the interrelationships among science, technology and society, by:**
3. Environmental pathogens can disrupt the homeostasis of the human organism.	Pathogens, as living systems, can cause disruptions in the internal homeostasis of the human organism, by: • ***describing how noncommunicable disease can affect the human organism, e.g., food poisoning, water contamination, direct contact*** • describing how communicable diseases are transmitted by various pathogens; e.g. Viruses, bacteria, fungi, protozoa and by a variety of methods • explaining the actions that can be taken to reduce the contamination by pathogens.	• performing an experiment to demonstrate the conditions necessary for the growth of various non-pathogenic bacteria and/or fungi • observing prepared slides of various disease - causing microbial organisms, using the compound microscope and accurately representing those organisms in clearly labelled diagrams • ***preparing a visual representation of the method of infection/transmission of a specific human pathogenic organism and presenting this information in the form of an oral presentation tot he peer group*** • ***researching how a specific food handling or preparation industry prevents the microbial contamination of their final product*** • researching the physiological effects of a specific human pathogen and communicating the information in a clearly written report.	understanding how pathogens disrupt human homeostasis by, describing the nature of disease, and explaining actions that reduce pathogen contamination; and by performing experiments demonstrating bacteria growth, observing and drawing pathogens from slides and researching and communicating information on human pathogens and contamination technology, withing the context of: • assessing how the invention of the electron microscope made possible the study of viruses and cellular structures which in turn led to great advancements in detection and treatment of disease, as an example of how science advances science OR • ***tracing, from a historical perspective, the connection between drinking water and poor sanitary conditions, e.g. Cholera*** OR • evaluating public health department food handling guidelines OR • investigating a specific disease that is directly related to personal hygiene, or drinking water contamination OR • assessing the societal impact, from an historical perspective of pandemic diseases; e.g. Black Plague, 1918 Influenza, AIDS OR • ***any other relevant context.***

Table 5. ...cont'd.

MAJOR CONCEPTS	**KNOWLEDGE** **Students should be able to demonstrate an understanding that:**	**SKILLS** **Students should be able to demonstrate the skills and thinking processes associated with the practice of science , by:**	**STS CONNECTIONS** **Students should be able to demonstrate the interrelationships among science, technology and society, by:**
NWT Science 25 Unit 3 Understanding Common Energy Conversion Systems			
1. ***Energy from the Sun moving through the hydrosphere and atmosphere drives weather systems on Earth.***	Weather can be explained by the movement of water and air driven by the energy from the Sun, by: • describing why movement of air and water requires an energy source and identifying and describing the energy sources and energy conversions involved in such movements • describing how forces cause specific patterns of movement of air and water and relating this constant flux to weather patterns • ***investigating various weather patterns describing their impact on the Earth's surface*** • describing how weather can be predicted • describing how weather climate have have changed over time and how conditions on Earth during the Carboniferous period led to the formation of fossil fuels.	• ***researching temperature and precipitation data for various climate areas of the world and constructing and communicating this information using climatograms*** • collecting and comparing daily temperature data for cities of similar latitudes and listing possible explanations for differences and similarities • charting global ocean current and explaining in general terms how they influence the climate patterns of specific land masses; e.g., Vancouver Island, New Brunswick • communicating meteorological data in SI units; e.g., temperature, wind velocity, atmospheric pressure, precipitation • interpreting weather chart data from a local resource, e.g., newspapers, or television news forecasts.	Understanding how weather is the result of the movement of water and air driven by energy from the Sun, describing various weather patterns, how weather can be predicted, how weather and climate have changed over time; and by collecting and interpreting and communicating weather data, constructing climatograms, charting global ocean current patterns and explaining how they influence climate, within the context of: • ***explaining how a variety of technologies are used to understand historical changes in climate, e.g., tree rings, fossils, ocean levels, ice cores*** OR • assessing the limitations of current in technology in accurate weather prediction OR • explaining how technology plays a key role in monitoring weather e.g. weather satellites OR • explaining how the accumulation of data may support or refute a theory that explains a weather phenomenon OR • any other relevant context.

DISTRIBUTION OF HIGH SCHOOL MATERIALS

The following materials:

- A six-poster set of Northern Ecozones
- Class reading set of Contaminants in Northern Canada Booklet
- Manual for Science Teachers, NWT Science 15-25
- CD-ROM version of Teachers Manual

have been distributed to all NWT High Schools offering Grades 10 and 11. The packages were addressed to the attention of the Science Teacher for Science 15 and 25. Schools can request additional copies, if required. Materials were mailed out at the beginning of the 1997/98 school year. Program materials (minus the poster set) have been sent to the District Education Council Offices and Yellowknife School Boards.

There are 37 NWT High Schools, 8 Divisional Education Councils and 2 School Boards. Reference copies will also be made available to NCP Partner Agencies and other Education Authorities that express an interest in this program.

Table 6. Distribution List for High School Program

Council/Board	Number of High Schools
Baffin Divisional Council	12
Beaufort-Delta Divisional Council	4
Deh Cho Divisional Council	3
Dogrib Divisional Council	1
Keewatin Divisional Council	6
Kitikmeot Divisional Council	4
Sahtu Divisional Council	3
South Slave Divisional Council	2
Yellowknife Education District #1	1
Yellowknife Education District #2	1
Total	37 + 10 for District Offices

NCP Overview Booklet, "Contaminants in Northern Canada"

In cooperation with the 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. This booklet was produced with separate funding, but complements our program. Due to demand, this booklet has been reprinted twice since the original run.

RESULTS

To date the project has produced:

- a data base of NCP contaminant research, school reference materials, community profiles and Health Risk Assessments.
- Junior High Books, which have been distributed to Schools, School Board Regional Resource Centres in the Northwest Territories, Aurora Research Institute and Nunavut Research Institute.
- program materials for Grades 10 and 11, NWT Science 15 and 25, which have been distributed to all NWT schools offering those grades.
- the overview booklet entitled 'Contaminants in Northern Canada', which is available for educators, professionals working in the contaminant field as well as the general public.

DISCUSSION/CONCLUSIONS

Generally, reaction to the program has been very positive. Requests for the schoolbooks have exceeded the quantities available. Distribution via bulletin boards and the Internet may prove useful. A survey of Junior High Teachers from the Baffin Region, attending an in-service session on the Northern Contaminants Program revealed:

- a high percentage of teachers new to the North
- most of the new teachers were not aware of our program materials and had not seen copies of the books
- most indicated that they would prefer hard copy to CD-ROM format

Teachers attending the workshop were provided with photocopies of the books. There is clearly a need to address the issue of distribution to ensure that the materials are received by those teachers who need them and to address the issue of ongoing availability. The Junior High Books were sent to the Regional Education Centres, with a request to distribute the books to schools in their area. Although the books were prepackaged and addressed to school principals, in some cases they appear not to have reached their intended users or as teachers moved from the school, the books appear to have moved with them. In an attempt to resolve these problems, the High School materials have been addressed to the attention of the Science 15–25 teachers, with packages being mailed directly to schools. Teachers have been asked to fax back a confirmation of receipt and indicate if extra copies are required. We hope that this strategy will enable us to establish direct communication with the classroom teachers. The experience of the past year demonstrates the importance

Table 7. List of NWT High Schools

Baffin	Arctic Bay	Inuujaq School
Baffin	Broughton Island	Inuksuit School
Baffin	Cape Dorset	Peter Pitseolak School
Baffin	Clyde River	Quluaq School
Baffin	Grise Fiord	Umimmak School
Baffin	Hall Beach	Arnaqjuaq School
Baffin	Igloolik	Ataguttaaluk High School
Baffin	Iqaluit	Inukshuk High School
Baffin	Kimmirut	Qaqqalik School
Baffin	Pangnirtung	Attagoyuk School
Baffin	Pond Inlet	Takijualuk School
Baffin	Sanikiluaq	Nuiyak School
Beaufort-Delta	Aklavik	Moose Kerr School
Beaufort-Delta	Fort McPherson	Chief Julius School
Beaufort-Delta	Inuvik	Samuel Hearne Secondary High School
Beaufort-Delta	Tuktoyaktuk	Mangilaluk School
Deh Cho	Fort Liard	Echo Dene School
Deh Cho	Fort Providence	Deh Gah School
Deh Cho	Fort Simpson	Thomas Simpson School
Dogrib	Rae-Edzo	Chief Jimmy Bruneau School
Keewatin	Arviat	Qitiqliq School
Keewatin	Baker Lake	Jonah Amitnaaq School
Keewatin	Chesterfield Inlet	Victor Sammurtok School
Keewatin	Coral Harbour	Sakku School
Keewatin	Rankin Inlet	Maani Ulujuk Ilinniarvik
Keewatin	Repulse Bay	Tusarvik School
Kitikmeot	Cambridge Bay	Kilinik High School
Kitikmeot	Kugluktuk	Kugluktuk School
Kitikmeot	Gjoa Haven	Quqshuun Ilihakvik Centre
Kitikmeot	Taloyoak	Netsilik School
Sahtu	Deline	?Ehtseo Ayah School
Sahtu	Fort Good Hope	Chief T'selihye School
Sahtu	Norman Wells	Mackenzie Mountain School
South slave	Fort Smith	Kaeser High School
South Slave	Hay River	Diamond Jennesse High School
Yellowknife #1	Yellowknife	Sir John Franklin High School
Yellowknife #2	Yellowknife	St. Patrick High School

of in-service training with classroom teachers and development of an ongoing distribution system.

Expected Project Completion Date: Phase V has been completed. The project continues in NCP Phase II with draft program development for Grade 12 High School courses and revision of Junion High Materials, in 1997/98.

APPENDIX 1

Publications produced by the Métis Nation Northern Contaminants Education Program.

Title	Contaminants in Northern Canada - Arctic Environmental Strategy: Northern Contaminants Program
Author	Judy Farrow, Education Co-ordinator Contaminant Program, Environment Division, Métis Nation - NWT.
Publisher	Métis Nation - NWT, Yellowknife.
Date	1995; 2nd printing 1995; 3rd printing (revised) 1996
Format	Illustrated Booklet.
Description	This booklet, written in plain language, contains a straightforward explanation of the sources and effects of contaminants in the North. It covers contaminants in general, their effects on wildlife and possible effects on human health. The booklet includes a discussion of the various programs in place to study contaminants in the North. As well, it provides a list of ways that people can learn more about the Northern Contaminants Program.
Length	15 pages
Community	N/A
Keywords	Contaminants, organochlorines, metals, radionuclides, food chains, bioaccumulation, biomagnification, human health, NCP.
Location	Métis Nation - NWT, Box 1375 Yellowknife NT X1A 2P1 403 873 3505 FAX 403 873 3395 and DIAND, Hull, Quebec.

Title	Contaminants in Northern Canada. Lesson Plans for Grade 7 Science 1. Environmental Concerns 2. Nuclear Energy.
Author	Judy Farrow, Education Co-ordinator Contaminant Program, Environment Division, Métis Nation - NWT.
Publisher	Métis Nation - NWT, Yellowknife.
Date	1995
Format	Spiral bound teachers' manual.
Description	Background information on AES: NCP, lesson plans and student activities referenced to the required NWT Science Curriculum. Spiral bound to allow easy copying of student activity sheets. Set of overhead transparency masters are also included. Lists ways to access more information about NCP.
Length	144 pages
Community	Applicable to all NWT communities offering Grade 7.
Keywords	Contaminants, organochlorines, metals, radionuclides, food chains, bioaccumulation, biomagnification, lesson plans, Grade 7, NWT science curriculum, teacher manual.
Location	Métis Nation - NWT, Box 1375 Yellowknife NT X1A 2P1 403 873 3505 FAX 403 873 3395

Title	Contaminants in Northern Canada. Lesson Plans for Grade 8 Science 1. Northern Food Chains and Webs 2. Pulp and Paper.
Author	Judy Farrow, Education Co-ordinator Contaminant Program, Environment Division, Métis Nation - NWT.
Publisher	Métis Nation - NWT, Yellowknife.
Date	1995
Format	Spiral bound teachers' manual.
Description	Background information on AES: NCP, lesson plans and student activities referenced to the required NWT Science Curriculum. Spiral bound to allow easy copying of student activity sheets. Set of overhead transparency masters are also included. Lists ways to access more information about NCP.
Length	108 pages
Community	Applicable to all NWT communities offering Grade 8.
Keywords	Contaminants, organochlorines, metals, radionuclides, food chains, bioaccumulation, biomagnification, pulp and paper, fresh water food chains, lesson plans, Grade 8, NWT science curriculum, teacher manual.
Location	Métis Nation - NWT, Box 1375 Yellowknife NT X1A 2P1 403 873 3505 FAX 403 873 3395

Title	Contaminants in Northern Canada. Information for Science Teachers Grades 7, 8 and 9.
Author	Judy Farrow, Education Co-ordinator Contaminant Program, Environment Division, Métis Nation - NWT.
Publisher	Métis Nation - NWT, Yellowknife.
Date	1996
Format	Spiral bound teachers' reference manual.
Description	Background information on AES: NCP, curriculum guide, guides teachers to where NCP information may be used with the required curriculum. Reference list of NCP projects, listed by species being studied and reference section on contaminants. Lists ways to access more information about NCP.
Length	58 pages
Community	Applicable to all NWT communities offering Grades 7, 8 and 9
Keywords	Contaminants, organochlorines, metals, radionuclides, food chains, bioaccumulation, biomagnification, lesson plans, Grades 7, 8 and 9, NWT science curriculum, teacher manual.
Location	Métis Nation - NWT, Box 1375 Yellowknife NT X1A 2P1 403 873 3505 FAX 403 873 3395

Title	Contaminants in Northern Canada. Lesson Plans and Reference Materials for NWT Science 15 and NWT Science 25.
Author	Judy Farrow, Education Co-ordinator Contaminant Program, Environment Division, Métis Nation - NWT.
Publisher	Métis Nation - NWT, Yellowknife.
Date	Distributed to NWT schools September 1997
Format	CD - ROM and quick print hard copy on three-hole paper.
Description	Background information on AES: NCP, lesson plans, and student activities referenced to the required NWT Science 15 and 25 Curriculum. CD - ROM Format provides the opportunity to access reference information by computer or provide hard copy print out capabilities. Reference materials and appropriate graphics are provided to assist teachers. Lists ways to access more information about NCP.
Length	650 MB
Community	Applicable to all NWT communities offering Grades 10 and 11.
Keywords	Contaminants, organochlorines, metals, radionuclides, food chains, bioaccumulation, biomagnification, lesson plans, Grades 10 and 11, NWT science curriculum, teacher manual, CD-ROM.
Location	Métis Nation - NWT, Box 1375 Yellowknife NT X1A 2P1 403 873 3505 FAX 403 873 3395

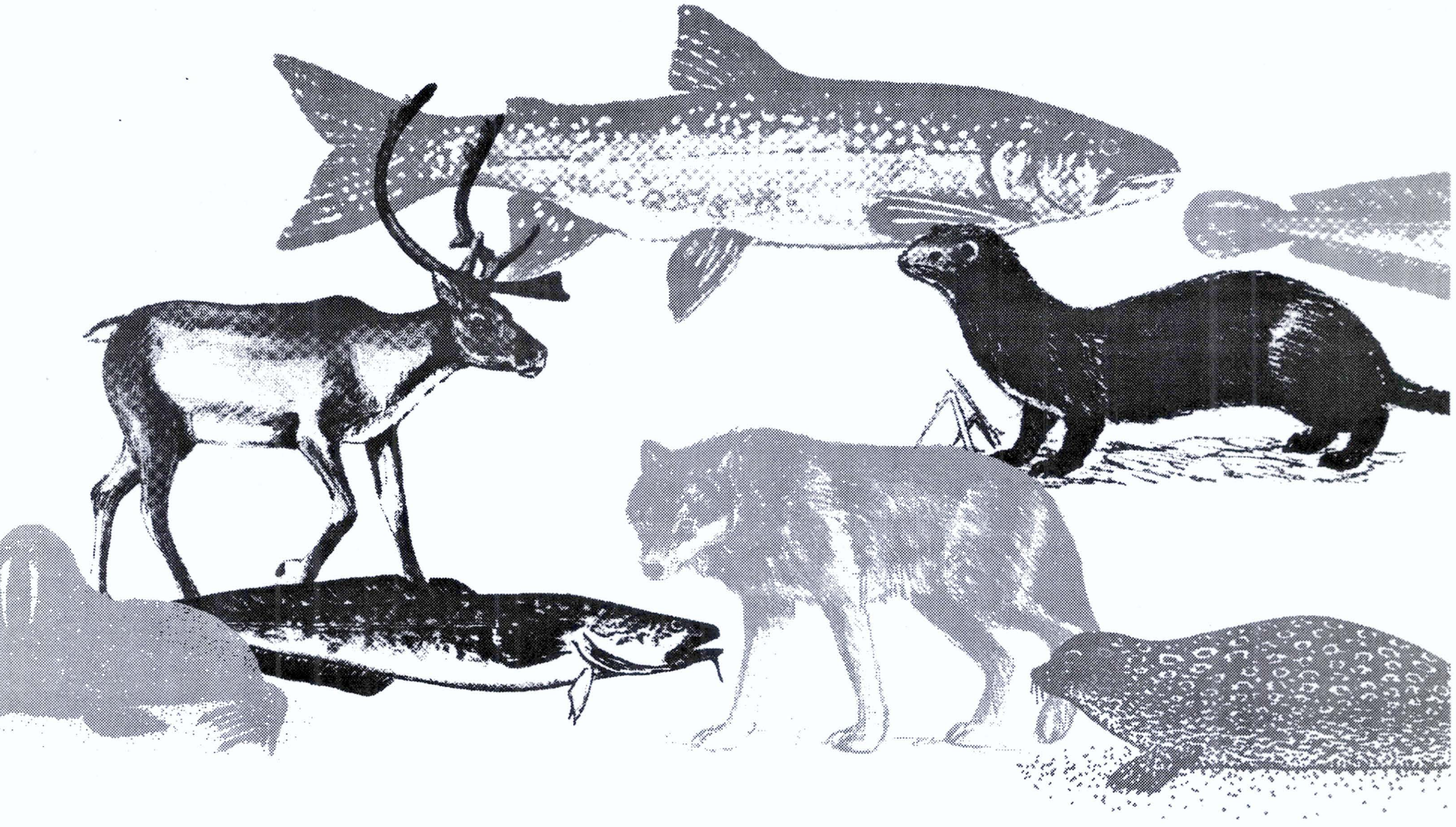
Sample pages from these publications follow.

APPENDIX: SAMPLE CURRICULUM

ARCTIC ENVIRONMENTAL STRATEGY • STRATÉGIE POUR L'ENVIRONNEMENT ARCTIQUE

Contaminants in Northern Canada

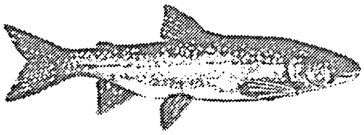
Information for Science Teachers
Grades 7, 8 and 9

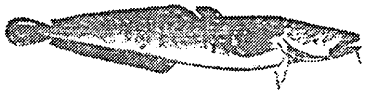


Métis Nation Northern Contaminants Education Program
Box 1375, Yellowknife, NT X1A 2P1 Tel.: 403-873-3505 Fax: 403-873-3395
eMail: metisnwt@internorth.com

Northern Contaminants Program

As Northerners, our relationship to the environment is usually closely linked with our personal life styles and that of the cultural group to which we belong. One of the most important values is respect, respect for yourself, for others and for the environment. Many of our northern traditions and legends revolve around food gathering and eating. These respected traditions helped to preserve the balance between us and the environment. Traditional northern foods are particularly important because of their superior nutritional value and their special spiritual and cultural significance. As well, traditional harvesting is an important economic factor in many northern communities. The stated objective of the Northern Contaminants Program is to reduce and wherever possible get rid of contaminants in traditional food. The result of this program should be renewed confidence in these foods as a safe diet.





In the last decade, there has been more and more evidence that the North, which doesn't have a lot of pollution sources of its own, is collecting chemical contaminants released elsewhere on the Earth. Contaminants from industry and agricultural practices, travel to the North by natural processes. In 1991, the Northern Contaminants Program (NCP) began to look at the problem in Canada, and to try and answer some important questions, such as:

- What Are Contaminants?
- Why Should I Be Concerned About Contaminants?
- How Do Contaminants Get To The North?
- Where Do Contaminants End Up Once They Reach The North?
- How Does The Wildlife Become Contaminated?
- What Are The Effects On Wildlife?
- What Does This Mean For Human Health?
- Is Traditional Food Safe To Eat?
- What Is Being Done About This Problem?

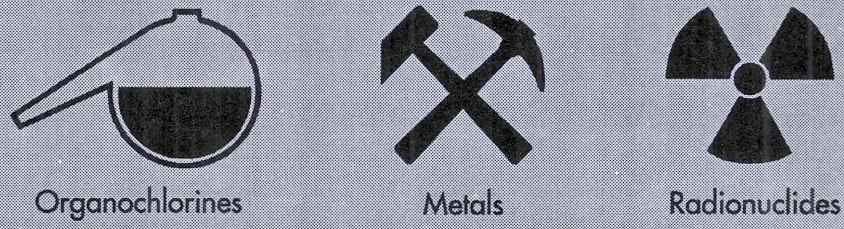
"Contaminants from industry and agricultural practices travel to the North by natural processes."

Under the Arctic Environmental Strategy (AES): Northern Contaminants Program, scientific studies are trying to find answers to these questions.

It is important to be matter-of-fact and not alarmist when presenting information regarding contaminants. People who eat traditional foods should be aware of the contaminant accumulation and biomagnification, but it is generally accepted that the nutritional and social benefits of eating traditional food, far out weigh the current risks from contaminants. However, people must be educated so that they can make informed decisions about what to eat. What better place to start than in the schools.

What Are Contaminants?

A contaminant is a substance that is found in a place where it should not be. This does not necessarily mean that it is harmful, but depending on what it is and the amount that is present, it may be. In an environmental context, however, the word contaminant has generally come to mean a substance that is potentially harmful to plants, animals and humans. Contaminants can be human made or naturally occurring. The contaminants of priority concern for this program are organochlorines, metals, and radionuclides.



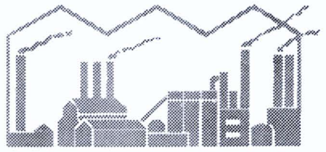
Contaminant particles are often so small that you cannot see them or even smell them. Because it is hard to visualize something that you can't see or even smell we use icons to represent the priority groups of contaminants.

Organochlorines are manufactured chemicals, they do not occur naturally. Often they are pesticides or products from industrial processes, old electrical components or they are released from burning garbage. Some examples of organochlorines are DDT, PCBs and toxaphene.

Metals are elements that occur naturally in rock or soils. Some metals are essential for life processes and cannot fall below critical levels without harm to plants or animals, but metals can also produce harmful effects at excessive concentrations. There are also some non-essential metals such as mercury, cadmium and lead, which are called "heavy metals", that are toxic to most living things, even at relatively low concentrations.

Radionuclides are a variety of radioactive forms of atoms; they can be naturally occurring or result from industrial activity. Most radionuclides occur naturally at very low concentrations, but incidents such as the 1986 Chernobyl nuclear accident reveal how easily contamination of a wide area can occur.

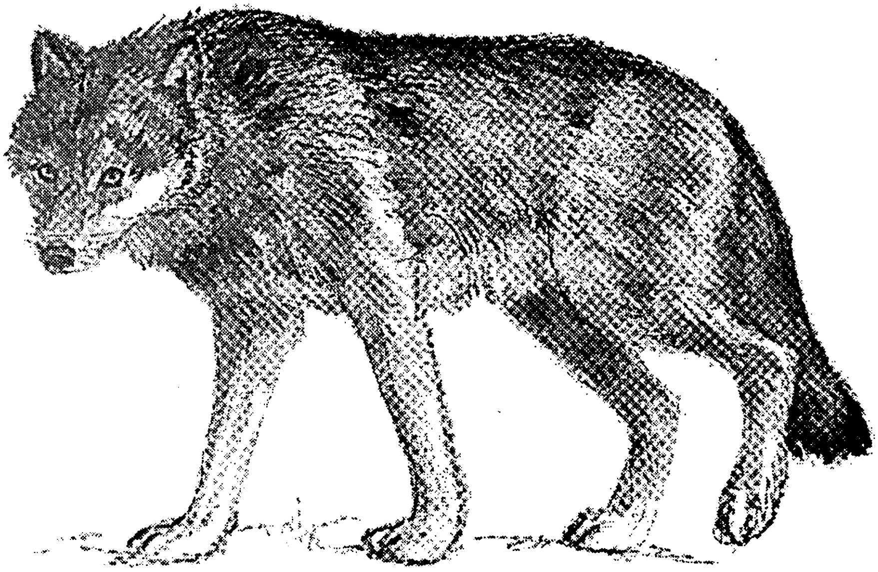
For a list of contaminants measured by the Northern contaminants program and more details regarding specific contaminants see the contaminant reference section towards the back of this book.



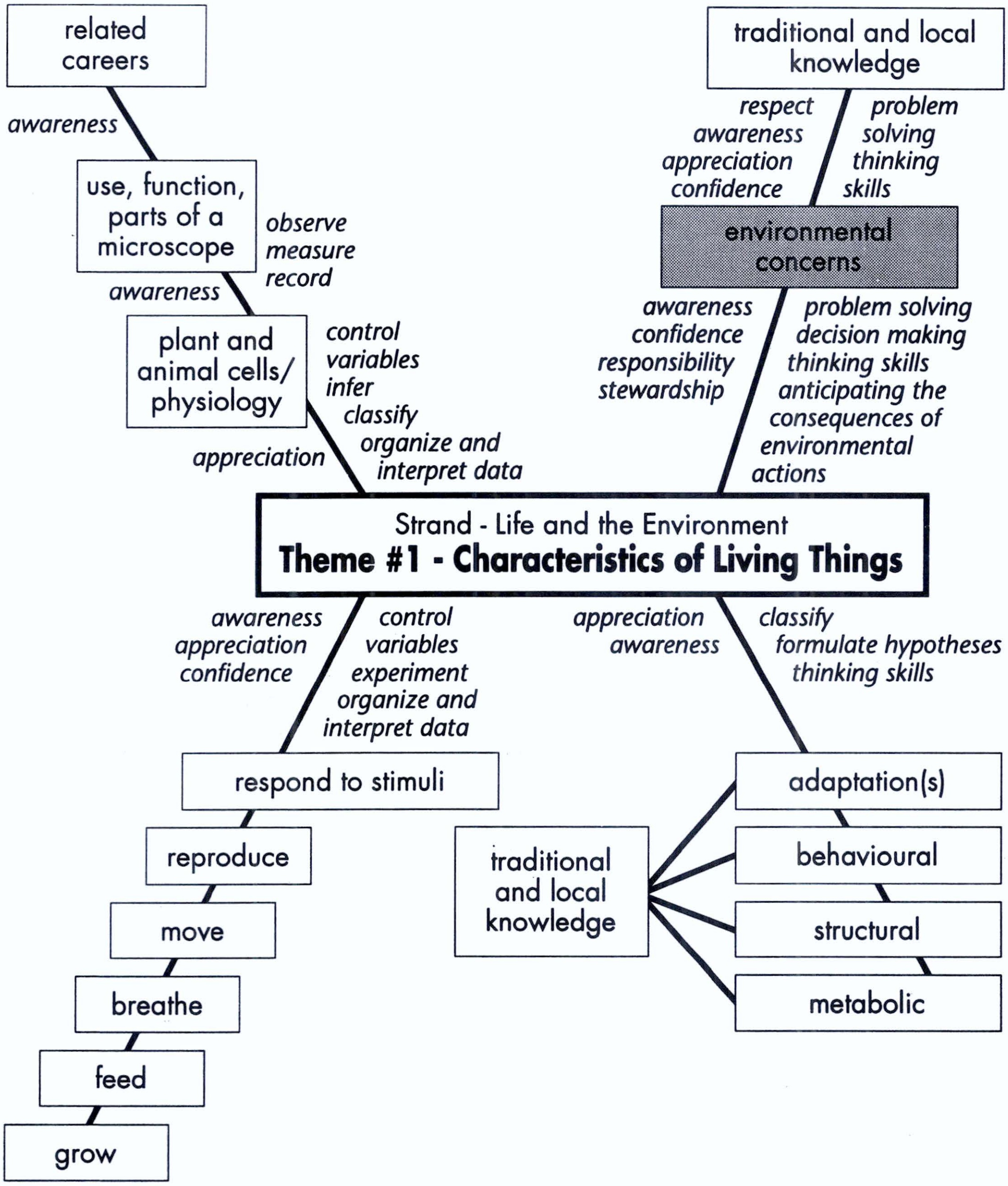
Industry in other parts of the world produce a lot of the contaminants that reach the Arctic.

How Does This Fit into Our Science Curriculum?

The lesson plans provided in previous publications and the suggestions made here, conform to the suggested sequencing for single grade classrooms, to be found on page fifty of the Junior High Science Curriculum Document. As some schools have adopted different sequences or use multi-grade classrooms, the following diagrams demonstrate where the information in this book most easily fits into the Junior High Science Curriculum.

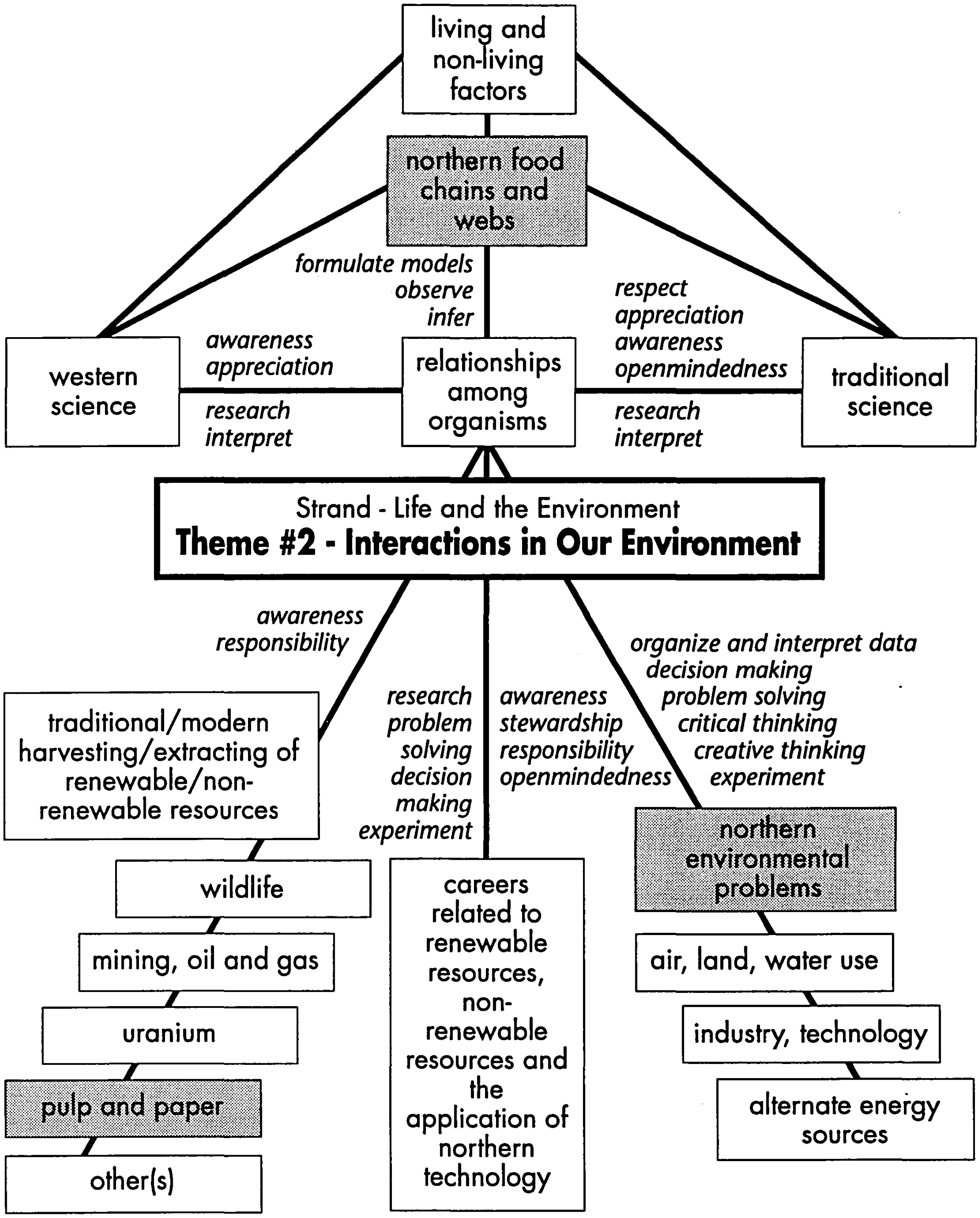


Theme 1



Lesson plans for the unit Environmental Concerns are published in Contaminants in Northern Canada, Lesson Plans for Grade 7 Science.

Theme 2

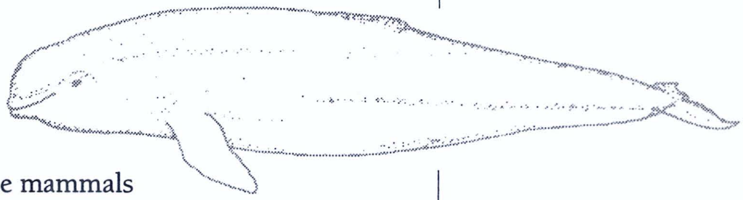


Lesson plans for Northern Food Chains and Webs and Pulp and Paper are published in Contaminants in Northern Canada, Lesson Plans for Grade 8 Science.

In Northern Environmental Problems, teachers may wish to review and/or build upon the lessons from Environmental Concerns for Grade 7.

NCP Projects Listed By Species Being Studied

Marine Mammals



Beluga

Who?	R.F. Addison of DFO
What?	Long term trends in OC residues in marine mammals
When?	1993/94
Where?	Ungava Bay, Hudson Strait, Gulf of St. Lawrence
Why?	To measure temporal trends in PCBs, DDT and other OC levels in seals and beluga.

Who?	B. Hargrave, Bedford Institute, DFO
What?	Organochlorines in the Arctic marine food web
When?	1993/94
Where?	Resolute Bay (South Camp), Barrow Strait (Cape Martyr), Arctic Ocean, Ice Island
Why?	To quantify long range atmospheric marine transport of organic contaminants and their incorporation into the Arctic marine food web.

Who?	D. Muir, DFO
What?	Circumpolar survey of PCBs in Beluga
When?	1990/91, 1991/92
Where?	White Sea, Beaufort Sea, Chukchi Sea, Bering Sea, Norton Sound
Why?	To determine the temporal and spatial trends in PCBs and other OCs in belugas and other marine mammals on a circumpolar basis and provide data for use in surveys of dietary contamination.

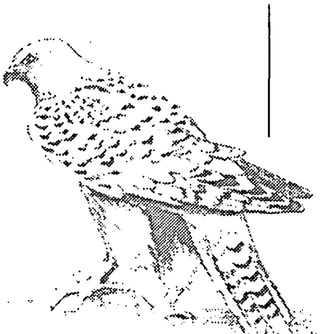
Who?	D. Muir, DFO
What?	Co-planar PCBs in Arctic marine mammals and fish
When?	1991/92, 1992/93
Where?	Cresswell Bay
Why?	To provide geographic and temporal information on toxic PCB congeners.

Who?	D. Muir, DFO
What?	Spatial and temporal trends in OCs in Arctic marine mammals
When?	1992/93
Where?	Cresswell Bay, Norton Sound, Hudson Bay
Why?	To determine temporal and spatial trends in PCBs and other OCs in Arctic marine mammals.

Who?	D. Thomas, Axys Group Ltd.
What?	OCs in beluga whales of the Beaufort Sea
When?	1991/92
Where?	Tuktoyaktuk, Beaufort Sea
Why?	To improve the database for OC contaminants in beluga whales of Beaufort Sea.

Birds

Peregrine/Gyr Falcon



Who?	R.M. Johnstone, University of Saskatchewan
What?	Temporal trends in organochlorine levels in peregrine falcons and their prey, in the Keewatin
When?	1993/94
Where?	Rankin Inlet
Why?	To establish temporal trends of contaminants.

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Ptarmigan

Who?	B.M. Braune, CWS
What?	Trends and effects of contaminants in seabirds, waterfowl and other wildlife
When?	1993/94
Where?	NWT
Why?	To determine levels of contaminants in game birds.

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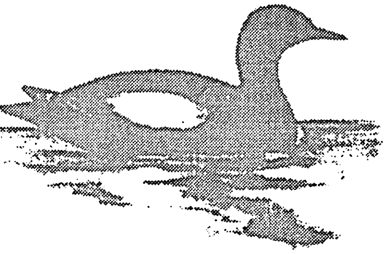
Seabirds and Waterfowl



Who?	B.M. Braune, CWS
What?	Contaminants in aquatic birds of Great Slave Lake
When?	1992/93
Where?	Great Slave Lake
Why?	To establish baseline data.

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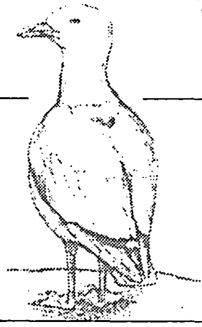

Who?	B.M. Braune, CWS
What?	Contaminants in Arctic seabirds
When?	1993/94
Where?	Cape Dorset, Hall Beach, Coppermine
Why?	To establish temporal trends.

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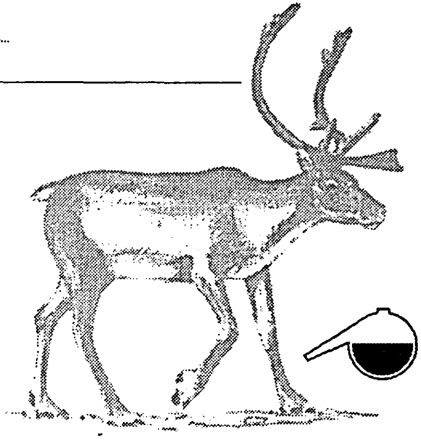
Terrestrial Mammals

Caribou



Who?	B. Elkin, GNWT RR
What?	Organochlorine, heavy metal and radionuclides in the lichen - caribou - wolf food chain
When?	1991/92, 1992/93, 1993/94
Where?	NWT
Why?	To establish baseline data and demonstrate biomagnification.

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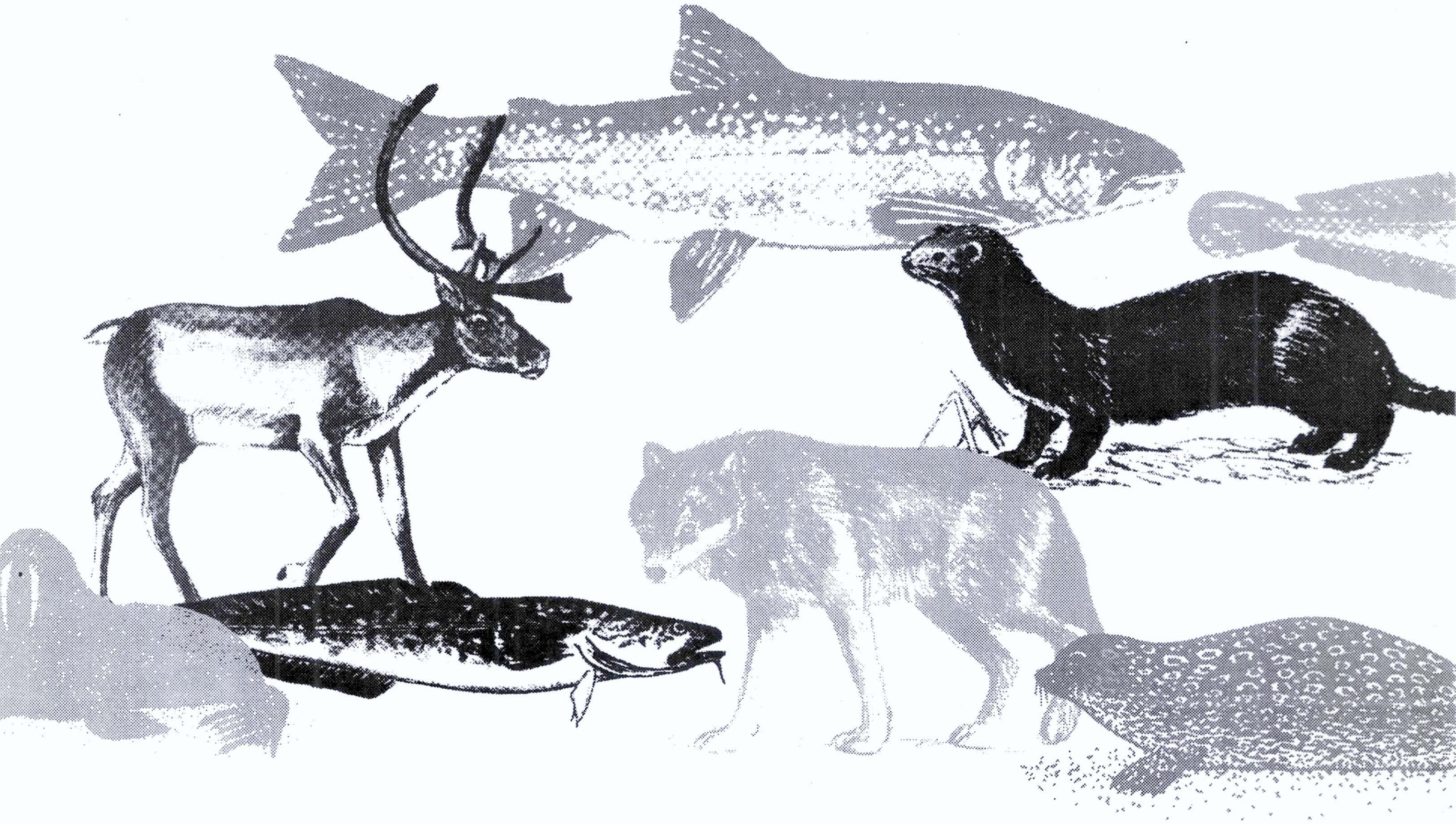
ARCTIC ENVIRONMENTAL STRATEGY • STRATÉGIE POUR L'ENVIRONNEMENT ARCTIQUE

Contaminants in Northern Canada

Lesson Plans For Grade 7 Science
1. Environmental Concerns
2. Nuclear Energy



Métis Nation Northern Contaminants Education Program
Box 1375, Yellowknife, NT X1A 2P1 Tel.: 403-873-3505 Fax: 403-873-3395

Name: ______________________________

EC4

Marine Arctic Food Chain/Food Web

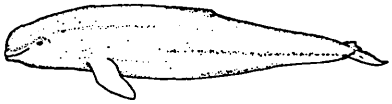
Student Activity Sheet for Environmental Concerns Lesson 4

Instructions:

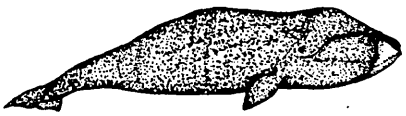
1. Cut out the drawings on the following pages.
2. Arrange the cut-outs to form food chains. The 'clues' on what each animal eats are given below.
3. When you are satisfied with your arrangement, glue them to the paper provided. Add arrows to show the direction of flow of food and energy.
4. Make a second arrangement to turn your food chains into a food web.

Food Chain "Clues"

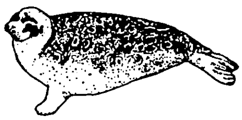
Belugas or white whales feed on fish and invertebrates. Humans and killer whales are their only enemies.



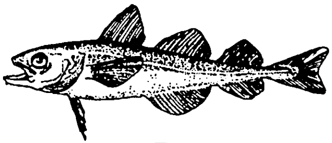
Bowhead whales have large mouths with baleen plates to filter out plankton which is their main food. They are hunted under strict regulations.



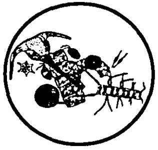
Ringed seals are the most common northern seal. They feed on invertebrates and cod. Ringed seals are eaten by polar bears and humans.



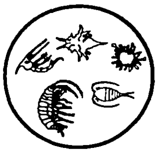
Arctic cod feed on other fish and invertebrates.



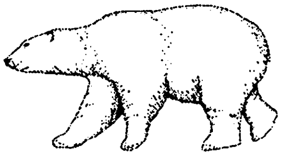
Plankton are very small plants and animals that float around in the sea currents.



Invertebrates are small animals without a backbone, like shrimp and jellyfish. They feed on plankton or dead and decaying matter.

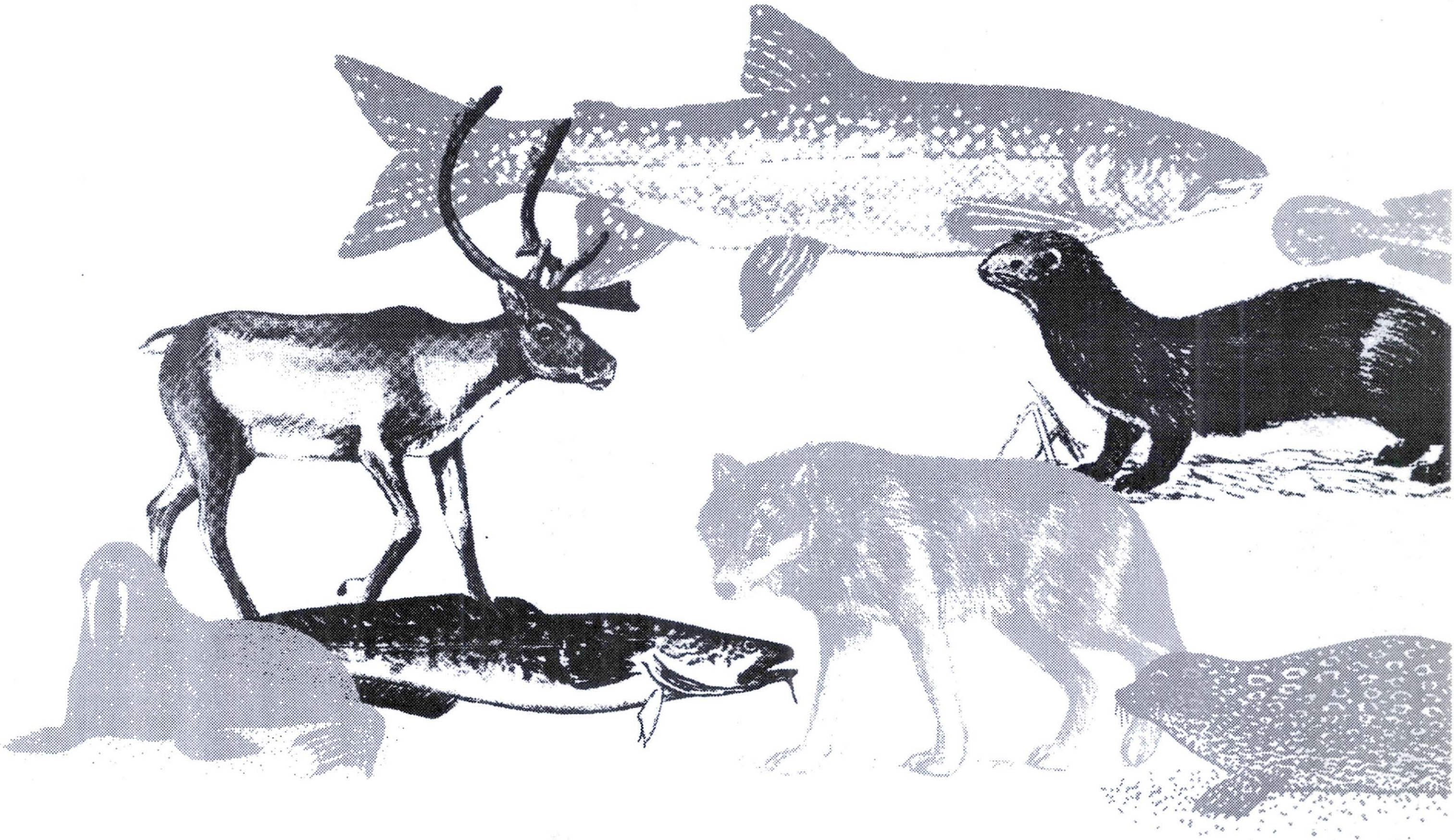


Polar bears are the largest of the bears. Their favourite food is ringed seal. Polar bears live and travel mostly on pack ice. Their only enemies are humans.

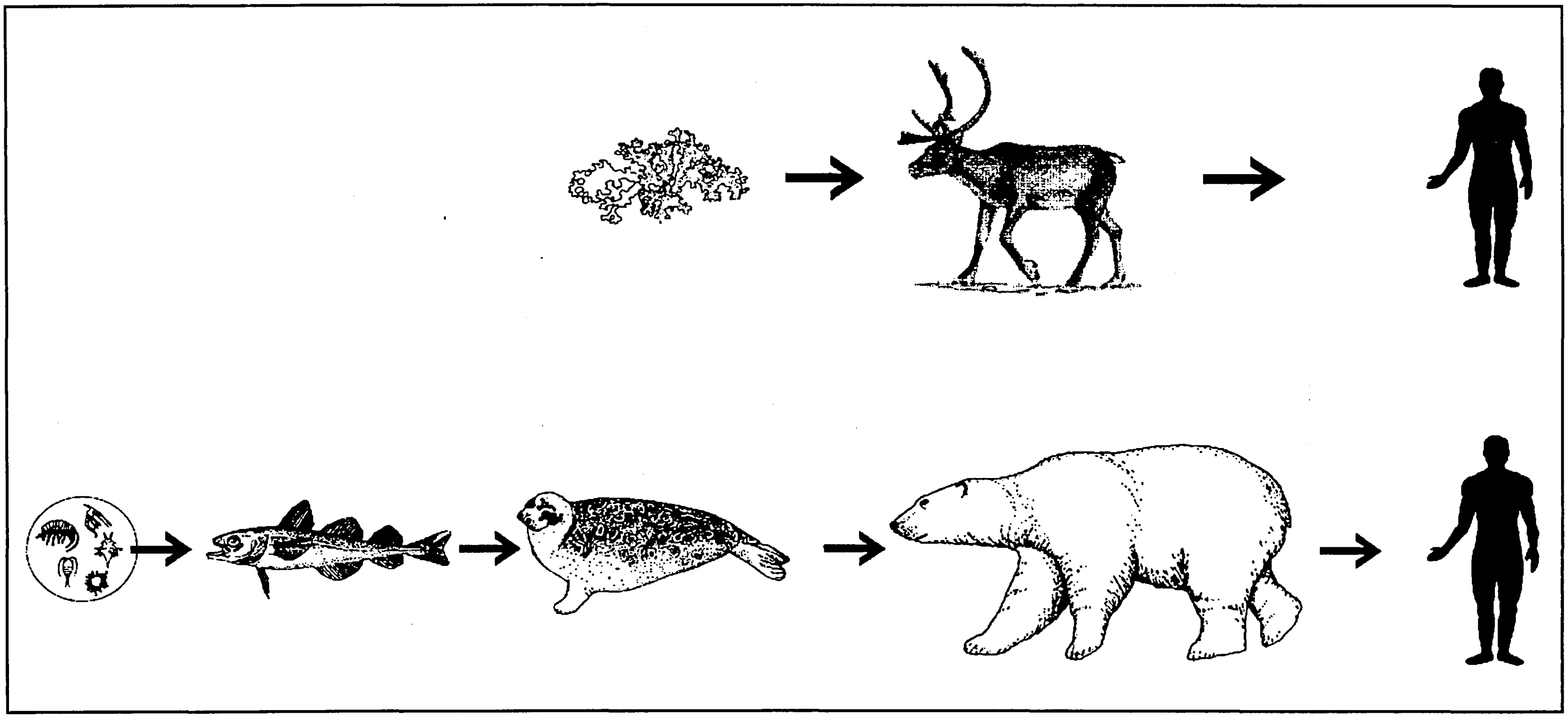


Environmental Concerns and Nuclear Energy

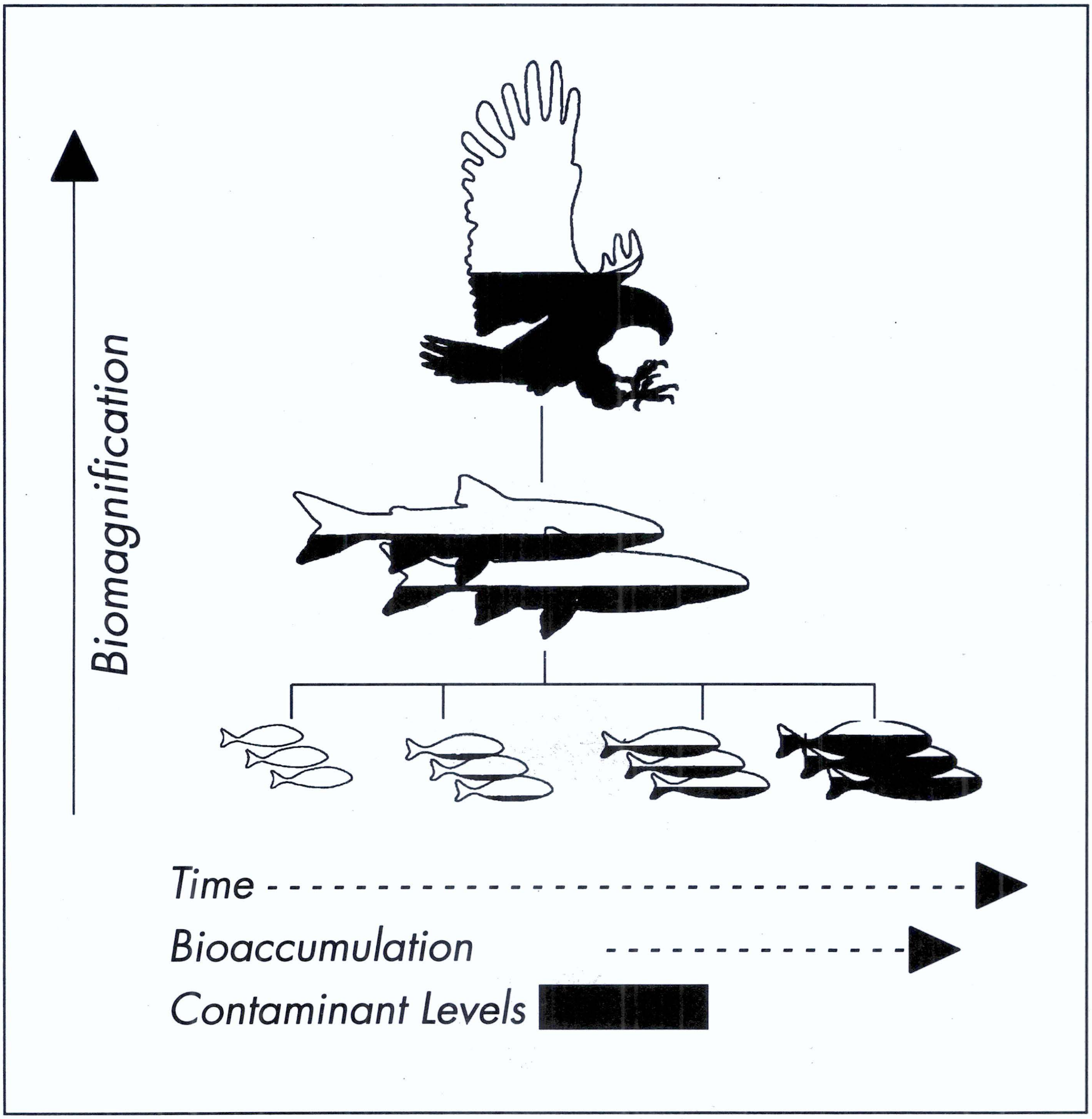
Overheads



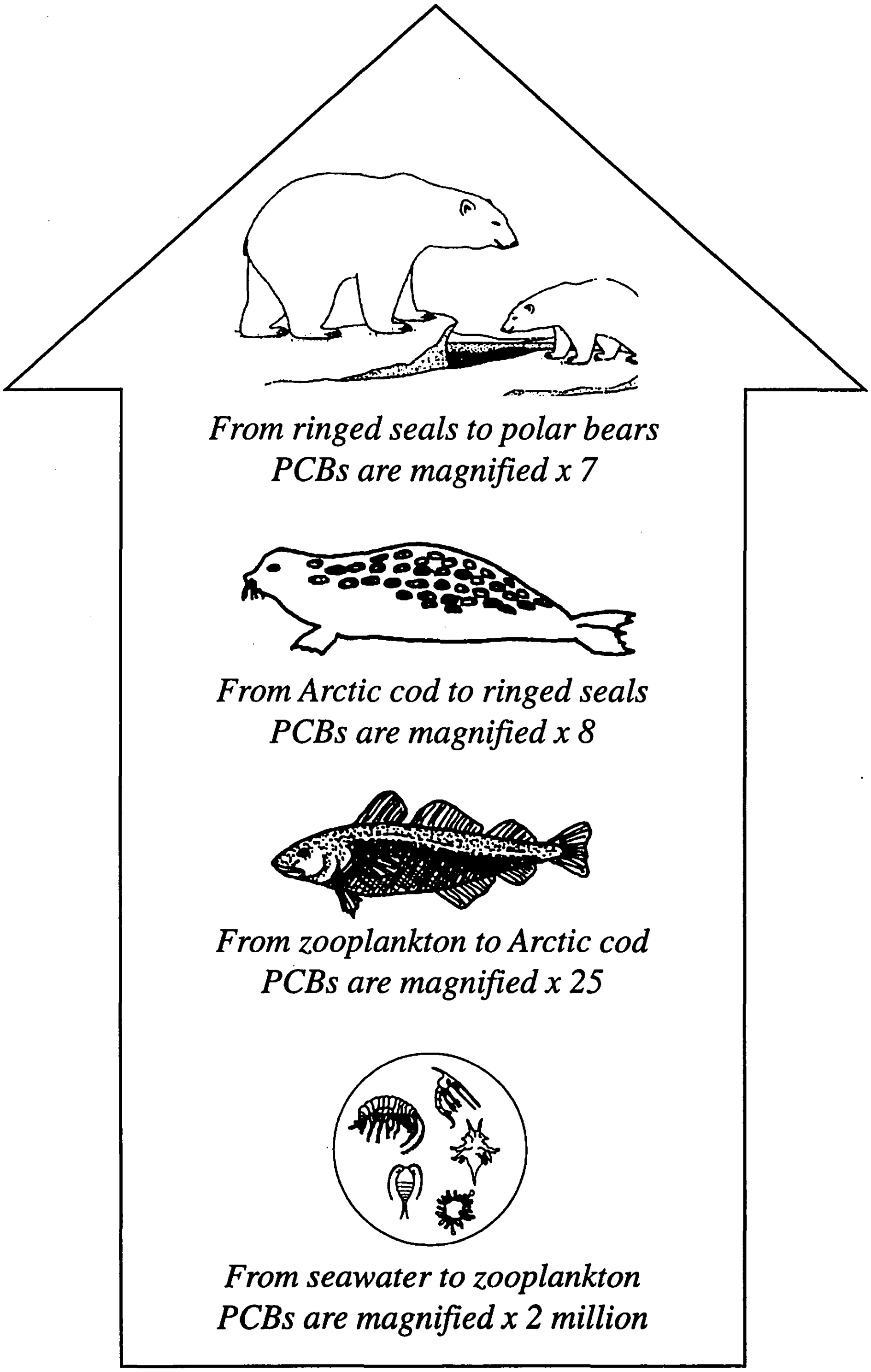
Food Chain



Bioaccumulation and Biomagnification of Contaminants



Biomagnification of PCBs in Marine Arctic Food Chain



From ringed seals to polar bears
PCBs are magnified x 7

From Arctic cod to ringed seals
PCBs are magnified x 8

From zooplankton to Arctic cod
PCBs are magnified x 25

From seawater to zooplankton
PCBs are magnified x 2 million

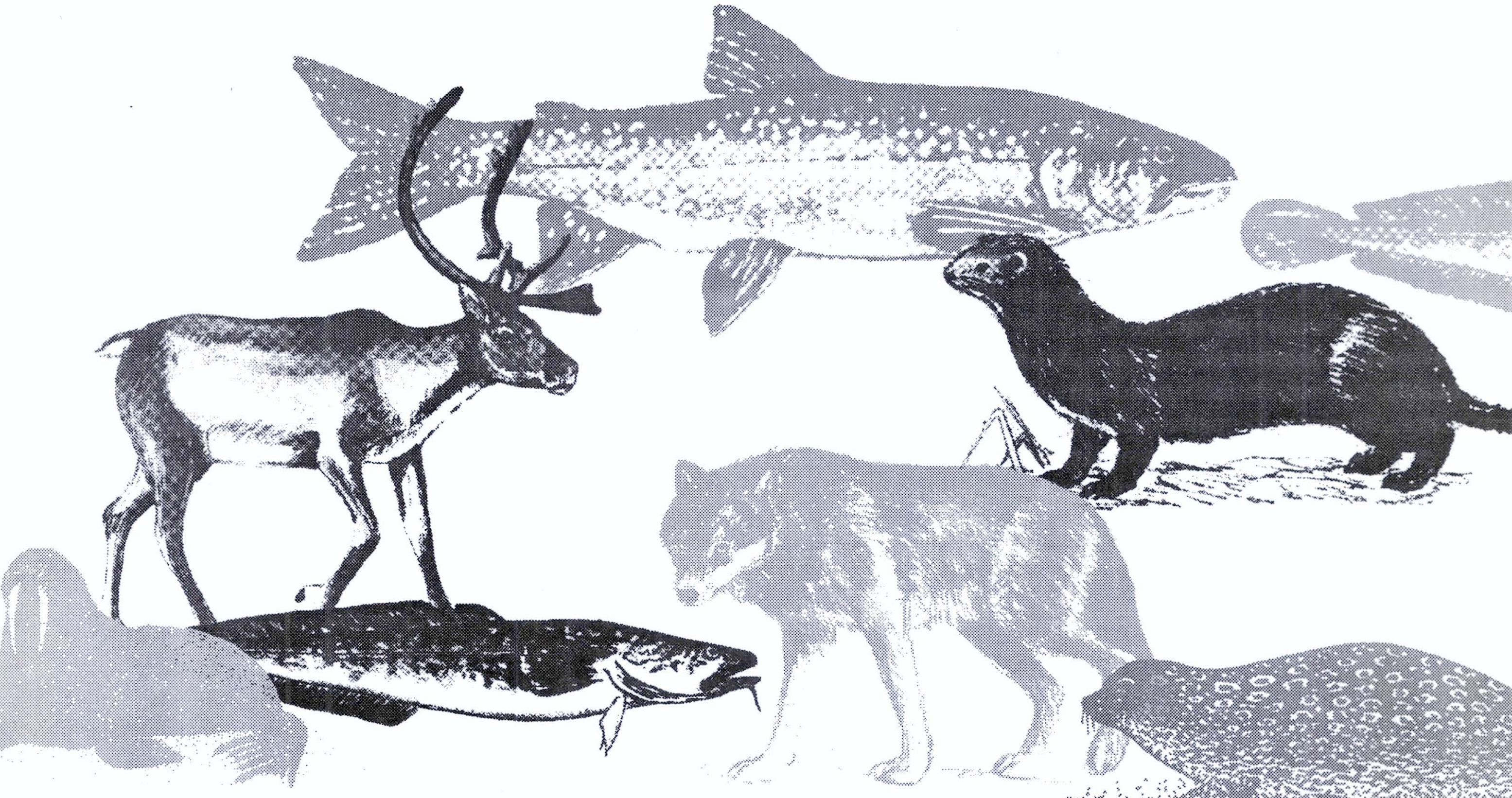
ARCTIC ENVIRONMENTAL STRATEGY • STRATÉGIE POUR L'ENVIRONNEMENT ARCTIQUE

Contaminants in Northern Canada

Lesson Plans For Grade 8 Science

1. Northern Food Chains and Webs

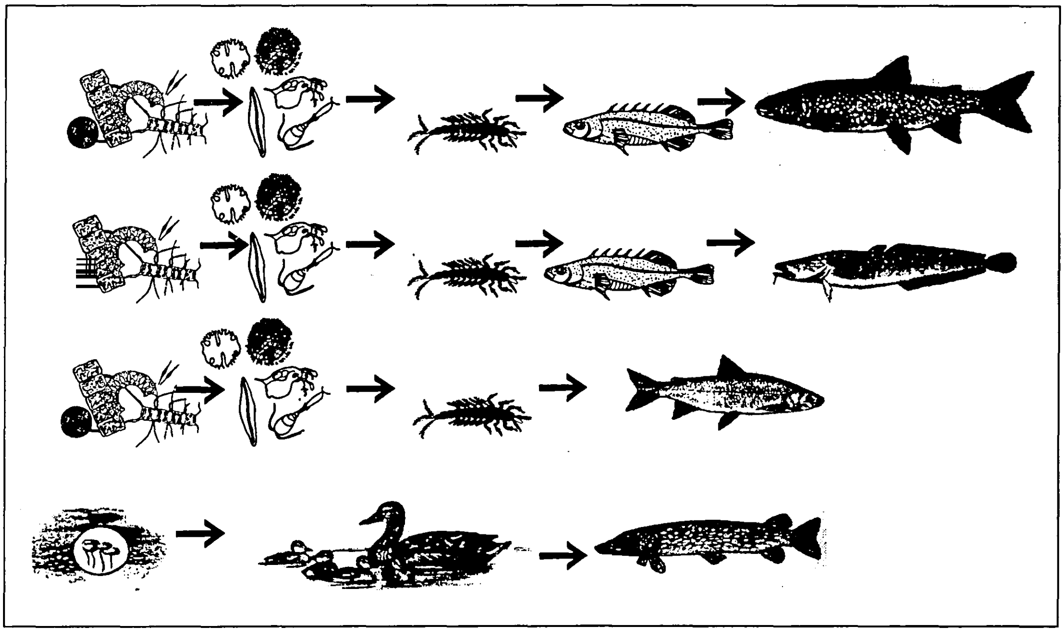
2. Pulp and Paper



Métis Nation Northern Contaminants Education Program

Box 1375, Yellowknife, NT X1A 2P1 Tel.: 403-873-3505 Fax: 403-873-3395

Possible Food Chains



Phytoplankton → Zooplankton → Mayfly Larva → Frog → Mink

Cattails → Muskrat → Mink

Phytoplankton → Zooplankton → Shiners → Pike

Phytoplankton → Zooplankton → Shiners → Mink

Answers to questions:

1. What would happen if one of the food chain links were damaged by an oil spill?

   Because oil spills stay at the surface, many waterfowl (ducks) and surface-feeding fish (whitefish, pike) would die.

2. Give other examples of contaminants that can harm the freshwater food chain.

   Garbage or sewage dumped in a river, a gold mine or pulp and paper mill dumping chemicals in a lake or river.

3. Contaminants are found in every food chain. What are contaminants?

   A contaminant is a substance that is found in a place where it should not be. This does not necessarily mean that it is harmful, but depending on what it is and the amount that is present, it may be. A contaminant may be something that you can see, such as spilled oil, or it may be so small that it cannot be seen or smelt.

4. Where do contaminants come from?

   There are many sources, such as garbage dumps and sewage, but most come from far away sources like smoke stacks and farmers spraying their fields.

Distribute Student Activity Sheets.

Contaminants

Student Activity Sheet for Northern Food Chains and Webs Lesson 5

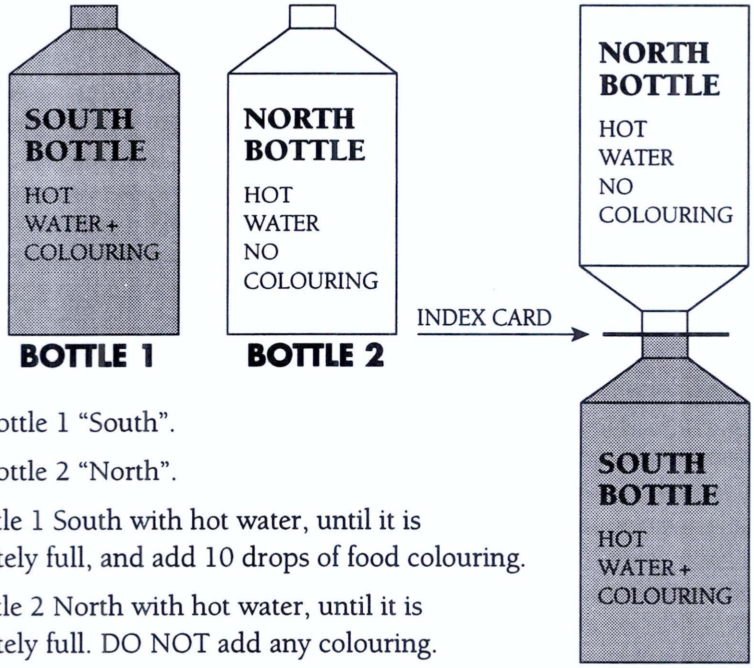
Instructions:

1. In this activity, hot and cold water represents a hot southern climate and a cold northern climate respectively.
2. The food colouring represents the contaminants and the demonstration shows that there is a movement along the temperature gradient from hot to cold.
3. This demonstrates the general rule that contaminants from warmer climates migrate towards the colder polar regions.

You will need the following equipment:

- two transparent plastic "pet"-type bottles (Coke, Pepsi)
- an index card
- a container of red dye (food colouring)

Part A: The "Control" Experiment



1. Label bottle 1 "South".
2. Label bottle 2 "North".
3. Fill bottle 1 South with hot water, until it is completely full, and add 10 drops of food colouring.
4. Fill bottle 2 North with hot water, until it is completely full. DO NOT add any colouring.
5. Place an index card over the top of bottle 2, holding it in place to stop the water coming out, and place it upside down over the South bottle.
6. Carefully remove the card, trying not to let any water escape.
7. Watch what happens and record your observations.

   In this control experiment, students will see no difference because there is no difference in temperature. The red dye from the hot South bottle will NOT rise into the hot North bottle.

MÉTIS NATION CONTAMINANTS COMMUNICATION WORKSHOP, JULY 8TH, 1995

Project Leader: William Carpenter, Environmental Director, Métis Nation - NWT

Project Team: Russel Shearer, Acting Chair, Technical Committee on Arctic Contaminants, Northern Contaminants Program (NCP), DIAND; Ron Allen, District Manager, Fisheries & Oceans Canada; Brett Elkin, Resources, Wildlife and Economic Development, GNWT; Harriet Kuhnlein, Centre for Indigenous Nutrition and the Environment (CINE), McGill University; Laura Seddon, Maternal/Cord Blood Monitoring Program Co-ordinator Mackenzie Regional Health Services (MRHS); Jill Christensen, Nutritionist, MRHS

OBJECTIVES

Short-term:

1. To give the Métis Nation Contaminant Project team an opportunity to learn first hand, the grass roots concerns and information gaps with regard to contaminant information.

2. To further the dialogue of "What AES:NCP needs to tell" and translating it to "What we want to know" from a northern perspective.

Long-term:

1. To ensure the Northern Contaminants Program's ability to fulfill its commitments to meaningfully communicate results to Northerners thereby giving northern Aboriginal residents some of the necessary information and tools to make informed decisions regarding health risks from human-made industrial contaminants that are present in the Northern food chain.

DESCRIPTION

As part of the Northern Contaminant Program (NCP) Communications Strategy the Métis Nation was funded to hold a Contaminants Communication Workshop for delegates attending the 23rd Annual Assembly of the Métis Nation–NWT. The Métis Nation designed the presentations for delivery by professional individuals from the AES–NCP partner agencies. Following the presentations, the Workshop participants divided into six 'Breakout' discussion groups. Facilitators guided each group through the process of determining "What AES/NCP needs to tell" and translating it to "What we want to know" from a northern perspective. (e.g. to answer the question "What do people need to know at the community level?") The facilitators also assisted the group members to deal with questions that could be classified into five main categories:

1. Where do people generally go for help and information on contaminants?
2. How would people like to receive information?
3. Where is more information is needed?
4. What are the concerns of local communities?
5. Recommendations?

Delegates also answered written questionnaires.

ACTIVITIES IN 1995/96

The Workshop

The Métis Nation–NWT held the "Contaminants Communication Workshop" on Saturday July 8th, 1995 at 9:00 AM during the 23rd Annual Assembly of the Métis Nation–NWT in Hay River, Northwest Territories. The workshop was attended by 70 registered delegates representing the 7,000 Métis peoples from 15 community-based locales in the Western Arctic. Workshop proceedings were open to the general public as well.

Table 1 provides details of the Workshop agenda.

Mid-year report

It had been agreed at the onset of this project that the proceedings and results from the workshop would be shared with partnership agencies to further the understanding of what needs to be communicated under the NCP. This was done in the way of a mid-year report entitled *Métis Nation–NWT Environmental Contaminants Workshop, July 8, 1995.* This report was circulated at the October, 1995 mid-year meeting of the Science Manager's Committee in Whistler, BC.

Table 1. Agenda for the Métis Nation Contaminants Communication Worship, July 8th, 1995.

TIME	SUBJECT	SPEAKER
9:00 to 9:05 AM	Welcome and introduction	Gary Bohnet, President Métis Nation
9:05 to 9:10 AM	The Métis Nation's AES Environmental Program & its four components	William Carpenter, Environmental Director, Métis Nation
9:10 to 9:30 AM	"Contaminants in Northern Canada", an overview of the AES Northern Contaminants Program (one of the four components of the AES)	Russel Shearer, Acting Chair, Technical Committee on Arctic Contaminants, Northern Contaminants Program, DIAND.
9:30 to 9:40 AM	Contaminants research in freshwater fish in Northern Canada.	Ron Allen, District Manager, Fisheries & Oceans Canada
9:40 to 9:50 AM	Contaminants research on birds and animals in Northern Canada.	Brett Elkin, Wildlife Disease Specialist, Renewable Resources, GNWT
9:50 to 10:00 AM	Variance in Traditional Food Use in Métis/Dene Communities - Preparing for the results of the dietary survey.	Harriet Kuhnlein, Centre for Nutrition & the Environment of Indigenous Peoples (CINE), McGill University
10:00 to 10:10 AM	Preparing for results from the Maternal/Cord Blood Monitoring Program.	Laura Seddon, Maternal/Cord Blood Monitoring Program Co-ordinator, MRHS.
10:10 to 10:30 AM	NUTRITION BREAK	
10:30 to 10:40 AM	Nutrition & traditional foods	Jill Christensen, Nutritionist, MRHS
10:40 to 12 noon	BREAKOUT GROUPS (to address the questions related to "What do people need to know at the community level?")	Facilitators for each breakout group will be the above invited speakers, other invited NWT facilitators and staff of the Métis Nation Environmental Division
12:00 to 12:45 PM	Reports from breakout groups & questions and answers.	Chaired by William Carpenter

RESULTS

The reports from the breakout discussion groups provided the following points when they dealt with the questions that were classified into the five main categories.

1. Where do people generally go for help and information on contaminants? For contaminant information people turn to:

- Public Health
- Métis Nation Office
- Band office
- Renewable Resource office
- Métis Locals
- Trappers
- Elders
- Schools
- Community Health Representatives (CHRs)
- Nursing station
- RCMP

2. How would people like to receive information?

A clear need for up-to-date information, quicker feed back, and better distribution of information was indicated. Suggestions for channels of information include:

- A published list of contacts where more information may be obtained.
- Distribution in the schools. It is very important that this message reaches the youth; the next generation must be educated in these matters. This was a very strong message from the groups.
- Posters showing esults of research.
- The media, especially local radio and TV, should be used to provide contaminant information. Use programs like Nedaa and Focus North.
- Agencies such as Métis locals, Hunters and Trappers Associations (HTAs), Band offices, Local government, Public health organizations, and schools, should be encouraged to present information at local level.
- Community workshops on specific topics.
- One-on-one dialogue with trappers and elders...very important.

- Local clean-ups should be encouraged to increase public awareness.
- Improved distribution of information is important; reports should be sent to all local agencies.
- Information should be presented in non-technical language or visual or point forms.
- Presentation of facts should be non-judgmental.
- Recommend having an environmental specialist in each region.

3. Where is more information needed?

More information is needed on:

- Traditional foods: are they safe to eat.
- Levels of contaminants in plants and animals?
- If we don't know what the levels are, conduct more testing to determine what they should be.
- How do contaminants move through food chain?
- Why are restrictions put on food consumption?
- How much traditional food can be eaten safely?
- What are the benefits and risks of eating traditional food?
- What can be done to minimize the effects of contaminants?
- What are the procedures for submitting samples for testing?

4. What are the concerns of local communities?

Local communities expressed concerns regarding:

- Contaminants from mine emissions.
- More local responsibility for our own pollution.
- Radionuclides and caribou.
- Needs to be better ways to deal with those who violate the environment.
- Cross-border pollution from pulp and paper industry in Alberta and British Columbia.
- A need for adequate resources (money) so that local people can express their concerns about contaminants
- There need to be more opportunities for community input and consultation.
- There needs to be more involvement of local people in scientific studies on contaminants and greater use of Traditional Knowledge.
- There is concern regarding the security of research information of personal nature, e.g. blood monitoring.

5. Recommendations?

Recommendations made by delegates include the following:

- Progress on international conventions is needed.
- There needs to be an international policy to cut down release of contaminants internationally.
- There needs to be more action on local clean-up.
- People want more input into research.
- Encourage openness about research.
- People need to know where they can complain if there is a problem with research.
- More testing for contaminants is wanted.
- There needs to be more emphasis on individual responsibility.
- Community responsibilities and roles need to be defined.
- More money should be spent on bringing information back to the communities.

Questionnaire Results

During the group discussions, delegates also answered written questionnaires. The following quotes from individual questionnaires represent the trends of thought from the workshop:

- 'It is very important that programs like this keep going so that people are informed on a regular basis. If a study is done once every ten years, nobody learns anything as it is basically forgotten, then we have to start over from scratch every time. Thank you and keep up the good work.' *Samantha Bohnet, Métis Local #66 (Yellowknife).*
- 'I would like to know how you decide what locations to study and for which wildlife species? Where do people go when they have concerns about types of research being conducted.' *Dolly Carmichael, Métis Local #62 (Inuvik).*
- 'This program should be integrated in the school system.' *Lawrence Mercredi, Métis Local #66 (Yellowknife).*
- 'In my community we use lots of fish and caribou and moose meat.' *Rose McNeely, Métis Local #54 (Fort. Good Hope).*
- 'An educational component should be put in place immediately in the schools. Another concern is that biologists are paid high wages to do studies (long term) but when elders do their presentations for example in schools, the education system is reluctant to pay these elders for their time and expertise.' *Steve Lafferty, Métis Local #66 (Yellowknife).*
- 'Should be introduced to the schools. It is important to get our children educated so that they can pass it on to the elders when they talk with them. It should also be introduced to the adults through the newly formed Métis Women's Group.' *Loreen Foye, Métis Local #50 (Ft. Smith).*

DISCUSSION/CONCLUSIONS

1. The foregoing list identifying where people generally turn for contaminants information, represents a consistent response from all discussion groups. A concerted effort should therefore be made by the NCP to reach all of the above agencies and groups with a consistent and co-ordinated message in appropriate non-technical language with program results.

2. The one very strong message from all group discussions was that the contaminant information should be in the schools and that the next generation must be educated in these matters.

3. The obvious final conclusion from the July 1995 Métis Nation Contaminants Communication Workshop at the 23rd Annual Assembly of the Métis Nation–NWT in Hay River, Northwest Territories, was that the AES Northern Contaminants Program is good program in that it has helped to raise community awareness and the program should be continued with the same Aboriginal partnership theme of the existing program.

Expected project completion date: The project has been completed.

CONTAMINANT MONITORING AND COOPERATIVE RISK MANAGEMENT IN THE NORTHWEST TERRITORIES

Project Leader: GNWT Health and Social Services, in collaboration with Mackenzie Regional Health Service, Kitikmeot Health Board, Baffin Regional Health Board, Keewatin Regional Health Board, and the Inuvik Regional Health Board

DESCRIPTION

Resources developed previously under the Northern Contaminants Program by the Department of Health and Social Services, in collaboration with regional health agencies and boards, were evaluated, and selected materials were translated into Inuktitut. The results of this work are summarized below.

CONTAMINANTS RESOURCES AND THEIR AVAILABILITY AND USE IN THE NWT

NWT contaminants resource summary

The NWT Contaminants Resource Summary was prepared to describe the scope of contaminants resources developed by the Department of Health and Social Services (and/or in collaboration with others) that are used in the NWT for communicating about contaminants issues as they may relate to human health. This summary includes information on; type of resource, title, description, purpose, date developed, extent of distribution, location of and attendance at workshops, and languages in which the resource is available.

Inuit Traditional Food Fact Sheets

Feedback on their use in Communities and Regions

The Inuit Traditional Food Nutrition Fact Sheets Series, consisting of 26 fact sheets, was added to the *Contaminants and Your Health* Fact Sheet Binder. This binder was distributed in the summer and fall of 1995 to Regional Health Boards, Community Health Centres, Band offices, Métis Locals and Renewable Resources Offices across the NWT. This series, along with the Dene/Métis Nutrition Fact Sheet Series (also in the binders) provides a more complete representation of nutritional information on NWT traditional foods.

To find out how these fact sheets are being used, whether there are important information gaps (missing food species and/or food uses etc.), and whether the fact sheets are useful in all communities and/or health centres, we asked for feedback on their use from community and regional health workers, and others.

A questionnaire was sent out to members of the NWT Technical Committee on Arctic Contaminants, Regional Nutritionists/Health Promotion Officers, members of the Department of Health and Social Services Contaminants Advisory Group, Regional Environmental Health Officers, Regional Contaminants Program Coordinators, Regional CEOs, Community Health Representatives and/or working group members. We asked for their feedback on the use of the Inuit Traditional Food Nutrition Fact Sheets. People were also asked to identify other resources they were aware of that are being used in communications about contaminants and human health.

We also requested that the questionnaire be forwarded to other people who may use these fact sheets.

Although questionnaire response was limited in numbers, the information received was appreciated and has provided good information on how often and in what ways these fact sheets are being used and has also given suggestions for the development of additional sheets. One of the main weakness identified seems to be that the fact sheets are available in English and Inuktitut but not in Innuinaqtun, which would be useful in working with elders in some communities.

Terminology, Language Development and Glossary Work

Translation of the Inuit Traditional Food Nutrition Fact Sheets Series

The Inuit Traditional Food Nutrition Food Fact Sheet Series was produced by the GNWT Health and Social Services, Community Health Programs, in collaboration with the Kitikmeot, Inuvik, Keewatin and Baffin Health Boards, to provide information on the nutritional benefits of eating traditional foods and to assist in communicating balanced interpretation of the results of contaminants work being done in the Northwest Territories.

Over the 1996/97 period, work done to further contaminants language development and terminology work included the completion of the translation of the Inuit Traditional Food Fact sheets series into the South Baffin dialect of Inuktitut. This was done to improve access by northerners to this information and is consistent with the frequently identified need for health information to be translated into an aboriginal language. Translation began with the 'priority' fact sheets - Seal, Walrus, Narwhal, Beluga, Polar Bear and Arctic Char. The priority fact sheets provided information on the nutritional benefits of eating these foods and were used to assist in communicating a balanced interpretation of the results of the marine mammal Health Assessment released in December 1995. The six priority fact sheets were translated by Sofie McRae and Siobhan Moss in the Baffin Regional Health Board. Translation of the remaining 20 fact sheets was completed by the Inuktitut terminologist Norman Keenianak who had previously participated in and directed the contaminants terminology work at the Cambridge Bay Contaminants Workshop (March 1996).

MARINE MAMMAL HEALTH ASSESSMENT

Health Assessment Sheet #1

A Health Assessment Sheet prototype was developed collaboratively during a two-day meeting of the NWT Technical Committee on Arctic Contaminants in November 1995. This meeting was also attended by a number of invited participants. The development of this Health Assessment Sheet was undertaken in anticipation of the upcoming need to communicate results from the Marine Mammal Health Assessment. Development of this sheet took into consideration the need expressed by NWT northerners, community representatives including CHRs, representatives from Aboriginal organizations and others, for a brief plain language summary of results from health assessments of residue data. Specifically this summary needed to include information on benefits as well as risks, and provide information that was contextualized, meaningful and available for general distribution.

Health Assessment Sheet #1 was developed to summarize the message agreed upon by Inuit representatives, scientists and health representatives in December 1995 in response to the results of the Health Canada Assessment of marine mammal residue data. It was distributed by the GNWT Department of Health and Social Services to NWT Health Boards, who then forwarded it on to Community Health Centres where Community Health Representatives (CHRs) passed this information on to community members. At the same time, this information was circulated through the communication channels maintained by representatives sitting on the NWT Technical Committee on Arctic Contaminants.

At the Nunavut Contaminants Workshop held in Cambridge Bay (March 1996) break-out groups discussed this assessment sheet, its format, content, effectiveness, and extent of its circulation, and provided comments and suggestions to be considered in developing future Health Assessment Sheets. Not many participants had actually seen the health assessment sheet. More participants were aware of the December marine mammal assessment results through radio interviews with Inuit representatives. Those who had heard about the marine mammal results felt comfortable about the information they had: "when we hear we do not panic, we keep eating our foods", but felt they needed to know more about amounts because: "we will still eat our foods", "we have heard the information and we were told not to panic, we still eat the things because of the information...", "I know Inuit have lots of concerns about marine mammals—they're scared to eat them". Others had more specific comments about the sheet: "the contents of this paper is very clear. Things are more scary when you don't know. Now it is less scary."

WESTERN NORTHWEST TERRITORIES AND NUNAVUT CONTAMINANTS WORKSHOPS

Project Leaders: J. MacKinnon and J. Walker, NWT Technical Committee on Arctic Contaminants

Project Team: Michelle Clusiau, GNWT Health and Social Services; NWT Technical Committee on Arctic Contaminants: Bill Carpenter (Métis Nation); Carole Mills (Dene Nation); Valoree Walker (Aurora Research Institute); Richard Isnor (Nunavut Research Institute); Marianne Demmer (Inuit Tapirisat of Canada); Brett Elkin, Jim Sparling, Kelly Robertson, GNWT Renewable Resources; Norm Snow (Inuvialuit Game Council/Joint Secretariat); John Witteman/Murray Swyripa, DIAND; David McKenna, DFO; Paul Latour, CWS; Andy Gilman, Vicki Jerome, Health Canada.

OBJECTIVE

1. To continue the process of human health-related information exchange with Northerners about contaminants.

DESCRIPTION

Participants at previously held workshops have requested:

- more discussion of research projects and their results
- more translation and interpretation of scientific information about contaminants (plain language)
- greater community control over research
- more opportunities for community networking on contaminants issues
- more involvement of various community groups/ individuals in contaminants discussions

Accordingly, the NWT Technical Committee, proposed to organize two workshops: one in the Western Arctic and one in Nunavut.

The membership of this Committee, and a brief description of its focus as presented in the Inuvik Contaminants Workshop Report (June, 1995) is appended.

RESULTS

To continue information exchange activities, the NWT Technical Committee on Arctic Contaminants (NWTTCAC) collaboratively organized the following two workshops during 1995/96.

The Inuvik Region Contaminants Workshop

The Western Arctic workshop—the Inuvik Region Contaminants Workshop—was held June 14–16, 1995. It was hosted by the Inuvialuit Game Council (IGC), and the Gwich'in Renewable Resource Board. The Science Institute of the NWT(Aurora College) organized it, with assistance from various Technical Committee members, and funding from the Arctic Environmental Strategy's (AES) Contaminants and Waters Programs.

Community representatives from Sachs Harbour, Aklavik, Holman, Paulatuk, Tuktoyaktuk, Tsiigehtchic, Inuvik and Fort McPherson participated in the two and one-half day workshop, along with resource people and presenters from Inuvik, Winnipeg, Yellowknife, Ottawa, Montreal, and Cambridge Bay—59 people altogether.

The purpose of the workshop was to:

- exchange information about contaminants with community representatives
- report results of recent AES research activities in the region
- seek recommendations from participants about current and future contaminants- related activities

At the workship, a series of presentations and discussions covered the following topics: introduction to contaminants; benefits of traditional living; introduction to cooperative risk management; results of regional water and sediment studies; results of regional fish and marine mammal studies; contaminants in birds and wildlife; human health monitoring; national and international initiatives; water quality; and waste management.

Recommendations resulting from these presentations and discussions included:

- form a working group of local people, committee representatives and government agencies
- set up a northern based Contaminants Lab run by local people

- involve and train youth in the contaminants field
- involve local people in all aspects of research from start to the final results
- train hunters and trappers in what contaminants to look for on the land
- incorporate traditional knowledge into studies and research
- participate in the First Ministers' Conference in Inuvik in March 1996 and other national and international conferences
- locate and obtain funding for work on contaminants
- set up a computerized information network, and
- distribute a summary report

Conclusions resulting from this workshop included:

- caribou are safe to eat in unlimited quantities
- most of the Arctic's contaminants problems are from pollution that comes from other provinces and countries
- people want to be informed about contaminants issues
- people want to be involved in research and monitoring activities
- there is currently a lack of communication between local people and researchers, industry and government agencies about contaminants
- local people want a say in what studies are done and who will do the studies
- education is needed to train local people to carry out research

A comprehensive report, *Environmental Contaminants Workshop - Summary Report,* was produced and distributed by the Aurora Research Institute.

The Nunavut Environmental Contaminants Workshop

The Nunavut Environmental Contaminants Workshop, the second workshop initiated by the NWT Technical Committee, occurred in Cambridge Bay, March 29–30, 1996.

At the recommendation of the Nunavut Tunngavik Inc., a member of the Technical Committee, this workshop was planned to take place immediately after the Pauktuutit Annual General Meeting (AGM to provide a chance for delegates of the AGM to extend their stay in Cambridge Bay to participate.

This collaborative effort between the Technical Committee and Pauktuutit (the Inuit Women's Association) resulted in a unique opportunity for delegates/participants that would otherwise not have been possible because of the high travel costs of bringing such a group together. Nunavut Tunngavik Inc. managed the logistical details and the financial management of the workshop, which was funded by the Arctic Environmental Strategy's Contaminants Program, the Community Animation Program of Health Canada, Environment Canada, and the GNWT Health and Social Services. Resource people covered their own costs of participating, which made possible such a range of expertise.

Participants at this contaminants workshop included:

- 44 Pauktuutit Delegates—women who had been elected by the women from their communities across Nunavut, Nunavik (Northern Quebec), Labrador and the Western Arctic.
- 5 Members of the NWT Technical Committee on Arctic Contaminants
- 10 Pauktuutit staff from Nunavut, Nunavik and Ottawa
- 20 resource people from Kitikmeot Health Board, Baffin Regional Health Board, Keewatin Regional Health Board DIAND(Ottawa and Yellowknife), GNWT Yellowknife (Language Bureau, Health and Social Services, Renewable Resources),Health Canada, Univ. of Waterloo
- Interested residents from Cambridge Bay

Workshop invitations were sent to regional health agencies, regional Aboriginal organizations and others via membership of the Technical Committee, although it was not possible to offer financial support for their participation.

Simultaneous translation occurred during the entire two-day workshop, both in plenary and small group sessions by four translators.

The purpose of this workshop was as follows:

- to learn about environmental contaminants;
- to discuss contaminants issues, particularly as they relate to people's health in Nunavut, as well as Nunavik, Labrador and the Western Arctic;
- to recommend ways of communicating new information to people
- to identify contaminants terminology that needs interpretation and translation into Inuktitut

To accomplish these objectives, there were presentations on: a general introduction to contaminants; viewing and discussing the videos *"Environmental Contaminants in the North"*, and *"Contaminants and Your Health"*; an overview of the Arctic Environmental Strategy and a circumpolar update; an overview of human health monitoring in the North; an update by the Kitikmeot Contaminants Consultation Working Group; an overview of the health hazard assessment process; and a well-received presentation about Health and the Whole Body—what things affect our health?.

Additionally, there were smaller group presentations and discussions about nutritional values of traditional foods, wildlife, human health, research, terminology, communications, and community action about contaminants.

Recommendations that emerged during the course of the workshop included those to:

- involve Northerners/local people in research activities from the beginning
- ensure that research benefits the participants or the residents of that community
- ensure that communities have ownership and control over the research in the community or within the region
- respect traditional Inuit knowledge and expertise
- consult more and especially with women about health research
- acknowledge where good research is being done and build on it and use it as examples and precedents
- target communications/information toward the youth
- communicate with several groups in each community so that information is widely available
- recognize the importance and need for terminology work to be done to facilitate accurate communications about contaminants in Inuit languages/dialects

Participant feedback indicated the workshop had been a success, with the main concern being a lack of time to fully discuss all their areas of interest. Several participants noted that this the first workshop of its kind that they had attended and were glad to learn more about contaminants and environmental issues.

A workshop Summary Report was produced and translated into English/Inuktitut from notes, flipcharts, and recordings taken at the workshop, and distributed to all who participated.

A limited number of copies of the *Nunavut Environmental Contaminants Workshop Report* are available from GNWT Health and Social Services.

DISCUSSION/CONCLUSIONS

Specific recommendations and conclusions arising from each of these workshops are described above.

Participants from both workshops identified the need for ongoing communications about contaminants with people in communities and regions, and that coming together in the workshop setting is a useful way of exchanging information.

Linking the Nunavut workshop with the Pauktuutit AGM provided an opportunity for participants from all regions in the North to attend the workshop, which would have been out the question otherwise, because of high travel costs. This approach is recommended for future workshops/meetings, when feasible, for the considerable cost savings and opportunities it provides.

Expected completion date: ongoing

REFERENCES

Walker, V. and J. Castleden. 1995. Environmental Contaminants Workshop - Summary Report; Inuvik, NWT, June 12–14, 1995. Aurora Research Institute, Aurora College.

File, P. 1996. Nunavut Environmental Contaminants Workshop Report. Cambridge Bay, NWT, March 29–30, 1996.

DENENDEH ENVIRONMENTAL COMMUNICATIONS STRATEGY

Project Leader: C. Mills and S. Papik, Environment Manager, Denendeh National Office

Project Team: Denendeh Environment Committee (includes representatives/observers from the five regions of Denendeh)

OBJECTIVES

1. To develop a Denendeh Environmental Communications Strategy based on four components: the message, the mode of transmission, the messenger (the source of information) and the recipient.
2. Provide pertinent information to Dene regions and communities on contaminants issues, research and results in a relevant and understandable manner. This includes information and advice on local, specific issues as well as the most current research.
3. Provide information to assist Dene regions, communities and individuals to make informed decisions. This information includes the benefits of traditional living and health advisories.
4. Enable regions and communities to have input into on-going research and results communications, to set priorities and to ask the next set of questions regarding future initiatives.
5. Provide more comprehensive input into existing contaminants committees including international initiatives.

DESCRIPTION

The Denendeh Environmental Communications Strategy (DECS) was developed to promote a better dialogue between the Northern Contaminants Program and Dene communities. As directed by the Science Manager's Committee, the last two years of the Arctic Environment Strategy (AES) have focused on collating research results and communicating the results to Northern communities.

In communication activities, we recognized that it was important to ensure the following:

- the message being received by Northerners, is the same message, regardless of who the messenger is (i.e., Chief, Community Health Worker, Renewable Resource Office, elder, etc.)
- the information given is the information received; in other words, that the message is delivered accurately. This is challenging when communicating across cultures, languages and knowledge systems (traditional knowledge and Western science) .

When the message has great implications on the lives of the recipients, the need for proper communications is emphasized. This is the case for the Northern Contaminants Program. It must communicate information on contaminants, whose presence in the food chain has a direct impact on the lives of the Dene. It is vital that a reliable, trustworthy and respected communications network is available to Dene communities for dealing with contaminants issues. This is the premise for Dene Nation developing the DECS.

This project built on existing structures, knowledge and tools as well as previous work and identified deficiencies in present communications.

This synopsis is for the two fiscal years, 1995/1996 and 1996/1997.

ACTIVITIES/RESULTS FROM 1995/97

Past experience has shown us that the messenger can be as important as the message, especially when the message affects an integral component of the audience's identity.

The most important element in successfully communicating with the communities was the continued support for the Denendeh Environment Committee. This committee has representatives from the five Denendeh regions and provides a trusted venue for the flow of information to and from the communities.

With this in mind, the following components of the DECS were developed through consultation with communities and individuals during workshops, meetings and assemblies. A workshop, "A Dene Environment Gathering: Exploring Kinds of Knowledge for Taking Care of the Land", was held in March. This workshop, which included participation of scientists, youth and elders, resulted in many recommendations on communications of environmental information.

Mode:

a) 1995/1996

The process in which the message should be communicated (in order of success rate) is:

- personally: one-on-one, workshops/meetings
- visually: video-tapes, television
- orally: cassette, radio
- written: "interpreted" briefing notes/summaries
- fact sheets/resource materials
- electronically- most communities are not technically capable of accessing this type of information

b) 1996/1997

- "A Dene Environment Gathering" workshop held March 5–7 1996
- October 1996 workshop
- Elders/Scientists Retreat, February 23–24, 1997
- the Lands & Environment newsletter: "As Long As This Land Shall Last"
- monthly mail-out to the communities on information concerning contaminants, with summaries
- participated in the ICSL Live Broadcast: "The Hidden Price of Progress- Global Pollution in the Arctic" held March 11, 1997

Recipient

a) 1995/1996

Leaders and Elders: When community members receive complex information, they will turn to trusted individuals for their opinions and advice about this information. Traditionally, the Dene have depended on respected individuals such as leaders and elders to provide direction on important decisions. Therefore, we targeted Dene leaders (Chiefs and Councils), elders and trusted resource people (Denendeh Environment Committee) as initial recipients, knowing that they would also act as messengers.

High Consumers of Traditional Foods: The Dene depend on traditional foods for the majority of major nutrients in their diet, as well as for socio-economic reasons, and cultural health.

b) 1996/1997

The recipients of this strategy consisted of the Denendeh Environment Committee, which consists of representatives/observers from each of the five Denendeh regions, regional contaminants coordinators, elders, leaders, youth and northerners.

Messenger

a) 1995/1997

In the community, the recipient receives the message from one of many possible messengers, including media. Regardless of who the original messenger is, people will go to 'alternate messengers' for confirmation of the information they've received. A continuous shift from being a recipient to becoming a messenger occurs through the following pathway:

Northern Contaminants Program→Dene National Office→Denendeh Environmental Committee→Leaders and Elders→Community resource people→individuals

Message

The message delivered by Dene National Office, and alternate messengers, includes a substantial amount of information generated from many sources including the following:

a) General Information on Environment/ Contaminants:

1995/1996

- workshop held in Inuvik (June 1995)
- workshop held in Yellowknife (March 1996)
- quarterly newsletter *"As Long As This Land Shall Last"* detailing various environmental issues including contaminants information
- environmental updates at Annual Assemblies (Deh Cho, Treaty #8, Dene National)
- presentations at community, general and technical sessions of the public hearings for the BHP proposed Diamond Mine in the Lac de Gras area

1996/1997

- hosted a "A Dene Environment Gathering" workshop held March 5–7 1996

Some of concerns raised at this workshop were:

- nuclear contamination levels around abandoned radioactive mines, and the long-term effects that this contamination will have on the environment and the people
- the apparent lack of communication between government and Aboriginal organizations, and the need to work together as one voice for the sake of wildlife management

- a need to look at mining activities in the Fort Fitzgerald area because of the existence of environmental damage
- community concern worried about the safety of drinking water, eating fish, and swimming
- the need to address the human health and environmental impacts in the Pine Point area
- that contaminants are affecting the traditional way of life for the Dene: depletion of animals and birds; contamination of traditional foods; contamination of plant life used in traditional medicines; and contamination of lakes and rivers

b) Specific Contaminants Information:

1995/1996

- interactive television phone-in show on environmental contaminants (November 1995)
- contaminants booklet (Métis Nation)
- contaminants fact sheets (GNWT Health & Social Services)
- contaminants in caribou studies (GNWT Renewable Resources)
- communications process in place in the event of a health advisory
- development of the Canadian Arctic Contaminants Assessment Report
- memos and briefing notes to communities on specific issues (e.g., lead shot ban)

1996/1997

- reviewed draft "Highlights Report" with regional contaminants coordinators in October of 1996
- ICSL television show, March 11, 1997
- sat on the Advisory committee for the "Fort Resolution Domestic Fishing Zone Contaminants Research"
- provided input into "Ideas Workshop" held November 1996
- distributed to all communities, information: on non-toxic gunshots, a summary of the waterfowl advisory
- brought Dene concerns to workshop on "Polonium Dosimetry"

c) Specific Benefits Information:

1995/1996

- developed nutrition fact sheets on priority species in Denendeh (Mackenzie Regional Health Service and Dene Nation)
- nutrition fact sheets on eastern arctic species (GNWT Health & Social Services)
- collection of socio-cultural and economic information on these species
- workshop in Yellowknife (March 1996)
- gathering in Rae to discuss Centre for Nutrition and the Environment of Indigenous Peoples (CINE) Dietary Survey (October 1995)

1996/1997

- reviewed "Dene/Métis Dietary survey" report, distributed report to the Denendeh communities with a summary

d) Interpretation of Information:

1995/1996

- incorporation of Western Science and Dene Science (Traditional Knowledge) (workshop in Rae, October '95 -Dietary Surveys; workshop in Yellowknife, March '96 -Other contaminant research)
- provide information in varying degrees of detail from the highly technical research data through to a one-page fact sheet - some people will be happy with the smaller, summarized document, others will want to see the technical reports (less and less technical)
- balance benefits and risks (NWT Technical Committee Workshop - November 1995)
- translate the less technical documents!

1996/1997

- developed a Paper on "Human Health risk Assessment - review of the Process" —distributed at Ideas workshop
- co-presented "Communicating with Indigenous Communities - The AES as an example" at the International Public Participation Practitioners' Conference
- attempting to bring elders and scientists closer together through Elders/Scientists retreat, February 23–24, 1997

Problems Identified:

The Dene have identified several problems that have occurred or are still occurring in terms of communications of contaminants information. Such problems include the following:

1995/1996

- With all the research done, we still do not have answers to questions such as "What makes the water look and taste different" and "Are the fish safe to eat?"
- Don't do any more monitoring if you can't tell us what the existing levels of contaminants mean regarding the health of the animals and of humans.

- Western language is sometimes too technical and difficult to understand. It is even harder to translate. (need for a glossary of terminology).
- Media sources usually report on contaminant information only when the news is "bad". Unfortunately, this has created unnecessary fear about the safety of traditional food.
- Dene believe that there is no or little balance between Western and Dene Science. The Dene and non-Dene do not understand each other's values.
- Western and Dene Scientists do not work together enough. Elders encourage everyone to respect each other and to respect the animals.

1996/1997

- Mixed messages, for example: fish are okay for metals but maybe not for organochlorines, does this mean that the fish are okay to eat or not?; or messages like, "Contaminants are low, keep eating your food..", while at the same time say communities and regions have differing priorities in regards to contaminants
- The most relevant information on contaminants depends on the resource management

DISCUSSION

The communications strategy has reached many Dene regions and communities who are now better informed on contaminants issues. Therefore, strengthened communications amongst Dene regions and communities will help set priorities for the next set of research to be done after gaps are identified and a thorough evaluation is complete.

1995/1996

Future communications priorities include:

Provide a balanced picture:

- more information on benefits of traditional foods, alternate traditional foods with same nutritional value, effects of cooking technique on contaminant levels, confirmation of safe species/tissues to eat
- broadcast the 'good news' stories
- investigate the contribution of other health confounders (diet, alcohol, smoking, etc.)

Health Risk Assessments:

- include information on what's being done to reduce global levels, how one can reduce individual levels, list of 'alternate messengers', is the picture getting better or worse
- concentrate on research that will improve existing guidelines and look at effects
- revise the process—it takes too long right now

Integrate Western Science and Dene Knowledge:

- communicate Dene values to researchers and government agencies
- facilitate "getting to know each other"—research can only be done together if we trust and respect each other

1996/1997

- laymen's reports on contaminants reports
- interpretations and translation of reports
- results and health assessments must be delivered quickly
- next set of questions for research

CONTAMINANTS COMMUNICATION IN INUIT COMMUNITIES

Project Leader: Peter. J. Usher, Ph. D., Research Director, Inuit Tapirisat of Canada

Project Team: Leonie Kunnuk, Inuit Tapirisat of Canada; Craig Boljkovac, Inuit Tapirisat of Canada; Jamal Shirley, Inuit Tapirisat of Canada; Katie Harris, Eco-Research (Nain Labrador); Joan Killulark, Keewaitin Regional Health Center (Baker Lake, NWT); John Komiak, Keelinik Translation Services (Cambridge Bay, NWT); Allen Kogiak, Renewable Resources (Inuvik); Jacob Partridge, Kativik Regional Government (Kuujuaq, Nunavik); Rachel Qitsualik, Consultant (Ottawa); William Qamukaq, Consultant (Ottawa); J. Mark Stiles, Consultant (Ottawa).

OBJECTIVES

The work undertaken through this project constitutes a crucial step in realizing key, long-term objectives for contaminants communications in Inuit communities. These are:

1. To have relevant, complete, up-to-date and accessible information for Inuit to increase their control over contaminants-related issues and problems, and to assist them in making their own, informed lifestyle decisions. These may include, for example, more pressure on government and industry from the grassroots for preventing the generation of contaminants at their sources; making choices about preparing and eating country food in certain ways, and educating others about contaminants.

2. To develop the capacity among front-line communicators in Inuit communities to answer questions and serve as sources of knowledge and wisdom on contaminants-related matters.

More specifically, the objectives of this project are:

1. To develop, in cooperation with the Inuit regions a set of communications materials designed to address key contaminants related information needs.

2. To give Regional Project Officers within a number of Inuit communities the necessary tools to further their work in the contaminants field.

DESCRIPTION

Designing Regional Information Modules

The development of detailed community-specific information materials regarding contaminants was undertaken with the direct involvement of Regional Project Officers (RPOs) from all six Inuit regions of Canada. These RPOs designed and drafted a set of contaminants information modules, which were refined and tested by the RPOs at a workshop held in June, 1996 (see below) and later in their home communities. The modules consist of the following:

1) A glossary of key contaminants terms in English and Inuktitut. The glossary defines 12 key contaminants terms in a clear and sensitive manner. It is based on experiences on the development of other such glossaries (such as the Baffin Regional Health Board and the GNWT Department of Renewable Resources) and the experiences of a number of the project officers. It is currently being reviewed by Rachel Qitsualik, and will soon be finalized and distributed to translators in the North and in southern Canada.

2) Short information sheets outlining key contaminants of local concern in the Keewatin and Labrador regions. These included PCBs, pesticides, and ultraviolet radiation for the Keewatin. For Labrador, the contaminants of concern were asbestos, lead, uranium and PCBs. These contaminants had been identified by the RPOs as being of primary concern in their communities and regions.

3) A series of short articles describing contaminants in the environment. John Komak worked with Jamal Shirley of ITC to explain where contaminants come from, how they get into the food chain, their possible effects and controls. The first article, entitled "Arctic Contaminants: What are they and where do they come from"

was recently published in Nunavut's *Nunatsiaq News,* which has an extensive readership in the North. The second article, which has been submitted to a number of newspapers for publication, addresses the possible health effects of contaminants, documents what has been witnessed in Inuit and other aboriginal communities, and discusses what can be done at the local level to deal with the general problem of contaminants in the Arctic.

4) A television interview script on contaminants in the Northern environment. The script, which was developed with ITC by Jacob Partridge in Nunavik, is intended as a template for use across the north. It explains:

- how contaminants get into the food chain
- some of the effects which contaminants-related research has had on Inuit communities
- who is doing what and why with regard to contaminants
- suggestions as to how Inuit could view the benefits and costs of country food consumption

5) An educational curriculum for Kindergarten to Grade 7 concerning contaminants in the Northern environment. Modelled on the Canadian Wildlife Federation's "Project Wild", this curriculum provides an interactive set of lessons designed to teach students vocabulary, relevant contaminants such as how food chain processes work and where contaminants come from. Alan Kogiak, the project officer, cited examples relevant to his home region, the Inuvialuit region of the Western Arctic.

6) A guide to making presentations in Northern Communities. Prepared with the assistance of Mark Stiles, it is intended for use by environmental scientists and health professionals in presenting information to aboriginal groups. It also serves as a training resource. The guide is currently undergoing a peer review by a selection of NCP scientists and other interested professionals.

PRE-TESTING AND PREPARATION: 1996/97

From June 4 to 7, 1996, four of the RPOs attended a workshop with ITC staff to begin finalizing their modules. At the meeting, materials were assessed for technical accuracy and necessary revisions were suggested. Members of Ottawa's Inuit community participated with the RPOs in a two-day session which pre-tested contaminants information and messages focusing specifically on the RPOs' work. This pre-testing was key in ascertaining the lay person's comprehension of the materials' key messages, and its results were very encouraging.

The RPOs left the workshop with the necessary tools to continue pre-testing in their home communities. In addition, they have identified the tasks for final production and distribution of their information modules. Jamal Shirley of ITC is currently assessing the RPOs' technical revisions and pre-testing results and is finalizing the materials for distribution in the communities they were meant to serve.

An information package consisting of the RPOs' information sheets is currently being prepared and will be distributed to community health representatives (CHRs), hunter and trapper associations (HTAs) and Hamlet offices across the North.

DISCUSSION/CONCLUSIONS

It appears that the activities undertaken through this project will meet the near-term objectives outlined above. In fact, one RPO has been appointed to a regional contaminants committee; another has conducted a series of radio spots on contaminants; and all have indicated they are interested in increasing their knowledge and capacity to communicate about contaminants issues.

This project has helped Inuit organizations prepare for greater regional participation in the contaminants field. This is consistent with the endorsement by the Science Managers Committee of the NCP in further developing capacity at the regional level with regard to contaminants.

This project is just one step towards realizing a future in which Inuit are adequately empowered regarding the contaminants issue, but important lessons have been learned in how to communicate with communities which, it is hoped, can be repeated elsewhere in the future.

Expected Completion Date: March 31, 1997.

ITC'S SIXTH ANNUAL NORTHERN ENVIRONMENT WORKSHOP: FEBRUARY 9–11, 1997 IQALUIT, NWT

DESCRIPTION

1. Workshop Goals

The following objectives guided all planning and preparation for the workshop:

- to allow Inuit from across Canada to share information and ideas with each other and with ITC on how to address current environmental issues of concern in the North.
- to establish and strengthen environmental communications links between Canada's Inuit regions
- to assist regional representatives in strategic planning for environmental protection, conservation and management by providing timely and accessible information on key issues
- to provide a forum for regional representatives to discuss and influence the content and scope of ITC's future research activities.

2. Workshop Discussion Topics

Discussions at the workshop focused primarily, but not exclusively, on the four following subject areas:

Communicating About Contaminants:

i) Global pollution reaching the Arctic: After years of research, how successfully has this problem been communicated? What is still needed to improve community level understanding of global pollution in Arctic food chains?

ii) What might improve the current policies and processes for assessing health risks posed by contaminants in country food, and for determining acceptable levels of contaminants in human blood? How should health related advice and information be crafted and communicated? Who should be responsible for this?

Fur and Harvesting:

i) The European Union's Humane Trapping Standards Agreement: what are its implications for the fur industry in general and Aboriginal trappers in particular?

ii) The International Sealing Industry: What are the remaining barriers to its revitalization and how should Inuit confront these?

iii) Article 8j of the United Nations' Convention on Biodiversity: How should traditional knowledge best be incorporated into conservation principles and practice?

Climate Change:

i) International Context: What is being done at the international level to address climate change? What role can and should Canadian Inuit play in international protocol development aimed at reducing global greenhouse gas emissions?

ITC's role as a Co-ordinating Body on Environmental Issues:

i) What are the most effective ways ITC can work with Canada's six Inuit regions in addressing environmental issues of concern? What significant activities does ITC plan for the future?

3. Outcome

Delegates to ITC's Sixth Annual Environment Workshop were extremely pleased with its outcome. Discussions on all the subject areas outlined above were active, creative and highly participatory, involving all those present. In their discussions, delegates identified and shared their knowledge about the areas most in need of improvement. Likewise, they agreed on clear and practical ways to address some pressing environmental challenges faced by Canada's Inuit. Unfortunately, delegates from the Kivalliq, Kititkmeot and Inuvialuit regions were unable to attend the workshop due to bad weather, but Labrador, Nunavik and the Baffin were strongly represented alongside ITC, ICC, Pauktuutit, the Arctic Council and the Nunavut Wildlife Management Board (NWMB). A complete list of attendees, and a final report of the workshop's proceedings is available from ITC.

4. Products

- Final Report of Workshop Proceedings
- All briefing materials (English and Inuktitut)

V QUALITY ASSURANCE

INTERLABORATORY QUALITY ASSURANCE PROGRAM FOR ANALYTICAL DATA PRODUCED BY THE NORTHERN CONTAMINANTS PROGRAM RESEARCH PROJECTS

Project Leader: Dr. Jiping Zhu, JP Ztech Company

Project Team: Members of Quality Assurance Sub-committee, AES
All laboratories in the Northern Contaminants Program

OBJECTIVES

Short-term:

1. To conduct interlaboratory comparisons on various contaminants among participating laboratories.

2. Analyse sampling procedures and associate uncertainties related to total 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 Northern Contaminants Program; and,

2. Provide a scientifically sound base to evaluate the data quality of the Northern Contaminants Program.

DESCRIPTION

This project is aimed at identifying sources of measurement uncertainties and variation of analytical results to provide information on data quality to the Northern Contaminants Program (NCP). The project focuses on interlaboratory comparison exercises. Laboratories participating in projects under the NCP analyse a wide range of contaminants in various matrices and species.

A siginificant amount of analytical work was performed in 1996/97 for human health and country foods data, which have very rigorous demands for quality and comparability of analytical data. It is important to link the comparability of human health and country foods data to the other analytical data through interlaboratory comparisons among NCP laboratories. This is particularly important to estimate the bioaccumulation of contaminants in the human body from its surroundings. Evaluation of data quality and its impact on overall NCP program conclusions/results is essential to translate the research findings of the NCP to the public, and to the northern communities in particular.

ACTIVITIES IN 1996/97

Interlaboratory comparison on PCBs and OCs in solution was conducted as the continuation of previous years activities to monitor quantification standards and laboratory performance. The selection of congeners was the same as in previous years. The check sample for this year's interlab comparison contained both PCBs and OCs in one single solution to reflect the fact that in real environmental samples, PCBs, and OCs co-exist in many instances. The standard was analysed with laboratory clean-up and separation procedures.

Results of the second international round-robin on toxaphene in cod liver, which had been conducted by Dr. Paul Andrews of Health Canada in 1996, were examined and evaluated in the context of the NCP. The use of raw data for NCP projects was permitted by Dr. Andrews.

RESULTS

The analytical results are summarized in Table 1. A total of 26 laboratories, six of which are associated with the NCP (NCP laboratory), reported analytical results. An extremely high value of PCB 31 (1.64 instead of 0.164 ng/uL) initially reported by Lab 4 was found to be a computing error in their data processing. The value of

Table 1: NCP Intercomparison Results of PCBs and OCs (ng/μL) - 1996/97

Compound	Assigned Value	Lab1	Lab2	Lab3	Lab4	Lab5	Lab6	Mean	S.D.	%RSD
1245-Tetrachlorobenzene	0.28	0.32	NA	0.26	0.31	**NA**	0.30	0.30	0.03	8.7
Pentachlorobenzene	0.41	0.35	0.37	0.54	0.44	0.45	0.47	0.44	0.07	15.9
Hexachlorobenzene	0.83	0.76	0.62	0.70	0.91	0.99	0.82	0.80	0.14	17.1
a-HCH	0.51	0.43	0.54	0.34	0.49	0.78	0.52	0.52	0.15	28.6
β-HCH	0.50	0.46	0.43	0.47	0.50	0.38	0.62	0.48	0.08	17.0
γ-HCH	0.35	0.36	0.38	0.40	0.34	0.21	0.34	0.34	0.07	19.9
p,p'-DDD	0.33	0.30	0.35	0.45	0.30	0.46	0.28	0.36	0.08	22.5
p,p',-DDE	0.84	0.80	0.78	0.64	0.93	0.75	0.95	0.81	0.12	14.3
p,p'-DDT	0.27	0.24	0.31	0.16	0.23	0.35	0.26	0.26	0.07	25.4
Heptachlor	0.29	0.34	0.30	0.33	0.23	**NA**	**NA**	0.30	0.05	16.2
cis-Chlordane	0.45	0.41	0.43	0.39	0.42	0.43	0.48	0.43	0.03	7.2
trans-Chlordane	0.58	0.56	0.56	0.56	0.52	0.54	0.63	0.56	0.04	6.5
cis-Nonachlor	0.26	0.15	0.28	0.32	0.42	0.34	0.25	0.29	0.09	31.2
trans-Nonachlor	1.20	1.10	1.04	1.26	**2.51**	1.60	1.15	1.23	0.18	14.8
Mirex	0.23	0.22	0.24	0.22	0.27	0.30	0.29	0.26	0.04	13.7
Photomirex	0.59	**NA**	0.64	0.71	0.58	0.74	0.56	0.65	0.08	12.3
Dieldrin	0.45	0.42	0.47	0.60	0.43	0.20	0.37	0.41	0.13	31.6
Heptachlor epoxide	0.92	0.77	1.17	0.96	0.88	0.81	0.85	0.91	0.14	15.9
Oxychlordane	0.81	1.10	0.78	0.90	0.72	**ND**	0.89	0.88	0.15	16.6
PCB 28	0.49	0.45	0.49	0.46	0.19	**Co-el**	**Co-el**	0.40	0.14	35.2
PCB 31	0.23	0.15	0.20	0.25	0.16	**Co-el**	**Co-el**	0.19	0.04	23.4
PCB 28+31	0.72	0.60	0.68	0.71	0.35	0.57	0.50	0.57	0.13	23.1
PCB 74	0.26	0.30	0.27	0.32	0.29	0.40	0.26	0.31	0.05	16.5
PCB 99	0.27	0.22	0.23	0.27	0.32	0.25	0.28	0.26	0.04	14.2
PCB 105	0.28	0.29	0.30	0.31	0.21	0.38	0.17	0.28	0.08	27.2
PCB 118	0.32	0.33	0.29	0.36	0.33	0.49	0.31	0.35	0.07	20.4
PCB 138	0.32	0.28	0.30	0.41	0.33	**Co-el**	0.31	0.33	0.05	15.5
PCB 158	0.08	0.08	0.08	0.10	0.04	**Co-el**	0.08	0.08	0.02	28.1
PCB 138+158	0.39	0.36	0.37	0.51	0.37	0.49	0.40	0.42	0.07	15.8
PCB 149	0.25	0.27	0.28	0.32	0.29	**ND**	0.30	0.29	0.02	6.8
PCB 153	0.34	0.35	0.35	0.43	0.33	0.55	0.36	0.40	0.08	21.0
PCB 156	0.22	0.22	0.23	0.32	0.22	0.43	0.20	0.27	0.09	33.3
PCB 170	0.13	0.12	0.17	0.12	0.18	0.18	0.17	0.16	0.03	18.1
PCB 180	0.26	0.27	0.26	0.35	0.31	0.28	0.30	0.29	0.03	11.2
PCB 187	0.26	0.21	0.24	0.29	0.26	0.31	0.25	0.26	0.04	13.8
PCB 194	0.27	0.21	0.25	0.36	0.24	0.26	0.22	0.26	0.05	21.1

Values in bold are not included in statistic calculation
NA: not analysed
ND: not detected
Co-el: co-eluting peaks

trans-nonachlor (2.51 ng/μL) from Lab 4 was significantly different from other laboratories, and therefore was not included in the statistical analysis of the data. Lab 5 did not detect oxychlordane and PCB 149 in the check solution. They also reported combined values only for PCB 28 and PCB 31, and for PCB 138 and PCB 158. The combined value for PCB 28 and PCB 31 was reported by Lab 6 as well.

Most of participants used either ECD (12 laboratories) or ECNI-MS (8 laboratories), or both detectors (4 laboratories). Only one laboratory used high resolution MS, and another used MS-MS as the detector. For the purposes of interpreting the round-robin results, a laboratory using both ECD and ECNI-MS is considered as two laboratories. The total number of laboratories in this report is therefore 30. Of the six NCP laboratories participating in the round-robin, only two reported values of the individual toxaphene congeners. Table 2 summarizes the mean values and %RSDs of total toxaphene and individual congeners in unknown solution, cod liver oil and adipose tissue among the NCP laboratories and all participating laboratories respectively.

DISCUSSION/CONCLUSIONS

The interlaboratory comparison results of PCBs and OCs this year showed %RSDs in the range of 15% to

Table 2: Analytical results of second international round-robin on toxaphene: comparison of mean values and %RSDs between AES labs and all participating labs

	Total toxaphene	#26	#32	#50	#60
Unknown solution					
All labs		68.9 (40)*	61.7 (41)	43.8 (27)	51.5 (30)
AES labs		76.3 (25)	64.2 (20)	46.5 (15)	54.1 (17)
NIST 1588 cod liver oil					
All labs	4.93 (59)	0.47 (178)	0.12 (258)	0.51 (149)	0.36 (159)
AES labs	3.72 (22)	0.54 (169)	0.07 (107)	0.33 (27)	0.19 (60)
Adipose tissue					
All labs	54.9 (68)	4.39 (166)	1.06 (224)	6.48 (91)	2.05 (121)
AES labs	62.0 (36)	3.24 (24)	0.31 (77)	5.83 (32)	1.10 (52)

* Mean value with %RSD in ( ). The zero number and one total toxaphene value in adipose tissue (1114 µg/g) were excluded from statistical calculation.

30% for most PCBs and OCs. This degree of variation is consistent with the results from previous years (Zhu 1993, Zhu 1994a, Zhu 1995). The %RSDs of interlaboratory comparisons on PCBs and OCs in solution obtained in 1994/95, 1995/96 and this year (1996/97) are illustrated in Figure 1. With the exception of PCB 74 and PCB 28+31, the %RSDs of all compounds in the three interlaboratory comparisons were generally below 30%. The means of the three comparisons were 10% to 25%. OC compounds had more consistent mean %RSD values than the PCB congeners.

The mean values of the target compounds obtained from this intercomparison were in good agreement with the assigned values which was calculated from the quantity of each compound added to the check solution. The correction between the two, expressed as R^2 was 0.9734 (Figure 2). In general the difference between the mean value and the assigned value for majority of compounds was within 10%. Since PCBs and OCs are the two major groups of contaminants in the North, the interlaboratory comparisons on PCBs and OCs in solution should be conducted on a yearly basis to continue monitoring performace of NCP laboratories on these two groups of contaminants.

The %RSDs of unknown solution in the toxaphene round-robin were about 15% to 25% among the six NCP laboratories compared to 30% to 40% among all participating laboratories. The mean value of total toxaphene in NIST 1588 sample from the NCP laboratories was 3.72 ppm with an RSD of 22%, compared to a mean value of 4.93 ppm with 59% RSD from all participating laboratories. NCP laboratories also demonstrated relatively good precision for congeners #50 (%RSD = 27) and #60 (%RSD = 60) in NIST 1588 cod liver oil sample. For the adipose tissue sample, NCP laboratories obtained good precision for the total toxaphene value (%RSD = 36) and two individual congeners (%RSD = 24 for #26 and 32 for #50).

Results of the first and second international round-robins on toxaphene showed that the analytical precision among participants remained the same in the past four or five years (Zhu 1997, Zhu 1994b, Andrews 1995). Since the last two international round-robins have provided useful information for assessing the interlaboratory variation of toxaphene data for the NCP, there is no further need to conduct our own interlaboratory comparison of toxaphene for NCP program.

At least one computing error in data reduction was discovered in this interlaboratory comparison. A similar error in data processing had been noticed in previous intercomparisons as well (Zhu 1995, Zhu 1994c). This emphasizes the importance of quality assurance measures in data reporting including independent data review.

Expected project completion date: March 31, 1997

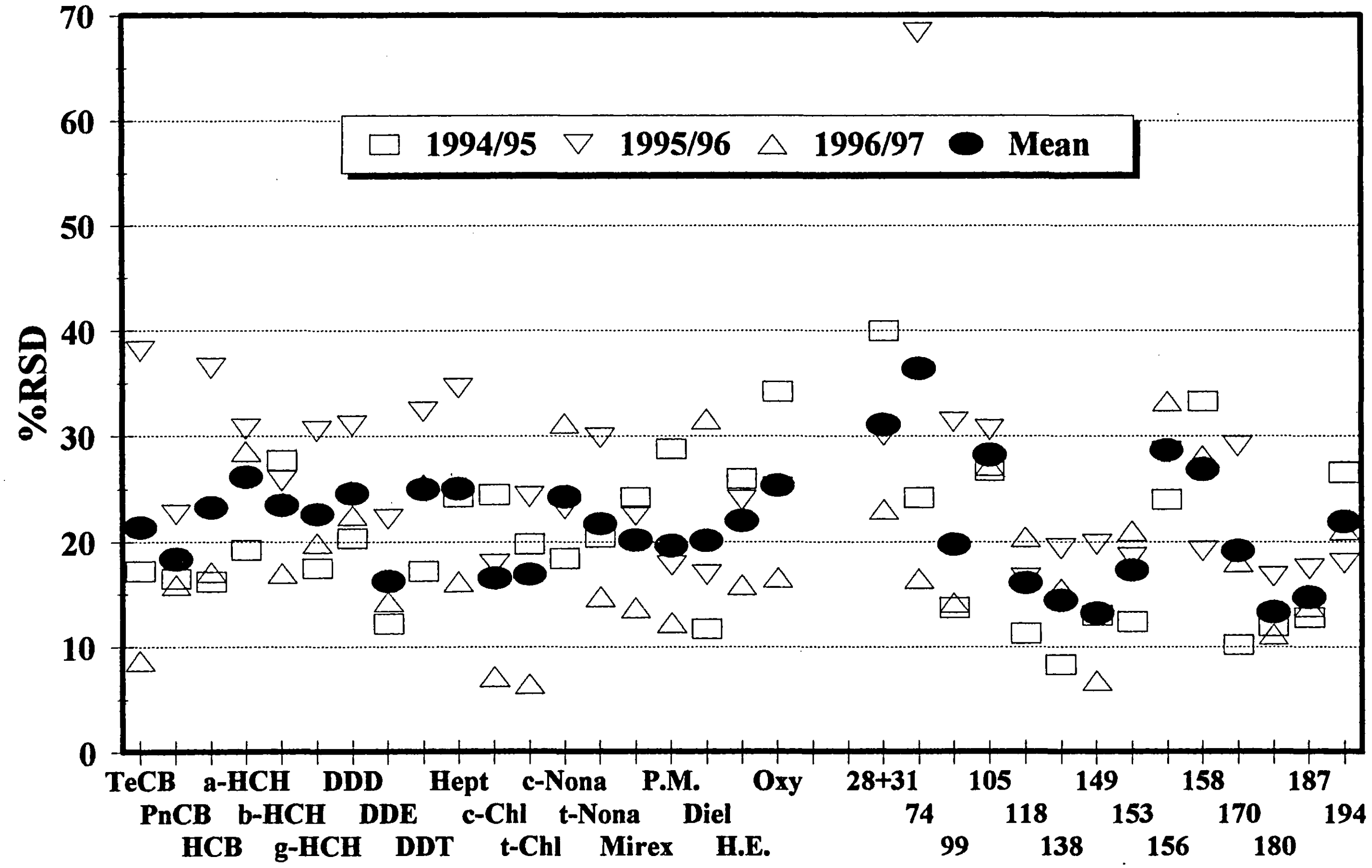


Figure 1. Relative standard deviations of PCBs and OCs in solution: Summary of three years' interlaboratory comparison results.

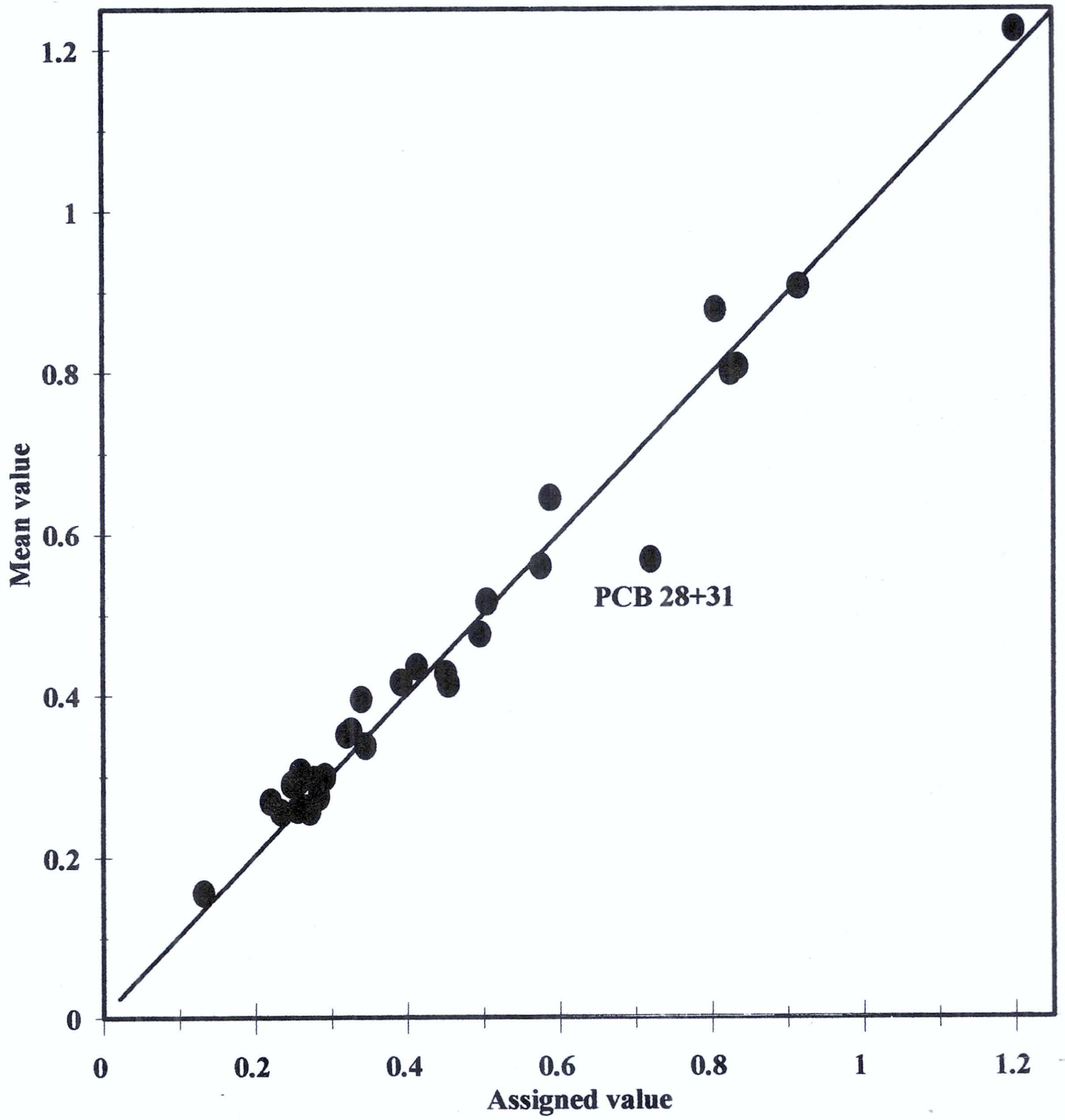


Figure 2. XY graph of mean values of PCBs and OCs in solution from participating laboratories and assigned values.

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