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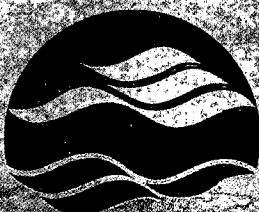
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**VARIATIONS IN THE STABLE ISOTOPE  
COMPOSITION OF MERCURY IN SEDIMENT  
SEQUENCES AND ORGANISMS IN  
NORTHERN LAKES**

**T.A. Jackson, D.C.G. Muir, and M.S. Evans**

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Environment Canada**

**NWRI Contribution No. 04-369  
National Water Research Institute  
Burlington, Ontario  
2004**

**FINAL REPORT ON A RESEARCH PROJECT SUPPORTED BY A NORTHERN  
ECOSYSTEM INITIATIVE (NEI) GRANT IN THE FISCAL YEAR 2002-2003**

1. **TITLE:** Variations in the Stable Isotope Composition of Mercury in Sediment Sequences and Organisms in Northern Lakes
2. **PROGRAMME PRIORITY:** Contaminants (in this case the toxic heavy metal mercury) in freshwater ecosystems in the North.
3. **PROJECT LEADER:** Dr. Togwell A. Jackson, National Water Research Institute, Burlington, Ontario (telephone no.: (905) 336-4795; fax no.: (905) 336-6430; e-mail address: t.a.jackson@ec.gc.ca).
4. **PROJECT TEAM MEMBERS:** Dr. Derek C. G. Muir, National Water Research Institute, Burlington, Ontario (telephone no.: (905) 319-6921; fax no.: (905) 336-6430; e-mail address: derek.muir@ec.gc.ca); and Dr. Marlene S. Evans, National Water Research Institute, National Hydrology Research Centre, Saskatoon, Saskatchewan (telephone no.: (306) 975-5310; fax no.: (306) 975-5143; e-mail address: marlene.evans@ec.gc.ca).
5. **SUMMARY:** Variations in the stable isotope composition of mercury (Hg) in cores and food web organisms from two widely separated boreal forest lakes characterised by marked differences in environmental conditions and pollution history were investigated, with emphasis on relationships between Hg isotope abundances and other variables, such as the age and chemical composition of the sediment and the methylmercury ( $\text{CH}_3\text{Hg}^+$ ) content, trophic levels, habitat preferences, and taxonomy of the organisms. The purpose of the research was to achieve new insight into the origin and biogeochemistry of Hg in freshwater ecosystems of the North. The isotopic makeup of Hg in the environment and in organisms could provide a wealth of important new information about the biogeochemical cycling of Hg, but little is known about its variations in nature.

The samples were taken from Shipiskan Lake, Labrador and Cli Lake, Northwest Territories. The cores were sectioned and, following measurement of physical properties, were dated radiometrically and analysed for total Hg, stable isotopes of Hg,  $\text{NH}_2\text{OH}\cdot\text{HCl}/\text{HNO}_3$ -extractable ("reactive") manganese (Mn) and iron (Fe), and organic carbon (C) and nitrogen (N). The biological samples, which consisted of zooplankton, forage fish, and top predator fish (i.e. representatives of three trophic levels) were analysed for  $\text{CH}_3\text{Hg}^+$  and for stable isotopes of Hg, C, and N, and were identified taxonomically; the fish were also characterised by measurement of fork length, weight, and lipid content and, whenever possible, by determination of age and sex. Hg isotope abundances in the sediments and organisms were determined by the highly precise technique of multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) and were expressed as per mil deviations of isotope ratios relative to a standard.

The total Hg profiles of the cores from both lakes reveal an increase in Hg content over time from the 19<sup>th</sup> to the late 20<sup>th</sup> century; in contrast, the profiles of the Hg isotope data differ profoundly from one lake to the other and are independent of the total Hg profiles. However, the isotope composition of the Hg in the cores correlates with environmentally and biologically meaningful chemical parameters such as the organic C and N and reactive Mn and Fe concentrations, and with the N/C and Mn/Fe ratios. Yet many of these relationships apply only to certain sequences of horizons within the cores (i.e. to certain historical intervals but not others), and the relationships differ from one lake to the other; moreover, some core horizons yielded anomalous isotope data.

The stable isotope composition of Hg in the food web organisms was found to correlate with trophic level and hence with CH<sub>3</sub>Hg<sup>+</sup> content. For a given Hg isotope ratio, however, the relationship is more strongly developed and significant in one of the two biotic assemblages than in the other, reflecting the physicochemical and biological differences between the lakes. One species of fish (lake whitefish) was anomalous in both assemblages, possibly owing to a physiological peculiarity of this species. Habitat factors such as preferred depth, and hence temperature, of water also appear to have affected Hg isotope composition.

The results suggest that Hg isotopes in lakes are fractionated *in situ* by natural processes, notably biological processes such as microbial methylation of Hg, bioaccumulation of CH<sub>3</sub>Hg<sup>+</sup> by aquatic organisms, biomagnification of CH<sub>3</sub>Hg<sup>+</sup> from lower to higher trophic levels, special physiological processes of individual fish species, and microbial activities involved in oxidation-reduction reactions in sediments. Environmental variables, such as water temperature and chemistry, may also affect the fractionation process. We infer that isotope fractionation produces systematic variations in the stable isotope composition of Hg in sediments and biota, yielding different patterns of variation in different lakes and in different historical periods within the same lake, owing to differences in environmental conditions and corresponding differences in the aquatic biota and sedimentary microflora. Our findings demonstrate that the study of temporal and spatial variations in the stable isotope composition of Hg and related physicochemical and biological factors, could yield valuable new information on the biogeochemical cycling of Hg in Northern lakes and other Hg-contaminated ecosystems. However, we found no evidence for the presence of isotope signatures indicative of the sources of the Hg. Any distinctive source-related isotope signatures initially possessed by the Hg were probably obliterated or obscured by fractionation in the environment, although the possibility that measurable traces of them are preserved in sediments under certain conditions has not been ruled out. Further research is needed to extend these promising and novel results.

6. **BACKGROUND:** Contamination of Northern aquatic ecosystems with Hg by long-range atmospheric transport from various anthropogenic and natural sources, followed by accumulation of the Hg in fine-grained sediments and biota, is a serious, widespread problem which poses a threat to the health of human and wildlife populations that habitually consume fish (Jackson, 1997; Fitzgerald *et al.*, 1998). Of particular concern is conversion of inorganic Hg(II) to the hazardous, relatively bioavailable neurotoxin CH<sub>3</sub>Hg<sup>+</sup> by free-living microorganisms in natural waters and sediments under a wide

range of conditions.  $\text{CH}_3\text{Hg}^+$  is readily accumulated by aquatic organisms and, unlike inorganic Hg, undergoes biomagnification from lower to higher trophic levels, generally becoming highly concentrated in the muscle tissues of fish and fish-eating animals at and near the upper end of the aquatic food chain (Jackson, 1998). Since the onset of industrialisation there has been a large progressive increase over time in the emission of anthropogenic Hg into the atmosphere, as well as discharge into natural waters, from point sources such as chlor-alkali plants, coal-burning power plants, incinerators, and smelters, and from various diffuse sources, although a decline in annual emissions occurred in some regions in the second half of the twentieth century. These trends are frequently seen in the total Hg profiles of sediment cores from lakes (Lockhart *et al.*, 1995, 1998; Jackson, 1997; Fitzgerald *et al.*, 1998; Bindler *et al.*, 2001; Muir *et al.*, 2003). Typical profiles show progressive enrichment in Hg from lower (older) to higher (younger) core horizons, the trend either continuing to the sediment-water interface or peaking below the top of the sequence and then declining, reflecting regional or local abatement of pollution starting in the middle or latter part of the twentieth century (Engstrom and Swain, 1997; Jackson, 1997). Moreover, anthropogenic Hg is accompanied by Hg from many different natural sources, such as volcanoes, hot springs, faults, and rocks undergoing chemical weathering. Although there are grounds for believing that the annual atmospheric fluxes of natural and anthropogenic Hg are of comparable magnitude on a global scale and that the greater part of the anthropogenic component comes from combustion of fossil fuels, especially coal, as in electric power plants (Jackson, 1997), it is difficult, if not impossible, to differentiate clearly between Hg emissions from different sources once they are mixed together in the environment and widely disseminated. This uncertainty is compounded by the fact that Hg originally emitted by the multitude of primary anthropogenic and natural sources and then deposited in the environment may be reemitted by secondary sources (e.g. soil, forest fires, and ocean water). Consequently, attempting to quantify the contributions of different sources of Hg and to trace the pathways of Hg in the environment is a challenging task (Jackson, 1997). In addition, the biogeochemistry of Hg is extremely complex, and much remains to be learned about the fundamental processes involved in it.

In theory, variations in the stable isotope composition of Hg could provide much valuable untapped information about the origins and biogeochemical cycling of Hg in the environment. Hg has seven stable isotopes (De Bièvre and Taylor, 1993), and it is possible that Hg emitted by different sources of contamination is distinguished by characteristic isotope signatures indicative of its origins; if so, detectable traces of these signatures could conceivably be preserved in the environment (e.g. in sediment, peat, and ice cores). Alternatively (or in addition), Hg isotopes could be fractionated by natural processes in the environment (e.g. the microbial conversion of inorganic  $\text{Hg(II)}$  to  $\text{CH}_3\text{Hg}^+$ , and the microbial reduction of  $\text{Hg(II)}$  to gaseous  $\text{Hg(0)}$  and subsequent escape of the  $\text{Hg(0)}$  into the atmosphere), with the result that whatever isotope signatures were imprinted on the Hg at its points of origin are obscured or obliterated. Thus, the study of temporal and spatial variations in the isotope composition of Hg (and particular species of Hg) in various natural materials could greatly advance our knowledge of the biogeochemical cycling of Hg. The literature on the stable isotopes of lighter elements (notably C, O, H, N, and S) is replete with examples of the usefulness of these isotopes

for both fingerprinting (e.g. the use of C isotope ratios to distinguish between organic substances of terrestrial and aquatic origin) and the elucidation of natural processes (e.g. the use of O isotope ratios of core sections to measure historical variations in mean water temperature) (Degens, 1965; Hoefs, 1973; Petersen and Fry, 1987). The same general principles could apply to stable isotopes of Hg.

However, the possibility that the proportions of the stable isotopes of Hg vary significantly in nature has rarely been investigated. The literature contains a few reports of experimental separation of Hg isotopes and evidence for natural fractionation of Hg isotopes found in Hg ores, meteorites, and moon rocks (see publications cited by Jackson *et al.*, 2004), but to the best of our knowledge there has never been any published evidence for variations in the isotopic makeup of Hg in ecosystems except for the recent work of T.A. Jackson and associates (Jackson, 2001a, b; Jackson *et al.*, 2003, 2004; Jackson and Whittle, 2003a, b). The dearth of knowledge about the isotope geochemistry of Hg probably stems from the fact that Hg is such a heavy element that any variations in its isotope composition are apt to be very small and therefore incapable of being measured except by extremely precise techniques of mass spectrometry. Multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) is the most precise method currently available and hence the method of choice for heavy elements such as Hg, but it is very expensive, and few laboratories possess the requisite facilities and expertise. Jackson (2001a, b) and Jackson and Whittle (2003a, b) used quadrupole inductively coupled plasma mass spectrometry, a less precise method (the only method available to them at the time), but, despite the limitations of the analytical method, their data showed highly significant systematic variations in the isotope composition of Hg in a core and assemblage of food web organisms from Lake Ontario. Subsequently, Jackson *et al.* (2003, 2004) were able to have Hg isotope analyses performed by MC-ICP-MS. Their results revealed that the isotope composition of Hg in a core from a meromictic lake in the High Arctic desert of Ellesmere Island, Nunavut varied as a complex function of the age and chemical composition of the sediment, suggesting fractionation of the isotopes by bacterial activities linked to oxidation-reduction reactions. MC-ICP-MS was employed in the present research project as well.

## 7. PURPOSE:

1. To investigate possible variations in the stable isotope composition of Hg in sediment cores and biota in selected lakes in the eastern and western regions of the boreal forest zone of Canada and to examine relationships between the abundances of the Hg isotopes and other variables, such as the age and chemical composition of the sediment and the  $\text{CH}_3\text{Hg}^+$  content, taxonomy, trophic categories, and habitat preferences of the organisms.
2. To assess the possible causes of any nonrandom variations in the stable isotope composition of the Hg and their wider implications for the biogeochemical cycling of the Hg, with particular attention to the question of whether the variations are due to isotope fractionation by natural processes in the environment

or variations in the abundances of Hg derived from different sources whose emissions are identifiable by distinctive Hg isotope signatures, or both.

3. To evaluate the potential usefulness of Hg isotopes in research on Hg in the environment, and to make recommendations regarding future research initiatives.

## 8. PROJECT DESIGN:

### Sampling sites and sample collection.

Cores and samples of aquatic organisms representing different trophic levels were collected from Shipiskan Lake, Labrador and from Cli Lake in the southwestern part of the Northwest Territories (Figure 1). Shipiskan Lake is located at latitude 54°-55°N, longitude 62°-63°, and Cli Lake is situated at latitude ~62°N (61°-63°N), longitude 122°-123°. Both lakes lie in remote, rugged subarctic regions of the boreal forest zone and are virtually pristine except for trace quantities of Hg and other contaminants presumably introduced by long-range atmospheric transport from many different sources. In these respects, the lakes are broadly comparable. However, they differ considerably in their physicochemical properties; thus, according to available background data, the surface water of Shipiskan Lake is mildly acidic and has a relatively low conductivity and high turbidity, whereas the surface water of Cli Lake is mildly alkaline and has a much higher conductivity but lower turbidity (Table 1). In addition, the rate of sedimentation is much higher in Shipiskan Lake than in Cli Lake (see section 9, below). Furthermore, Shipiskan Lake has undoubtedly been much more strongly affected by airborne anthropogenic Hg and other pollutants of North American origin owing to transport of emissions northeastward by the prevailing westerlies from major industrial and urban sources, such as coal-burning power plants, in the northeastern and north-central U.S.A. and adjoining parts of southern Canada (Lockhart *et al.*, 1995; Muir *et al.*, 2003).

**Shipiskan Lake.** Cores of fine-grained sediment were collected from sites 95-100 m deep in Shipiskan Lake on 29 April, 2002 using a Technical Operations gravity corer with an internal diameter of 10 cm (Machine All Inc., Mississauga, Ontario). The lake was frozen at the time, and the corer was lowered through holes cut in the ice (a separate hole for each core). The cores were cut into 1-cm sections, which were frozen at -20°C and freeze-dried. Biological samples and water quality data were collected in July, 2002. Zooplankton was collected by 5 vertical hauls from a depth of 50 m at open water sites (total depth of water: 83-133 m) using a Wildco (Saginaw, Michigan) net 3 m long and 1 m in diameter with a mesh size of 110 µm. Fish (longnose sucker, lake whitefish, northern pike, and lake trout) were caught during the night of 19-20 July using nets tied to the shore and set at right angles to the shoreline. All biological samples were frozen at -20°C except for a subsample of the zooplankton which was preserved in formalin for taxonomic identification. Measurements of the pH, conductivity, turbidity, dissolved oxygen content, and temperature of the water were performed using a Horiba meter within a depth of ~2 m, and Secchi disk depths were recorded. Horiba readings were also



made at 1 m depth intervals to depths of 4 to 9 m at selected sites ranging from littoral to pelagic.

**Cli Lake.** A core of fine-grained sediment was collected with a gravity corer on 28 March, 1999. The core, which had a diameter of 10 cm, was cut into 0.5-cm sections to a depth of 5 cm and then 1-cm sections over the depth range 5-8 cm, and the sections were frozen and then freeze-dried. Samples of ninespine stickleback and pond smelt were collected on 20 and 23 August, 1999, respectively, using a beach seine. Zooplankton samples were collected on 4 August, 2002 by three 5-10 min. horizontal tows 1-2 m below the surface of the water using a no. 10 (153  $\mu$ m) plankton net, whereupon the samples were frozen and then freeze-dried except for a sample preserved in formalin for taxonomic identification. Specimens of lake trout, lake whitefish, and round whitefish were collected with a gill net on 3 and 16 February, 2003. All samples were frozen at -20°C. Hydrolab measurements of the pH, conductivity, turbidity, dissolved oxygen content, oxidation-reduction potential, and temperature of the water at different depths were made on 4 August, 2002.

#### **Measurement of physical properties and radiometric ages of core sections.**

The Shipiskan Lake core sections were freeze-dried, their porosity and specific gravity were measured, and they were dated by the  $^{210}\text{Pb}$ - $^{210}\text{Po}$  method using the Constant Initial Concentration (CIC) model for calculating the mean absolute age (the estimated year of deposition) for each section (Yang, 2003). The same method was used to date the Cli Lake core sections. The  $^{210}\text{Pb}$ - $^{210}\text{Po}$  technique yields measurable ages for the past 150 years, although the most accurate and reliable data are obtained from sediments no more than 100 years old.

#### **Identification and characterisation of biological samples.**

**Zooplankton.** The organisms were identified at the genus and species level whenever possible, and the abundances of the different components of the community were determined. For information on characteristics of the different kinds of planktonic organisms, see Thorp and Covich (1991).

**Fish.** The species of fish were identified, and the total length, fork length, and weight, and, whenever possible, the sex, of each individual were determined. In addition, the age of each Cli Lake fish was measured; but the ages of the Shipiskan Lake fish could not be ascertained, as the aging structures (along with some other tissue) had been excised. Information on fish biology (e.g. dietary and habitat preferences) was obtained from Scott and Crossman (1998) and Carlander (1969).



### Chemical and isotopic analyses of cores and biological samples.

**Cores.** The core sections were digested with  $\text{HNO}_3/\text{HCl}$  (1:3, v/v) at  $120^\circ\text{C}$  and the extracts were made up to final volume with deionised water. Aliquots of the extracts were mixed with additional  $\text{HNO}_3$  and  $\text{HCl}$  together with  $\text{KMnO}_4$ , and total Hg was determined by reduction of dissolved  $\text{Hg(II)}$  to  $\text{Hg(0)}$  gas with  $\text{SnCl}_2$  followed by cold vapour atomic absorption spectrophotometry (CVAAS) using a Perkin Elmer Flow Injection Mercury System. The stable isotopes of Hg in the sample extracts were determined by means of an automated, computerised ThermoFinnigan Neptune MC-ICP-MS unit employing argon (Ar) as the carrier gas and Faraday cups as the detectors (a separate one for each Hg isotope). Following reduction of  $\text{Hg(II)}$  to  $\text{Hg(0)}$  with  $\text{SnCl}_2$ , the  $\text{Hg(0)}$  and associated solution were entrained by a stream of Ar, and the  $\text{Hg(0)}$  was stripped from the liquid phase in a liquid-gas separator (nebuliser) and injected into the plasma of the MC-ICP-MS unit by the Ar. A standard solution of Hg in 3.5%  $\text{HNO}_3$  (lot S-HG02027, Inorganic Ventures Inc.) was analysed before and after each sample, and three reference samples (two soil samples and a specimen of copper-mill heads) were analysed as well. Each sample and standard solution was automatically analysed 25 times in rapid succession, and the mean values and standard deviations were computed. The raw data were expressed as the ratios  $^{196}\text{Hg}/^{202}\text{Hg}$ ,  $^{198}\text{Hg}/^{202}\text{Hg}$ ,  $^{199}\text{Hg}/^{202}\text{Hg}$ ,  $^{200}\text{Hg}/^{202}\text{Hg}$ ,  $^{201}\text{Hg}/^{202}\text{Hg}$ , and  $^{204}\text{Hg}/^{202}\text{Hg}$ , and the per mil (‰) deviations of the sample ratios from the standard ratios (i.e. the  $\delta^{196}\text{Hg}$ ,  $\delta^{198}\text{Hg}$ ,  $\delta^{199}\text{Hg}$ ,  $\delta^{200}\text{Hg}$ ,  $\delta^{201}\text{Hg}$ , and  $\delta^{204}\text{Hg}$  values) were calculated using the following formula:

$$\delta^X\text{Hg} = [({}^X\text{Hg}/^{202}\text{Hg})_{\text{sample}} - ({}^X\text{Hg}/^{202}\text{Hg})_{\text{standard}}] \cdot 10^3 / ({}^X\text{Hg}/^{202}\text{Hg})_{\text{standard}},$$

where X = 196, 198, 199, 200, 201, or 204.

The standard value used to compute a given  $\delta$ -value was, in each case, the mean of the two standard values bracketing the sample value. This report will be concerned solely with  $\delta^{198}\text{Hg}$ ,  $\delta^{199}\text{Hg}$ ,  $\delta^{200}\text{Hg}$ , and  $\delta^{201}\text{Hg}$ , because  $\delta^{196}\text{Hg}$  and  $\delta^{204}\text{Hg}$  are subject to possible interference by  $^{196}\text{Pt}$  and  $^{204}\text{Pb}$ , respectively, and because  $^{196}\text{Hg}$  is one to two orders magnitude less abundant than the other stable isotopes of Hg and therefore cannot be measured as precisely as the others. Furthermore,  $\delta^{204}\text{Hg}$  values are not necessarily reproducible in sample reruns, even when interference by  $^{204}\text{Pb}$  has been ruled out, whereas  $\delta^{198}\text{Hg}$ ,  $\delta^{199}\text{Hg}$ ,  $\delta^{200}\text{Hg}$ , and  $\delta^{201}\text{Hg}$  are highly reproducible (Jackson *et al.*, 2004). A more detailed account of the analytical methods is given by Jackson *et al.* (2004).

The chemical analysis of the sediments included determination of "reactive" manganese (Mn) and iron (Fe) by extraction with  $\text{NH}_2\text{OH}\cdot\text{HCl}/\text{HNO}_3$  followed by analysis of the extracts for total Mn and Fe by inductively coupled atomic emission spectrometry using a Thermo Jarrell Ash IRIS unit. (Reactive Mn and Fe are defined as labile Mn and Fe species, such as oxyhydroxides, which are subject to formation and transformation in the lake and its watershed by processes such as oxidation-reduction reactions, solubilisation, and precipitation.) Organic carbon (C) and organic nitrogen (N) were determined with a Perkin Elmer 2400 CHN analyser (organic C being defined as all C remaining after removal of inorganic C by treatment with dilute  $\text{H}_2\text{SO}_4$ ).

**Biological samples.** The fish were ground and homogenised using a commercial meat grinder, and the samples were stored at  $-20^{\circ}\text{C}$  until they were analysed. The frozen and freeze-dried zooplankton samples were assumed to be homogeneous to begin with. The lipid content of the homogenised fish samples was determined by extraction with chloroform/methanol (2:1) and analysis of the extracts using a Büchi 810 lipid extractor. For total Hg and Hg isotope analyses, portions of the samples were digested with  $\text{HNO}_3$  at  $170^{\circ}\text{C}$  in a microwave oven (MARSX), and the extracts were analysed using the same techniques that were used to determine the total Hg content and Hg isotope ratios of the sediments (see above). Separate subsamples of the frozen and freeze-dried samples were analysed for  $\text{CH}_3\text{Hg}^+$ . Following treatment with  $\text{H}_2\text{SO}_4$  in the presence of acid-washed elemental copper (Cu) powder, they were mixed with KBr and toluene in an ultrasonic water bath, resulting in conversion of  $\text{CH}_3\text{Hg}^+$  to  $\text{CH}_3\text{HgBr}$ , which was taken up by the toluene. Two additional extractions with toluene were carried out, and the extracts were combined with the original extract. The  $\text{CH}_3\text{HgBr}$  was then converted to a hydrophilic complex by treatment of the toluene solution with aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution, and was taken up in the aqueous phase. The complex was then converted to  $\text{CH}_3\text{HgI}$  by treatment with excess KI, and extracted with toluene. The solution was dried with anhydrous  $\text{Na}_2\text{SO}_4$ , and the  $\text{CH}_3\text{HgI}$  was reacted with butylmagnesium chloride to form a butylmethylmercury derivative. The reaction was quenched with HCl, and the butylmethylmercury was taken up in toluene and analysed by gas chromatography (GC) using an Agilent 6890 GC unit equipped with an Agilent 7683 automatic sample injector, an HP-1 capillary column with He as the carrier gas, and an Agilent G2350A atomic emission detector (AED) employing a microwave-induced He plasma.  $\text{CH}_3\text{Hg}^+$  was determined as elemental Hg. In addition, freeze-dried specimens of zooplankton and homogenised fish tissue were analysed for stable isotopes of C and N to verify the trophic relations and other ecologically important characteristics of the food web species. Organic C and N were converted to  $\text{CO}_2$  and  $\text{N}_2$ , respectively, by combustion in a Carlo-Erba NA 1500 elemental analyser, whereupon they were separated chromatographically and analysed with a VG Optima triple collector isotope ratio mass spectrometer. Internal reference substances (Princeton University Gelatin and bowhead whale baleen calibrated with respect to the international PDB and AIR standards for C and N isotopes, respectively) were used to calculate the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values, i.e. the per mil ( $\text{‰}$ ) deviations of the  $^{13}\text{C}/^{12}\text{C}$  and  $^{15}\text{N}/^{14}\text{N}$  ratios of the samples from those of the standards.

## 9. RESULTS AND DISCUSSION:

### The core from Shipiskan Lake.

**Chronology.** The radiometric dates show that approximately the upper half of the stratigraphic sequence spans the entire 20<sup>th</sup> century, the measured average years of deposition for the core horizons in this region ranging from 1904 to 2000. The lower half of the sequence presumably represents much, if not all, of the 19<sup>th</sup> century.

**Hg isotope abundances and chemical composition.** The core profiles of selected chemical and Hg isotope data are shown in Figures 2a and 2b. The total Hg concentration (Figure 2a) increases progressively from the latter part of the pre-1904 era (probably the late 19<sup>th</sup> century) to 1979, forming a small maximum at 1979, and shows no significant or consistent change from 1979 to 2000. In the region of background Hg below this long-term trend all Hg levels are relatively low, and there is no variation over time apart from a series of minor short-term fluctuations. Reactive Mn and organic C and N (Figure 2b), along with the Mn/Fe ratio of the  $\text{NH}_2\text{OH}\cdot\text{HCl}/\text{HNO}_3$ -extractable fraction and the porosity and water content of the sediment (not shown), exhibit similar overall tendencies, and organic C and N, like total Hg, show a small peak at 1979. These observations suggest a progressive increase in biological productivity (and hence an increase in the organic content of the sediment) from the late 19<sup>th</sup> century to the end of the 20<sup>th</sup> century – possibly the result of a long-term warming trend and accompanying increase in productivity which is known to have affected many Northern lakes, starting in the 19<sup>th</sup> century and continuing through the 20<sup>th</sup> (Douglas *et al.*, 1994; Gajewski *et al.*, 1997; Huguen *et al.*, 2000; Joynt and Wolfe, 2001; Koerner and Fisher, 1990; Overpeck *et al.*, 1997; Smol and Cumming, 2000). The 1979 maximum superimposed on this long-term trend probably represents a short-term local phenomenon. The correlation of reactive Mn with organic C and N is consistent with this tentative interpretation of the core profiles, as it suggests the existence of connections, as would be expected, between biological activity, oxidation-reduction reactions, and Mn geochemistry in the lake. The tendency of organic C and N to increase upward could also reflect progressive postdepositional decomposition of organic matter, but the buried maximum superimposed on the trend does not fit this interpretation. Another conceivable, though hypothetical, explanation of the organic C and N profiles is that they reflect temporal variations in other environmental factors, such as the grain size of the sediments or the proportion of refractory allochthonous humic substances to labile autochthonous substances in the organic matter; however, the entire core appeared to be composed of very fine-grained sediment, and the strong correlation between C and N throughout the stratigraphic sequence implies that there was no major change in the ratio of allochthonous to autochthonous organic matter over time. Pending acquisition of more detailed information, temporal variation in biological productivity seems the most likely explanation for the C, N, and Mn profiles, although the core profiles could represent the combined effects of two or more different processes.

Returning to the total Hg profile, we may reasonably conclude that the tendency toward progressive enrichment in Hg over time is attributable to the combined effect of increased Hg loading (a result of rising emissions of anthropogenic Hg into the atmosphere) and the parallel increase in the concentration of organic matter (which accumulates Hg effectively, with the result that total Hg concentrations in sediments generally correlate with organic content). The Hg/organic C ratio (i.e. total Hg normalised with respect to organic C) was used to estimate variation in Hg loading as distinct from variation linked to the variation in organic content. The profile of the Hg/organic C ratio (Figure 2a) suggests that Hg loading increased from the late 19<sup>th</sup> century to the middle of the 20<sup>th</sup> century (the 1950's) and then declined slightly owing to reduced emissions from North

American sources of atmospheric Hg pollution (see section 6, above). The Hg/organic N ratio (not shown) gave essentially the same pattern of variation.

The  $\delta$ -values of the stable isotopes of Hg revealed a radically different pattern of variation. In Figure 2a this pattern is represented by the  $\delta^{199}\text{Hg}$  data, but  $\delta^{198}\text{Hg}$ ,  $\delta^{200}\text{Hg}$ , and  $\delta^{201}\text{Hg}$  gave essentially the same result. The Hg isotope profiles lack the long-term trend that characterises the upper half of the total Hg profile and the profile of each of the other chemical parameters discussed above. Instead, they show a series of peaks, including a small peak at 1904 and an anomalously large one at 1987, that do not coincide with any of the minor maxima or minima in the profiles for total Hg, reactive Mn, organic C and N, the Hg/organic C ratio, etc. (Figures 2a and 2b). Nevertheless, examination of relationships between Hg isotope data and chemical data showed highly significant relationships between the stable isotope composition of Hg and the organic C and N concentrations, reactive Mn content, and Mn/Fe ratio within certain segments of the stratigraphic sequence (not counting occasional anomalies), but not in other parts of the sequence. This implies that the isotope composition of Hg varied because of isotope fractionation caused by environmental processes and biological activities, and that changes in ambient conditions, and corresponding changes in the nature and activities of the biota, over time led to changes in isotope composition.

A typical example is the relationship between  $\delta^{199}\text{Hg}$  and organic C (Figure 3) and N (not shown). Over the depth range 0-7 cm (= the time interval 1947-2000),  $\delta^{199}\text{Hg}$  gives a highly significant positive correlation with organic C and N, not counting the  $\delta^{199}\text{Hg}$  value for the 2-3 cm (1987) horizon, which, for as yet unknown reasons, is anomalously high. In contrast, the  $\delta^{199}\text{Hg}$  values of the deeper, older (pre-1947) horizons are independent of organic C and N. Since total Hg in this particular core correlates very significantly with organic C and N,  $\delta^{199}\text{Hg}$  correlates as strongly with total Hg as with organic C and N, raising a key question: Is the observed variation in the isotope composition of Hg due to temporal change in the proportions of Hg from different sources, each characterised by a distinctive isotopic fingerprint, or is it due to environmentally and biologically induced fractionation in the lake? To address this question, we plotted  $\delta^{199}\text{Hg}$  against the total Hg/organic C ratio to eliminate the effect of the organic matter on the relationship between  $\delta^{199}\text{Hg}$  and total Hg. The result showed that  $\delta^{199}\text{Hg}$  varies independently of the total Hg/organic C ratio (not shown) in the 0-7 cm depth range, demonstrating that its variations are attributable solely to variations in the organic C concentration, not to variations in total Hg loading. Thus, the most plausible explanation for the systematic variation in isotopic composition in the second half of the 20<sup>th</sup> century is fractionation of the isotopes within the lake owing to environmental change and corresponding changes in biological activities.

Microbial activities in the sediments or water, or both, could well have been the immediate cause of the presumptive isotope fractionation. In any case, there is no evidence for the alternative hypothesis that the observed variation in the proportions of the Hg isotopes reflects variations in the quantities of Hg derived from different sources of contamination, although the existence of detectable source-related effects cannot, at this stage, be ruled out. The same general inferences have been drawn from data for

other lakes (Jackson *et al.*, 2003, 2004; Jackson, 2001a). Environmental changes that could have been the direct or indirect causes of the relationship shown in Figure 3 include the warming trend and resulting increase in biological productivity mentioned above (and quite possibly an associated change in the species composition of the aquatic biota and sedimentary microflora). Other environmental changes that could have played a part include temporal increases in the loadings of various toxic airborne pollutants, which may have altered the species composition and activities of the microflora (Jackson *et al.*, 2003, 2004). The possibility that airborne pollutants induced the observed effect gains credence from the fact that the observed relationship is limited to the second half of the 20<sup>th</sup> century, which saw a marked upsurge in rate of industrial pollution following World War II, and from the fact that Shipiskan Lake lies in the path of the prevailing westerlies (predominantly southwest winds), which blow from the general direction of industrial sources in the northeastern and north-central U.S.A. and adjoining regions of Canada.

### **The core from Cli Lake.**

**Chronology.** To a depth of only 3 cm the stratigraphic sequence goes back to the mid-19<sup>th</sup> century. Thus, the radiometric dates show that the average years of deposition for the top 6 horizons (approximately the upper half of the core) range from 1849 to 1994. The deeper (pre-1849) horizons could not be dated by the <sup>210</sup>Pb-<sup>210</sup>Po method, but, assuming that there was no drastic change in annual rate of sedimentation in the historical interval in which the stratigraphic sequence was laid down, they probably represent the first half of the 19<sup>th</sup> century and all or most of the 18<sup>th</sup>, possibly extending as far back as the 17<sup>th</sup> century. Clearly the annual rate of sedimentation has been very much lower in Cli Lake than in Shipiskan Lake.

**Hg isotope abundances and chemical composition.** Profiles of selected chemical and isotopic data are shown in Figures 4a and 4b. The total Hg profile (Figure 4a) is characterised by a large buried peak dating back to the pre-industrial era (spanning the depth range 5-8 cm and attaining its maximum at 6-7 cm). Further up the core, starting at ~3.0-3.5 cm (presumably in the first half of the 19<sup>th</sup> century), total Hg shows a general long-term tendency to increase upward to the top of the sequence (to the year 1994). Organic C (Figure 4b) gradually decreases upward within the deep pre-industrial region of Hg enrichment (~5-8 cm) and then, abruptly changing the direction of its trend, increases progressively, and more steeply, upward to the top, indicating a steady rise in the concentration of organic matter over time throughout the 19<sup>th</sup> and 20<sup>th</sup> centuries. Organic N (Figure 4b) shows a similar, though not identical, pattern of variation. The upward decrease giving way abruptly to an upward increase suggests that the C and N profiles represent changes in productivity owing to environmental changes over time rather than cumulative effects of decomposition after burial, although the profiles could reflect the combined effects of two or more different processes.

The total Hg and organic C and N profiles are roughly parallel except that C and N have no counterpart of the buried Hg peak, although the zone in which C and N decrease over time (the depth range 5-8 cm) coincides with it. Consequently, total Hg gives a positive

correlation with C and N (especially the latter) except in the 6-7 cm interval, where pre-industrial Hg reaches its highest concentration and is anomalously high relative to C and N. Reactive Mn, unlike the reactive Mn in the Shipiskan Lake core, varies independently of total Hg and organic C and N. Thus, reactive Mn content (Figure 4b) rises to a large maximum from ~8 cm to ~2 cm, with a smaller peak superimposed on it at ~2.5-3.0 cm, but the values are consistently low from ~2.5 cm to the top of the sequence; the Mn/Fe ratio shows a similar pattern of variation (not shown). However, the apex of the large reactive Mn peak coincides with the point at which the organic C and N trends change direction, suggesting a common cause. The core profiles suggest a temporal change in environmental conditions and biological activities, with involvement of oxidation-reduction reactions and Mn geochemistry in the lake or its watershed, or both (see Jackson *et al.*, 2004). Also note that the Hg/organic C ratio (Figure 4a) and Hg/organic N ratio (not shown) parallel the total Hg profile.

Except for anomalously low values at 1.0-1.5 cm and 7-8 cm, the  $\delta$ -values for the Hg isotope ratios (represented as  $\delta^{199}\text{Hg}$  in Figure 4a), tend to increase from lower to higher horizons throughout the stratigraphic sequence and correlate inversely with total Hg and with organic C and N. However, the isotope composition of the Hg correlates much more significantly with organic C (Figure 5a) than with total Hg (not shown), which gave far more scatter; and, as with the Shipiskan Lake core, it is independent of the Hg/organic C ratio (not shown). These observations suggest that in Cli Lake, as in Shipiskan Lake, variation in the  $\delta$ -values is due to fractionation mediated by biological activity in the lake rather than variation in the proportions of Hg from different sources. Yet the nature of the relationship between  $\delta^{199}\text{Hg}$  and organic C is radically different in Cli Lake (Figure 5a) than in Shipiskan Lake (Figure 3), implying effects of differences in site-specific environmental and biological processes and their historical patterns of variation. This contrast between the results for the two lakes reinforces the conclusion that the observed variations in the isotope composition of Hg were caused by *in situ* fractionation controlled by temporally and spatially varying physicochemical and biological processes.

A plot of  $\delta^{199}\text{Hg}$  against organic N (Figure 5b) gives an overall trend that is roughly similar to the trend observed in the plot of  $\delta^{199}\text{Hg}$  against organic C (Figure 5a) (though it is less significant); but, unlike the latter, it reveals intriguing systematic shorter-term variations superimposed on the long-term trend. In the seven deepest (3-8 cm) and oldest (pre-1849) core sections,  $\delta^{199}\text{Hg}$  varies *inversely* with organic N, the data from the 4.5-8 cm horizons forming one trend and the data from the 3.0-4.5 cm horizons resolving themselves into a separate but comparable trend. In contrast, the data from the three highest (0-1.5 cm) and youngest (1955-1994) horizons show a *positive* correlation. In the three horizons of intermediate depth (3-4.5 cm) and age (1849-1925),  $\delta^{199}\text{Hg}$  is independent of N, suggesting that these horizons represent a transition zone in which the two opposing tendencies are equally well developed and therefore cancel each other (see Jackson *et al.*, 2004). The radical shift in the nature of the relationship between  $\delta^{199}\text{Hg}$  and N concentration from the oldest to the youngest horizons, with a possible transition zone between them, suggests effects of long-term environmental change and resultant biotic change on the processes responsible for *in situ* fractionation of Hg isotopes. The trend toward climatic warming which is known to have started at high latitudes during the

19<sup>th</sup> century and continued throughout the 20<sup>th</sup> century (see above), or increased loading of airborne pollutants as a result of the growth of industrial activity in the 19<sup>th</sup> and 20<sup>th</sup> centuries, or a combination of these factors, could very well have been the ultimate cause of the observed effect (Jackson *et al.*, 2003, 2004). On the theory that Hg isotope fractionation was mediated by microbes, the immediate cause could have been a successional change in the species composition of the microflora in response to an environmentally induced shift in the species composition of the aquatic community over time. Similar results leading to the same conclusions have been reported for a lake in the high Arctic (Jackson *et al.*, 2003, 2004).

### **Food web organisms from Shipikan Lake.**

**Taxonomy, trophic rank, and C and N isotope abundances.** Ranked in order of rising trophic level, the biotic assemblage comprised the following trophic categories and taxonomic groups: (1) Zooplankton: crustaceans (84% copepods and 16% cladocerans). (2) Forage fish: longnose sucker (*Catostomus catostomus*) and lake whitefish (*Coregonus clupeaformis*). (3) Top predator fish: northern pike (*Esox lucius*) and lake trout (*Salvelinus namaycush*). As would be expected (Kiriluk *et al.*, 1995), the  $\delta^{15}\text{N}$  values (not shown) increase from lower to higher trophic levels, although they also vary somewhat within different trophic levels. Thus, the  $\delta^{15}\text{N}$  values increase in the order zooplankton < longnose sucker < lake whitefish < northern pike < trout. The observation that lake whitefish had a higher  $\delta^{15}\text{N}$  value than longnose sucker may reflect the fact that lake whitefish feed to some extent on small fish and fish eggs as well as invertebrates (Scott and Crossman, 1998). The  $\delta^{13}\text{C}$  values (not shown) exhibit a very similar trend, increasing in the order zooplankton < longnose sucker < lake whitefish < lake trout < northern pike, suggesting that N and C isotopes are, in large part, fractionated by the same processes during transfer up the food chains in this particular lake.

**Hg isotope abundances and  $\text{CH}_3\text{Hg}^+$  concentrations.** The Hg isotope ratios of the organisms were found to vary with trophic level and (among fish species) with certain habitat factors, specifically the preferred depth of water and therefore the ambient temperature (Scott and Crossman, 1998). Thus,  $\delta^{199}\text{Hg}$  increases in the order zooplankton < longnose sucker < northern pike < lake whitefish < lake trout (Figure 6). All other factors being equal, it would seem that  $\delta^{199}\text{Hg}$  tends to increase up the food chain, but fish that are known to prefer shallower, warmer water (northern pike) have lower  $\delta^{199}\text{Hg}$  values than fish that have a greater tendency to frequent deeper, colder water (lake whitefish and lake trout). In brief, the stable isotope composition of Hg in aquatic organisms is evidently a complex function of biological and environmental factors. The  $\delta^{199}\text{Hg}$  value of surface (0-1 cm) sediment was relatively low and therefore comparable to the values obtained for zooplankton and longnose sucker (Figure 6).

The relationship between the isotopic makeup of Hg and the trophic level of the organism appears to reflect involvement of  $\text{CH}_3\text{Hg}^+$ , which, as a rule, increases from lower to higher trophic levels in aquatic communities (Jackson, 1998). Accordingly, the variation in mean  $\delta^{199}\text{Hg}$  values among different species (Figure 6) parallels variations in mean



$\text{CH}_3\text{Hg}^+$  concentration (on a wet or dry weight basis) except in the case of whitefish, which had an anomalously high  $\delta^{199}\text{Hg}$  value relative to its  $\text{CH}_3\text{Hg}^+$  content (Figure 7). These results suggest that during microbial production of  $\text{CH}_3\text{Hg}^+$ , or the bioaccumulation and biomagnification of  $\text{CH}_3\text{Hg}^+$ , or both, Hg isotopes are fractionated, as inferred from data for a Lake Ontario food web assemblage (Jackson, 2001a; Jackson and Whittle, 2003a and 2003b). More research would be needed to explain the anomalous result obtained for lake whitefish, but possible reasons for it include the preference of adult whitefish for cold, deep waters and a special biochemical mechanism of  $\text{CH}_3\text{Hg}^+$  excretion inferred previously from indirect evidence (Jackson, 1991).

### **Food web organisms from Cli Lake.**

**Taxonomy, trophic rank, and C and N isotope abundances.** Listed in order of rising trophic level, the biotic assemblage was made up of the following trophic categories and taxonomic groups: (1) Zooplankton: crustaceans (mostly calanoid and cyclopoid copepods, with a few cladocerans). (2) Forage fish: pond smelt (*Hypomesus olidus*), ninespine stickleback (*Pungitius pungitius*), round whitefish (*Prosopium cylindraceum*), and lake whitefish (*Coregonus clupeaformis*). (3) Top predator fish: lake trout (*Salvelinus namaycush*). As in Shipiskan Lake,  $\delta^{15}\text{N}$  increases with trophic level, though it varies appreciably within the forage fish group (not shown). Specifically, the  $\delta^{15}\text{N}$  values increase in the order zooplankton < pond smelt < ninespine stickleback < lake whitefish  $\leq$  round whitefish < lake trout. The high values for lake whitefish and round whitefish relative to the other forage fish probably reflects the fact that the diet of both of those species includes small fish and fish eggs as well as invertebrates (Scott and Crossman, 1998). The Shipiskan Lake biota gave comparable results (see pp. 13-14). However, the  $\delta^{13}\text{C}$  values for the Cli Lake assemblage, unlike the  $\delta^{13}\text{C}$  values for the Shipiskan Lake assemblage, were independent of trophic level except for the fact that the zooplankton had a much lower  $\delta^{13}\text{C}$  value than any of the fish, possibly reflecting its purely pelagic environment. The  $\delta^{13}\text{C}$  values increased in the order zooplankton < lake trout  $\leq$  ninespine stickleback < lake whitefish < pond smelt < round whitefish. Note that the forage fish, without exception, had the highest  $\delta^{13}\text{C}$  values. The contrasting patterns of variation exhibited by the  $\delta^{13}\text{C}$  values for the Cli Lake and Shipiskan Lake assemblages may reflect the differences in environmental conditions in the two lakes and the differences in the nature of the aquatic organisms that make up the two assemblages.

**Hg isotope abundances and  $\text{CH}_3\text{Hg}^+$  concentrations.** Making allowances for the differences in species composition, the Cli Lake biota yielded results that were roughly comparable to those given by the Shipiskan Lake biota. The zooplankton, pond smelt, nine-spine stickleback, and round whitefish all had relatively low  $\delta^{199}\text{Hg}$  values, whereas lake whitefish had an appreciably higher  $\delta^{199}\text{Hg}$  value, and lake trout had the highest value (Figure 8). As with Shipiskan Lake, the  $\delta^{199}\text{Hg}$  value of the surface (0-0.5 cm) sediment was closest to the lowest values for the organisms (Figure 8). Again, the fish at the top of the food chain (lake trout) had the highest  $\delta^{199}\text{Hg}$  value, and lake whitefish had a higher  $\delta^{199}\text{Hg}$  value than any of the other forage fish. The possibility that conditions in the cold, deep waters preferentially frequented by lake whitefish account for the

relatively high  $\delta^{199}\text{Hg}$  value for this species is confirmed by the difference between round whitefish and lake whitefish: Round whitefish prefer shallower water (Carlander, 1969; Scott and Crossman, 1998) and have a correspondingly lower  $\delta^{199}\text{Hg}$  value (Figure 8).

As with the Shipiskan Lake biota,  $\text{CH}_3\text{Hg}^+$  concentrations in the Cli Lake biota increased from lower to higher trophic levels, being lowest for zooplankton and highest for lake trout (Figure 9). Unlike the Shipiskan Lake biota, however, the Cli Lake biota showed only a weak positive correlation between  $\delta^{199}\text{Hg}$  value and  $\text{CH}_3\text{Hg}^+$  content: The relationship owes its significance solely to the fact that lake trout had a higher  $\delta^{199}\text{Hg}$  value and  $\text{CH}_3\text{Hg}^+$  concentration than the organisms at lower trophic levels; among the zooplankton and forage fish there was no correlation between  $\delta^{199}\text{Hg}$  and  $\text{CH}_3\text{Hg}^+$ . This is yet another indication that other factors besides  $\text{CH}_3\text{Hg}^+$  content and trophic level affect the stable isotope composition of Hg in aquatic organisms. Habitat preferences, dietary preferences, physiological peculiarities of individual species, and factors such as the ages and growth rates of individual fish, along with the differing physicochemical properties of the individual lakes (Table 1), probably have to be taken into account. Note that round whitefish had much higher  $\text{CH}_3\text{Hg}^+$  levels than lake whitefish did (Figure 9). This may reflect the fact that round whitefish tend to inhabit shallower waters closer to shore, where rates of  $\text{CH}_3\text{Hg}^+$  production by bacteria are likely to be higher owing to higher temperatures and, above all, a greater abundance of labile organic matter.

## 10. CONCLUSIONS AND RECOMMENDATIONS:

Our results lead to the conclusion that stable isotopes of Hg are fractionated by natural processes, notably biological activities, in lacustrine ecosystems. The data for the biota provide especially strong support for this inference, as the proportions of Hg isotopes in different species clearly vary with  $\text{CH}_3\text{Hg}^+$  concentration and trophic level and appear to be affected by habitat factors and peculiarities of individual species as well. The cores support the same general conclusion, though more indirectly: Within certain depth ranges (i.e. historical intervals) in the stratigraphic sequences the isotopic makeup of the Hg varies with biologically significant chemical parameters such as the concentrations of organic C and N, but in other depth ranges the relationship may not exist or may be radically different. These findings suggest that historical changes in environmental conditions and related shifts in the nature of the biota (including changes in the species composition of the sedimentary microbial community) affected the processes whereby Hg isotopes are fractionated, altering the relationships between the isotopic makeup of Hg and the chemical properties of the sediment. Our results provide no grounds, however, for inferring that source-related isotopic signatures have been preserved. Any distinctive isotopic signatures indicative of the sources of Hg contamination were probably obliterated by fractionation in the environment. Results and interpretations broadly comparable to the ones reported here have been reported for two other lakes (Jackson *et al.*, 2003, 2004; Jackson, 2001a). If our inferences are applicable to lakes in general, not just to the two lakes encompassed by this research project and the two lakes investigated earlier, they imply that stable isotopes of Hg may yield much valuable, as yet

untapped information about the biogeochemical cycling of Hg but cannot be used to extract information about the origins of the Hg.

We recommend further research on the biogeochemistry of the stable isotopes of Hg to follow up on the promising beginning represented by our findings and the other recent observations reported previously. The work accomplished thus far has opened up a new a potentially important field of inquiry, but at this point there are many questions and few answers. There is a need for detailed comparative investigation of various lakes with widely differing geographical settings, environmental conditions, biological communities, and histories so that well-founded generalisations can be formulated and the results properly interpreted in terms of cause and effect. Both spatial and temporal variations in the isotopic makeup of Hg and related physical, chemical, and biological variables need to be examined in depth. Moreover, empirical research on field sites should be combined with controlled experiments on the fractionation of Hg isotopes by natural processes (together with experiments designed to detect and eliminate any artifacts that might be produced during sample storage, preparation, extraction, or analysis). One question that must be resolved is whether Hg emissions from different natural and anthropogenic sources have characteristic isotopic signatures indicative of their origins, and, if so, what happens to them after the Hg is released into the environment: Are they invariably obliterated by isotope fractionation (and obscured by the mixing of emissions from different sources), or can they be at least partially preserved? Another major objective will be to elucidate the mechanisms and results of Hg isotope fractionation by various physical, chemical, and biological processes in the environment.

## **11. COMMUNITY CONSULTATION AND COMMUNICATION:**

The Shipiskan Lake field work was done in consultation and communication with elders of the Innu Nation, including Innu Environmental Guardian Jack Selma, and with the two Innu communities of Labrador. During the field work at Cli Lake the Deh Cho First Nations (Dene) community at Fort Simpson, Northwest Territories was kept informed about our activities through regular communication with the local band office.

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The Shipiskan Lake core was collected by M. Mawhinney and R. Neureuther (Technical Operations Branch, National Water Research Institute (NWRI), Burlington). David Wilson and the late Geoffrey Howell (Department of the Environment (DOE), Atlantic Region, Dartmouth, Nova Scotia) kindly provided valuable assistance with logistical arrangements for the Shipiskan Lake field work and supplied the biological samples from Shipiskan Lake, as well as the data for physicochemical properties of the lake water. Others who assisted with the field work included R. Whalen (Department of Fisheries and Oceans (DFO)), J. Carreau (Université de Québec), J. Pomeroy (DOE, Atlantic Region), and J. Selma (Innu Nation). The Cli Lake field work was carried out with the technical assistance of J. Keating (NWRI, Saskatoon), E. Walker, J. Inkster, K. Gerein, A. Plante, C. Beres, A. Gent, C. Allsop, and L. Doetzel, and R. Tsetso served as a guide in the field. We thank L. and R. Letcher (North Nahanni Naturalist Lodge), South Nahanni Air, and Simpson Air for cooperation and logistical support in the field.

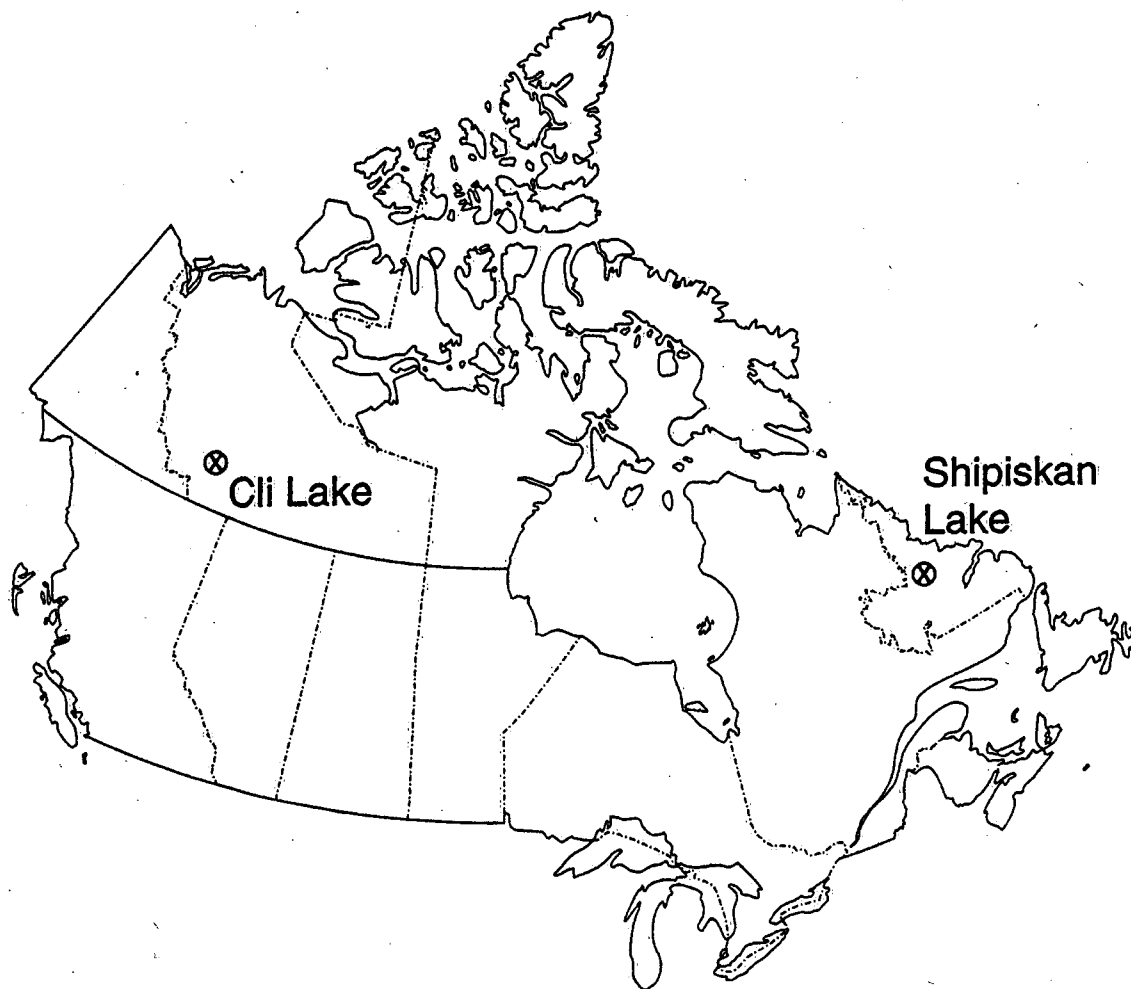
The Shipiskan Lake core was dated by F. Yang (NWRI, Burlington), and the Cli Lake core was dated by P. Wilkinson (DFO). The Hg isotope and total Hg analyses were performed by Activation Laboratories Ltd. (Ancaster, Ontario) under the direction of Y. Kapusta using methods developed by the company. The reactive Fe and Mn were extracted by N. Nguyen (NWRI, Burlington), and the Fe and Mn analyses, as well as the organic C, organic N, and  $\text{CH}_3\text{Hg}^+$  analyses were done by technicians of the National Laboratory for Environmental Testing (NWRI, Burlington). The C and N isotopes were determined by G. Koehler (NWRI, Saskatoon). The fish were processed and identified by D.M. Whittle (DFO, Burlington), and taxonomic identification of zooplankton from Shipiskan Lake was performed by D. Geiling of Limnoservices (Landsdowne, Ontario).

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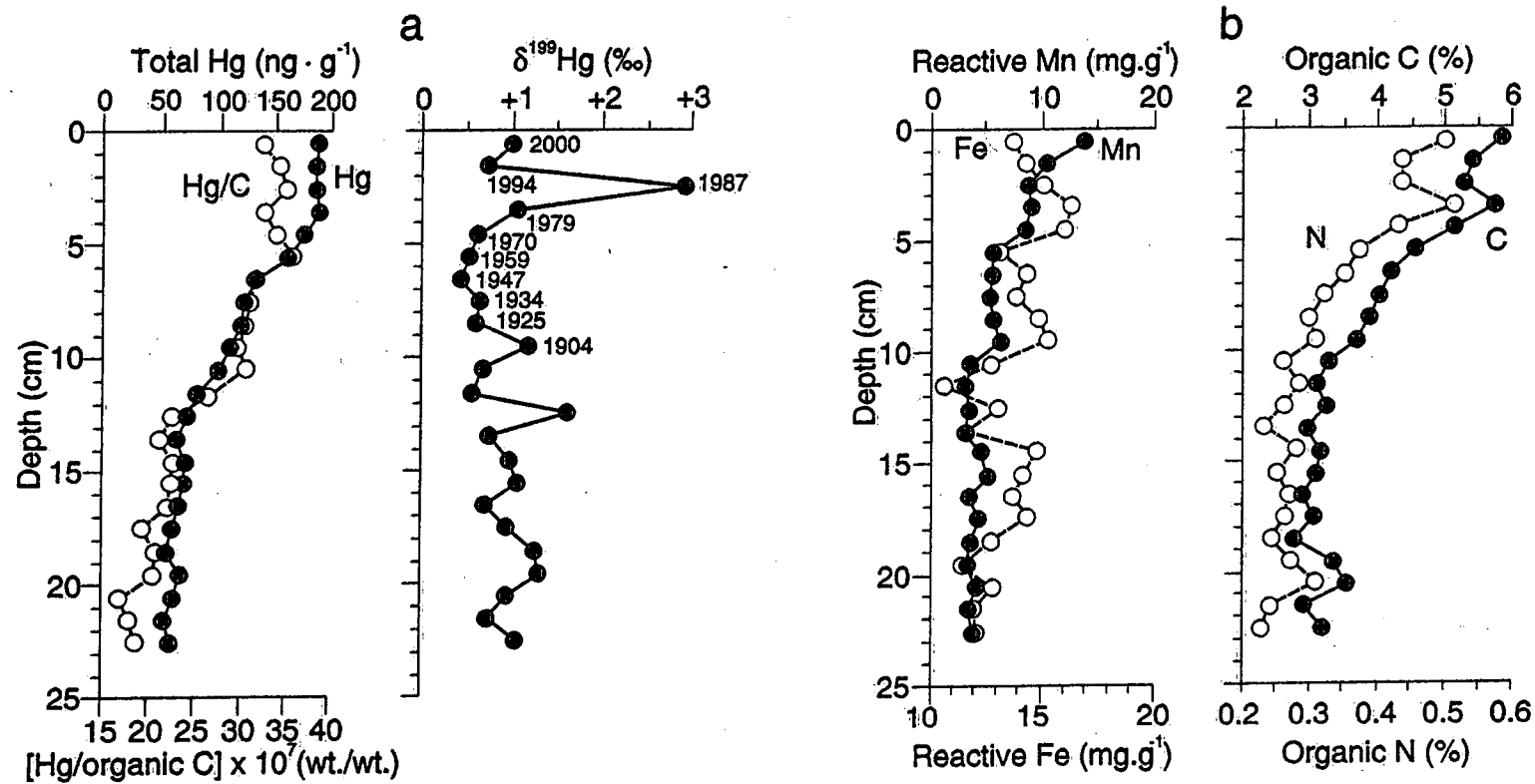
**Table 1.** Values of selected physicochemical parameters of the surface waters at pelagic sites in Shipiskan Lake (Horiba measurements made in July, 2002; courtesy of D. Wilson) and Cli Lake (Hydrolab measurements made in August, 2002).

Lake	pH	Conductivity ( $\mu$ S/cm)	Turbidity (NTU)	Dissolved O <sub>2</sub> (mg/L)	Temperature (°C)
Shipiskan Lake	5.91	23	2.0	11.91	12.4
Cli Lake	8.04	204	0.4	10.73	11.87

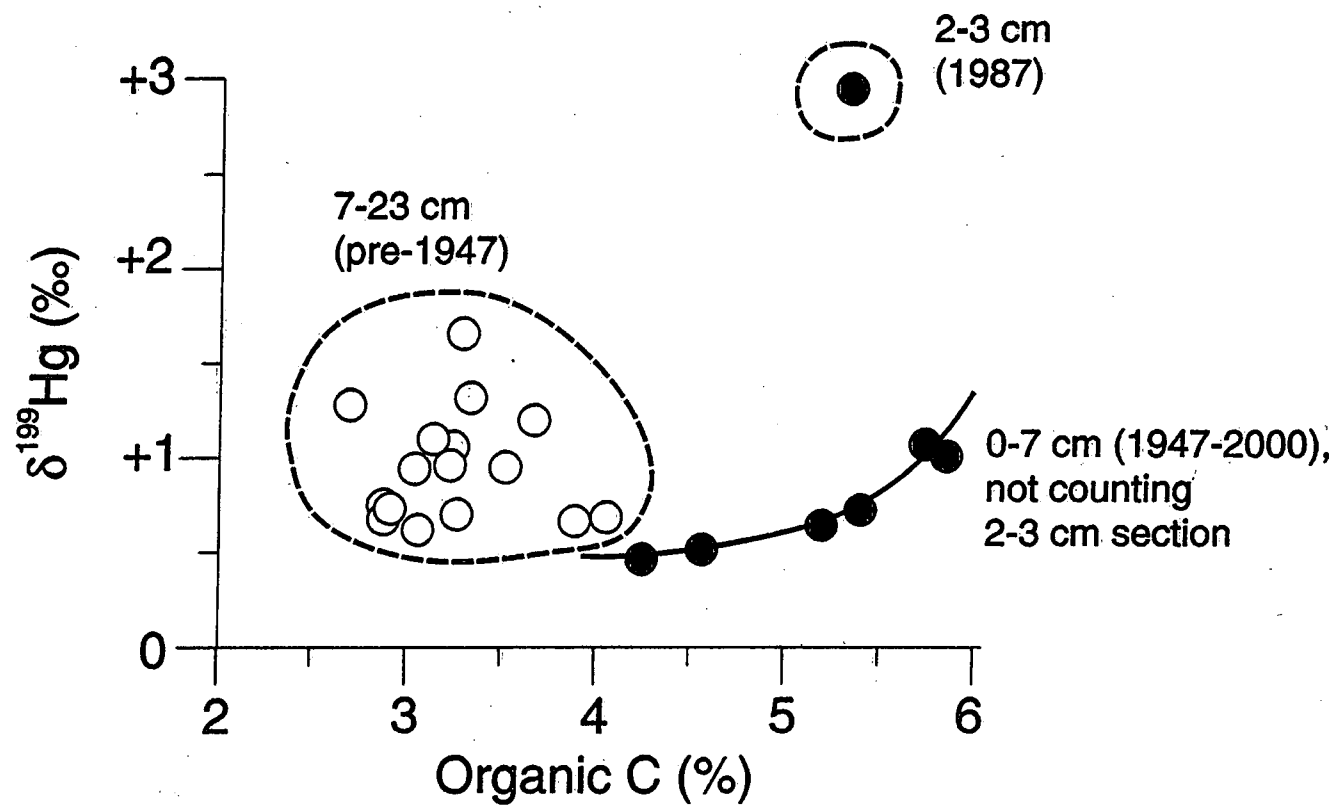




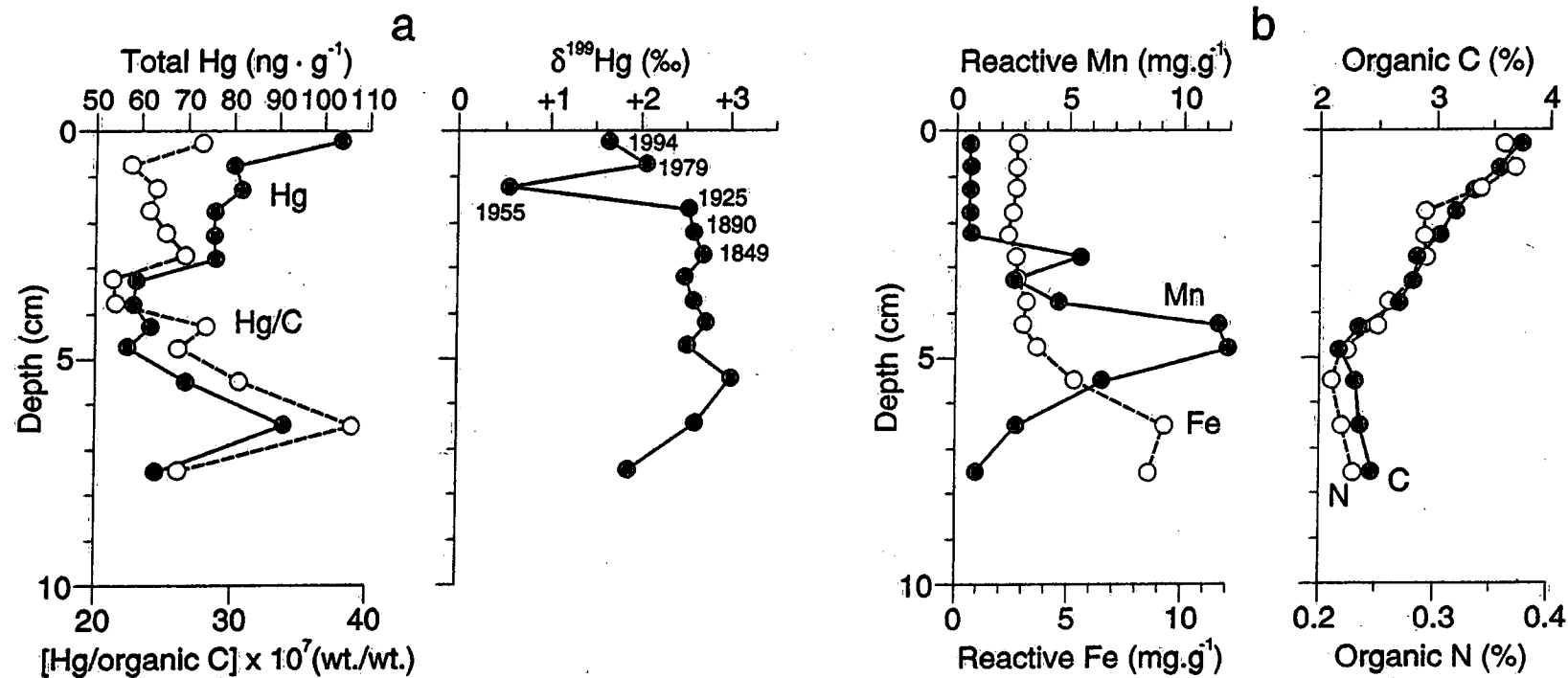
**Figure 1.** Map of Canada showing the locations of the sampling sites.



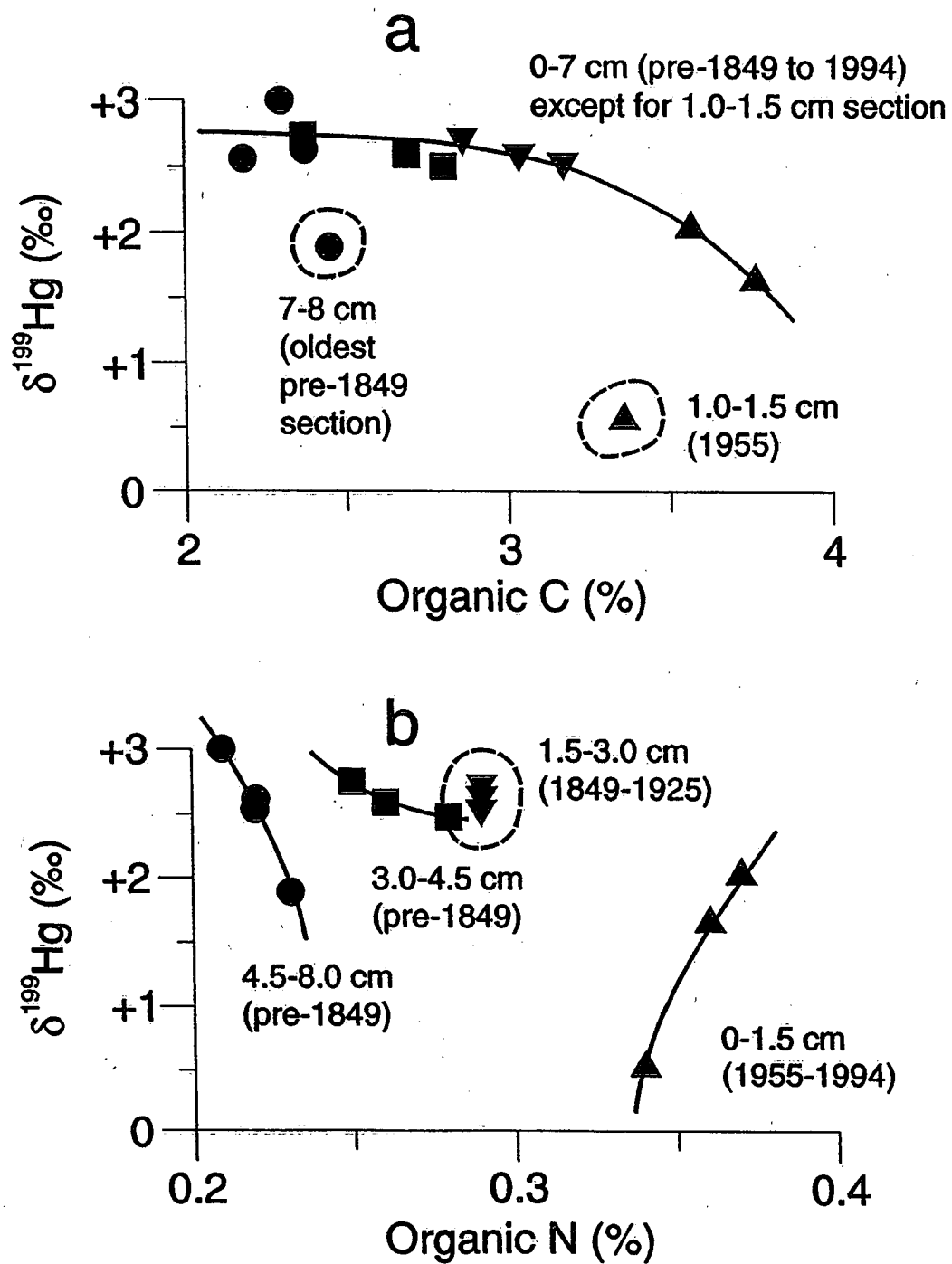
**Figure 2.** The Shipiskan Lake core profiles of (a) total Hg, the Hg/organic C ratio, and  $\delta^{199}\text{Hg}$ , and (b) reactive Mn and Fe and organic C and N. The radiometric dates of the uppermost ten horizons are shown in the profile of  $\delta^{199}\text{Hg}$ .



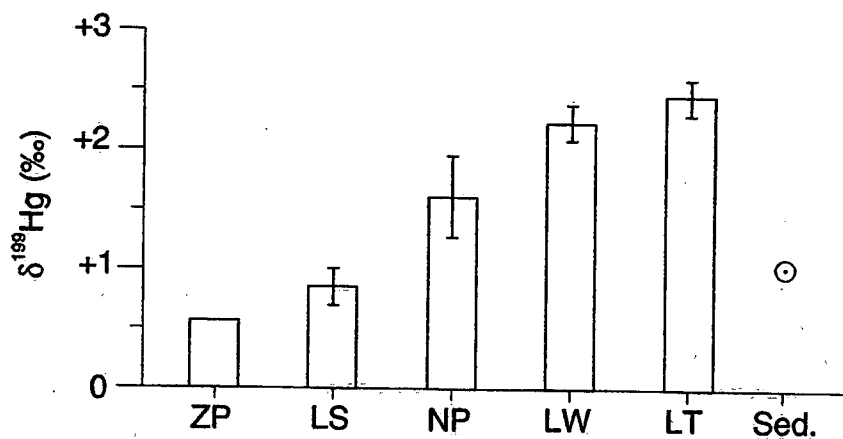
**Figure 3.** The relationships between  $\delta^{199}\text{Hg}$  and organic C in the 0-7 cm (1947-2000) horizons (●) and 7-23 cm (pre-1947) horizons (○) of the Shipiskan Lake core.



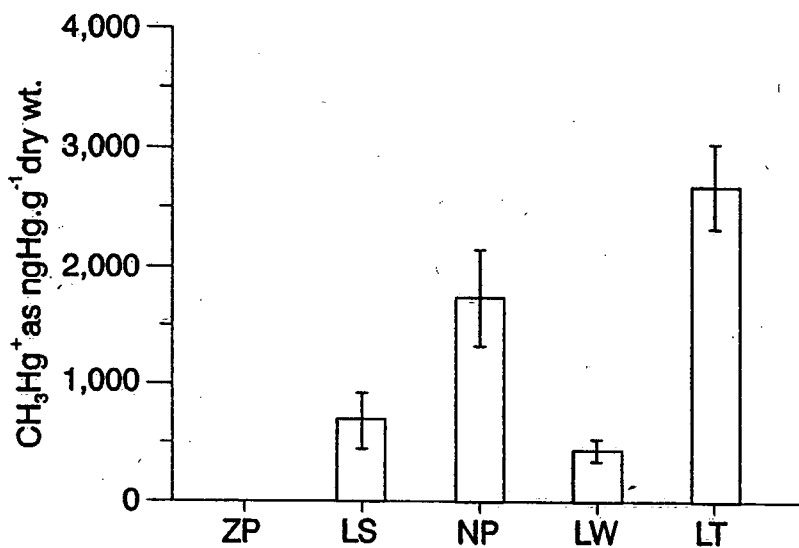
**Figure 4.** The Cli Lake core profiles of (a) total Hg, the Hg/organic C ratio, and  $\delta^{199}\text{Hg}$ , and (b) reactive Mn and Fe and organic C and N. The radiometric dates of the uppermost six horizons are shown in the profile of  $\delta^{199}\text{Hg}$ .



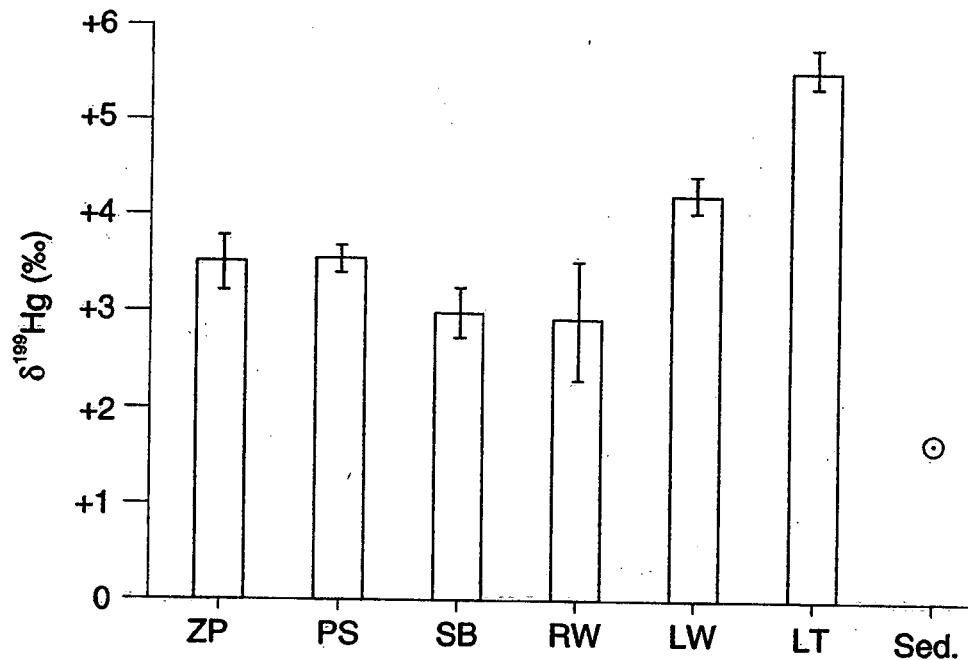
**Figure 5.** Relationships between  $\delta^{199}\text{Hg}$  and organic C (a) and organic N (b) in the Cli Lake core. Explanation of symbols: 0-1.5 cm (1955-1994), ▲; 1.5-3.0 cm (1849-1925), ▼; 3.0-4.5 cm (pre-1849), ■; 4.5-8.0 cm (pre-1849), ●.



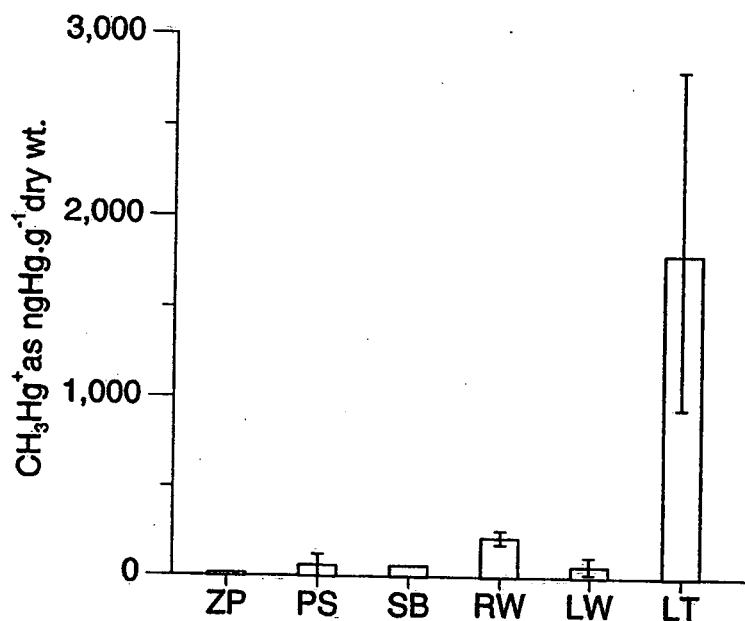
**Figure 6.** The mean  $\delta^{199}\text{Hg}$  values for organisms and surface sediment from Shipiskan Lake. Each error bar represents mean  $\pm$  standard error. Explanation of abbreviations: ZP = zooplankton; LS = longnose sucker; NP = northern pike; LW = lake whitefish; LT = lake trout; sed. = sediment in the depth range 0-1 cm.



**Figure 7.** The mean  $\text{CH}_3\text{Hg}^+$  content of organisms from Shipiskan Lake. Each error bar represents mean  $\pm$  standard error. Explanation of abbreviations: ZP = zooplankton; LS = longnose sucker; NP = northern pike; LW = lake whitefish; LT = lake trout.



**Figure 8.** The mean  $\delta^{199}\text{Hg}$  values for organisms and surface sediment from Cli Lake. Each error bar represents mean  $\pm$  standard error. Explanation of abbreviations: ZP = zooplankton; PS = pond smelt; SB = nine-spine stickleback; RW = round whitefish; LW = lake whitefish; LT = lake trout; sed. = sediment in the depth range 0-0.5 cm.



**Figure 9.** The mean  $\text{CH}_3\text{Hg}^+$  content of organisms from Cli Lake. Each error bar represents mean  $\pm$  standard error. Explanation of abbreviations: ZP = zooplankton; PS = pond smelt; SB = nine-spine stickleback; RW = round whitefish; LW = lake whitefish; LT = lake trout.





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