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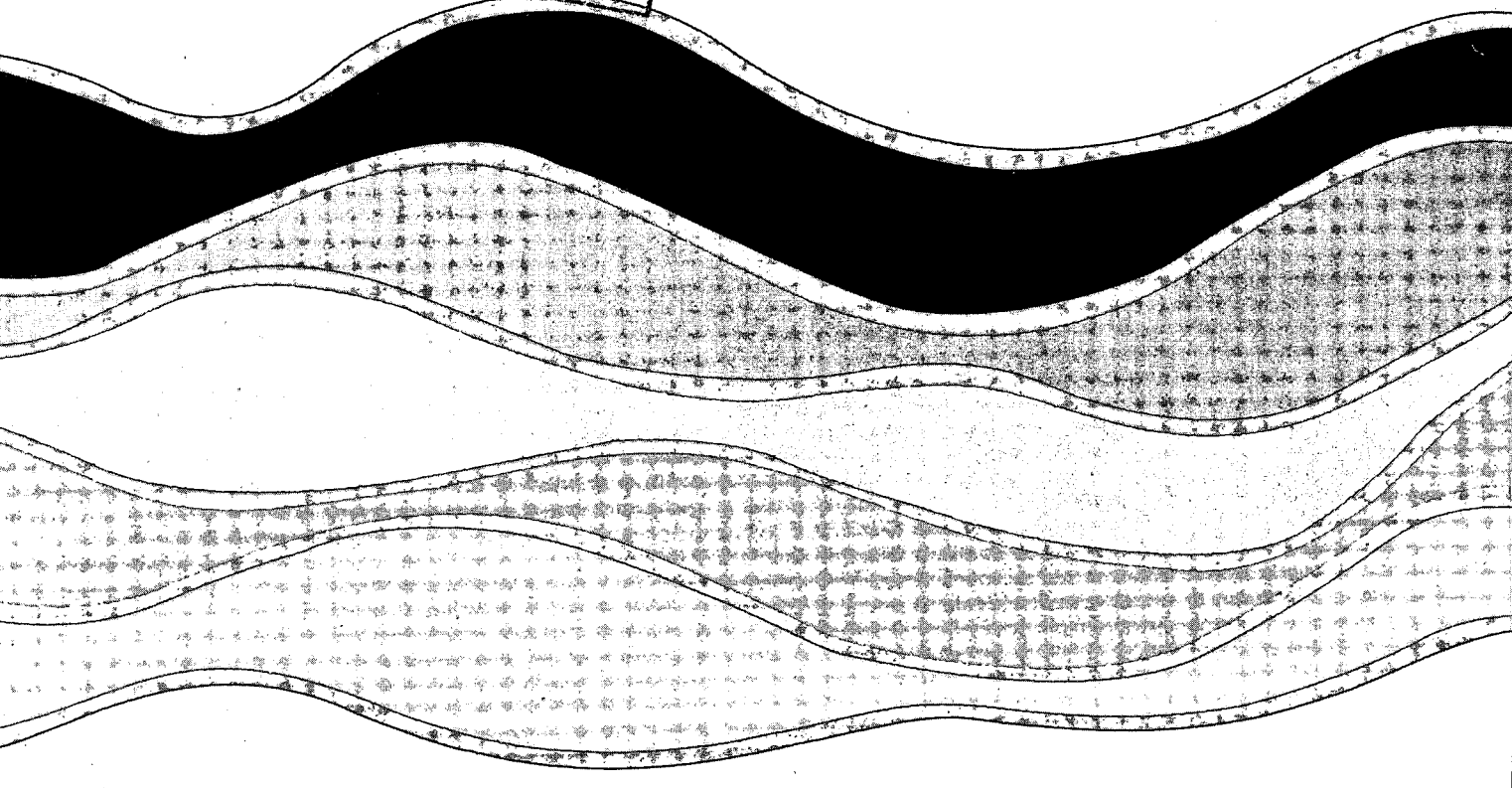

LAKE SEDIMENTS IN MONITORING POLLUTION

Alena Mudroch

NWRI Contribution No. 92-56

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MANAGEMENT PERSPECTIVE

Following the comprehensive study of the Niagara River/Lake Ontario pollution in the 1980's, it was recommended to use Lake Ontario bottom sediments in monitoring the effectiveness of remedial actions implemented in the lake's drainage basin. However, limited information existed for selection of the sediment monitoring sites in Lake Ontario.

This investigation was carried out to make a recommendation for selection of sampling sites for the long-term monitoring using bottom sediments as an 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. The results of the investigation showed that fine-grained sediments in the western, central and eastern basins of Lake Ontario are considerably homogeneous, and that sediment cores for the long-term monitoring of inputs of contaminants can be recovered at any location within the basins. However, more than one sampling site should be considered in each basin. Further, the sedimentation rate should be determined for each long-term monitoring site to confirm the trends in input of contaminants to the lake. The results of the investigation suggested that surficial sediments are unsuitable and only sediment cores should be used in the long-term monitoring.

SOMMAIRE À L'INTENTION DE LA DIRECTION

À la suite de l'étude de synthèse portant sur la pollution de la rivière Niagara et du lac Ontario dans les années 1980, il a été recommandé d'utiliser les sédiments de fond du lac Ontario pour surveiller l'efficacité des mesures d'assainissement appliquées dans le bassin versant du lac. Toutefois, il existait peu d'informations concernant le choix des sites de surveillance des sédiments dans le lac Ontario.

La présente étude a été menée en vue de formuler une recommandation concernant le choix des sites d'échantillonnage pour la surveillance à long terme au moyen des sédiments de fond comme registre de l'histoire des apports de contaminants dans le lac Ontario, en utilisant, notamment, un nombre minimal de sites de surveillances en fonction du coût des dosages des différents contaminants dans des échantillons de sédiments. Les résultats de l'étude ont révélé que les sédiments de faible granulométrie dans les bassins ouest, du centre et est du lac Ontario sont très homogènes, et que des carottes de sédiments pour la surveillance à long terme des apports de contaminants peuvent être prélevées n'importe où dans les bassins. Toutefois, il faudrait prévoir plus d'un site d'échantillonnage dans chacun des bassins. De plus, la vitesse de sédimentation devrait être établie pour chaque site de surveillance à long terme afin de confirmer les tendances au niveau de l'apport de contaminants dans le lac. Il semble, d'après les résultats de l'étude, que les sédiments de surface ne conviennent pas, et que seules des carottes de sédiments devraient être utilisées pour ce genre de surveillance.

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 (Si, Al, Ca, Mg, Fe, Na, K, Ti, Mn, P, As, Co, Cu, Cr, Ni, Pb and Zn) in the sediments. Results of the investigation indicated that fine-grained sediments in three Lake Ontario depositional basins are considerably homogeneous, and that few sediment cores should be collected within each basin for the long-term monitoring of inputs of contaminants to the lake.

RÉSUMÉ

Une étude a été menée pour choisir des sites en vue de la surveillance à long terme des apports de contaminants dans le lac Ontario en utilisant des sédiments de fond de faible granulométrie comme registre de l'histoire de la pollution. Le programme d'échantillonnage des sédiments a été conçu afin d'établir l'hétérogénéité des sédiments dans les bassins de sédimentation ouest, centre et est du lac. Des sédiments de surface et des carottes de sédiment ont été recueillis dans chaque bassin afin d'obtenir des renseignements sur la répartition horizontale et les profils de concentration des principaux éléments et des éléments à l'état de trace (Si, Al, Ca, Mg, Fe, Na, K, Ti, Mn, P, As, Co, Cu, Cr, Ni, Pb et Zn) dans les sédiments. D'après les résultats de l'étude, les sédiments de faible granulométrie dans trois bassins de sédimentation du lac Ontario sont très homogènes, et peu de carottes de sédiments devraient être prélevées dans chacun des bassins pour la surveillance à long terme des apports de contaminants dans le lac.

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 an 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 long-range atmospheric transport of different contaminants (for example, Eisenreich, 1987). This capacity of lake bottom sediments can be utilized in the long-term monitoring of effectiveness of remediation of inputs of contaminants into the environment from different sources.

In the 1980s, a comprehensive study was carried out on pollution of the Niagara River (Allan et al., 1983). The study showed that there is no deposition of fine-grained sediments on the bottom of the river, and that particle-associated contaminants are transported into Lake Ontario where they become deposited on the lake bottom (Mudroch and Williams, 1989). Durham and Oliver (1983) used Pb-210 and Cs-137 radiodating to trace the history of chlorinated hydrocarbon contamination of Lake Ontario sediments by the Niagara River. The historical record found in the sediments for most compounds studied was in good agreement with known production and usage pattern of the chemicals.

The results of a comprehensive study of pollution from the Niagara River 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. In the early 1970s, a geochemical survey of sediments was carried out in all the Great Lakes. The survey used only 3 cm of surficial sediments (Thomas and Mudroch, 1979). The results of the survey were used to evaluate horizontal distribution of metals and PCB in Great Lakes surficial sediments. 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 to locate sampling stations 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 to obtain data which would represent deposition of contaminants over the entire lake. Considering 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 selection of sampling sites for long-term monitoring using bottom sediments as an 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 x 0.5 m x 0.5 m) was collected at each sampling station and a surficial 3 cm of sediment were sampled from the core into polycarbonate plastic bags. At selected stations, sediment cores were collected by gently pushing polycarbonate core tubes 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). The core sections were collected into polycarbonate bags. One-half of the surface sediment samples was used for particle size distribution. The other half and all core sections were freeze-dried and pulverized to about 150 um 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). 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 (Mudroch and Mudroch, 1992) using powder pellets and different sediment, soil and rock material as standards. 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 to 35% silt-size particles (4 to 63 um) with the rest of clay-size particles (<4 um). Heterogeneity of the surface 0 to 3 cm sediment in a single box core 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 exception of Mn and As, the concentrations of major and trace elements were similar in all nine samples collected from the single box core, considering the precision of the analytical method. The difference in the

concentration of Mn was, most likely, due to 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 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.

Generally, concentrations of major and trace elements in the surficial 3 cm sediments were similar in all three depositional basins with exception of Fe, Al, Cu and Zn. 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 shown in Figure 2. Greater concentrations of Fe, Zn and Cu in the western basin than in the other two basins originated from inputs of these elements by the steel industry located at the west end of the lake, on the shore of Hamilton Harbour. Concentrations of Fe, Zn and Cu in suspended solids collected in Hamilton Harbour were up to 12%, 3,200 ug/g and 200 ug/g, respectively (Mayer and Manning, 1990), and up to 15%, 5,500 ug/g and 500 ug/g, respectively, in bottom sediments in the harbour (Mudroch A.,unpublished data). 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.

3.2 Vertical Distribution of Major and Trace Elements in Sediments

Concentrations 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 past 40 years. 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 Ca in the lake (Mudroch, unpublished data). 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 changes in concentration profiles of the trace elements was similar in all cores collected in the three basins. An example of 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. The increase in the concentrations of Pb and Ni above the background level reflected changes in inputs of these elements to the lake. The concentrations of Pb and Ni started to increase at about 8 cm sediment depth (Figure 3). This increase reflected the commencement of inputs of Pb and Ni from different anthropogenic activities in the Lake Ontario drainage basin, including atmospheric inputs, particularly Pb, to the lake. The greatest concentrations of Pb and Ni were found between 2 to 4 cm and 0 to 5 cm sediment depth, respectively (Figure 3). The pattern of the concentration profiles of both elements was similar in all four cores collected in the western basin. However, due to the variability in sedimentation rates within and among the basins of Lake Ontario (J.A.Robbins, NOAA, Great Lakes Environmental Laboratories, personal communication), the concentration profiles differed from one core to the other (Figure 3).

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 to 6. Minimum and maximum concentrations shown in the figures represent variability among individual cores collected in each basin. Following the fast 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 in the past 10 to 15 years.

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 eastern basin in 1971, 1981 and 1985. Determination of 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 to 7 cm of the cores. The decrease of lead concentration at the surface of the sediment profile appears to reflects the implementation of unleaded gasoline in Canada and the U.S.A. Trefry et al. (1985) found a relationship between 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 buried by settling particles containing less Pb.

4 CONCLUSIONS

The results of the investigation can be used in the selection of sampling sites for long-term monitoring of inputs of contaminants to Lake Ontario. The geochemistry of the sediments indicated that fine-grained sediments in the western, central and eastern basins are considerably homogeneous, and that sediment cores for the long-term monitoring of inputs of contaminants 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 make surficial

sediments unsuitable for monitoring. A protocol has to be developed describing details of sediment collection and methods used in sample preparation and analysis of the sediments to ensure consistency of sediment sampling techniques and analytical methods for determination of concentrations of contaminants in sediments in the long-term monitoring program.

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TABLES

TABLE I

Concentrations of major and trace elements in 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

ug/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 analysis of one sample.

TABLE II

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

ELEMENT	BASIN	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

TABLE III

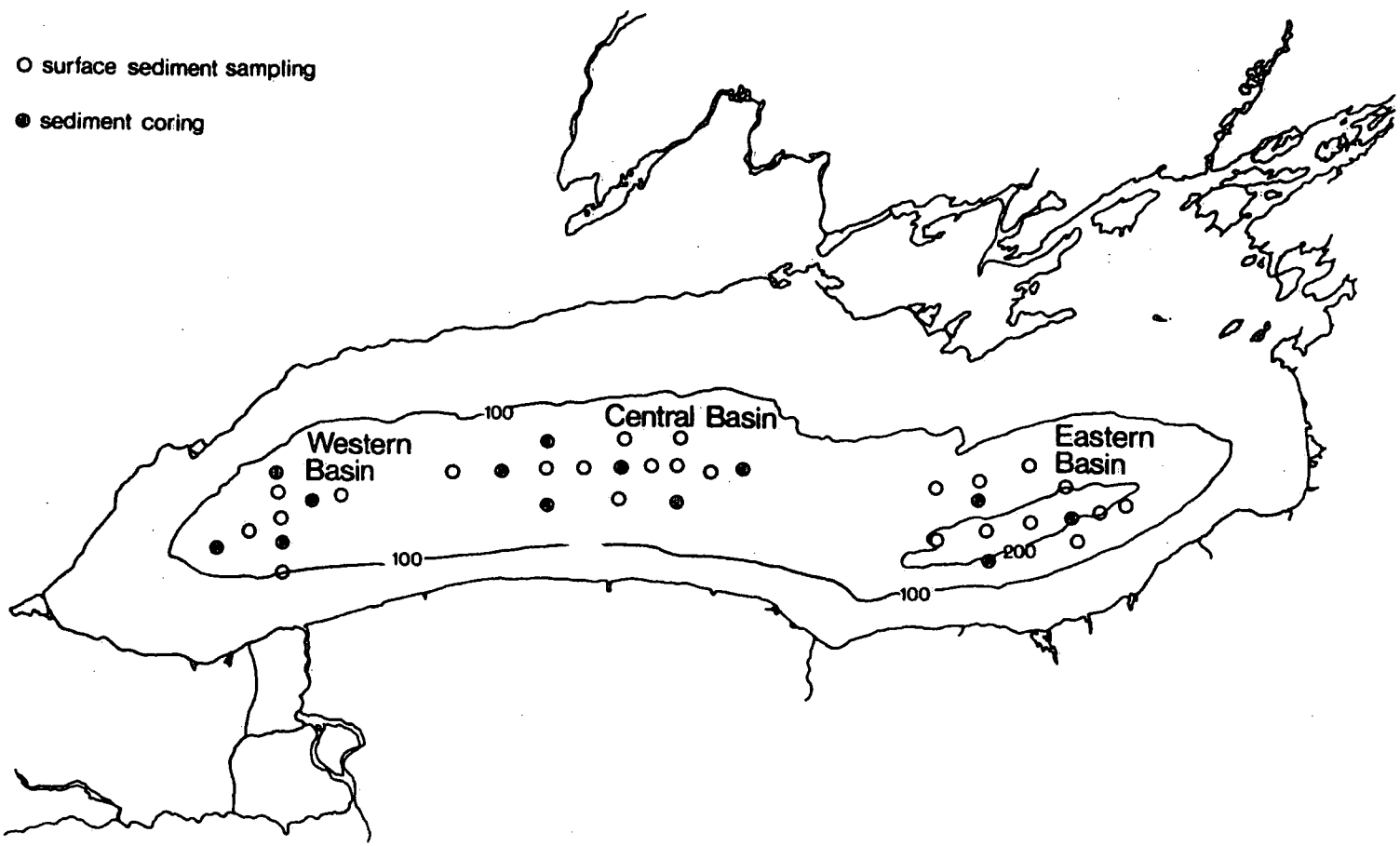
Concentrations of trace elements in surficial sediments (ug/g dry weight)

ELEMENT	BASIN	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

FIGURES

LIST OF FIGURES

LAKE ONTARIO - SEDIMENT SAMPLING GRID



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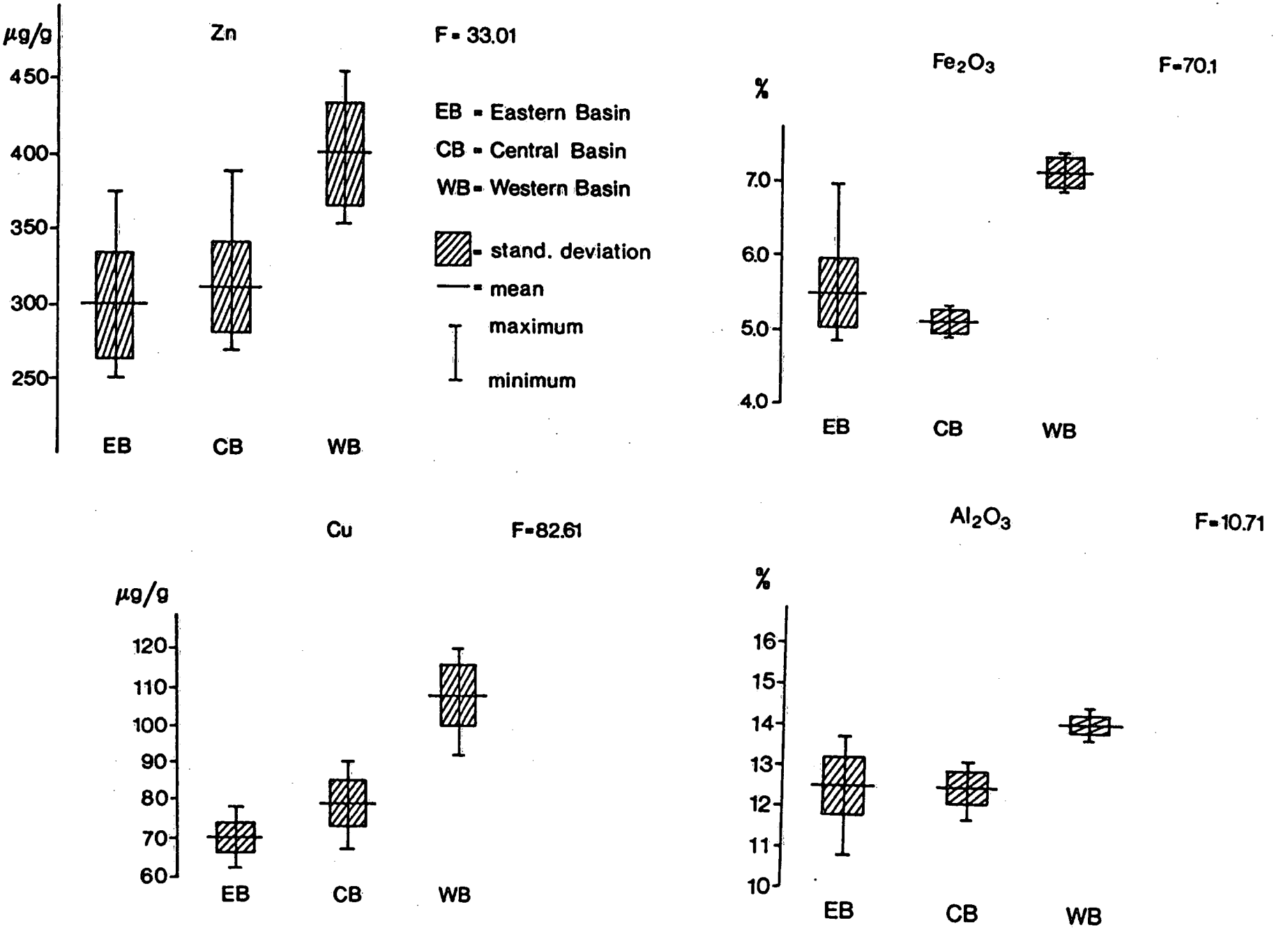
µg/g
Zn
F = 33.01
450
400
350
300
250
EB
CB
WB
EB = Eastern Basin
CB = Central Basin
WB = Western Basin
= stand. deviation
= mean
maximum
minimum
Cu
F=82.61
µg/g
120
110
100
90
80
70
60
EB
CB
WB
Fe2O3
F=70.1
%
7.0
6.0
5.0
4.0
EB
CB
WB
Al2O3
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%
16
15
14
13
12
11
10
EB
CB
WB

FIGURE 2

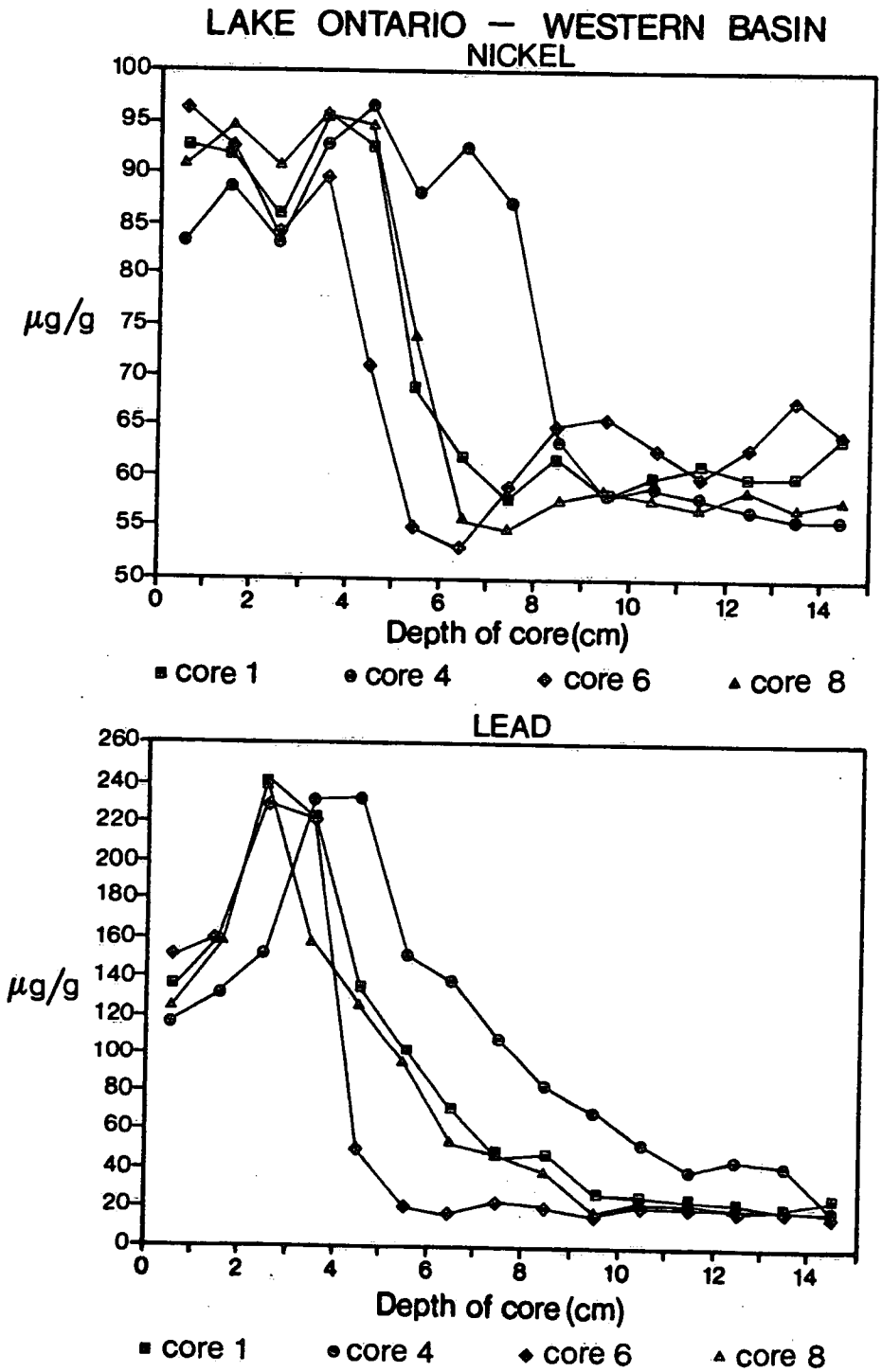
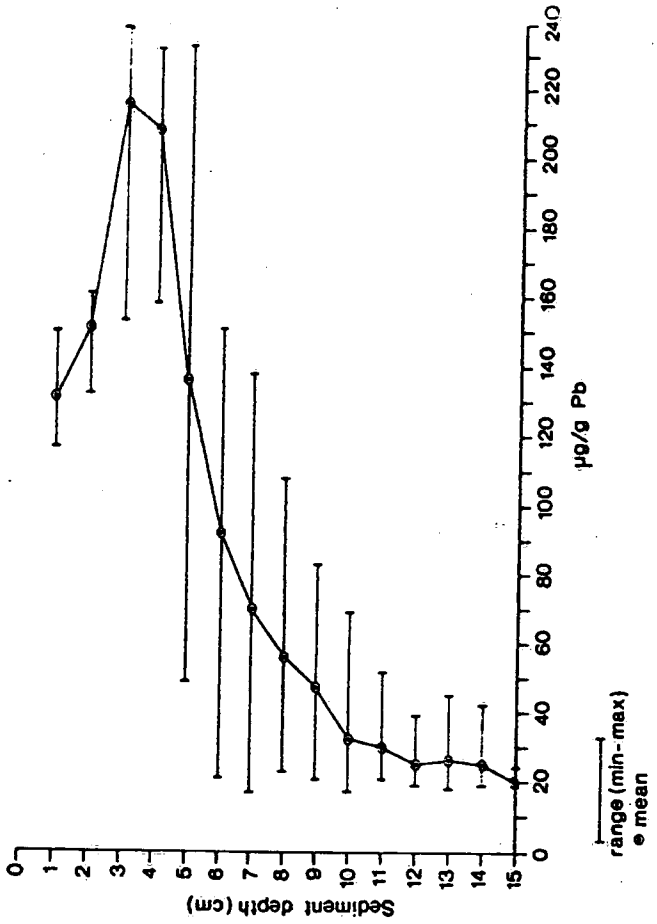
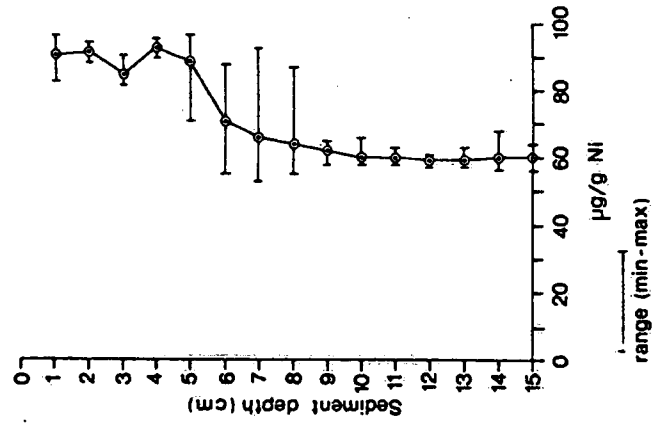
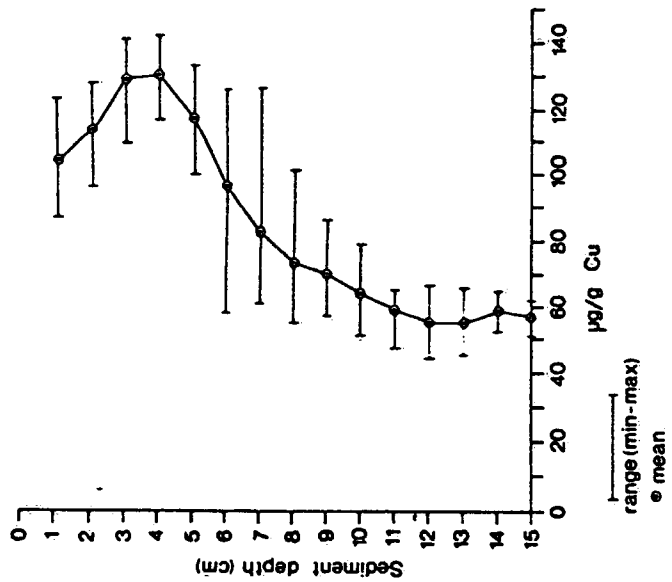

LAKE ONTARIO — WESTERN BASIN
NICKEL
μg/g
100
95
90
85
80
75
70
65
60
55
50
0
2
4
6
8
10
12
14
Depth of core (cm)
core 1
core 4
core 6
core 8
LEAD
μg/g
260
240
220
200
180
160
140
120
100
80
60
40
20
0
0
2
4
6
8
10
12
14
Depth of core (cm)
core 1
core 4
core 6
core 8

FIGURE 3


Sediment depth (cm)
µg/g Pb
range (min-max)
mean


Sediment depth (cm)
µg/g Ni
range (min-max)
mean


Sediment depth (cm)
µg/g Cu
range (min-max)
mean

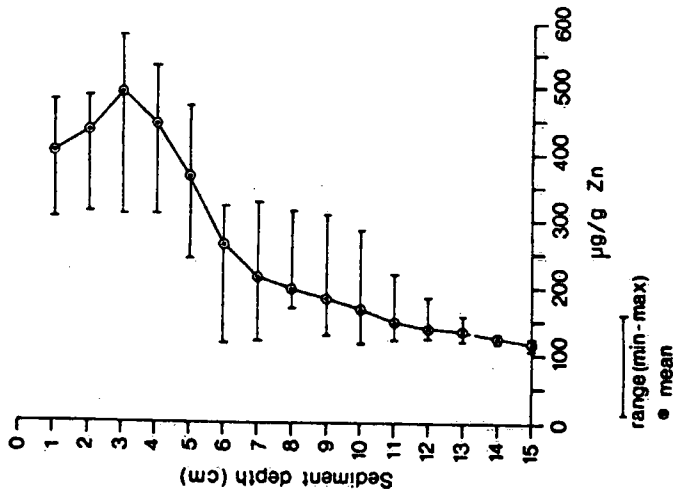
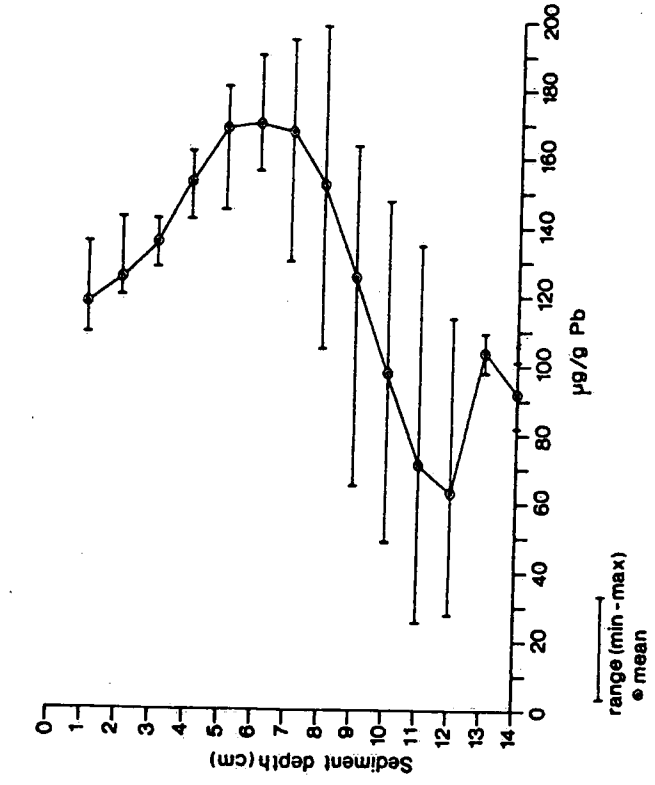
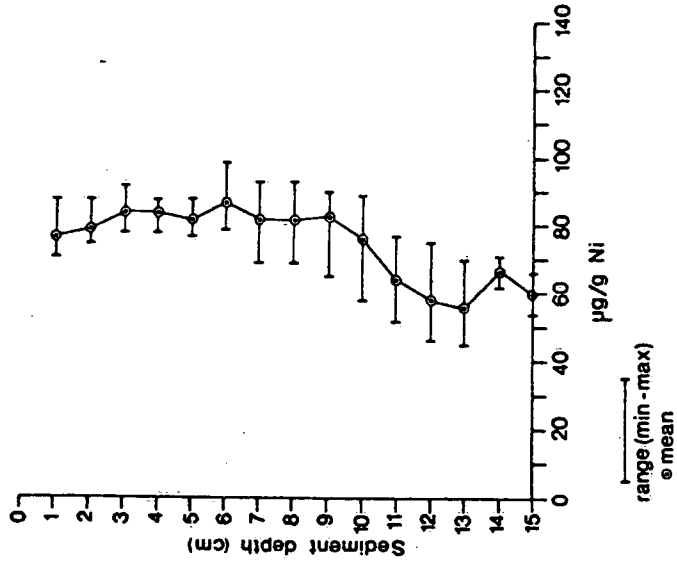
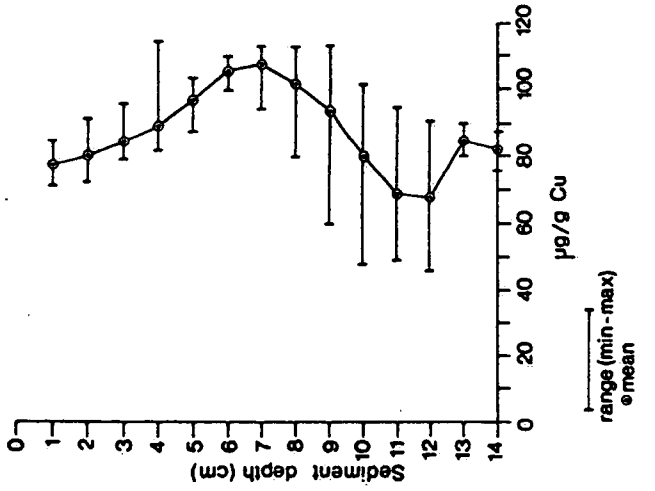

Sediment depth (cm)
µg/g Zn
range (min-max)
mean

FIGURE 4


Sediment depth (cm)
µg/g Pb
range (min-max)
mean


Sediment depth (cm)
µg/g Ni
range (min-max)
mean


Sediment depth (cm)
µg/g Cu
range (min-max)
mean

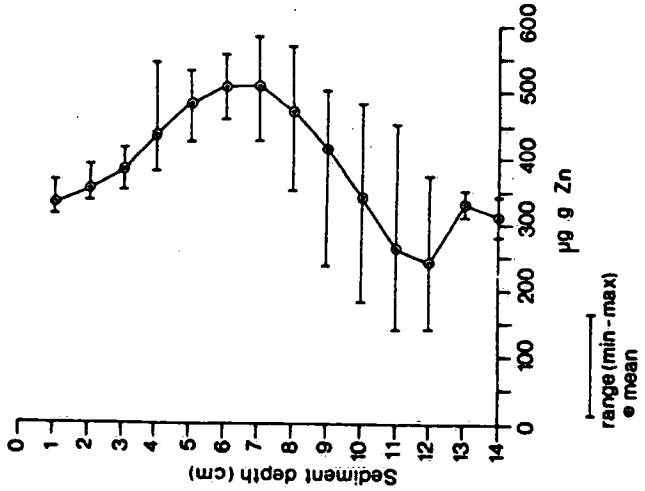
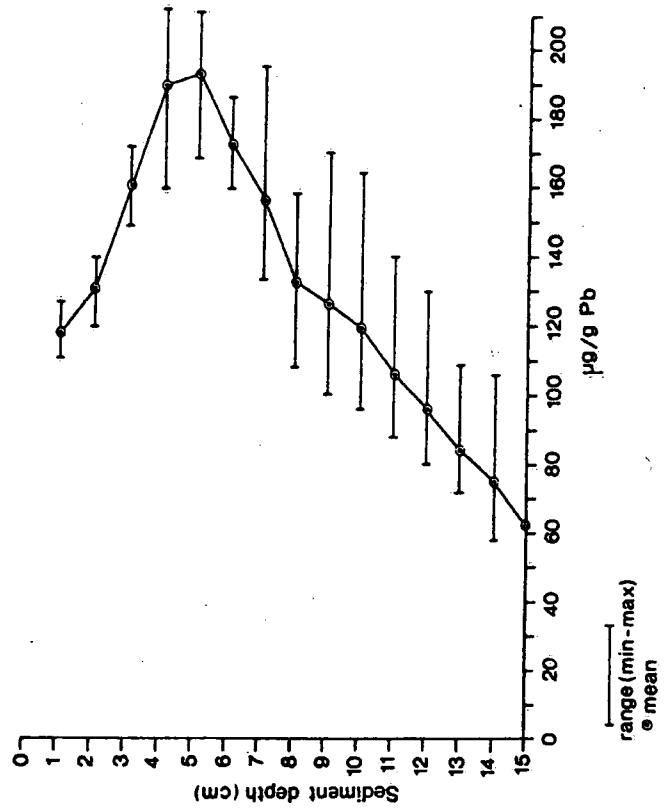
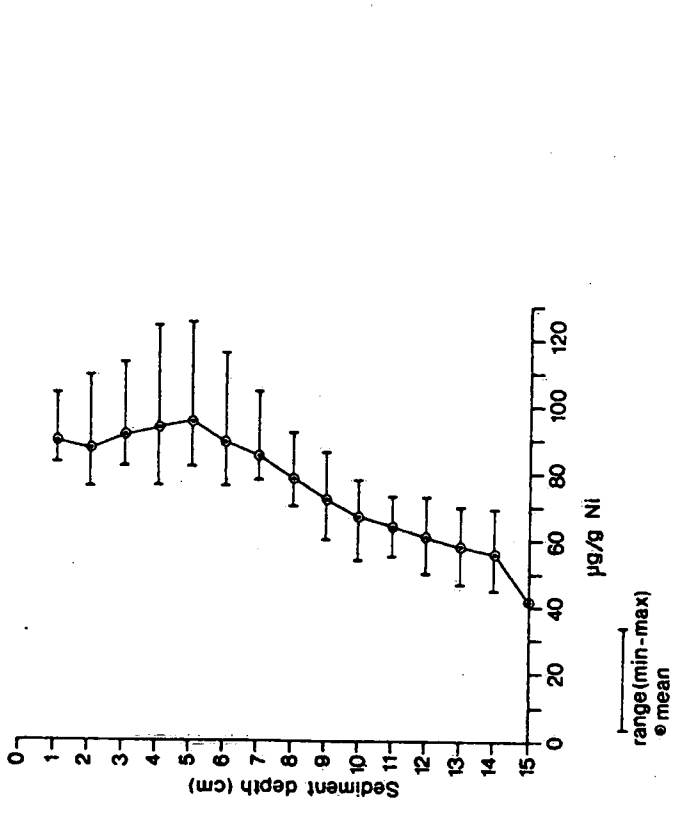
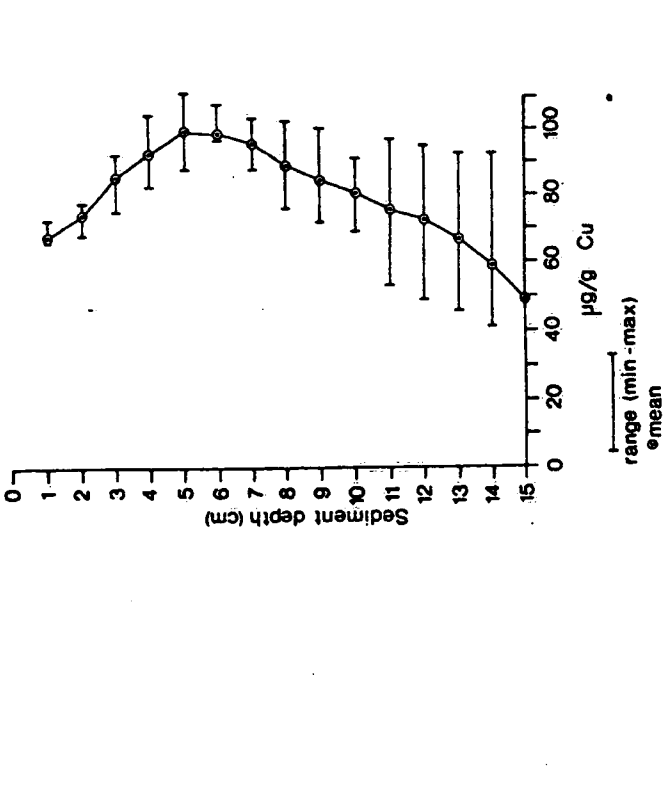

Sediment depth (cm)
µg g Zn
range (min-max)
mean

FIGURE 5


Sediment depth (cm)
µg/g Pb
range (min-max)
mean


Sediment depth (cm)
µg/g Ni
range (min-max)
mean


Sediment depth (cm)
µg/g Cu
range (min-max)
mean

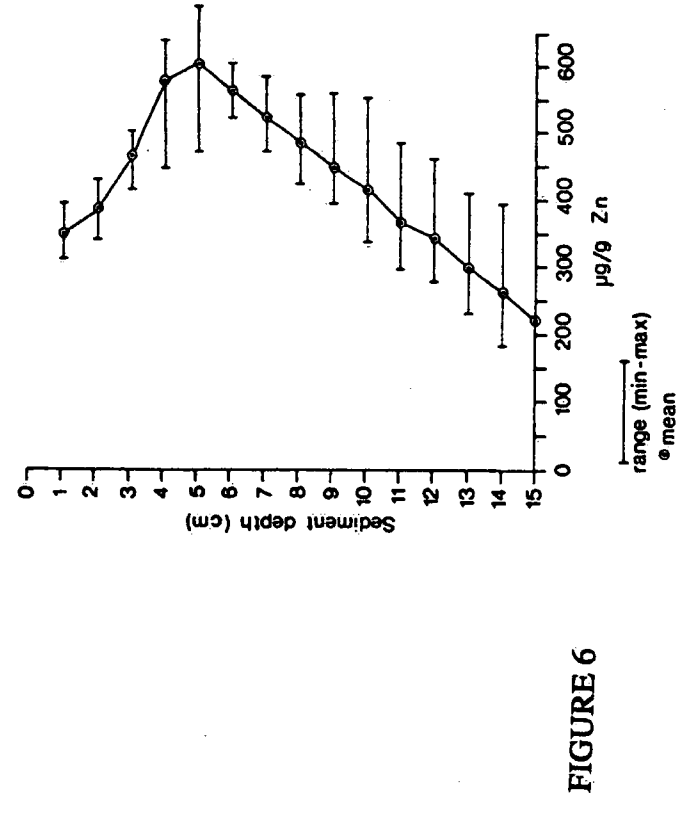

Sediment depth (cm)
µg/g Zn
range (min-max)
mean

FIGURE 6

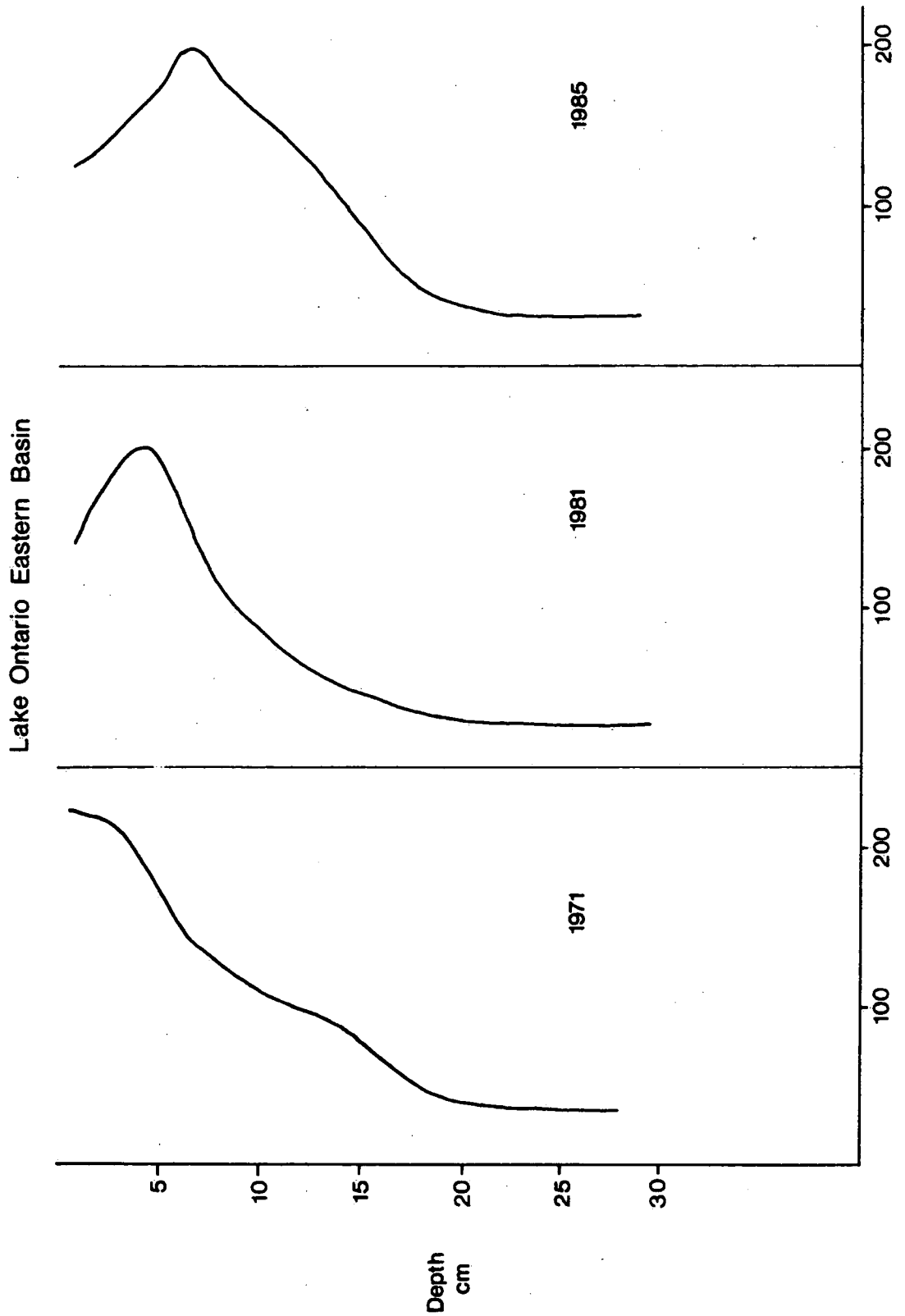
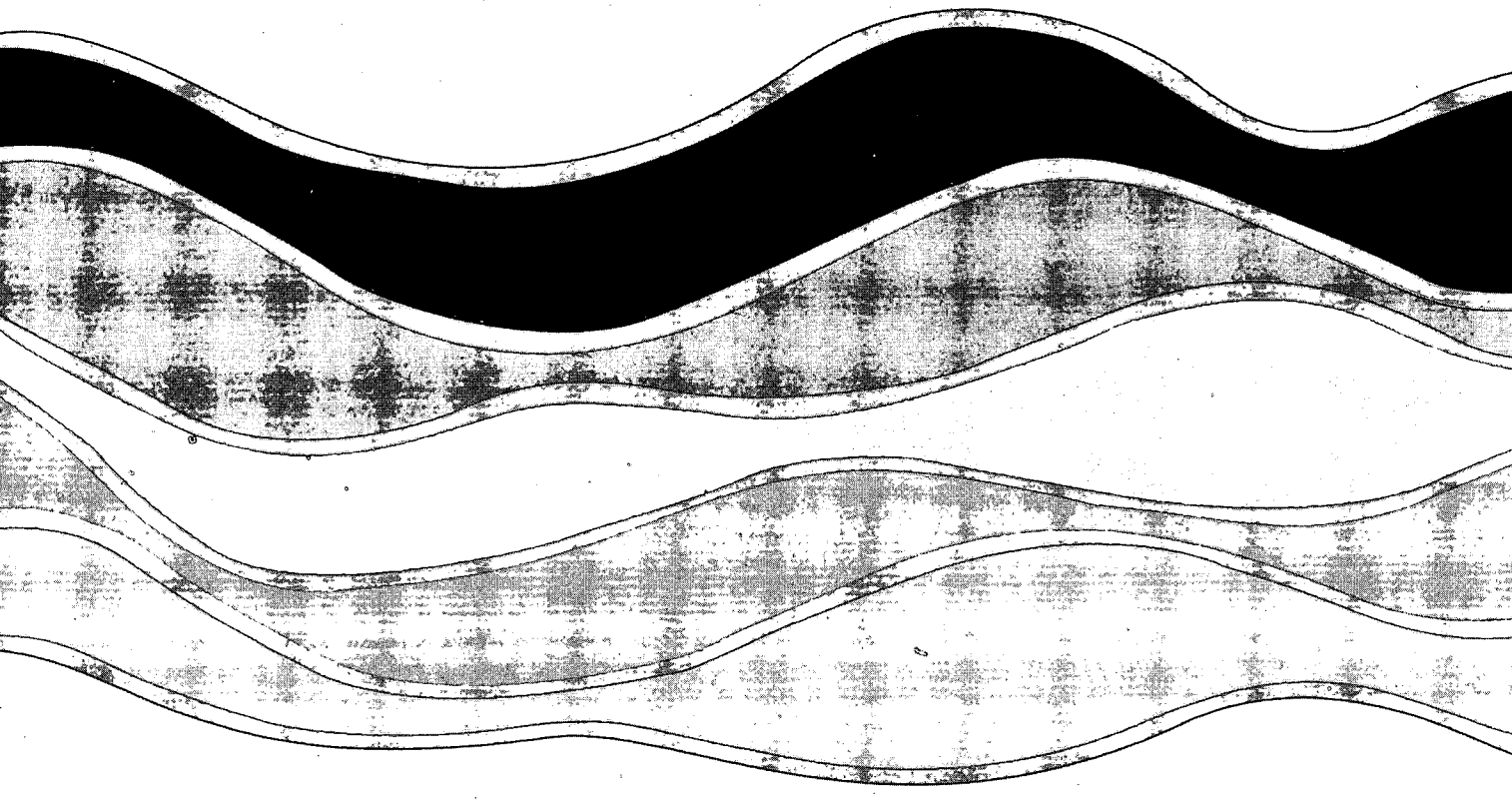

Lake Ontario Eastern Basin
1971
1981
1985
Depth cm
5
10
15
20
25
30
100
200
Pb µg/g

FIGURE 7



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