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Occurrence of Polychloro-*n*-alkanes in Canadian Mid-latitude and Arctic Lake sediments

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ABSTRACT

Sediment cores from 4 lakes in Canada ranging from 49°N to 81°N, were analyzed for polychloro-*n*-alkanes (PCAs), with the intent of: (1) examining depositional trends with increasing latitude, and (2) studying the historical profiles of dated sediment slices. Concentrations of total PCAs in surface sediments from Lake Winnipeg (50°N/96°W, Manitoba) and Hazen lake (81°N/71°W, High Arctic) were 176 and 4.5 ng/g (dry wt.), respectively; corresponding surficial fluxes were 147 and 0.9 ug/m^2 yr. The high flux of PCAs to Lake Winnipeg suggests local contamination. In fact, PCAs were detected in water collected from the Red River, a river that discharges into the southern basin of Lake Winnipeg, ranging from 16 to 55 ng/L. The surficial flux of PCAs to Fox lake (61°N/135°W), a sub-arctic lake in theYukon, was also high, 34 ug/m^2 yr, but much lower in Lake Nipigon (49°N/89°W, N.Ontario), 3 ug/m^2 yr. PCA profiles showed maxima in sediment slices dated from the early 1980s to the 1990s. The detection of PCAs in lakes from both populated and remote regions suggests that these organochlorines, which are the components of commercial chlorinated paraffins (CPs), are widespread trace contaminants of freshwater environments in Canada. The change in congener profiles with increasing sediment depth observed in sediments from Fox lake and Lake Winnipeg suggests that biodegradation is occurring.

INTRODUCTION

Commercially produced PCAs, of the general formula $C_nH_{2n+2-z}Cl_z$, have carbon chain lengths from C_{10} to C_{30} and chlorine content from 30 to 70% by mass. Also known industrially as chlorinated paraffins, they are formed by direct chlorination of *n*-alkane feedstocks with molecular chlorine under forcing conditions. These reactions, which have low positional selectivity, yield complex formulations consisting of mixtures of optical isomers and congeners. Owing to varying carbon chain length and chlorine percentages, PCAs provide a range of properties for different applications. The extent, and conditions, of chlorination used depend ultimately on the desired application.

In Canada, PCAs are classified as Priority Toxic Substances under Canada's Environmental Protection Act (CEPA), and in the U.S., have been placed on the Environmental Protection Agency (EPA) Toxic Release Inventory (TRI). Presently, PCAs represent the largest group of high molecular weight chlorinated hydrocarbons produced in Western Europe and in

North America, and are among the last industrially produced high molecular weight organochlorine compounds in North America [1].

Of particular interest are the C_{10}-C_{13} PCAs, which have the greatest potential for environmental release and appear to exhibit the highest toxicity. Because of their environmental mobility, persistence and almost ubiquitous appearance in industrialized countries, there is a risk that these compounds may in fact have adverse effects on terrestrial and aquatic organisms and on humans [2]. C_{10}-C_{13} PCAs have even been detected in Arctic marine mammals and in air samples from northern Ontario [3]. In a recent study, researchers in Sweden have found that the C_{10}-C_{13} PCAs inhibit intercellular communication in rat liver epithelial cells, a phenomenon which suggests that these chemicals may be acting as tumour promotors [4].

To date, there has been limited information on the behavior of these compounds in the environment. This is due both to a lack of published analytical methods for their analysis, and hence unreliable determination of environmental levels, and to the limited knowledge on their physicochemical properties.

Recently, Tomy *et al.* (1997) reported a highly specific and sensitive method for quantifying PCAs [5]. ΣPCA levels in biota and sediment samples from the Detroit River were estimated to be 1148 ng/g (wet wt.) and 288 ng/g (dry wt.), respectively.

We report here on the historical profiles and fluxes of ΣPCAs to lake sediments ranging from 49°N to 81°N. Variation in formula group ion profiles for sediment slices from a few lakes will also be discussed. ΣPCA concentrations will also be compared to those of other organochlorines (OCs).

EXPERIMENTAL

Sediment Extraction and dating. Sediment cores, collected using a KB corer (10 or 16 cm diameter), were sliced at 1 cm intervals and kept at 0°C to -10°C. Extractions were performed as described by Muir *et al.* [6]. Excess ^{210}Pb and ^{137}Cs profiles were used to calculate the median age of each core slice. Sedimentation rates were calculated from a simple linear model by assuming a constant ^{210}Pb flux, and focusing factors based on latitude specific atmospheric fluxes of ^{210}Pb [7].

Quality Control. Reagent blanks consisting of solvents and extraction thimbles/glassware were analyzed to check laboratory contamination. Where possible, samples from *pre*-1900 slices were also analyzed from each site to examine possible contamination from sample collection and handling.

Mass Spectrometry. ECNI was performed on a Kratos Concept HRMS (*EBE* goemetry) controlled by a Mach 3 data system. Selected ion monitoring (SIM) was performed at a resolving power of ~12 000, with a cycle time of 1 sec for each window, and equal dwell times for each ion monitored. Argon was used as the moderating gas and PFK as the mass calibrant. Optimum sensitivity was obtained at a gas pressure of ~ 2×10^{-4} torr as recorded by the source ion gauge. The electron emission current was 100 µA, the initial electron energy was ~ 180 eV, and the ion accelerating voltage was 5.3 kV. The ion source temperature was maintained at 120°C.

Formula group profiles. The generation of SIM chromatograms has been described previously [5]. In brief, the MS, operating in the SIM mode, is tuned to monitor the two most intense ions in the $[M-Cl]^-$ cluster, one for quantitation and the other for confirmation, for the following formula groups in their respective homologue groups: C_{10} (Cl_5 to Cl_{10}), C_{11} (Cl_5 to Cl_{10}), C_{12} (Cl_6 to Cl_{10}) and C_{13} (Cl_7 to Cl_9). Retention time windows are also used to improve the efficiency of SIM. Profiles are generated by correcting the electronically integrated ion signals for each formula group for isotopic and response factors and then plotting them in a bar graph format.

Method of Quantitation. Visual inspection of these graphs, which are created for the sample(s) and standard, then allows us to: (*i*) select the most intense ion (corresponding to the most abundant formula group) for which the quantitation is based, and (*ii*) apply correction factors which account for variations in the abundances of formula groups in the standard and sample. Further details of the method are described elsewhere [5].

Gas Chromatography. Analyses were performed on a Hewlett-Packard (HP) 5890 Series II gas chromatograph, fitted with a high resolution DB-5 fused silica column (30 m x 0.25 mm i.d., 0.25 μm film thickness), connected to the mass spectrometer through a heated transfer line maintained at 280°C. All sample injections were made by a CTC A200SE autosampler under data system control. The injector port temperature was 220°C and helium carrier gas flow rate of 0.75 mL/min was maintained by an electronic pressure program. The column temperature program was: initial 150°C; hold for 1 min; ramp to 260°C at 7°C min^{-1}; hold for 8:18 min; ramp to 280°C at 10°C min^{-1}; hold for 13 min.

RESULTS and DISCUSSION.

The concentration profiles of sediments from the four lakes under investigation are shown in Figure 1. The most important observation that can be made regarding PCAs in these sediments is that they are *present*; even in sediments from the most northerly site, Lake Hazen, which is situated at the northern end of Ellesmere Island.

The high ΣPCA levels in surface slices were observed in Fox Lake (257 ng/g dry wt.). Compared to other OCs, ΣPCAs are 8 times higher than ΣPCB (31 ng/g), 100 times higher than ΣCHB (chlorobornanes) (2.1 ng/g) and an order of magnitude times higher than ΣDDT (0.01 ng/g) [8,9]. The high concentration of ΣPCAs in Fox lake, which is adjacent to the Alaska Highway, suggests contamination by point sources, although actual sources for PCAs are not known.

ΣPCA concentrations in surface sediments from Hazen lake (4.5 ng/g) were 2 times higher than ΣPCB (2.42 ng/g), 5 times higher than toxaphene (CHB) (0.9 ng/g) and 20 times higher than ΣDDT (0.2 ng/g) [6,10]. The remote location of this lake and the low levels of ΣPCAs, as well as other OCs, imply that long range atmospheric transport is the only mode of input of contaminants to this lake. The decline of ΣPCA in older sediment slices, however, is not apparent, and may be due to diffusion of PCAs into the sediment bed because of the low sedimentation rate of this lake.

The focus corrected surface fluxes of ΣPCA (ng/m^2 yr) and other OCs for the lakes studied are shown in Table 1. The high flux of PCAs to Lake Winnipeg suggests local contamination. In fact, PCAs were detected in water collected from the Red River, a river that discharges into the southern basin of Lake Winnipeg, ranging from 16 to 55 ng/L [5]. The flux of ΣPCA to Lake Winnipeg was 4 times higher than that of Fox lake and 55 times higher than Lake Nipigon. The surface flux of ΣPCA to Hazen lake was also lower, 200-fold, than that in Lake Winnipeg.

PCA concentrations in all the lakes studied were highest for sediment slices dated from the 1980s and 1990s, which is consistent with the usage patterns of CPs. Further inspection of the formula group profiles for sediments from Fox lake revealed that ΣC_{10} and ΣC_{12} congeners in the top slice accounted for 31 and 19% of the ion current, respectively. Further down the sediment bed (slice 9), however, we observed that the relative abundance of ΣC_{10} congeners accounted for 46% of the ion current, while the ΣC_{12} decreased to 9%. Similar observations were observed for the Lake Winnipeg slices, although the variation is less pronounced. These observations would suggest biodegradation is occurring in these sediments.

Table 1. Focus corrected fluxes of ΣPCAs (ng/m^2 yr) and characteristics of the lakes studied.

Lake	Sed. rate (g/m^2 yr)[a]	Focusing Factor[b]	Conc. of ΣPCAs in surface slice (ng/g dry wt.)	Surface Flux (ng/m^2 yr)[c]			
				ΣPCA	ΣPCB	ΣCHB	ΣDDT
Winnipeg	1000	1.2	176	146666	27500	2733	500
Nipigon	411	2.83	18	2658	6405	298	171
Fox	126	0.95	257	34086	4155	280	1.3
Hazen	278	1.4	4.5	893	340	120	5

[a] Sedimentation rates were calculated using a linear model which assumes a constant ^{210}Pb flux and constant dry-mass sedimentation rate [7].

[b] Focusing factors were calculated using latitude-specific atmospheric fluxes of ^{210}Pb.

[c] Surface flux = (sedimentation rate x conc. in surface slice) / (focusing factor)

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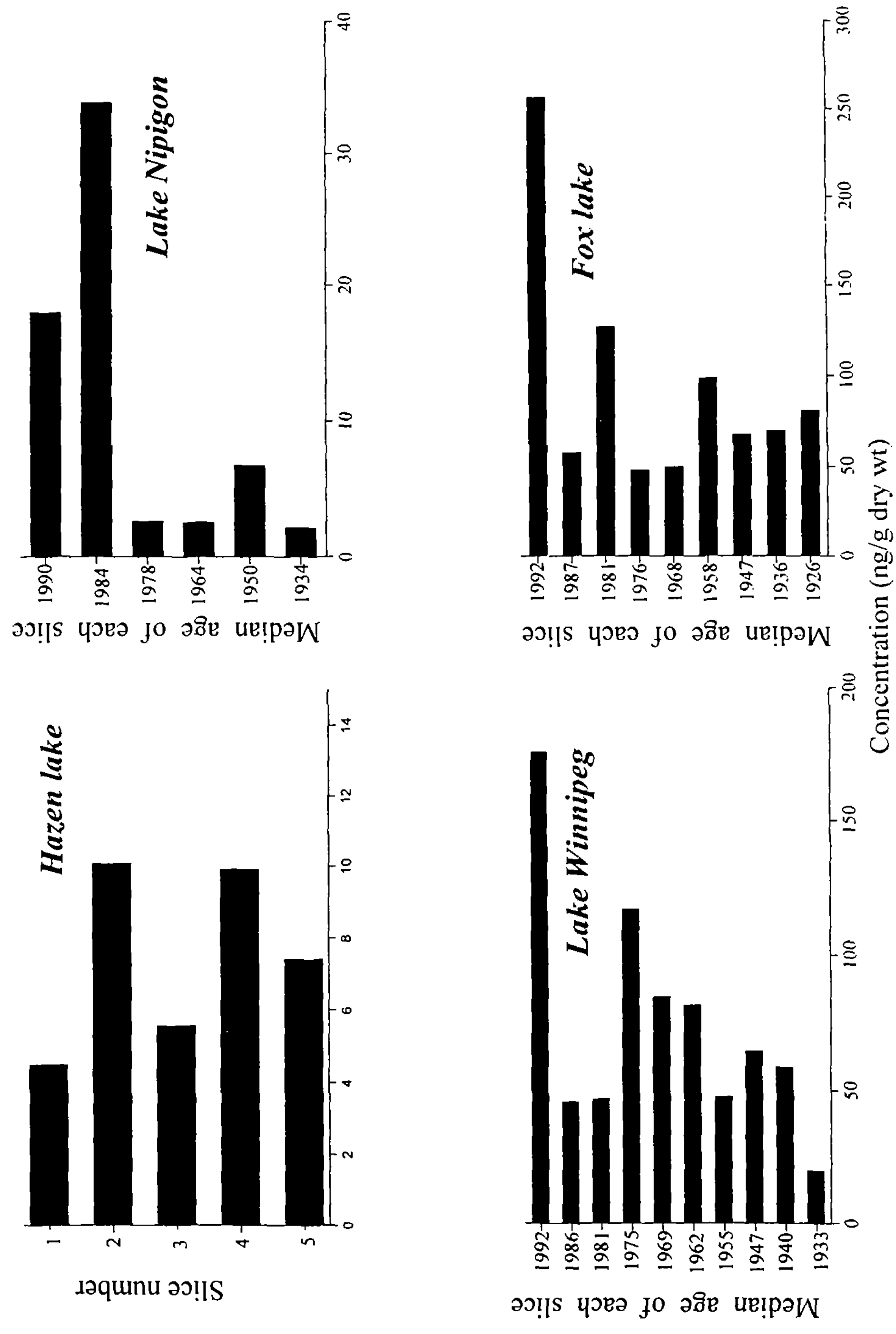

Figure 6.1 Concentration (ng/g dry wt) profiles of ΣPCA in lakes from Canada. Dates are median ages of each slice determined by ^{210}Pb. Sediment slices from Hazen lake have yet to be dated.