LAKE ONTARIO SEDIMENTS IN MONITORING POLLUTION

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Abstract. An investigation was carried out to select locations for long-term monitoring of inputs of contaminants into Lake Ontario using fine-grained bottom sediments as an historical record of pollution. The sediment sampling program was designed to determine sediment heterogeneity in the western, central and eastern depositional basins of the lake. Surficial sediments and sediment cores were collected in each basin to obtain information on horizontal distribution and concentration profiles of major and trace elements in the sediments (Si, Al, Ca, Mg, Fe, Na, K, Ti, Mn, P, As, Co, Cu, Cr, Ni, Pb and Zn). The results of the investigation indicated that fine-grained sediments in three Lake Ontario depositional basins are homogeneous to a high degree, and that only a few sediment cores need to be collected within each basin for the long-term monitoring of inputs of contaminants to the lake.

Key words: Lake Ontario, bottom sediments, heterogeneity, major and trace elements.

1. Introduction

Most hydrophobic organic contaminants, metal compounds and nutrients entering rivers and lakes become associated with fine-grained particulate matter. The particulate matter is carried by currents into areas of reduced flow where it settles and accumulates in bottom sediments. Consequently, fine-grained bottom sediments are a sink of contaminants in aquatic environments. The fine-grained sediments can be used as a historical record of usage pattern for different chemicals in a river or lake drainage basin. Lake bottom sediments have often been used to evaluate the sources and changes in anthropogenic inputs of different metals into a lake (for example, Kemp and Thomas, 1976; Christensen and Chien, 1981). This capacity of lake bottom sediments can be utilized in the long-term monitoring of the effectiveness of remediation of inputs of contaminants into the environment from different sources.

The results of a comprehensive study of pollution from the Niagara River (Allan *et al.*, 1983) were used in the recommendation for planning of long-term management and remedial actions to clean up and prevent the pollution of Lake Ontario. Further, it was recommended that Lake Ontario bottom sediments should be used to monitor the effectiveness of remedial actions implemented in the lake's drainage basin. However, limited information was available for selection of the monitoring sites in Lake Ontario. Data from a few sediment cores were available to assess the trends of metal inputs to Lake Ontario. These data were collected in early 1970 to compare metal inputs to the Great Lakes (Kemp and Thomas, 1976). For the long-term monitoring, it was suggested that sampling stations be located

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in Lake Ontario depositional basins. However, there was a lack of knowledge of the effects of sediment heterogeneity on the selection of sites in each depositional basin. Further, it was necessary to decide how many monitoring stations needed to be established in order to obtain data which would represent the deposition of contaminants over the entire lake. In consideration of these issues, a study was initiated with following objectives: (1) to design a sediment sampling program for the investigation of heterogeneity of fine-grained sediments in three depositional basins (western, central and eastern) in Lake Ontario; (2) to assess the difference in sediment geochemistry among the three depositional basins; and (3) to make a recommendation for the selection of sampling sites for long-term monitoring using bottom sediments as a historical record of inputs of contaminants to Lake Ontario, particularly using a minimum number of monitoring sites with respect to the cost of quantitative determination of different contaminants in sediment samples.

2. Materials and Methods

Sediment sampling was carried out along two transects in each of the three depositional basins (western, central and eastern) in Lake Ontario. The sampling grid is shown in Figure 1. A box core (0.5 m $\times$ 0.5 m $\times$ 0.5 m) was collected at each sampling station and the top 3 cm of sediment were sampled from the core into polycarbonate plastic bags. Thirteen stations were randomly selected, four, six and three in the western, central and eastern basin, respectively, for collection of sediment cores. The cores were collected by gently pushing polycarbonate core tubes (10.5 cm inside diameter) into the box core to prevent compression of the soft, fine-grained sediments (Mudroch and MacKnight, 1991). To investigate the heterogeneity of the surface 3 cm sediments in a single box core, the surface of a box core collected in the western basin was divided into nine equally sized fields. Each field was treated as an individual sample. Hand-cores retrieved from the box corer were divided vertically into 1-cm sections using a piston extruder described by Mudroch and MacKnight (1991). Each core section was collected into a polycarbonate bag. One-half of the surface sediment samples was used for determination of particle size distribution. The other half and all core sections were freeze-dried and pulverized to about 150 μm size. Pulverized samples were used for the determination of concentrations of major and trace elements (Si, Al, Fe, Ca, Mg, Na, K, Ti, Mn, P, As, Co, Cr, Cu, Pb, Ni and Zn). The particle size distribution in the samples was determined by a sedigraph (Duncan and LaHaie, 1979). The concentrations of major and trace elements were determined by X-ray fluorescence spectrometry using powder pellets. The accuracy of the analysis was verified by running Canadian reference standard Syenite SY-2 and soils SO-2 and SO-4 obtained from Canada Centre for Mineral and Energy Technology, Ottawa, Ontario, and standard reference material 1645 (river sediment) obtained from U.S. Department of Commerce National Bureau of Standards, Washington, D.C., and comparing the analytical results with the stated reference values for major and trace

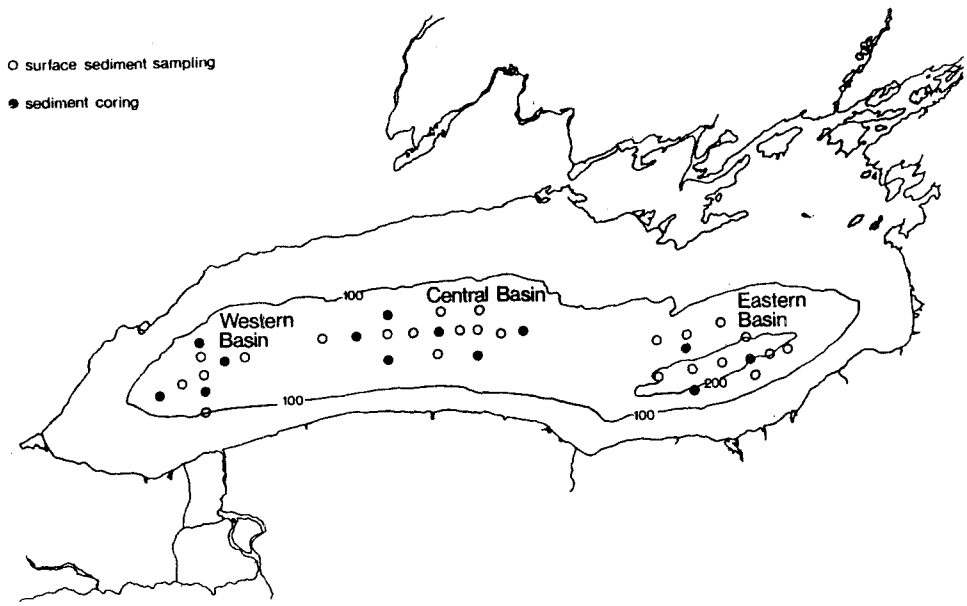

Fig. 1. Sediment sampling stations in Lake Ontario.

elements. The precision and accuracy of the analysis were described by Mudroch and Mudroch (1992). The reported results are based on sediment dry weight. The difference in the concentrations of major and trace elements in sediments in the three Lake Ontario depositional basins was tested using one-way analysis of variance (ANOVA).

3. Results and Discussion

3.1. Horizontal Distribution of Major and Trace Elements in Sediments

Sediments sampled at all stations consisted of 30–35% silt-size particles (4–63 μm); the rest was clay-size particles (< 4 μm). The heterogeneity of the surface 0–3 cm sediment in a single box core (i.e. an area of 0.25 m^2) collected in the western basin of Lake Ontario and the precision of the analytical method used for the analysis are shown in Table I. With the exception of Mn and As, the concentrations of major and trace elements were similar in all nine samples collected from the single box core. The difference in the concentration of Mn was most likely due to the irregular migration of Mn into the sediment surface in the box core (Marshall, 1979). The difference in the concentration of As was ascribed to the mobility of As in sediments and sediment pore water (Nriagu *et al.*, 1987). The results showed

TABLE I

Concentrations of major and trace elements in nine samples taken from a single box core.

Major Elements (concentration in %)				
Parameter	Range	Mean	S.D.[1]	S.D.[2]
SiO_2	57.0 – 57.2	57.1	0.08	0.05
Al_2O_3	13.9 – 14.1	14.0	0.07	0.04
Fe_2O_3	6.8 (in all nine samples)			
MgO	2.6 – 2.7	2.6	0.04	0.03
CaO	12.9 – 13.4	13.2	0.16	0.05
Na_2O	0.58 – 0.64	0.62	0.02	0.02
K_2O	3.39 – 3.44	3.42	0.17	0.10
TiO_2	0.60 – 0.62	0.61	0.07	0.05
MnO	1.14 – 1.37	1.28	0.10	0.05
P_2O_5	0.35 – 0.37	0.36	0.01	0.01
Trace Elements (μg/g)				
Parameter	Range	Mean	S.D.[1]	S.D.[2]
Ni	83 – 85	84	0.9	0.9
Co	15 – 21	18	1.7	1.7
Cr	101 – 110	107	3.0	1.5
V	87 – 95	90	3.0	3.0
Pb	125 – 133	130	3.0	2.4
Zn	394 – 419	407	8.0	4.5
As	28 – 49	40	8.0	5.1
Cu	105 – 113	108	3.0	2.1

S.D.[1] = Standard deviation calculated from analysis of nine samples from the box core.

S.D.[2] = Standard deviation calculated from nine repeated analyses of one sample.

that the heterogeneity of the sediment within a single box core will not affect the comparison of the heterogeneity of sediments within and among the three Lake Ontario depositional basins. Considering the results of the chemical analysis of the surficial sediments (Tables II and III) indicating a relatively homogeneous chemical composition of the sediments within each basin, no further attempt was made to investigate sediment heterogeneity within a smaller area, such as a hundred or a thousand square meters.

TABLE II

Concentrations of major elements in surficial sediments (% dry weight).

Parameter	Basin[1]	Mean	Max.	Min.	Std.dev
SiO_2	Western	57.5	58.0	56.7	0.45
F-test: 4.7	Central	57.9	59.7	55.9	1.20
	Eastern	59.7	66.9	56.8	2.5
MnO	Western	1.01	1.24	0.73	0.17
F-test: 3.4	Central	0.87	1.17	0.41	0.25
	Eastern	1.14	1.50	0.46	0.27
K_2O	Western	3.50	3.56	3.46	0.03
F-test: 0.9	Central	3.42	3.50	3.37	0.04
	Eastern	3.47	4.04	3.27	0.22
MgO	Western	2.85	3.20	2.70	0.16
F-test: 1.0	Central	2.81	2.93	2.75	0.05
	Eastern	2.79	2.97	2.64	0.08
TiO_2	Western	0.66	0.73	0.61	0.04
F-test: 14.1	Central	0.54	0.61	0.50	0.03
	Eastern	0.58	0.79	0.51	0.07
CaO	Western	12.16	13.10	10.90	0.69
F-test: 5.4	Central	15.57	17.61	12.84	1.54
	Eastern	13.61	17.33	10.37	1.99
Na_2O	Western	0.66	0.69	0.60	0.03
F-test: 16.2	Central	0.58	0.63	0.51	0.04
	Eastern	0.61	0.82	0.52	0.08
P_2O_5	Western	0.37	0.40	0.35	0.02
F-test: 9.4	Central	0.44	0.51	0.39	0.04
	Eastern	0.40	0.45	0.27	0.05

[1] Based on number of samples: Western Basin = 9; Central Basin = 15; Eastern Basin = 13.

Generally, the concentrations of major and trace elements in the surficial 3 cm of sediments were similar in all three depositional basins, with the exception of Fe, Al, Cu and Zn. The results of the ANOVA test showing the similarity of concentrations of major and trace elements in sediments in the western, central and eastern basins of the lake are shown in Tables II and III. Differences in the concentrations of Fe, Al, Zn and Cu in sediments among the three basins are

TABLE III

Concentrations of trace elements in surficial sediments (μg/g dry weight).

Element	Basin[1]	Mean	Max.	Min.	Std.dev.
Ni	Western	86	93	77	5.4
F-test: 3.2	Central	86	89	67	6.4
	Eastern	80	77	63	6.9
Cr	Western	113	120	108	3.6
F-test: 4.2	Central	108	120	93	9.7
	Eastern	105	128	93	10.4
As	Western	39	49	28	9.7
F-test: 1.4	Central	34	48	28	5.7
	Eastern	37	50	26	7.1
Co	Western	20	22	19	1.1
F-test: 26.7	Central	10	18	4	3.9
	Eastern	12	17	6	3.0
Cr	Western	114	120	108	3.6
F-test: 2.1	Central	108	120	93	9.8
	Eastern	105	128	93	10.5
Pb	Western	134	144	120	9.1
F-test: 8.5	Central	162	185	135	17.4
	Eastern	139	171	107	20.4
V	Western	94	106	89	5.6
F-test: 24.4	Central	69	79	61	4.6
	Eastern	82	106	66	11.8

[1] Based on number of samples: Western Basin = 9; Central Basin = 15; Eastern Basin = 13.

shown in Figure 2. The greater concentrations of Fe, Zn and Cu in the western basin than in the other two basins may have its origin in inputs of these elements by the steel industry located at the west end of the lake, on the shore of Hamilton Harbour. The concentrations of Fe, Zn and Cu in suspended solids collected in Hamilton Harbour were up to 12%, 3200 μg/g and 200 μg/g, respectively (Mayer and Manning, 1990), and up to 15%, 5500 μg/g and 500 μg/g, respectively, in bottom sediments in the harbout (Mudroch A., unpublished data). These are the highest concentrations in sediments from Lake Ontario harbours and embayments (Thomas and Mudroch, 1979; Mudroch *et al.*, 1988). The Zn and Fe concentrations in Hamilton Harbour sediments, the highest recorded at any harbour, can be related

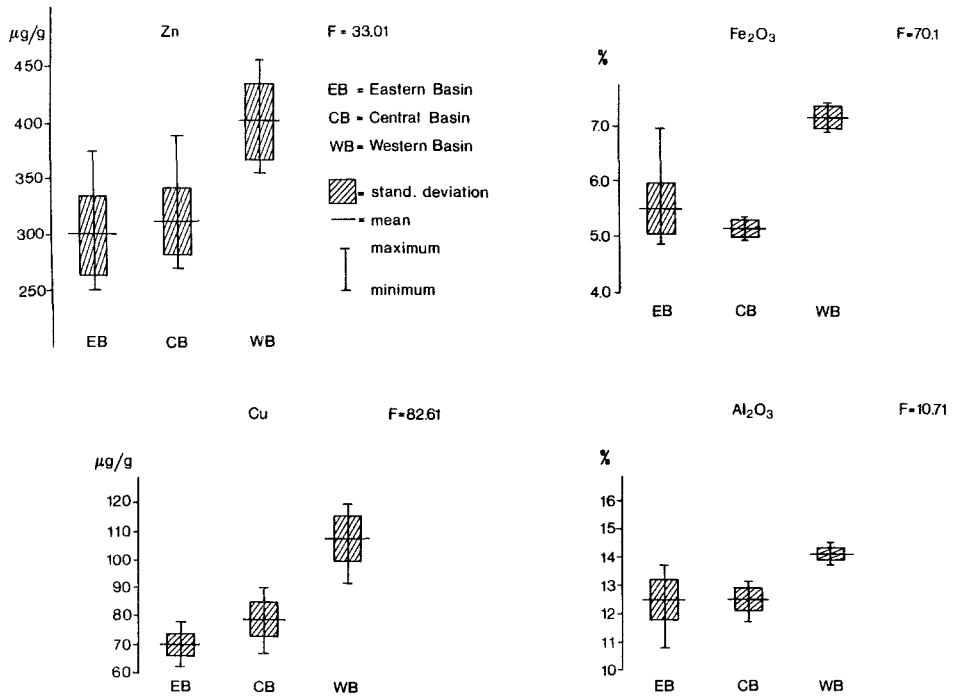

Fig. 2. Concentrations of Zn, Fe, Al and Cu in surficial sediments in three Lake Ontario basins.

to effluent discharges from the large local iron and steel plants (Nriagu *et al.*, 1983). The substantial exchange of water between the harbour and Lake Ontario serves to export most of the pollutant metal burden of the harbour to the Lake (Nriagu *et al.*, 1983), the western basin being affected more than the other two basins. A greater concentration of Al in the sediments in the western basin than in the other basins indicated elevated concentrations of naturally occurring alumino-silicates in the sediments associated with the fine-grained sediments (Thomas *et al.*, 1972).

3.2. Vertical Distribution of Major and Trace Elements in Sediments

The concentrations of each of Si, Al, Fe, Mg, K, Na and Ti were uniform from the surface down to a depth of 15 cm in all sediment cores collected from the three depositional basins, indicating inputs of geochemically similar material to the lake over the past 40 years. The concentrations of Ca and P increased towards the surface in all sediment cores. The increase in the concentration of these two elements in surficial sediments reflected changes of Ca loadings to the lake and coprecipitation of P with $CaCO_3$ in the lake, particularly during the peak of primary production in summer, with a subsequent increase of pH in the lake water (Sylvestre, Kuntz and Warry, 1985). The concentrations of trace elements (As, Cu, Co, Cr, Ni, Pb and Zn) changed from the surface to the bottom of each sediment core. The pattern of the

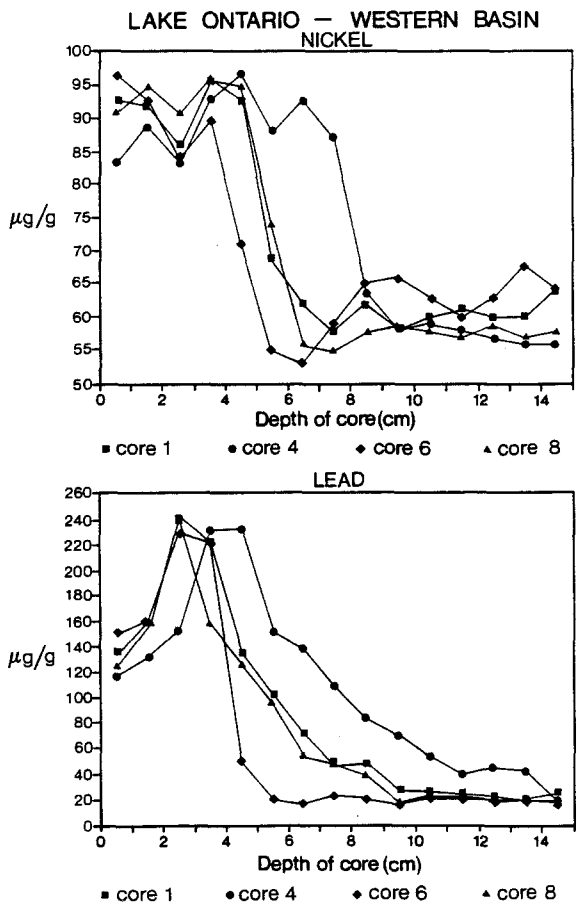

Fig. 3. Concentration profiles of Ni and Pb in sediments from western basin.

changes in concentration profiles of each of the trace elements was similar in all cores collected in the three basins. An example of the concentration profiles of Ni and Pb in sediment cores collected in the western basin is shown in Figure 3. The concentrations of Pb and Ni below the 10 cm sediment depth can be considered background concentrations, similar to those in the soils and bedrock of the lake's drainage basin (Kemp and Dell, 1976; Reeves and Brooks, 1978). The increase in the concentrations of Pb and Ni above the background are interpreted as increases in inputs of these elements to the lake. The greatest concentrations of Pb and Ni were found between 2–4 cm and 0–5 cm sediment depth, respectively (Figure 3). The pattern of the concentration profiles of both elements was similar in all four of the cores collected in the western basin. However, due to the variability in sedimentation rates within and among the basins of Lake Ontario (Robbins, NOAA, Great Lakes Environmental Laboratories, personal communication), the concentration profiles differed from one core to the other (Figure 3).

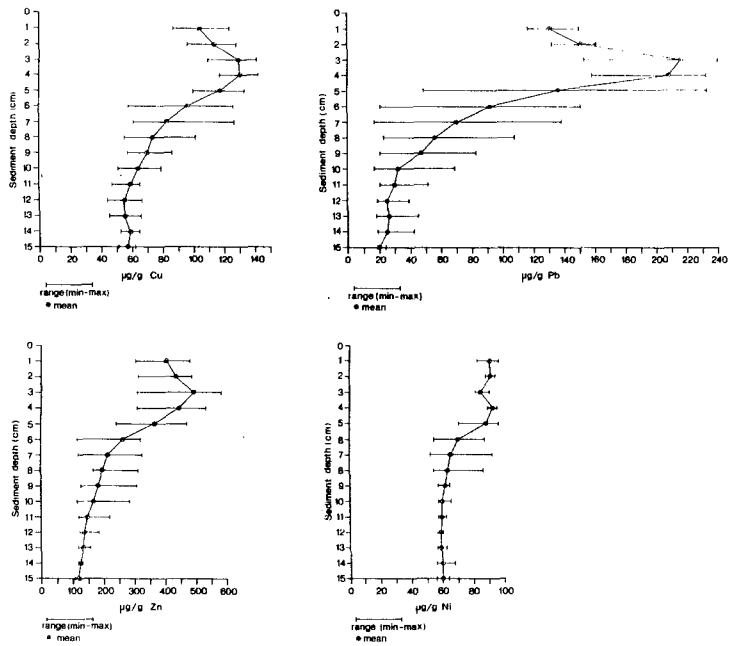

Fig. 4. Concentration profiles of Cu, Zn, Ni and Pb in sediments from western basin.

Changes in mean concentrations of Cu, Zn, Ni and Pb in the sediment cores from the western, central and eastern basins are shown in Figures 4–6. The minimum and maximum concentrations shown in the figures represent the variability among individual cores collected in each basin. Annual sedimentation rates in Lake Ontario depositional basins were estimated in past studies as follows: 1–2 mm, 2–2.5 mm, and 3–4 mm in the western, central and eastern basins, respectively (Kemp and Harper, 1976; Farmer, 1977; Oliver *et al.*, 1989). Following the rapid increase in concentrations of Cu, Pb and Zn above the background level to the greatest concentrations between 3 and 4 cm sediment depth, the concentrations of the three elements started to decrease near the sediment surface. The decrease reflected reduced inputs of Cu, Pb and Zn to Lake Ontario sediments in the past 10–15 years, which may be ascribed to several factors, such as the change in the usage of the metals, implementation of more efficient technology for waste treatment by different industries, etc.

Figure 7 shows an example of inputs of Pb to Lake Ontario recorded by fine-grained sediments. Sediment cores were collected at the same location in the deposition zone of the eastern basin in 1971, 1981 and 1985. The location was verified using the best electronic positioning system available on the research vessel during the sampling. It can be expected that the 1971, 1981 and 1985 sediment cores were collected within a 25 m^2 large area in the depositional basin. Although the sedimentation rate can vary slightly within the depositional basin,

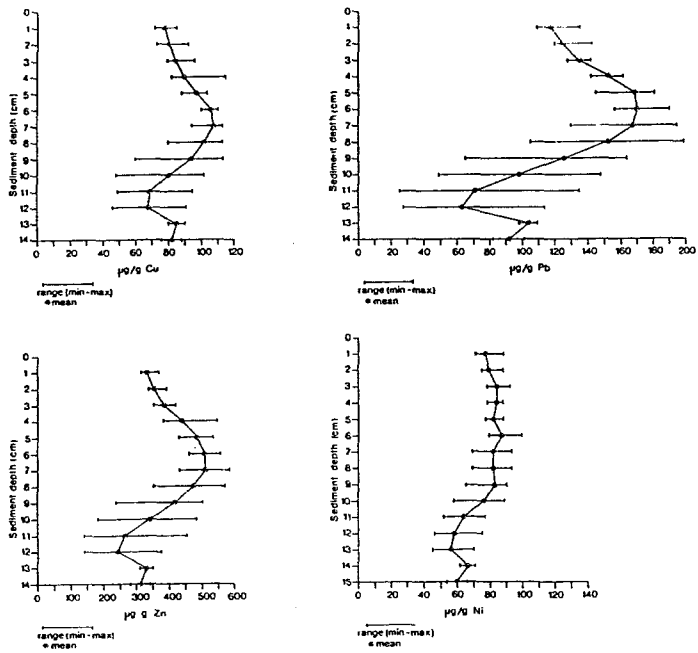

Fig. 5. Concentration profiles of Cu, Zn, Ni and Pb in sediments from central basin.

the pattern of the concentration profiles of Pb remains similar, as shown in Figure 3. The determination of the concentration profiles of Pb in the cores showed the greatest concentration of Pb at the sediment surface in the core collected in 1971. The concentration peak occurred between 5 and 7 cm sediment depth in cores collected in 1981 and 1985, followed by a decrease of the concentration of Pb in the top 5–7 cm of the cores. The decrease of lead concentration at the surface of the sediment profile appears to reflect the implementation of unleaded gasoline in Canada and the U.S.A. Christensen and Goetz (1987) reported similar observations of a Pb sedimentary record in Lake Michigan, indicating maximum inputs of Pb between 1954 and 1969, with a subsequent decrease. Eisenreich *et al.* (1986) found a decrease in annual Pb fluxes in precipitation in north-central Minnesota from 1979 to 1983. The decrease was closely correlated with that in Pb used in gasoline in Minnesota and nationwide. Trefry *et al.* (1985) found a relationship between the concentration profiles of lead in sediments collected at the Mississippi River delta and the annual consumption of lead in gasoline in the U.S.A. Automobile exhaust and atmospheric deposition are major contributors of Pb to Lake Ontario sediments (Nriagu, 1986). Consequently, sediments with the greatest concentration of Pb in Lake Ontario have been covered by settling particles containing less Pb.

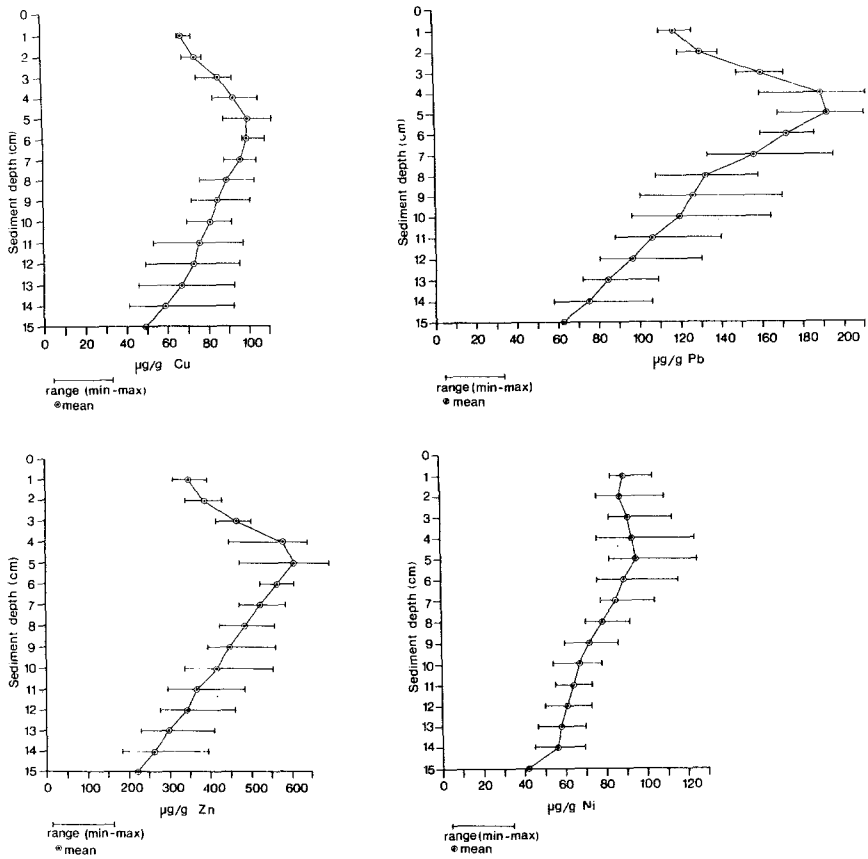

Fig. 6. Concentration profiles of Cu, Zn, Ni and Pb in sediments from eastern basin.

4. Conclusions

The results of the investigation can be used in the selection of sampling sites for the long-term monitoring of inputs of metals to Lake Ontario. The chemistry of the sediments indicated that fine-grained sediments in the western, central and eastern basins are relatively homogeneous, and that sediment cores for the long-term monitoring of inputs of metals can be recovered at any location within the basins. However, more than one sampling site should be considered in each basin. Due to the variability of sedimentation rates within and among individual basins the sedimentation rate should be determined for each long-term monitoring sediment sampling site to confirm that trends in the concentration profiles of contaminants are similar for the entire lake. The variability in concentrations of some trace elements within and among each basin makes surficial sediments unsuitable for the monitoring of those metals. A protocol has to be developed to describe the details of sediment collection and methods used in sample preparation and chemical

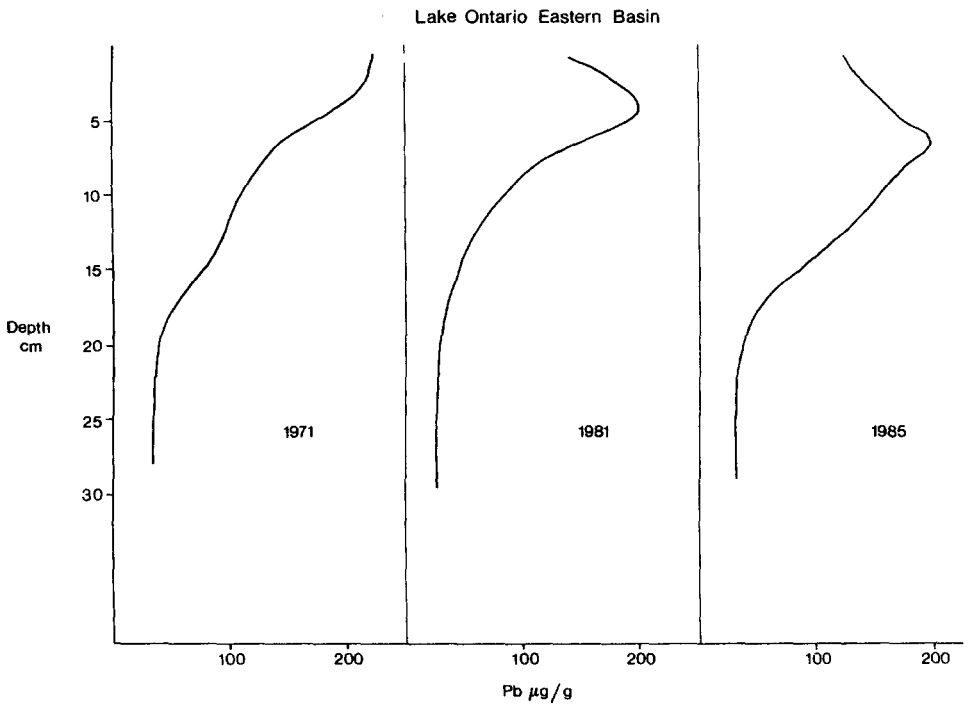

Fig. 7. Concentration profiles of Pb in sediment cores in 1971, 1981 and 1985 in eastern basin.

and chronological analysis of the sediments in order to ensure consistency in the sediment sampling techniques and analytical methods for the determination of concentrations of contaminants in sediments in the long-term monitoring program.

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