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Distribution of major and trace elements in  
sediments and pore water of Lake Erie

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## MANAGEMENT PERSPECTIVE

### DISTRIBUTION OF MAJOR AND TRACE ELEMENTS IN SEDIMENTS AND PORE WATER OF LAKE ERIE

Lake Erie plays an important role in the water quality of the Lower Great Lakes. The Central Basin occupies an area of 16,200 km<sup>2</sup>, and accounts for 63% of Lake Erie's surface area and total volume. Sedimentary records of trace elements in the 1970's showed severe anthropogenic pollution of Lake Erie bottom sediments, however, during the past 25 years various environmental control measures have been implemented in Lake Erie drainage basin. Therefore, there is now a need to update our knowledge of the distribution of major and trace elements and determine trends which may have recently developed in the Lake. The objectives of the study were: i) to investigate the distribution of major and trace elements in the sediments and pore water of the Central Basin of Lake Erie; ii) to identify the trend of anthropogenic inputs of the elements to the lake; and iii) to determine the role of sediment pore water in the remobilization of elements within the sediments. The results of this study showed that the concentrations of trace elements (As, Cd, Cr, Cu, Hg, Mn, Ni, Pb and Zn) in the sediments were greatest at approximately 18 cm sediment depth, corresponding to the early 1960's. The concentrations of all elements in the sediments have considerably decreased in the last decade. However, the concentrations of Hg, Pb, and Cd are still about 10, 5 and 4 times greater, respectively, than those in the pre-industrial sediments. The profiles of dissolved concentrations of the trace elements in pore water were characterized by maxima below the sediment-water interface, dropping off rapidly beneath the zone of reduced sediments. Estimates of concentration gradients in the sediment pore water indicated that upward diffusive remobilization from sediments to lake water is a significant transport process in the Central Basin of Lake Erie and may play an important role in the transport of trace elements from the sediments, particularly during periods of hypolimnetic anoxia.

# **DISTRIBUTION OF MAJOR AND TRACE ELEMENTS IN SEDIMENTS AND PORE WATER OF LAKE ERIE**

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## **ABSTRACT**

Concentration profiles of major and trace elements were determined in sediment cores (representing approximately 100 years of sediment deposition) from the Central Basin of Lake Erie. The concentrations of trace elements (As, Cd, Cr, Cu, Hg, Mn, Ni, Pb and Zn) in the sediments were greatest at approximately 18 cm sediment depth, corresponding to the early 1960's. The concentrations of all elements in the sediments have considerably decreased in the last decade. However, the concentrations of Hg, Pb, and Cd are still about 10, 5 and 4 times greater, respectively, than those in the pre-industrial sediments. The profiles of dissolved concentrations of the trace elements in pore water were characterized by maxima below the sediment-water interface, dropping off rapidly beneath the zone of reduced sediments. Concentrations of dissolved Pb and Zn below the sediment-water interface are 8 times greater than those in the lake water. Estimates of concentration gradients in the sediment pore water indicated that upward diffusive remobilization from sediments to lake water is a significant transport process in the Central Basin of Lake Erie and may play an important role in the transport of trace elements from the sediments, particularly during periods of hypolimnetic anoxia.

**INDEX WORDS:** Lake Erie, trace elements, sediments, pore water, fluxes.

## INTRODUCTION

Lake Erie plays an important role in the water quality of the Lower Great Lakes. It has been heavily polluted by toxic metals and, based on overall metal concentrations, probably comes second to Lake Michigan as the Great Lake most polluted by these contaminants (Rossmann, 1984). Due to its shallowness (mean water depth is 19 m) and high biological productivity, contaminants in Lake Erie are processed in a different way than in the other Great Lakes (Allan and Ball, 1990). Lake Erie is mesotrophic and at one time in the 1960's was approaching eutrophic status (Burns, 1985). Cultural eutrophication of Lake Erie has received considerable scientific attention (Burns, 1985). Sedimentary records of trace elements in the 1970's showed severe anthropogenic pollution of Lake Erie bottom sediments (Kemp et al., 1976; Nriagu et al., 1979; Walters et al., 1974). More recently, several groups have studied the environmental effects of Pb inputs to Lake Erie (Flegal et al., 1989; Ritson et al., 1994; Sturges and Barrie, 1987). During the past 25 years various environmental control measures have been implemented in Lake Erie drainage basin. Therefore, there is now a need to update our knowledge of the distribution of major and trace elements and determine trends which may have recently developed in the Lake.

Concentration profiles of major and trace elements in the bottom sediments have been extensively used to interpret the history of the aquatic environment in which the sediments have accumulated (Bricker, 1993; Hallberg, 1991; Owens and Cornwell, 1995; Ritson et al., 1994; Trefry et al., 1985). After the sediment is deposited, bioturbation and changes in the redox potential within the sediment layer can alter the mobility and bioavailability of major and trace elements (Aller, 1984; Azcue et al., 1994; Davis, 1974; Kramer et al., 1991). Sediment pore water is the medium of transport of different elements and compounds within the sediments, and plays an important role in the linkage between the chemistry of lake water and bottom sediments. Sediments

can act as either a source of contaminants and nutrients due to dissolution and desorption or as a sink due to precipitation and adsorption reactions. This study was carried out to find relationships between the concentrations of different chemical species in sediment pore water and those in the sediments of the Central Basin of Lake Erie. The Central Basin occupies an area of 16,200 km<sup>2</sup>, and accounts for 63% of Lake Erie's surface area and total volume. The objectives of the study were: i) to investigate the distribution of major and trace elements in the sediments and pore water of the Central Basin of Lake Erie; ii) to identify the trend of anthropogenic inputs of the elements to the lake; and iii) to determine the role of sediment pore water in the remobilization of elements within the sediments.

## MATERIAL AND METHODS

### Study Area and Sampling

All the samples analyzed in this study were collected in September 1994 from the Central Basin of Lake Erie (41°56'06"N, 81°39'30"W). A total of 3 sediment cores were hand collected by divers using Plexiglas tubes of 6.3 cm inner diameter. The core liners were 50 cm long and recovered approximately 30 to 40 cm of undisturbed sediment. After retrieval the cores were kept upright and tightly closed with nylon stoppers to minimize any disturbance of the sediment during transport. All three cores were immediately subsampled into 1 cm sections using an hydraulic extruder (Mudroch and Azcue, 1995). The subsamples were collected in plastic bags and kept refrigerated at 4°C during the transport to the laboratory at the National Water Research Institute, Burlington, Ontario.

Three dialysis samplers, or "peepers" (Hesslein, 1976), were used in this study to collect *in situ* sediment pore water at 1 cm depth intervals. All equipment used in this study was previously acid washed following the method recommended by Nriagu et al. (1993). To remove traces of oxygen stored in the samplers' acrylic

material, the peepers were placed in nitrogen for three days before assembling (Carignan et al., 1994). Each peeper contained 60 compartments which were filled with oxygen-free deionized, double distilled water (DDW) and assembled by covering the open side with a 0.45  $\mu\text{m}$  cellulose membrane (Gelman Scientific, Inc.) a few days prior to deployment. The peepers were assembled following standard procedures recommended by Rosa and Azcue (1993). Subsamples of the water used in the assembling and storage of peepers were kept for further analysis to monitor any possible contamination. The peepers were kept in oxygen-free double distilled water until they were vertically deployed by divers in flat areas of the lake bottom at the sampling station. The peepers were left for four weeks in the sediment to allow the water in the chambers to equilibrate with the sediment pore water (Carignan, 1984). At retrieval the peepers were quickly rinsed with lake water to dislodge adhering sediment particles. The pore water from each compartment (about 5 ml) was immediately removed using disposable syringes. The samples were stored in polystyrene vials pre-acidified with 50  $\mu\text{l}$  of Ultrapure Seastar concentrated  $\text{HNO}_3$  and stored at 4°C prior to the analysis.

#### **Analytical Procedures**

The water content was determined in all sediment subsamples from one sediment core by oven drying at 110°C. The concentration of organic matter was determined by loss on ignition at 450°C. All sediment samples were freeze-dried and homogenized by grinding to 189  $\mu\text{m}$  particle size. Approximately 0.5 g of homogenized sediments were placed in Teflon containers containing 6 ml of aqua regia and 1.5 ml of HF. All samples were allowed to de-gas overnight at room temperature to prevent a vigorous reaction during heating. The samples were digested in a microwave oven with closed pressure-relief containers (Floyd, Inc. Model RMS 150) using the following program: a) 3 min at 30 psi, b) 5 min at 50 psi, c) 5 min at 100 psi, and d) 5 min at 130 psi. After the microwave digestion the samples were heated on a hot plate at about 80 to 90°C to ensure all HF was removed before the analysis.

The quantitative determination of major elements (Al, Ca, Fe, K, Mg, Na, Si and Ti) and trace elements (As, Cd, Cr, Cu, Mn, Ni, Pb, Sr and Zn) was carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Jobin Ivon Model 74 spectrometer. The concentration of Hg was determined by cold vapour atomic absorption spectrometry. The calibration standards consisted of mixed solutions of high purity elements in 2% HNO<sub>3</sub> (Delta Scientific Laboratory Products, Canada). Reagent blanks and certified sediment reference materials of the National Institute of Standards and Technology (Buffalo River sediment, NIST-2704, and estuarine sediment, NIST-1646) were analyzed simultaneously with all samples. The coefficients of variations for triplicate analysis were <5%.

## RESULTS AND DISCUSSION

Despite its shallowness (mean depth 19 m), the Central Basin of Lake Erie exhibits a well defined thermal stratification from June to October. A strong thermocline develops at a depth of approximately 12 to 15 m by late June, deepens through the summer and stays until overturn in October when the lake re-establishes isothermal conditions. At the sampling time the hypolimnion temperature and oxygen concentrations were 14°C and 3 mg/L, respectively. For a historical perspective on oxygen depletion over time refer to Rosa and Burns (1987).

### Concentration Profiles of Major and Trace Elements in Sediments

Assuming sedimentation rates for the Central Basin of Lake Erie of 0.51 cm/y (Kemp et al., 1976), the 47 cm of sediment core represented about 100 years. The water content of the sediment decreased from around 90% at the surface to approximately 74% at 25 cm depth. The average content of organic matter ranged from 13.4% at the surface to 8.1% at 40 cm depth. The concentration profiles of major elements in the Central Basin of Lake Erie are shown in

Figure 1. No significant changes were observed in the total concentrations of Al, Fe, K, Si, and Ti through the sediment core. These elements represent the bulk of the sediment matrix, reflecting the content of major mineralogical species, such as illite  $[KAl_2(AlSi_3O_{10})(OH)_2]$  and chlorite  $[Mg_3Al(AlSi_3O_{10})(OH)_8]$  (Thomas, 1969). Surface sediments from the Central Basin of Lake Erie consist mainly of quartz, feldspar, organic matter, and clay minerals (Thomas, 1969). The concentration of the major elements fluctuates around a general uniform value in the sediment profile, suggesting that they are not affected by anthropogenic inputs and diagenetic effects. Nevertheless, due to the large concentrations of these elements in the sediments, it is very difficult to identify any potential precipitation or dissolution from and into the sediment pore waters. Regeneration of soluble Fe and precipitation of Fe oxyhydroxide phases may be masked by the total concentrations of Fe in the sediment profile and deserve further investigation in the sediment pore water (see below). The profile of total Na shows that after a sharp increase in the top 2 cm, the concentration remains relatively constant at 0.03%. The average concentration of Ca in the top 20 cm of the core was 0.9%, decreasing to approximately 0.45% in the deeper section of the sediments. The Mg profile showed a similar trend, with an approximately 10% increase in the concentration of the top 20 cm of the sediment core. Similar enrichments of Ca and Mg at the surface was observed by Kemp et al. (1976). The results indicate that the carbonates are undergoing *in situ* dissolution in the surface sediments.

The concentration profiles of trace elements in the sediments are shown in Figure 2. A similar trend was observed for all determined trace elements: an increase at approximately 30 cm sediment depth reaching the greatest concentrations at approximately 18 cm sediment depth with subsequent decrease in the concentrations towards the sediment-water interface. Approximately 90% of the benthic community, dominated by Oligochaete ranging from 5,000 to 10,000 per  $m^2$ , is present in the top 10 cm of the sediments



in Lake Erie (T.B. Reynoldson, personal communication). The distribution of major and trace elements in the uppermost sediment layers may be modified by bioturbation to a certain degree. However, the non-uniform concentration profiles of trace elements in the topmost layer of the sediments (Figure 2) support the theory of anthropogenic input as the main source of these elements.

Concentration profiles of Mn in sediments showed a peak at the sediment-water interface with concentrations in the top centimetres reaching 1,330  $\mu\text{g/g}$  (Figure 2). The near-surface enrichment of Mn indicated diagenetic precipitation at the oxic interface. The profile of Mn concentrations clearly showed the oxic top 3 cm layer of the sediment at the sampling time. Upward migration of Mn in sediment pore water under reducing conditions and precipitation in the surface oxidized sediment has been extensively reported (Mason, 1965; Lynn and Bonatti, 1965; Callender et al., 1974; Holdren et al., 1975; Burdige and Gieskes, 1983). The concentration profile of As in the sediments correlates with Mn, showing a sharp increase of the concentration at the sediment-water interface to 11  $\mu\text{g/g}$  (Figure 2). The results suggested co-precipitation of As with Mn oxides. Similar trends were observed in other lakes (Oscarson et al., 1981; Peterson and Carpenter, 1986; Azcue and Nriagu, 1993). The profile of As showed a considerable increase in concentration in the sediment section deposited in the 1960's. This increase may be partially correlated to the proliferation in the use of inorganic compounds of As as insecticides in the 1950's (Nriagu and Azcue, 1990).

According to the estimated sedimentation rates in 1976 (Kemp et al.), the maximum concentrations of trace elements in sediments correspond to the inputs in the early 1960's. The uncertainties of these calculations are greater for the deep sections of the core due to the assumptions of constant deposition rates and neglecting the effects of compactness. However, the history inferred from the sediments agrees qualitatively with the complex history of development and industrial growth in Lake Erie drainage basin

(Environment Canada-U.S. Environment Protection Agency, 1988). Our estimates are in agreement with the sediment chronology reported in previous studies where the greatest concentrations of As, Pb, and Hg occurred around 1960 (Thomas and Jaquet, 1976; Legault, 1986; Eadie and Robbins, 1987). At the same time, the concentrations of these elements in the deep sections of the sediment cores (Figure 2) correspond to those of the pre-colonial or natural sediments for this basin (Kemp et al., 1976; Allan and Ball, 1990).

The concentrations of Pb in the deepest section of the sediment cores are relatively constant at about 18  $\mu\text{g/g}$  (Figure 2), which is similar to the natural Pb concentrations measured in Lake Erie by Ritson et al. (1994). The concentration profile of Pb is similar to that of Zn. That is, confirming that Pb concentrations in Lake Erie sediments cannot simply be correlated with the combustion of leaded gasoline, because other Pb sources in the lake are relatively large and can account for more than 30% of the Pb deposited in the sediments (Nriagu, 1986; Ritson et al., 1994).

Until the early 1970's two chlor-alkali facilities located upstream of the Detroit River were the main sources of Hg to the Great Lakes (Wolery and Walters, 1974). In 1971, the concentrations of Hg in the surficial sediments of Lake St. Clair and the West and Central Basins of Lake Erie were 3,000, 1,622 and 500 ng/g, respectively (Thomas and Jaquet, 1976; Mudroch and Hill, 1987). The decrease of Hg concentrations in the top section of the sediment in the Central Basin (Figure 2) reflects the reduction of Hg emission to the Great Lakes in the early 1970's. Mercury is mainly bound to a number of mineral phases and organic matter occurring in finer fractions of sediments of the Great Lakes (Thomas, 1974). Therefore, resuspension and transport of sediments of the Detroit River and Lake Erie West Basin can be the main sources of Hg to the Central Basin. This is in agreement with the observed prevailing west to east water currents in the lake (Simons, 1976).

A comparison of the concentration of the trace elements in sediments deposited recently (3 to 5 years), those deposited in the 1960's and at the beginning of the century, are shown in Table 1. The maximum sediment enrichment factor (MEF) is determined by the method recommended by Förstner and Wittmann (1981), and is defined as the ratio of maximum trace metal concentration and background levels. The present enrichment factors (PEF), defined as the ratio of average trace element concentrations in the top 3 cm sediment layer to the average background levels, were also calculated. The results showed that Hg, Cd, and Pb were enriched during the 1960's by factors of approximately 14, 12 and 9, respectively. Although the levels of these elements in recent sediments have significantly decreased in the last decades, Hg concentrations are still about 10 times greater than those in the pre-industrial sediments. As previously mentioned, resuspension and transport of sediments of the Detroit River and Lake Erie West Basin could be considered as the main sources of Hg to the Central Basin. However, further investigation is been carried out by the authors to study the transport of Hg in Lake Erie.

#### **Concentration Profiles of Major and Trace Elements in Sediment Pore Water**

Concentration profiles of major elements in pore water at the Central Basin of Lake Erie are shown in Figure 3. The pore water profiles reflect the physico-chemical conditions (pH, O<sub>2</sub>, temperature, etc.) at the sampling period, being very sensitive to minor chemical changes. Concentration profiles of some trace elements, such as As, and Cd, are not available due to their low concentrations in the pore water and the analytical detection limits of the method used in this study or due to the small sample volume and specific preservation requirements for Hg. The concentrations of K, Na, and Mg fluctuated around generally uniform values (1, 5, and 10 mg/L, respectively). The concentrations of dissolved Al, Ca, Si, Fe, and Mn in pore waters showed a continuous increase below the sediment-water interface and the elements

remained in solution at high concentrations in the deeper sections of the sediment. The concentrations of Fe, Si and Mn in pore water at 30 cm sediment depth were 12, 10, and 5 times higher, respectively, than in the overlying lake water. The Fe and Mn profiles in the pore water from the Central Basin of Lake Erie showed strong similarities. Under oxygenated conditions Mn will persist in solution longer than Fe (Förstner and Wittmann, 1981). The diagenetic accumulation of Mn in the oxic layer (0 to 3 cm) of the sediment is evident in Figure 2. The concentration profile of Fe in the pore water indicated remobilization of soluble Fe in the anoxic sediments and precipitation in the oxic interface (Figure 3). The vertical movement of Fe in sediments is not discernible (Figure 2) due to the high concentration of Fe (approximately 4.5%) in the sediments compared to the concentration of dissolved Fe (<10 mg/L).

The concentration profile of dissolved Ca in the pore water (Figure 3) was in good agreement with the changes observed in the solid phase (Figure 1). The shape of the concentration profile for Ca in pore water suggested dissolution within the sediment column and upward migration, judging by the concentration gradient. The deduced dissolution and upward flux of Ca are compatible with the abundance of biogenic calcium carbonate and calcium silicates in the sediments (Sly, 1976). However, the determination of the precipitated authigenic mineral phases, which are likely to be chemically mixed and not pure phases (Matisoff et al., 1980), is out of the scope of this manuscript.

The profiles for total dissolved concentrations of trace elements in sediment pore water are characterized by maxima below the sediment-water interface dropping off rapidly beneath the zone of reduced sediments (Figure 3). The concentration maxima were always located within the top 3 cm of the sediment, which corresponded to the oxic layer of sediment. The two possible causes of the near-surface concentration maxima are the biodegradation of organic matter and/or reduction of oxyhydroxide complexes, which

both release metals to the pore water. No attempt is made in this study to discern between these two potential sources. Concentrations of dissolved Pb and Zn in the pore water below the sediment-water interface were 8 times greater than those in the lake water.

#### Fluxes at the Sediment-Water Interface

The flux of chemical species due to deposition of sediments ( $S$  in  $\mu\text{g}/\text{cm}^2\cdot\text{y}$ ) may be calculated as follows:

$$S = R (1-\phi) \rho C$$

where  $R$  is the sedimentation rate ( $\text{cm}/\text{y}$ ),  $\phi$  is the sediment porosity near the sediment-water interface,  $\rho$  is the dry density of the sediment ( $\text{g}/\text{cm}^3$ ), and  $C$  is the trace element concentration ( $\mu\text{g}/\text{g}$ ) (Lerman, 1979).

It is difficult to calculate the contemporary fluxes of trace elements being incorporated into the sediments because of the mixing and diagenetic processes within the sediment-water interface (Davis, 1974; Aller, 1984; Jahnke, 1985; Kramer et al., 1991; Sanford, 1992). For this reason, present day fluxes refer to the 1 to 3 cm depth interval and exclude the surface flocculant layer. Sedimentation rates for the Central Basin of Lake Erie estimated by palynological analysis averaged  $0.51 \text{ cm}/\text{y}$  (Kemp et al., 1976). The top 3 cm of sediments have an average porosity and density of 87% and  $2.65 \text{ g}/\text{cm}^3$ , respectively. Solid phase fluxes ( $S$ ) of major and trace elements to the sediments are presented in Table 2. Solid phase fluxes for Al, Fe, Ni, Cr, and Mg (Table 2) suggest that the incorporation of these elements into the sediments probably resulted from the deposition of metal-rich particles. Previous studies have shown that contemporary inputs of trace elements to Lake Erie are overwhelming derived from anthropogenic, rather than natural, sources (Kemp et al., 1976; Nriagu et al., 1979; Flegal et

al., 1989; Ritson et al., 1994). During the summer, algal blooms scavenging dissolved trace element species through particle complexation is important in Lake Erie (Flegal et al., 1989). The estimated depositional fluxes for trace elements, such as Cd, Cu, Pb and Zn, are similar to those previously calculated (Nriagu et al., 1979) and for freshwater lakes of similar characteristics (Hamilton-Taylor, 1979; Lerman, 1979). Due to the great variability on the sedimentation rates of Lake Erie (Kemp et al., 1977), these estimates should be considered as site specific, and not as a lake average.

The vertical diffusional flux of dissolved trace elements from the sediments to the overlying water may be calculated from the pore water dissolved gradient  $(dC/dZ)_{x,y}$  across the sediment-water interface and Fick's first law in one dimension:

$$F = \emptyset D_s (dC/dZ)_{x,y}$$

where  $F$  is the diffusive flux of the element ( $\mu\text{g}/\text{cm}^2\cdot\text{y}$ ),  $\emptyset$  is the porosity of the sediments, and  $D_s$  is the diffusion coefficient in pore water ( $\text{cm}^2/\text{y}$ ). In order to calculate the diffusive fluxes, the following assumptions have to be made: a) sediment-water interface is known; b) viscosity and charge coupling effects are negligible; c) there is no solid-phase consumption of dissolved species near the sediment-water interface; and d) concentration gradients are linear, so that  $(dC/dZ)_{x,y}$  is equivalent to  $\Delta C/\Delta Z$  (Lerman, 1979). The average porosity is for the sediments to the depth of the dissolved maximum. The diffusion coefficients ( $D_s$ ) were estimated from the empirical relationship  $D_s = \emptyset^n D$ , where  $n$  is a constant ( $n=2$ , Lerman 1978); and  $D$  is the diffusion coefficients of ions at infinite dilution, corrected by the Stokes-Einstein relation (Li and Gregory, 1974) to the *in situ* water temperature of  $10^\circ\text{C}$  (Rosa and Burns, 1987).

The sediment pore water concentrations shown in Figure 3 demonstrate the bidirectional nature of trace elements concentration gradients. The trace elements are transported from the region of high concentrations, about 3 cm below the sediment-water interface, deeper into the sediments and they are also migrating across the sediment-water interface into the overlying water column. The calculated upward diffusional fluxes (F) are presented in Table 2. These calculations, due to the assumptions of linearity and no solid-phase incorporation, could be considered as the maximum possible diffusion out of the sediment into the overlying water column.

The calculated fluxes showed sediment loss to overlying waters for all the elements except Al. Upward diffusion Al fluxes represented only 4% of the solid-phase depositional Al fluxes. Adams et al. (1982) calculated that the upward flux of the reduced species can represent more than a third of the oxygen demand at the sediment-water interface in the Central Basin of Lake Erie. Our estimates indicate that upward diffusive remobilization from sediments to lake water is a significant process of transport of trace elements in the Central Basin of Lake Erie. At the sampling period of this study the lake was stratified. Therefore, the majority of the dissolved reduced trace elements in the pore water lost from bottom sediments were oxidized at the sediment-water interface. The post-depositional remobilization due to diffusional gradients, may play an important role during periods of hypolimnetic anoxia. The seasonal variations of the fluxes of major and trace elements in Lake Erie is under investigation by the authors.

## CONCLUSIONS

The sampling site used in this study is not located near any major municipal or industrial discharge, thus, long-range hydrologic and atmospheric transport of the trace elements to this Central Basin region is most likely the mechanism of trace elements accumulation in bottom sediments. The concentrations of major elements in the sediments fluctuated around a generally uniform value in the sediment profile, suggesting that the major elements were not overly affected by anthropogenic inputs and diagenetic processes. The vertical profile of Mn in sediments indicated an upward migration of soluble Mn under reducing conditions in sediment pore water and precipitation at the oxic sediment/water interface. A similar profile was observed for As, suggesting coprecipitation with Mn oxides. Concentration profiles of trace elements in the sediment indicated a reduction in the trace element loadings during the last two decades. However, concentrations of Hg, Pb, and Cd in recent sediments (approximately last 5 years) were still about 10, 5, and 4 times greater, respectively, than those in the pre-industrial sediments. The profiles of total dissolved concentrations of trace elements in pore water were characterized by maxima below the sediment-water interface decreasing rapidly beneath the zone of reduced sediments. Concentrations of dissolved Pb and Zn below the sediment-water interface were 8 times greater than those in the lake water. Our estimates indicated that upward diffusive remobilization from sediments to lake water is a significant process of transport of trace elements in the Central Basin of Lake Erie.

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Table 1. Average concentrations of trace elements in recent, industrial, and pre-industrial sediments (concentrations in  $\mu\text{g/g}$ , except for Hg in  $\text{ng/g}$ ). (MEF= maximum enrichment factor; PEF= present-day enrichment factor)

	Recent sediments top 3 cm	Maximum (approx. 1960's)	Pre- industrial sediments	MEF	PEF
As	6	16	3.7	1.6	4.4
Cd	1.6	4.3	0.37	4.4	11.7
Cr	53	78	35	1.5	2.2
Cu	52	72	32.3	1.6	2.2
Hg	293	437	30.3	9.7	14.4
Mn	695	749	655	1.1	1.1
Ni	52	68	48	1.1	1.4
Pb	69	131	15	4.7	8.9
Zn	233	422	116	2.0	3.6

Table 2. Upward dissolved fluxes and solid-phase deposition rates for trace elements in Central Basin of Lake Erie in September.

	Diffusion coefficients ( $D_s$ ) ( $\text{cm}^2/\text{y}$ )	Diffusive flux (F) ( $\mu\text{g}/\text{cm}^2 \cdot \text{y}$ )	Deposition rates (S) ( $\mu\text{g}/\text{cm}^2 \cdot \text{y}$ )	(F/S)
Al	93.3	221	5390	0.04
Ca	138.2	228151	2347	97.2
Cd	125.5	480	0.42	1142
Co	123.7	1298	4.18	310
Cr	60.7	585	14.1	41.5
Cu	127.2	2030	13.8	147
Fe	125.7	155317	10290	15.1
K	351.4	64823	709	91.4
Mg	126.6	144556	2844	50.8
Mn	117.0	46154	184	251
Na	232.0	27184	146	186
Ni	117.0	349	14	25
Pb	166.4	14003	18.4	761
Sr	138.1	1589	8.62	184
Zn	124.4	5313	61.9	85.8



**Figure captions:**

**Figure 1. Total concentrations of major elements in sediments of the Central Basin of Lake Erie.**

**Figure 2. Total concentrations of trace elements in sediments of the Central Basin of Lake Erie.**

**Figure 3. Total concentrations of major and trace elements in sediment pore water of the Central Basin of Lake Erie.**

Figure 1. Total Concentrations of major elements in sediments of the Central Basin of Lake Erie.

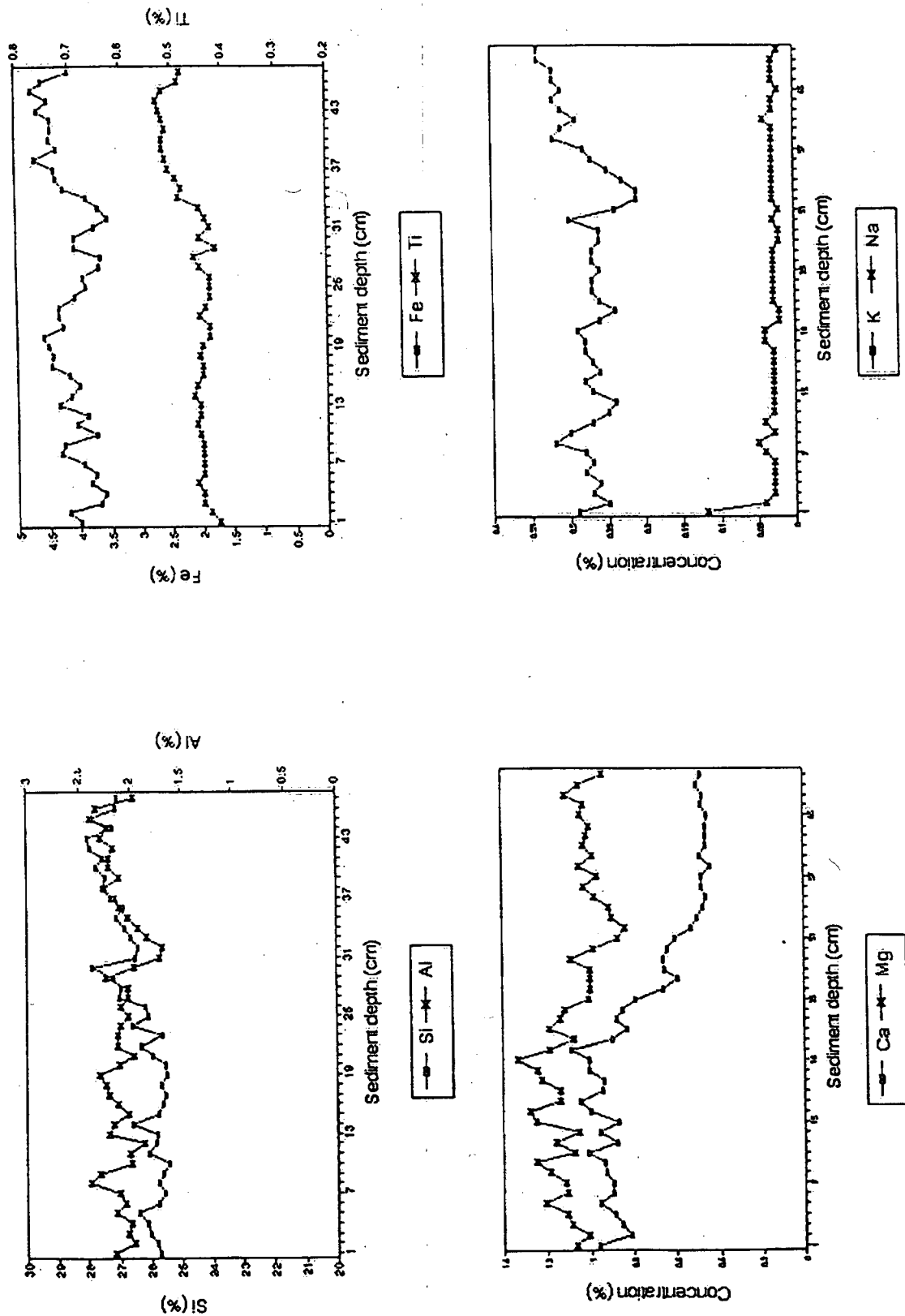


Figure 2. TOTAL concentrations of Trace elements in sediments of the central Basin of Lake Erie

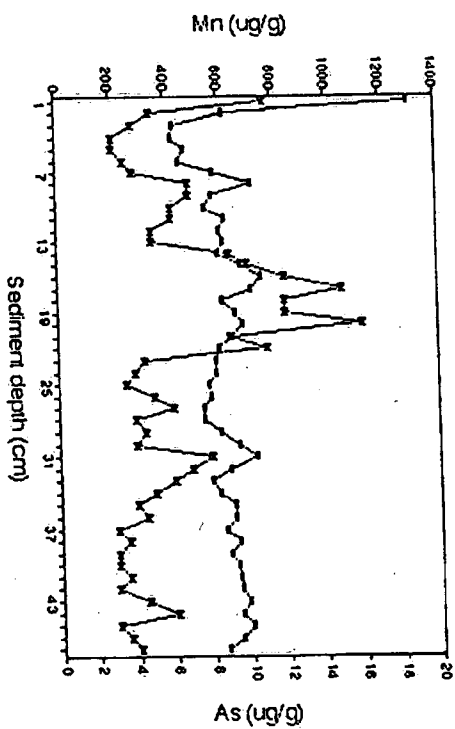
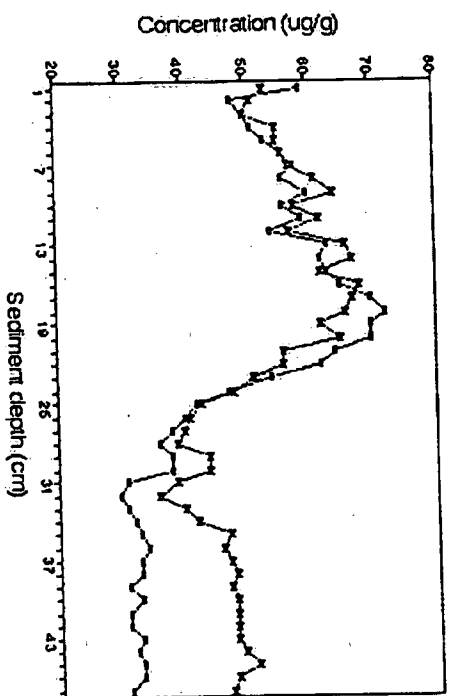
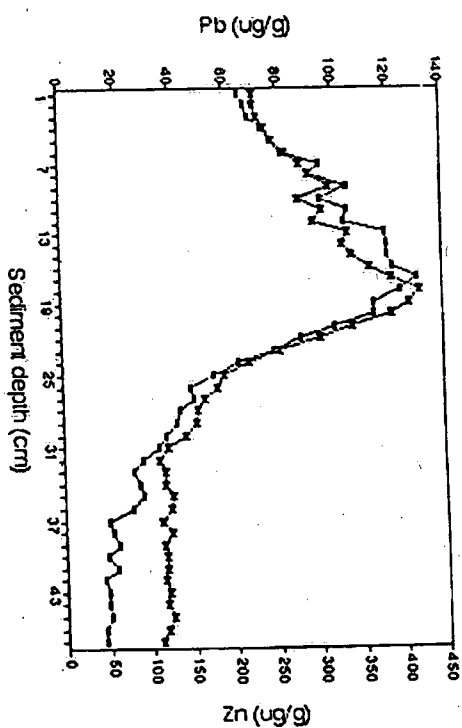
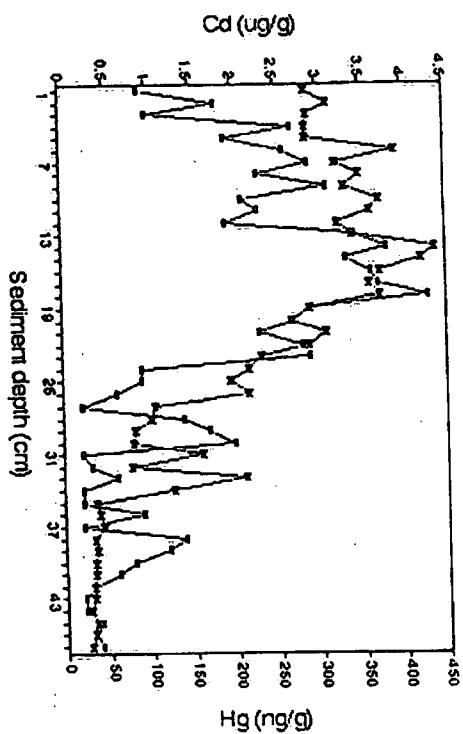


Figure 3. Total concentrations of major and trace elements in sediment pore water of Central Basin of Lake Erie

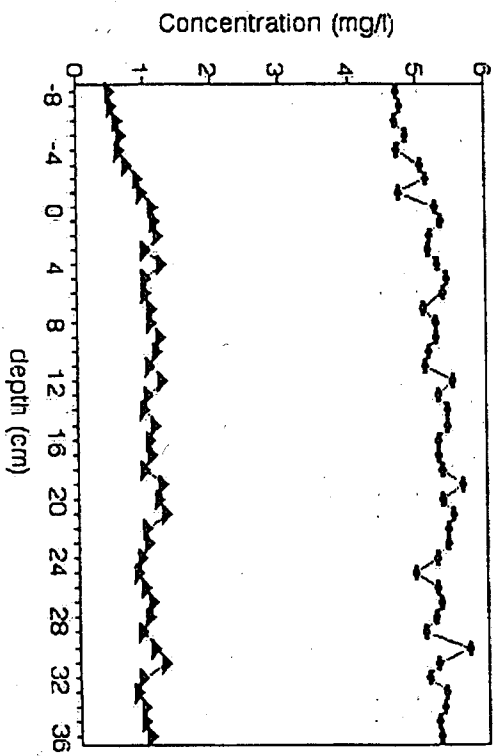
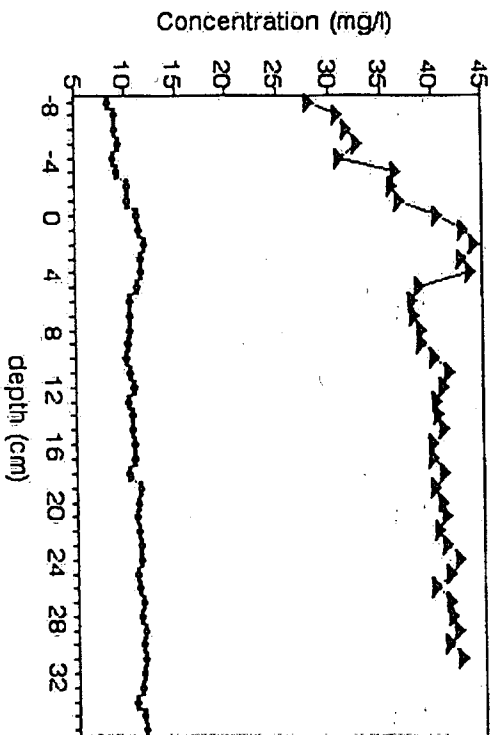
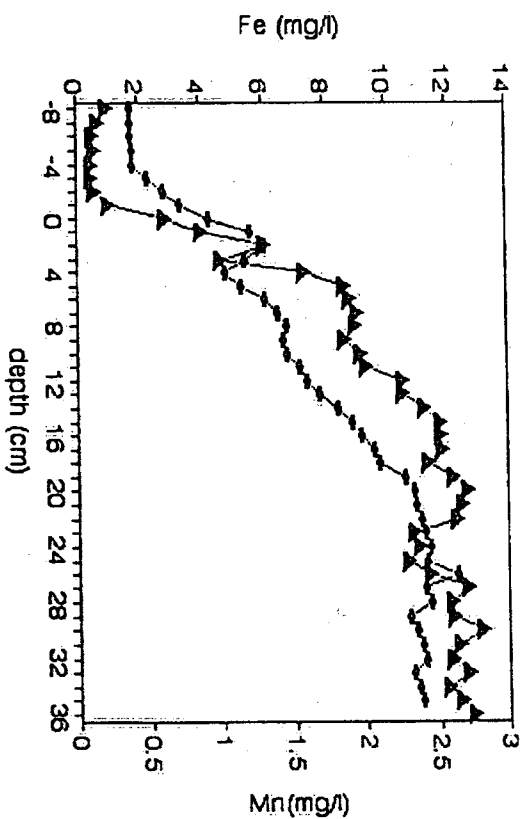
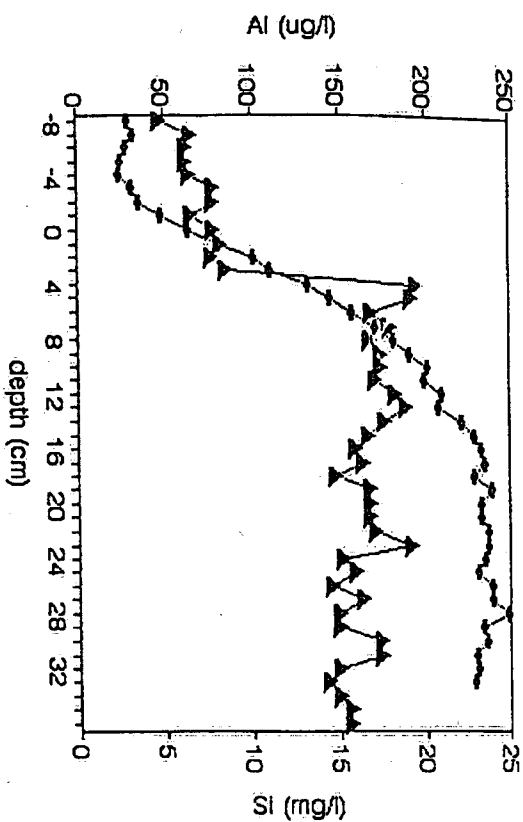
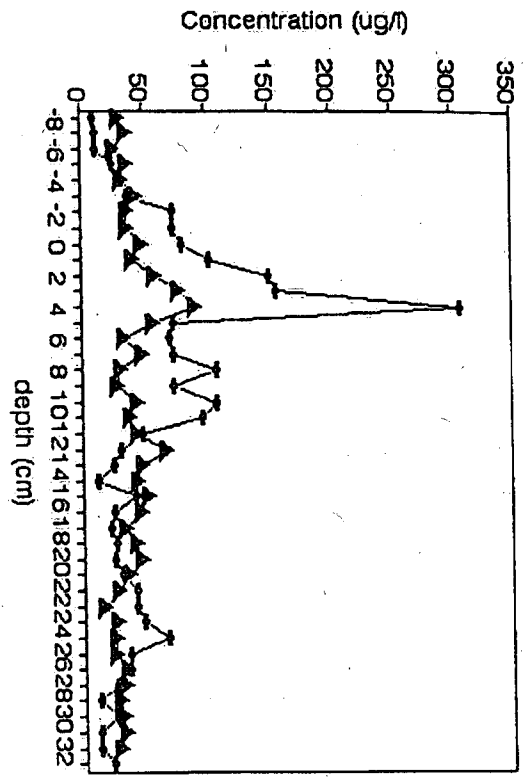
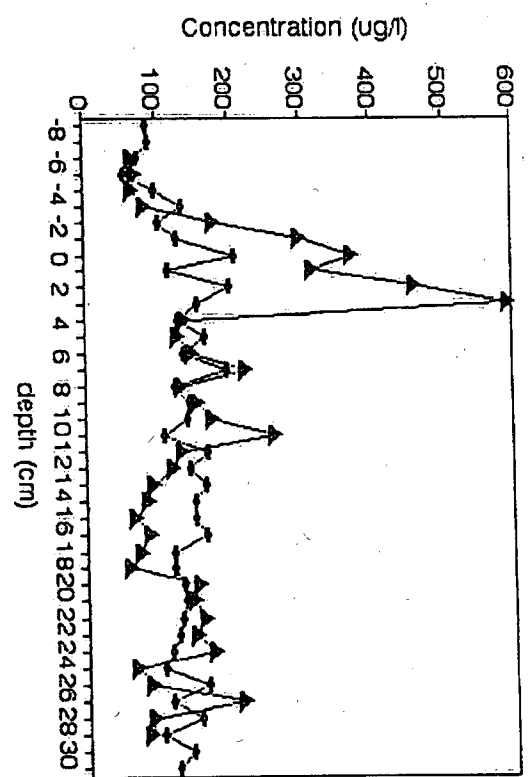


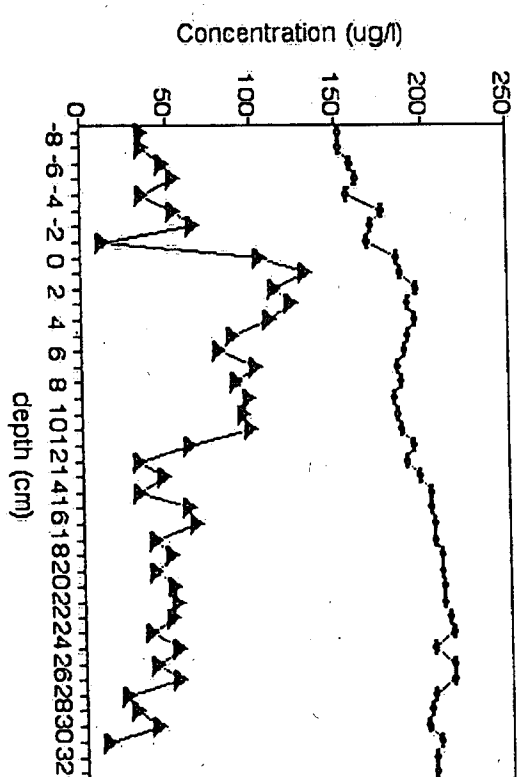
Figure 5 (Cont.)



—▲— Cu —◆— Ni



—▲— Pb —◆— Zn



—▲— Cr —◆— Sr

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