GEOCHEMISTRY AND DISTRIBUTION OF METALS IN RADIODATED SEDIMENT CORES FROM LAKE ST. LOUIS, ST. LAWRENCE RIVER

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ABSTRACT

Particle size distribution, geochemical composition and concentrations of metals (Cu, Cr, Pb, Co, V, Ni, Hg and Zn) were determined in radiodated cores collected from Lake St. Louis, St. Lawrence River. About 20 cm of fine grained sediment accumulated during the past 30 years at two sites near the centre of the lake. However, a 20 cm thick sediment layer was deposited over the past five years at two different areas in the southern part of the lake. The concentration profiles of major elements and most of the investigated metals in sediment cores indicated a continuous input of geochemically similar material at the sampling sites. A uniform particle size distribution within the sediment profile showed that these areas are settling zones for particles of similar hydrodynamic properties transported by the St. Lawrence River. The concentration profiles of Hg and Zn in the sediments indicated an input from local sources along Lake St. Louis. Observed concentrations of investigated metals in Lake St. Louis sediments were ascribed to the particle sorting, transport and deposition of silt-size (2 to 63 μm grain size) particles which may contain smaller concentrations of metals than clay-size (< 2 μm grain size) particles in the depositional basins of Lake Ontario.

MANAGEMENT PERSPECTIVE

The concentrations of metals in sediments in Lake St. Louis, St. Lawrence River, were smaller than those in depositional basins in Lake Ontario. It appears that Lake St. Louis provides only a temporal storage for metals associated with the clay-size (<2 µm grain size) sediment particles which become eventually resuspended and transported downstream St. Lawrence River and eventually become deposited in the river's estuary.

EXECUTIVE SUMMARY

The distribution of metals was investigated in radiodated sediment cores collected in Lake St. Louis, St. Lawrence River. The geochemistry of the sediments and concentrations of metals in a 20 cm sediment layer collected at two areas near the centre of the lake indicated a continuous input of geochemically similar material over past 30 years. Greater sedimentation rates were found in the southern part of the lake. A uniform particle size distribution through the cores showed that these areas are settling zones for particles of similar hydrodynamic properties transported by the St. Lawrence River. Observed concentrations of investigated metals in Lake St. Louis sediments were ascribed to the particle sorting, transport and deposition of silt-size (2 to 63 μm grain size) particles which may contain smaller concentrations of metals than clay-size (<2 μm grain size) particles in the depositional basins of Lake Ontario.

RÉSUMÉ

La répartition des métaux a été déterminée dans des carottes de sédiments, datées par la méthode des isotopes radioactifs, qui ont été prélevées dans le lac Saint-Louis (fleuve Saint-Laurent). La géochimie des sédiments et la teneur en métaux mesurée dans une couche de sédiments de 20 cm d'épaisseur prélevée à deux endroits près du centre du lac ont révélé qu'il y avait eu au cours des 30 dernières années un apport constant de matériaux à propriétés géochimiques semblables. On a relevé des taux de sédimentation plus importants dans la partie sud du lac. Une distribution granulométrique uniforme à l'intérieur des carottes a montré que ces endroits constituent des zones de sédimentation pour des particules à propriétés hydrodynamiques semblables charriées par les eaux du fleuve Saint-Laurent. La teneur en métaux mesurée dans les sédiments du lac Saint-Louis était attribuable au tri, au transport et au dépôt de particules de la taille des silts (granulométrie : 2 à 63 µm). La teneur en métaux de ces particules peut être plus faible que celle des particules de la taille des argiles (granulométrie inférieure à 2 µm) qui se trouvent dans les bassins de sédimentation du lac Ontario.

PERSPECTIVE-GESTION

La teneur en métaux des sédiments qui ont été prélevés dans le lac Saint-Louis (fleuve Saint-Laurent) était moins importante que celle des échantillons prélevés dans les bassins de sédimentation du lac Ontario. Il semble que le lac Saint-Louis ne soit qu'un lieu de dépôt temporaire pour les métaux associés aux particules de sédiments de la taille des argiles (granulométrie inférieure à 2 µm) qui, à la longue, redeviennent en suspension dans l'eau, sont transportés en aval du fleuve Saint-Laurent et se déposent finalement dans son estuaire.

RÉSUMÉ

La distribution granulométrique, la composition géochimique et la teneur en métaux (Cu, Cr, Pb, Co, V, Ni, Hg et Zn) ont été déterminées dans des carottes, datées par la méthode des isotopes radiactifs, qui ont été prélevées dans le lac Saint-Louis (fleuve Saint-Laurent). À deux endroits près du centre du lac, une couche de sédiments à grain fin d'à peu près 20 cm d'épaisseur s'est accumulée au cours des 30 dernières années. Toutefois, au cours des cinq dernières années, une couche de sédiments de 20 cm d'épaisseur s'est accumulée à deux endroits de la partie sud du lac. Les diagrammes de concentration des principaux éléments et une grande partie des métaux étudiés présents dans les carottes de sédiments ont révélé qu'il y avait eu un apport constant de matériaux à propriétés géochimiques semblables aux lieux d'échantillonnage. Une distribution granulométrique uniforme à l'intérieur du profil sédimentaire a montré que ces endroits constituent des zones de sédimentation pour les particules à propriétés hydrodynamiques semblables charriées par les eaux du fleuve

Saint-Laurent. Les diagrammes de teneur, pour le Hg et le Zn qui se trouvaient dans les sédiments, ont révélé un apport en provenance de sources locales se trouvant le long du lac Saint-Louis. La concentration de métaux étudiés qui a été mesurée dans les sédiments du lac Saint-Louis était attribuable au tri, au transport et au dépôt de particules de la taille des silts (granulométrie : 2 à 63 µm). La teneur en métaux de ces particules peut être plus faible que celle des particules de la taille des argiles (granulométrie inférieure à 2 µm) qui se trouvent dans les bassins de sédimentation du lac Ontario.

INTRODUCTION

The St. Lawrence River with a discharge 7400 m^3/sec and 450 km length drains the Great Lakes into the Gulf of St. Lawrence of the Atlantic Ocean. The river is primarily a collection and transport system for toxic contaminants. Some of the toxic chemicals come from Lake Ontario but many others are added from point and diffuse sources along the river's course (Allan, 1986; 1987). Water soluble and particulate contaminants from Lake Ontario and sources along the river become transported by the river into its estuary.

Lake St. Louis with an area of 148 km^2 (Prefontaine, 1942) is one of the four small riverine lakes which are an integral part of the St. Lawrence River (Figure 1). The lake is located at the confluence of the Ottawa and St. Lawrence Rivers. The mean and maximum depth of the lake are 2 and 28 m, respectively (Pageau et al. 1971). The spatial distribution of metals and PCB's in surficial sediments of Lake St. Louis was investigated by Jarry et al. (1985). The results of the investigation showed that the concentrations of contaminants in the sediments exceeded currently used Ontario Ministry of the Environment guidelines for the disposal of dredged material into open water.

The objectives of the present study were to investigate the temporal changes in sediment geochemistry and historical trends in concentrations of contaminants in the sediments to assess the significance of Lake St. Louis as a sink of contaminants transported through the St. Lawrence River.

MATERIALS AND METHODS

Sediment collection and sample preparation

Sediment was collected in the depositional areas identified by earlier surveys of Lake St. Louis (Jarry *et al*., 1985; Rukavina, 1986). Four sites were selected for the coring in the lake (Figure 1). Three cores were collected at each sampling station using a modified Kajak-Brinkman corer equipped with a plastic liner. All cores were subsampled into 1 cm sections. All sections from two cores from each station were freeze-dried, ground to about 190 μm particle size and used for the dating and geochemical analyses. The sections of third cores were used for the determination of particle size distribution.

Analytical methods

The determination of the particle size distribution was carried out by the method described by Duncan and LaHaie (1979).

The concentrations of major elements (Si, Al, Fe, Ca, Mg, K, Na, Ti, P and Mn) and metals (Co, Cu, Pb, V, Ni and Zn) were determined by X-ray fluorescence spectrometry using the method described by Mudroch (1985). The concentrations of Hg were determined in all samples by the method described by Mudroch and Kokotich (1987). The concentrations of organic and inorganic C were determined by a Leco carbon analyzer.

Sediment dating

The total Pb-210 and Ra-226 levels in the sediment core sections were measured by low-energy gamma-ray spectrometry using techniques described by Joshi (1987). The contribution of atmospherically-delivered or excess Pb-210 (hereafter referred to as Pb-210) was obtained by subtracting the amount of Pb-210 supported by Ra-226 from total Pb-210.

Calculation of sediment age

Assuming a constant rate of supply of Pb-210, it can be shown (Goldberg, 1963) that the age t (in years) of a sediment core section at depth x cm below the sediment/water interface is given by

$$t = \frac{1}{\lambda} \quad \ln \frac{A(o)}{A(x)} \tag{1}$$

where A(o) is the total Pb-210 (Bq cm^{-2}) in the sediment column, A(x) is the Pb-210 beneath sediments of age t, and the decay constant of Pb-210 (0.0311 y^{-1}). The activities A(o) and A(x) were estimated as described by Joshi _et al_. (1988) who have recently outlined the procedures used in the estimation of these parameters when the Pb-210 measurements are available only for a limited depth as is the case in the present study. The effect of mixing on sediment age has been estimated applying the equation (Oldfield and Appleby, 1984)

$$t = \frac{1}{\lambda} \quad \ln \frac{A(o)}{A(x) + A(m)} , \tag{2}$$

where $$A_m = \frac{C(x)}{C(s)} \cdot A_m(o)$$

In this equation $A_m(o)$ represents the integrated Pb-210 activity in the mixing zone, C(s) is the Pb-210 concentration (Bq g^{-1}), below the mixing zone, and C(x), in Bq g^{-1}, the concentration of Pb-210 at depth x.

RESULTS

All sediment cores consisted of grey silty clay with particles 63 μm. Generally, 54 to 77% of the particles were <8 μm and 21 to 46% were <2 μm. About 20 to 24 cm long cores were recovered at stations 21 and 17. The sediment below this depth was a mixture of fine sand and clay. Longer cores (up to 30 cm) were recovered at stations 3 and 9. The sediment below 30 cm depth was firm fine clay.

The age/depth profiles of four sediment cores from Lake St. Louis, obtained using equations (1) and (2) are shown in Figure 2. The mixing zone in core 21 could not be ascertained from the measured Pb-210 profile, and, therefore, no mixing-influenced ages were assigned to core sections. The estimated thickness of the mixing zone in cores 3, 9 and 17 was 5.3, 6.2 and 4.5 cm, respectively. In these cores, the incorporation of mixing parameter gives a lower estimate of the age. This is in agreement with theoretical predictions (Joshi *et al.*, 1988). The results indicated that the sediment deposited at each station is very recent, in particular at stations 17 and 21.

Generally, similar concentrations of major elements and organic and inorganic C were found in the sediment profiles at all stations. Consequently, only the concentration profiles of these elements in core 3 are shown (Figure 3). The concentration profiles of Cu, Ni, Co, Pb, Cr, Zn and V in the sediments at stations 3, 17 and 21 are shown in Figures 4 to 6 and those of Hg in the sediments from stations 3 and 21 in Figures 7 and 8. Sediment age shown in all cases is that obtained by the incorporation of the mixing parameter except for station 21 where, as noticed earlier, mixing depth could not be established.

DISCUSSION

The dating of the sediment cores showed that 20 cm of recent sediment was deposited during past five years at stations 17 and 21. The incorporation of the mixing parameter in the calculation of sediment age showed that about 4.5 cm of the surface sediment was mixed at station 17. The mixing zone in the sediment at station 21 could not be determined from the measured Pb-210 profile. It appears that these areas in Lake St. Louis are only transition zones for the deposition of fine grained sediments. On the other hand, 20 cm of recent sediment at stations 3 and 9 was deposited during the past 30 years indicating that these areas of the lake are the depositional zones for some of the fine grained sediments ($\leqslant$63 µm grain size) transported by the river.

The concentration profiles of major elements and inorganic carbon, which represents the concentrations of carbonates, indicated a continuous input of geochemically similar material over past 40 years to stations 3 and 9. Only small changes occurred in the accumulation of sediment-associated metals at both stations. A uniform particle size distribution and similar geochemistry within the 30 cm sediment layer at station 3 confirmed that this area is a settling zone for particles of similar hydrodynamic properties transported through the river. However, there was an indication of some mixing of the surface sediment layer at these stations. The concentration profile of Mn in the sediment at station 3 was compared to that from a depositional basin in Lake Ontario (Figure 9). The increase of Mn in surface 5 cm is due to the migration and precipitation of this element at the sediment surface in the relatively undisturbed depositional area of Lake Ontario. This migration and accumulation of Mn was not observed at the surface of the sediment in the depositional area in Lake St. Louis. The mixing of the surface sediment layer, rather than the anoxic regime at the sediment/water interface seems to be responsible for the lack of migration of Mn towards the sediment surface.

In depositional basins of Lake Ontario the concentrations of organic carbon increased two to three times towards the surface of the sediment. The concentration profiles of organic carbon at stations 3 and 21 in Lake St. Louis showed only a small accumulation of organic matter in surface sediments. A greater increase of organic carbon in 5 cm surface sediment at station 21 than at station 3 may be attributed to the deposition of more recent sediments (1984-85) containing less decomposed organic matter than in about eight years old sediment at station 3.

The only two metals with changes in concentration profiles were Zn and Hg. An increase in the input of Zn during past 30 years was observed at stations 3 and 9. On the other hand, a decrease in Zn input occurred recently at station 17. A uniform loading of Zn during past five years was observed at station 21. The concentration profiles in the sediments in Lake St. Louis most likely reflect the changes in local inputs of Zn to the lake. The concentrations of Hg were an order of magnitude greater in the sediments at station 21 than at stations 3 and 9. A chlor-alkali plant on the southern shore of Lake St. Louis is an important point source of Hg in the sediments at station 21 and the south part of the lake (Sloterdijk, 1983; Jarry *et al*., 1985). Consequently, the fluctuations in Hg concentrations in the sediment core from station 21 represent local events at the point source. This source may contribute to the Hg contamination of sediments in other depositional areas of Lake St. Louis. However, most likely Hg contaminated sediments will not be transported toward station 3 in the northern part of the lake (Figure 1). The increase in Hg loading at this station after 1964 indicates input of Hg from other sources along the St. Lawrence River.

The concentration of metals in about 5 to 7 cm surface sediments from Lake St. Louis are compared to those from Lake Ontario, Ottawa River and St. Lawrence River, about 3 km upstream from Lake St. Louis in Table 1. The concentrations of Cu, Cr, Co, Ni, Pb, V, Zn and Hg were higher in the sediments from Lake St. Louis than those of the sediments collected in the upstream area of the St. Lawrence River and Ottawa River. The concentrations of Cu and Ni were lower in the sediments from Lake St. Louis than those found in recent sediments from Lake Ontario. Similarly, concentrations of Pb were lower in Lake St. Louis surficial sediments whan compared with those from Lake Ontario; however, they were higher than Lake Ontario background levels. Similar concentrations of Zn were found in surficial sediments from Lake Ontario and Lake St. Louis. These concentrations were five to six times greater than the background for Lake Ontario. The concentrations of Cr, Co and V in surficial sediments from Lake Ontario and Lake St. Louis were similar to those in pre-colonial sediments of Lake Ontario. These metals are derived mainly from the materials of the regional geology of the lower Great Lakes (Thomas and Mudroch, 1979). Increased concentrations of Hg in surficial sediments of Lake St. Louis originated from local sources, and were greater in some areas than those in Lake Ontario surficial sediments.

The relationship between various sediment particle sizes and the concentrations of metals in Lake St. Louis is shown in

Figure 10. Each particle size fraction contained a different concentration of specific metals. Consequently, the concentrations of metals in sediments will be different at an area of accumulation of particles <13 µm than for example at an area with most particles of 18 to 38 µm grain size. The greatest concentration of metals in the sediment in a lake's depositional basin is usually associated with particles <2 µm (Mudroch, 1984). However, only 21 to 46% of the sediment particles were <2 µm at stations 3, 9, 17 and 21 in Lake St. Louis, indicating that these areas are accumulation zones for particles mostly 2 to 63 µm large. In addition, these areas may provide only a temporary storage for <2 µm particles which become eventually resuspended and transported downstream. Consequently, small particles with greatest concentrations of metals will be transported into an area with hydrodynamic conditions permitting their settling, which may be the estuary of the St. Lawrence River. These observations are supported by relatively small thickness of the recent sediment layer in Lake St. Louis depositional areas. The residual sediment in these zones is of sufficiently large grain size, high in density and cohesive so that it cannot be moved within the local energy regime.

CONCLUSIONS

1. About 20 to 30 cm of recent fine grained sediment (<63 μm grain size) accumulated in four areas of Lake St. Louis in the St. Lawrence River. At two of these areas, the age of a 20 cm sediment layer was about 30 years. At the other two areas the 20 cm thick sediment layer was deposited in past five years.
2. About 21 to 46% of sediment particles in sediment cores collected at these four areas were <2 μm, and 54 to 77% were <8 um. The concentration profiles of major elements and most of the investigated metals in sediment cores indicated a continuous input of geochemically similar material. A uniform particle size distribution through the cores showed that these areas are settling zones for particles of similar hydrodynamic properties transported by the St. Lawrence River.
3. The concentration profiles of Hg and Zn in the sediment indicated an input of these metals from local sources along Lake St. Louis. The concentrations of Cr, V and Co in sediments in the depositional zones were similar to both background and surficial sediment concentrations in depositional basins of Lake Ontario. The concentrations of Cu, Ni and Pb were lower than those in surficial sediments in Lake Ontario depositional basins. Observed concentrations of investigated metals in Lake St. Louis sediments were ascribed to the particle sorting,

transport and deposition of silt-size (2 to 63 μm grain size) particles which may contain smaller concentrations of metals than clay-size (<2 μm grain size) particles in the depositional basins of Lake Ontario. Consequently, Lake St. Louis provides only a temporal storage for metals associated with clay-size sediment particles which become eventually resuspended and moved downstream.

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FIGURE CAPTIONS

Figure 1 Sampling stations in Lake St. Louis

Figure 2 The age/depth profiles of sediment cores

Figure 3 Concentration profiles of major elements in the sediment from station 3

Figure 4 Concentration profiles of metals in sediment from station 3

Figure 5 Concentration profiles of metals in sediment from station 17

Figure 6 Concentration profiles of metals in sediment from station 21

Figure 7 Concentration profile of Hg in sediment from station 3

Figure 8 Concentration profile of Hg in sediment from station 21

Figure 9	Concentration profiles of Mn in sediment from depositional basin in Lake Ontario and from station 3 in Lake St. Louis
Figure 10	Concentrations of metals in different sediment particle size fractions in Lake St. Louis

TABLE 1. **Concentration of metals in surface sediments of Lake Ontario and St. Lawrence and Ottawa Rivers (µg/g dry weight)**

	Cu	Cr	Co	Ni	Pb	V	Zn	Hg
Lake Ontario								
Western Basin	87-142	110-190	20-31	83-97	170-240	94-145	310-580	0.55-1.89
Central Basin	74-115	85-140	11-20	75-88	120-190	70-96	390-545	0.62-2.47
Eastern Basin	68-110	86-136	13-22	76-92	136-210	77-103	338-38	0.65-3.12
Background*	44-55	90-105	20-25	56-65	19-27	135-145	120-135	0.20-0.30
Ottawa River								
Lake Des Deux Montagne	13-28	49-147	1-27	29-57	20-41	78-124	83-257	0.11-0.50
St. Lawrence River 3 km upstream of Lake St. Louis	22-43	100-103	11-18	47-52	15-40	75-77	125-213	0.39-0.50
Lake St. Louis								
Station 3	25-34	116-118	9-10	58-59	48-53	115-121	430-570	0.32-0.52
Station 17	26-30	81-90	13-14	51-57	53-54	88-96	401-636	NA
Station 21	36-40	93-104	14-17	59-61	45-50	93-109	288-320	3.4-5.4

* Pre-colonial sediments.
NA = not analyzed.

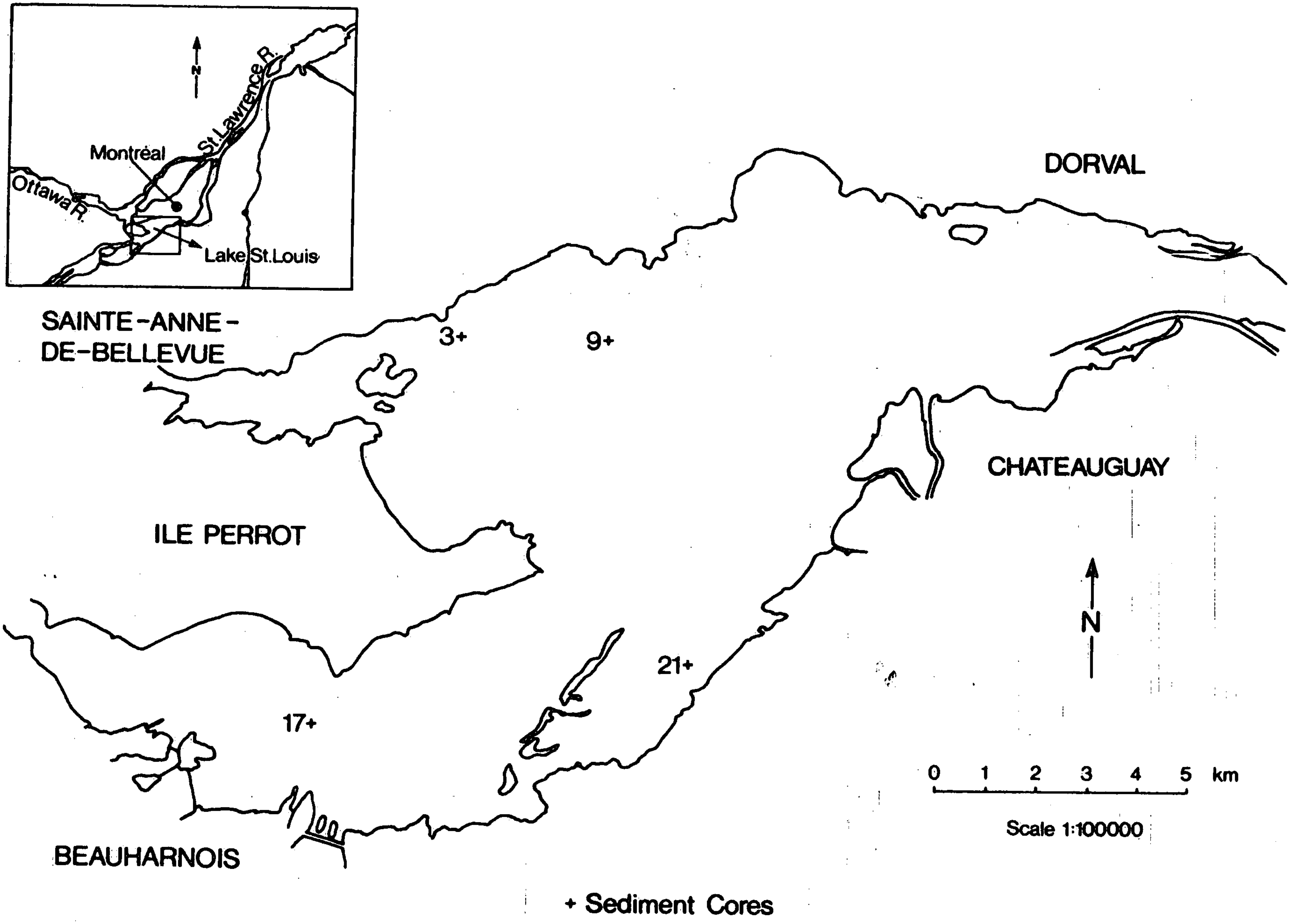

Figure 1   Sampling stations in Lake St. Louis

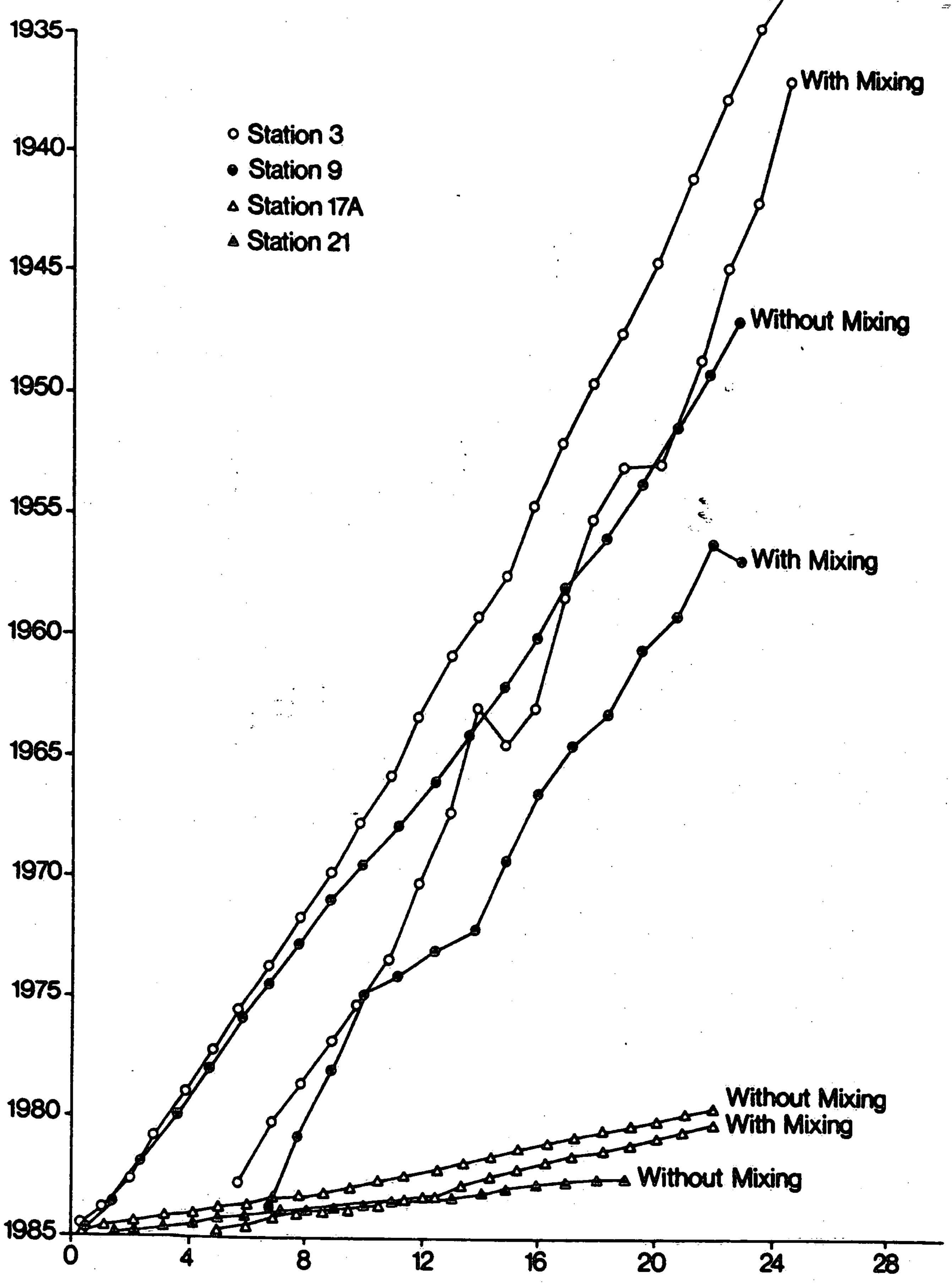

Figure 2 The age/depth profiles of sediment cores

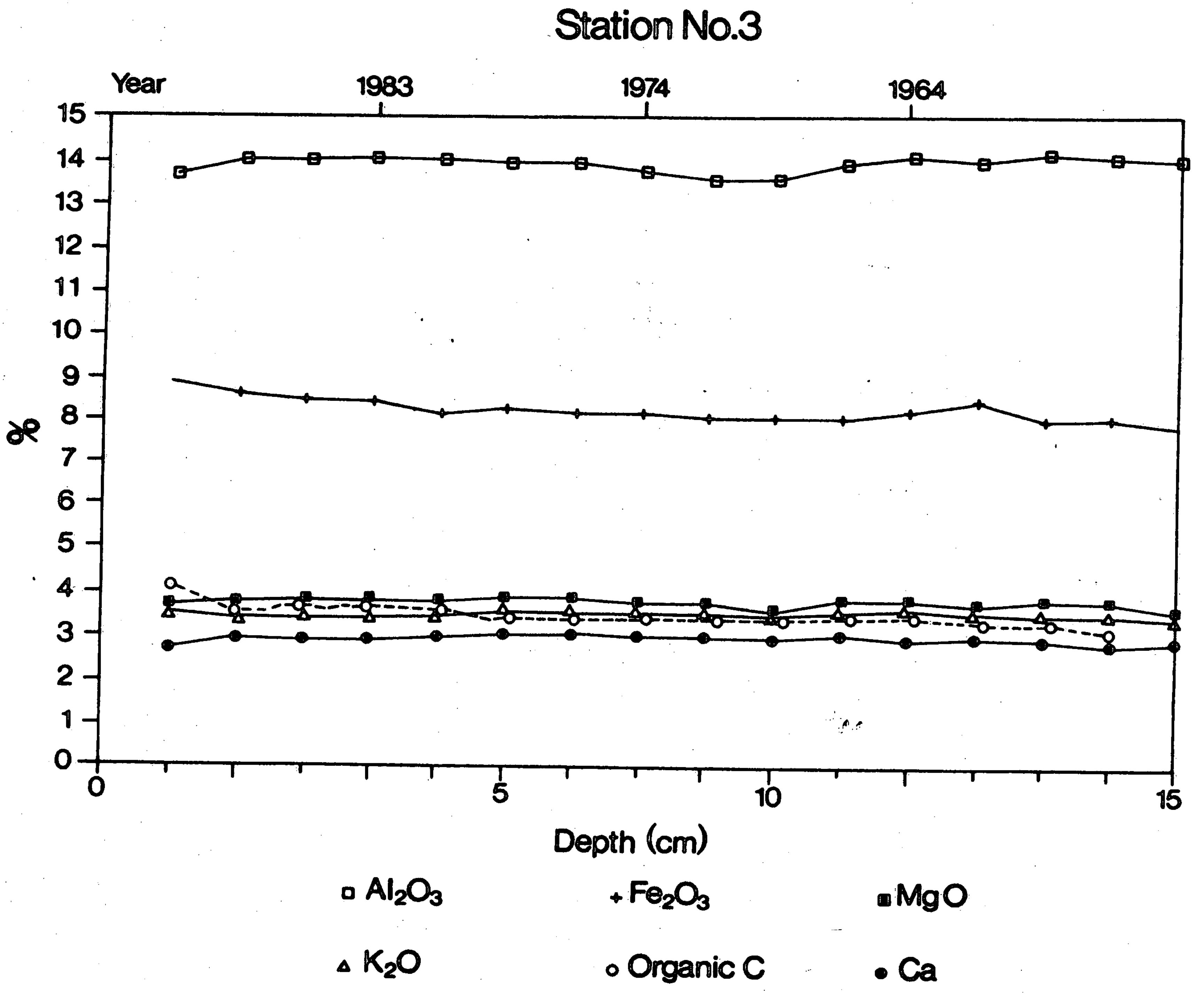

Figure 3 Concentration profiles of major elements in the sediment from station 3

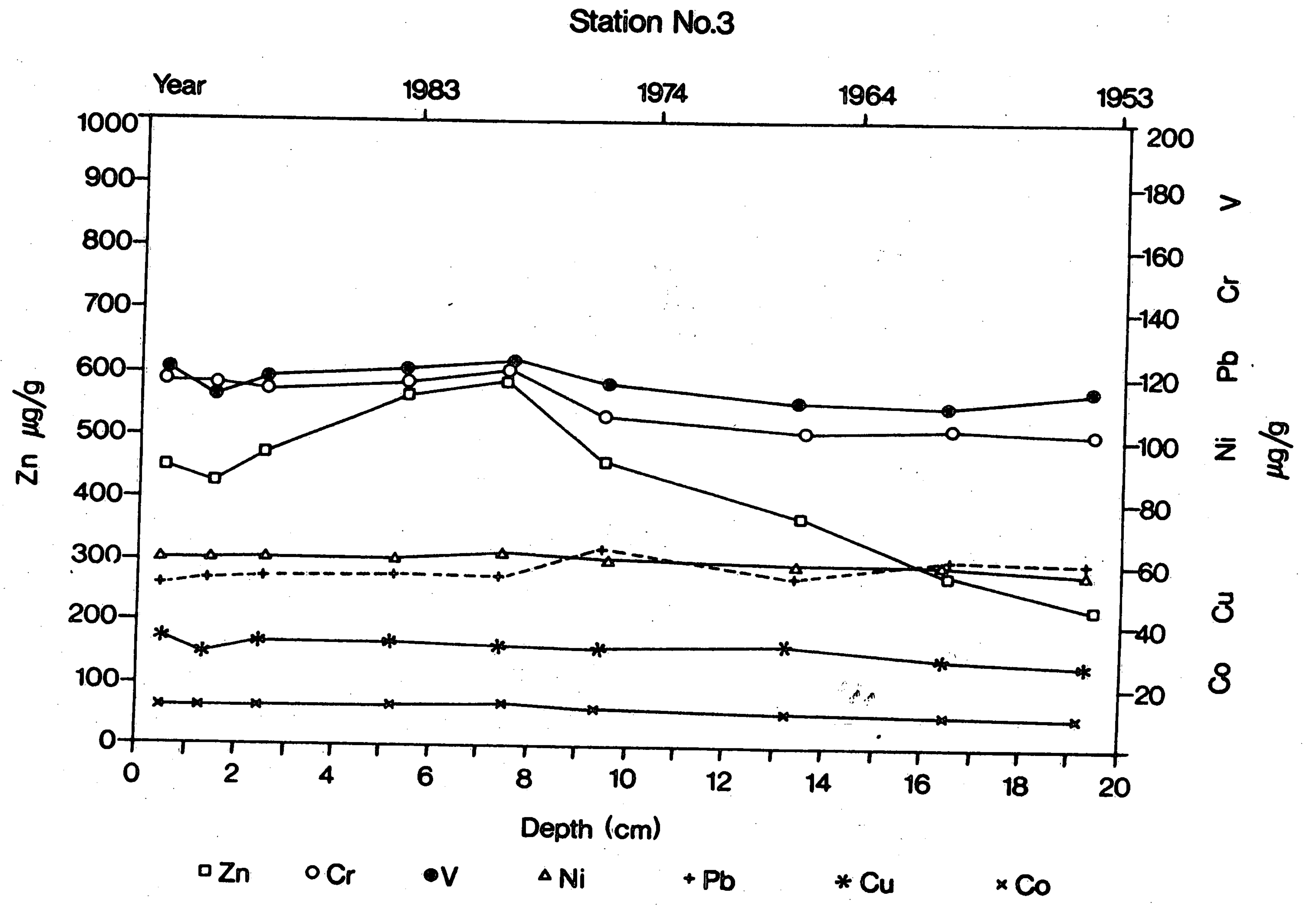

Figure 4 Concentration profiles of metals in sediment from station 3

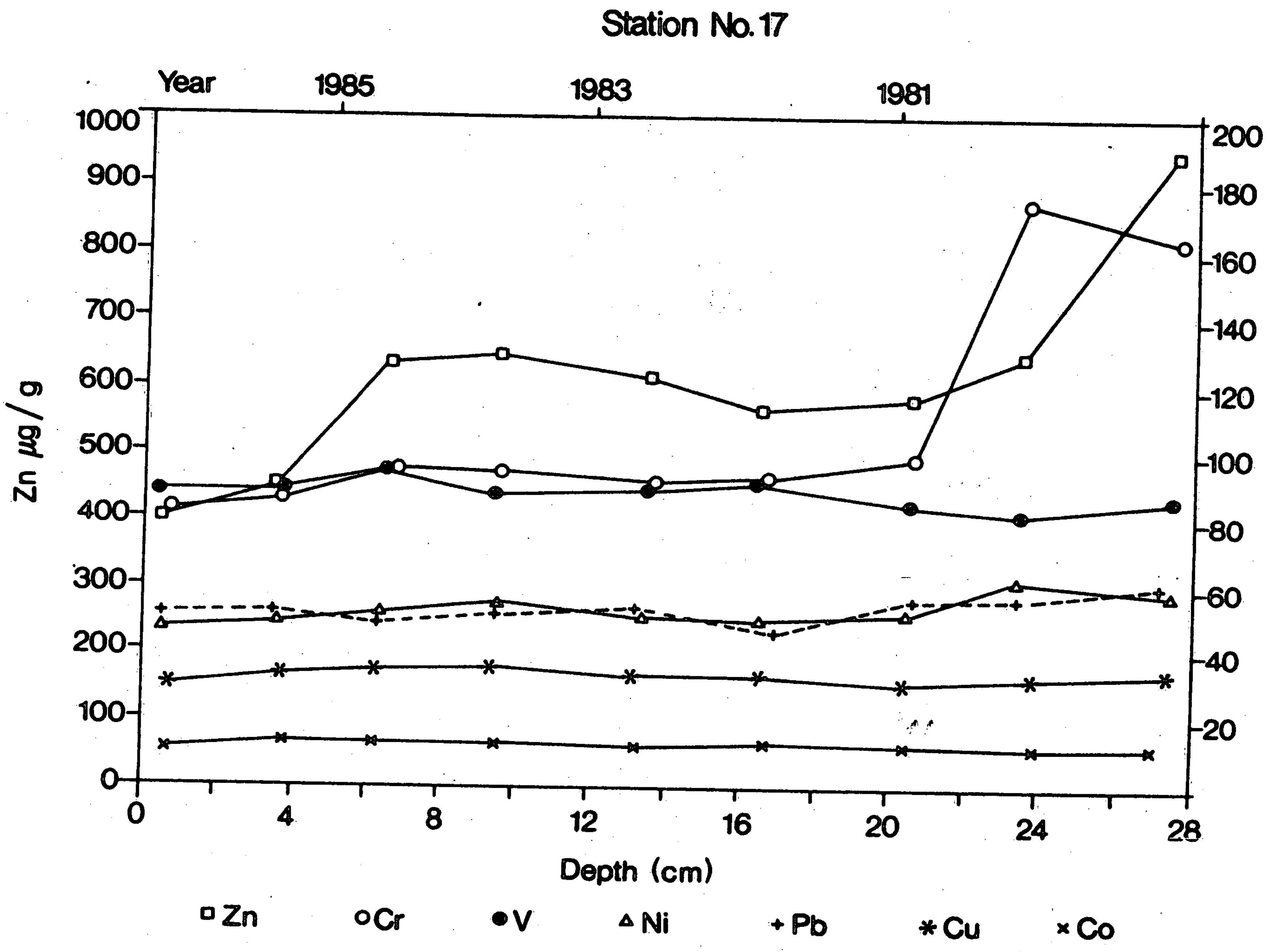

Figure 5 Concentration profiles of metals in sediment from station 17

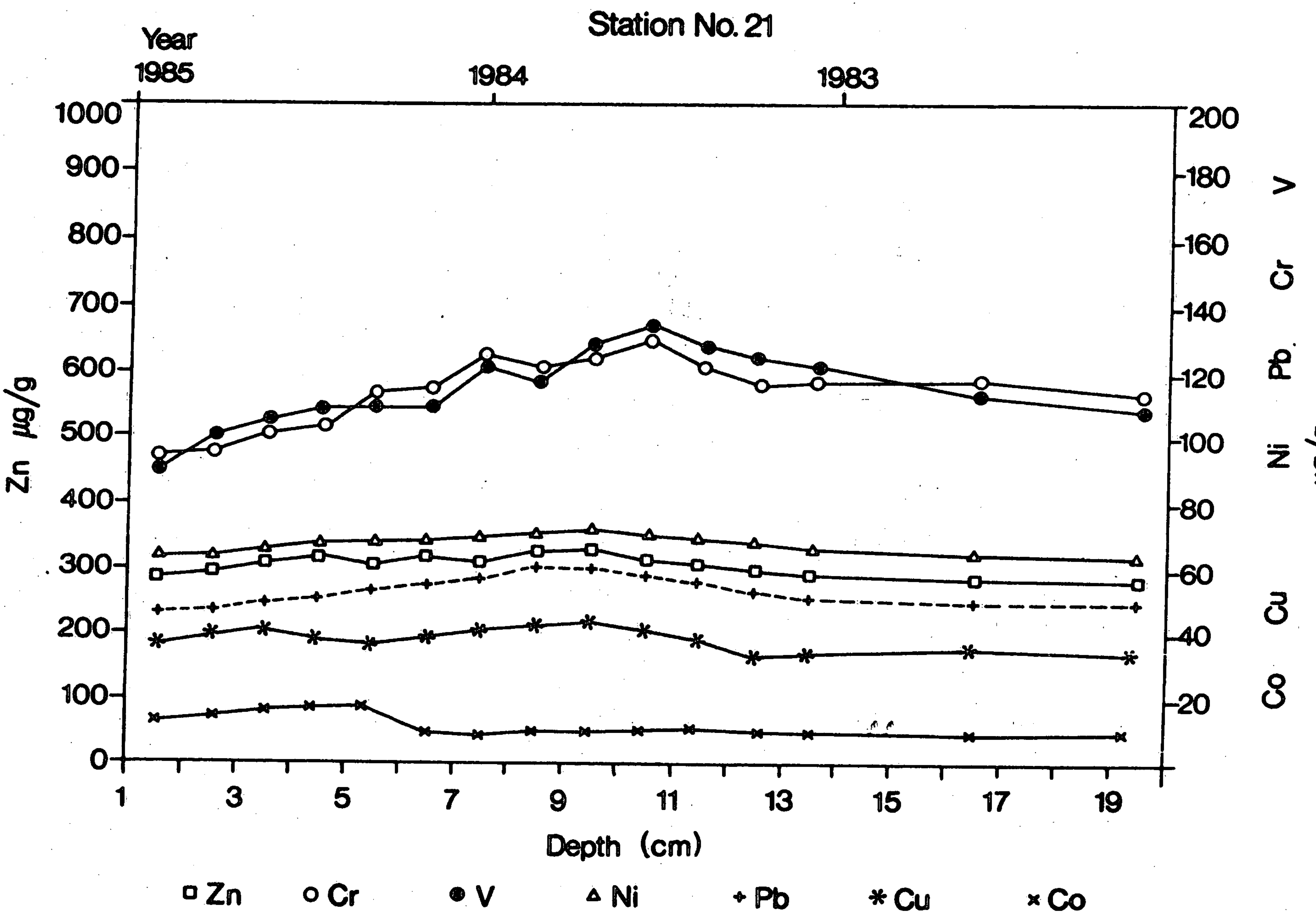

Figure 6 Concentration profiles of metals in sediment from station 21

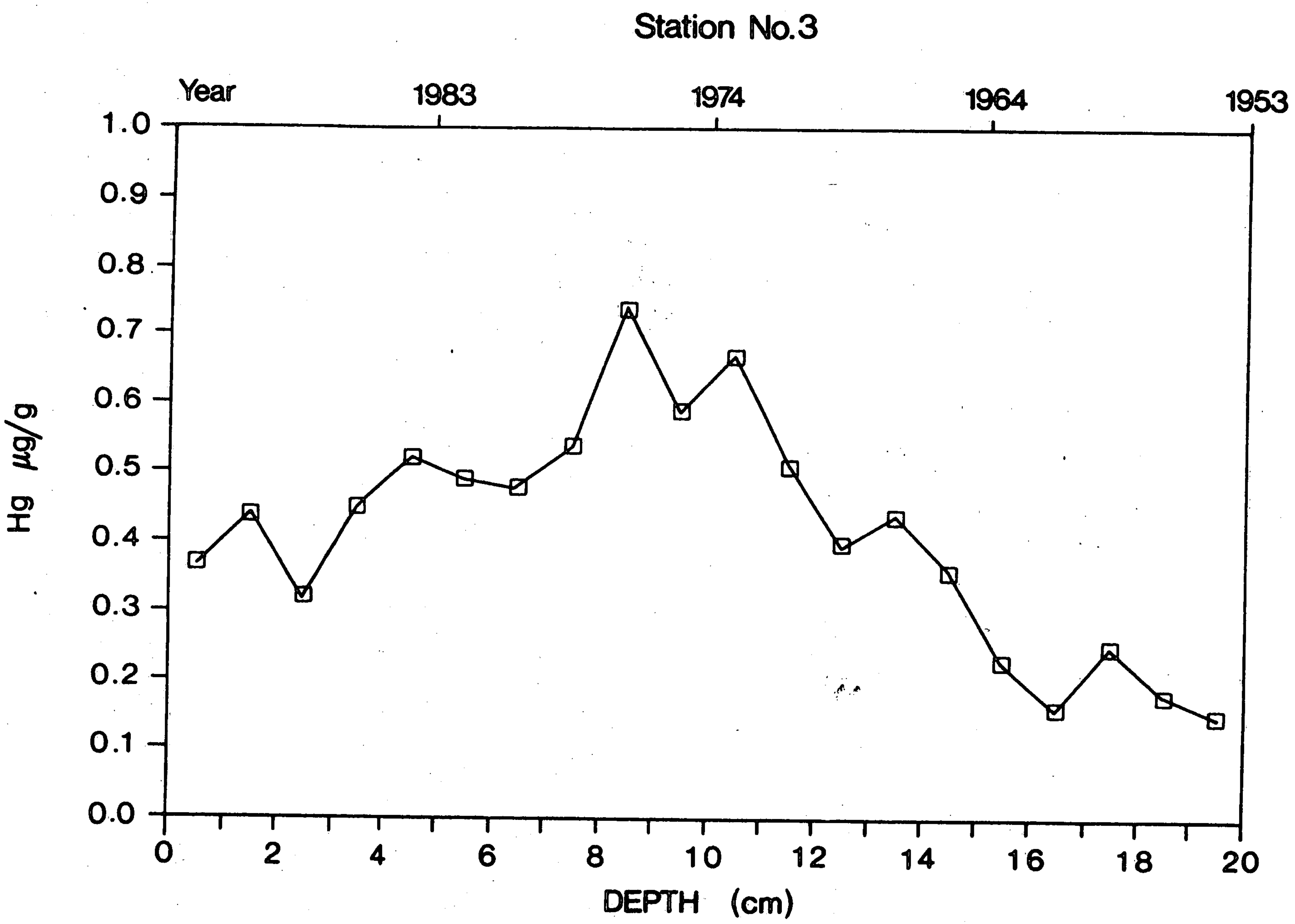

Figure 7 Concentration profile of Hg in sediment from station 3

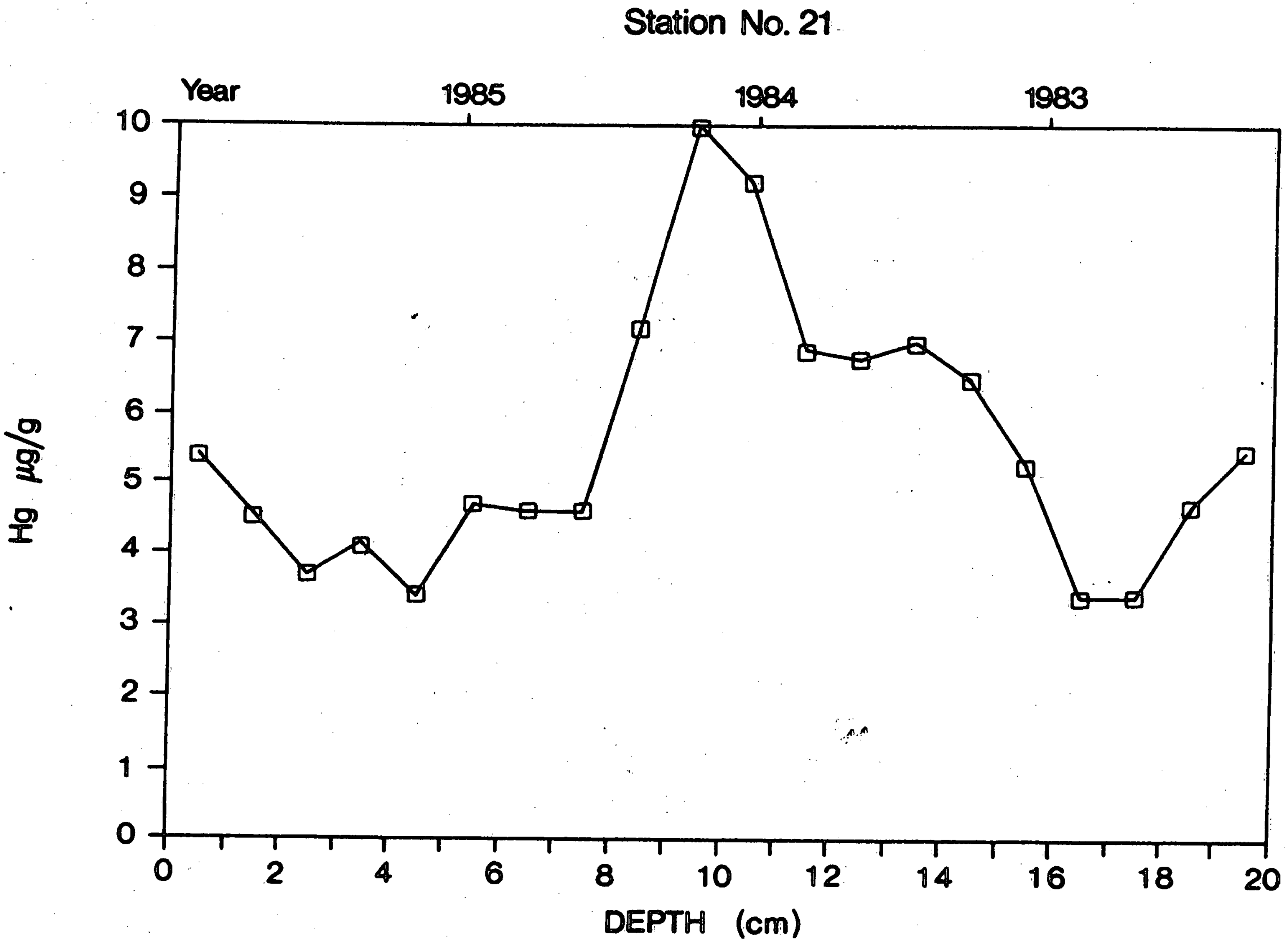

Figure 8 Concentration profile of Hg in sediment from station 21

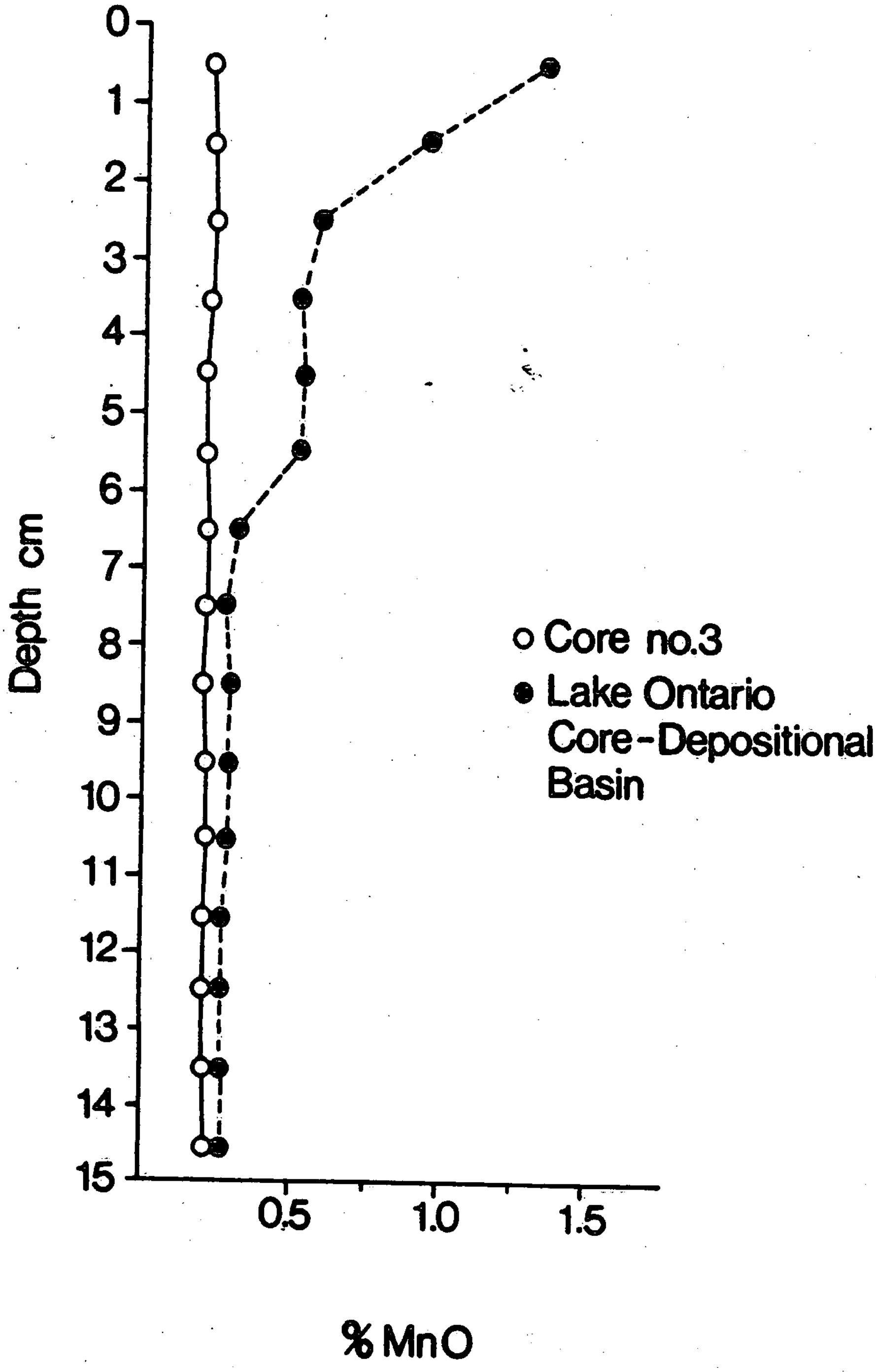

Figure 9 Concentration profiles of Mn in sediment from depositional basin in Lake Ontario and from station 3 in Lake St. Louis

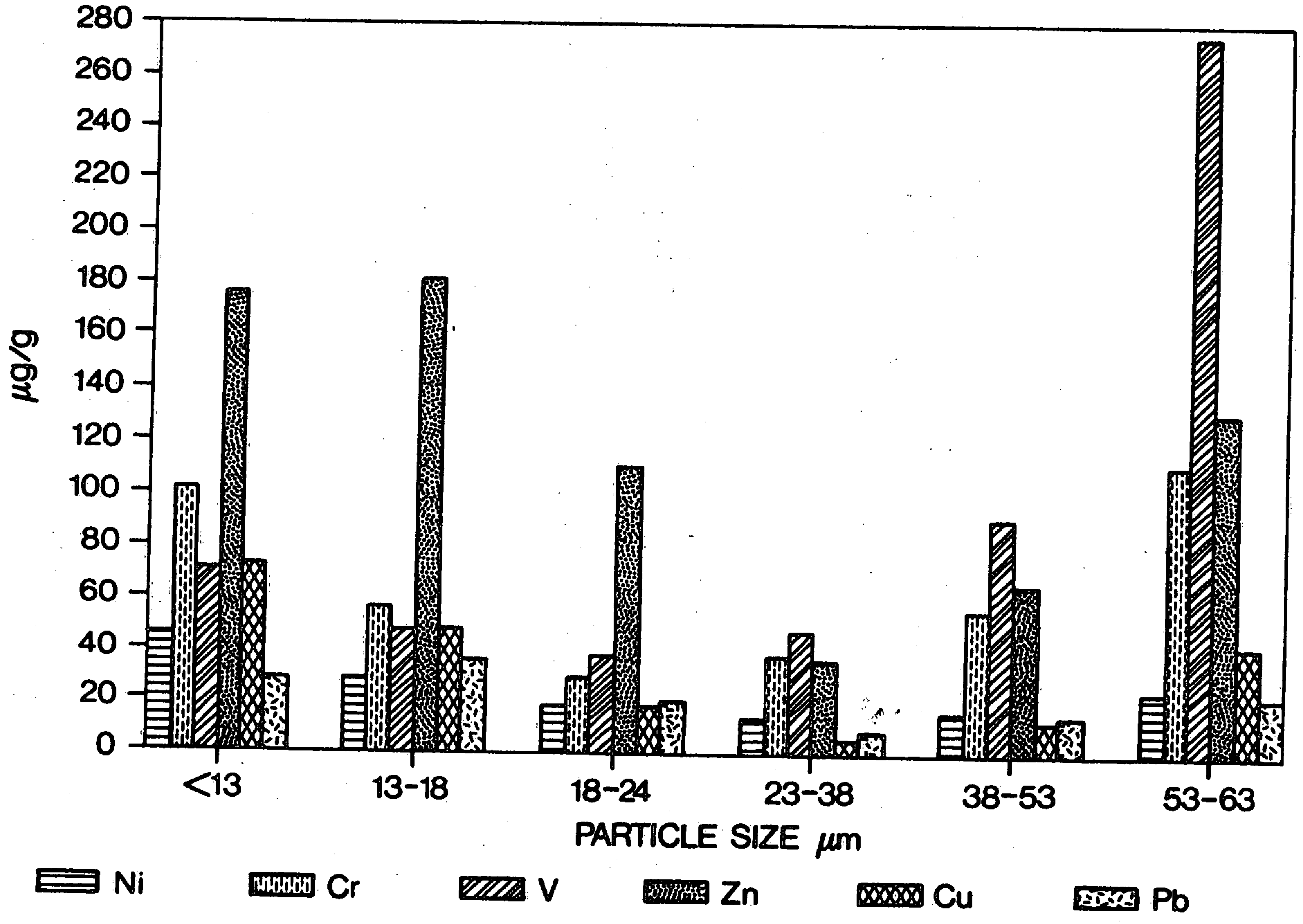

Figure 10 Concentrations of metals in different sediment particle size fractions in Lake St. Louis