

98-258



Environment
Canada

Environnement
Canada

Canada



NATIONAL WATER
RESEARCH INSTITUTE

INSTITUT NATIONAL DE
RECHERCHE SUR LES EAUX

TD
226
N87
No. 98-
258

Are Zebra Mussels Responsible for
the Layering of Phosphorus and metal ions
in the Near-Surface sediments of the Central
and Eastern Basins of Lake Erie?

BY:

P.G. Manning, X. Wang

NWRI Contribution No. 98-258

ARE ZEBRA MUSSELS RESPONSIBLE FOR THE LAYERING OF PHOSPHORUS AND METAL IONS IN THE NEAR-SURFACE SEDIMENTS OF THE CENTRAL AND EASTERN BASINS OF LAKE ERIE?

P. G. MANNING and X. WANG
Lake Remediation Branch

ABSTRACT

The bottom sediments of the central basin of Lake Erie, from the surface to approximately 18 cm depth, are marked by several sharply defined layers enriched in nonapatite inorganic phosphate ion and in trace metal ions. Layering is also observed at similar depths of burial in the offshore sediments of the deeper eastern basin, in which rates of sedimentation greatly exceed those in the central basin. The layers are probably formed by the precipitation of hydrated ferric and manganese oxides at oxidizing horizons generated beneath the sediment-water interface by the diffusion of molecular oxygen into the sediments. The sediments are healthy in terms of their oxid potential and their contaminant holding capacity. Layers are also present in sediments collected in 1984 and 1986. Their formation cannot, therefore, be linked to the recent infestation of zebra mussels. Provided there is no significant deterioration in trophic status, the layers should remain as permanent features and as important sinks for contaminants.

NWRI Cont # 98-258

Management Perspective

Title **Are Zebra Mussels Responsible for the Layering of Phosphorus and Metal Ions in the Near-Surface sediment of the Central and Eastern Basins of Lake Erie?**

Authors: P G. Manning and X. Wang
National Water Research Institute
Aquatic Ecosystem Restoration Branch

NWRI Publication #: 98-258

Citation:

EC Priority Issue **Conserving Ecosystems, Great Lakes 2000, LAMPs**

Current Status

Anthropogenic contaminants have been deposited in Lake Erie sediment for more than a century. The potential of the invading Zebra Mussels to disrupt the storage by altering redox reactions has been assessed. Much of the anthropogenic phosphorus and metals were stored in layers in the sediment. Although these layers are only in the top 18cm of sediment they predate the arrival of the Zebra Mussels and they persist today 10 years after the mussel invasion. Thus, the mussels have not altered the storage of contaminants. Unless there is a deterioration in the trophic status of the lake (more eutrophic) the layers should remain as permanent features and a sinks for contaminants in Lake Erie.

Next Steps: The lead author has retired. The importance of the work will be communicated to the LAMP process. Phosphorus work in Lake Erie is being extended by other members of the Lake Remediation Project of AERB/NWRI

INTRODUCTION

The binding capacity of lacustrine bottom sediments for contaminants is an important issue in lake management and restoration. This capacity is dependent to a large degree on redox potentials within the sediments. For example, the brown oxidized surface layer commonly seen in the offshore sediments in the Great Lakes contains elevated concentrations of iron and phosphorus. The surface layer inhibits the release of contaminant ions to the overlying water. Also, the precipitation of hydrated ferric oxides at oxidizing horizons several centimetres beneath the sediment-water interface sediments is not uncommon in freshwater lakes (Manning *et al.* 1985, Nembrini *et al.* 1983). The oxides provide the substrates for the adsorption and co-precipitation of phosphate and metal ions. In other lakes, phosphate enriched horizons are due to the precipitation of vivianite (Manning *et al.* 1991).

In this paper, we discuss the origin of layers enriched in phosphate ion and trace metal ion in the offshore sediments of the central and eastern basins of Lake Erie. Rates of sedimentation are much higher in the eastern basin (Kemp *et al.* 1977, Robbins *et al.* 1978, Turner 1994, 1996). We attempt to answer the question "Has the recent infestation of Lake Erie by zebra mussels had a significant change on the binding capacity of the offshore sediments for contaminant ions?"

EXPERIMENTAL DETAILS

Gravity cores of bottom sediment were collected from the western (stations 349 and 350), central (station 84, the primary, and station 352), and eastern (station 351) basins of Lake Erie on several occasions in the mid 1980s and 1990s. Station 349 is in 10 m of water at 41°45' 37" N and 82°59' 20" W; station 350 is nearshore in 4m of water at 41°56' 46" N and 82°49' 50" W. The offshore stations 84 and 352 in the central basin are in 25 m of water and are at 41°56' 24" N and 81°39' 18" W, and at 41°55' 52" N and 81°55' 00" W, respectively. Station 351, the "deep hole" in 58 m of water, is at 42°32' 12" N and 79°30' 45" W. The cores were sectioned into 1 cm slices over the top 20 cm of the sediment column and into 1 cm slices every 5 cm down to 40 cm. The sections were frozen immediately and freeze dried within one week of collection. The sediments are silty clay, except for a small sand fraction at station 350.

Replicate cores were collected for the purposes of ²¹⁰Pb chronology (Turner 1994, 1996) from station 84 in September 1993 and from station 351 in September 1995.

Core sections were analyzed for concentrations of nonapatite inorganic phosphorus (NAIP), insoluble apatite and organically bonded P using the methods of Williams *et al.* (1976a). Concentrations of NAIP, the principal form of bioavailable phosphorus in sediments (Williams *et al.* 1980), are accurate to 5%. Concentrations of Fe, Mn, Pb and Zn were measured by acid dissolution and plasma emission

spectrometry. Concentrations of metal ions are accurate to 5%.

Sections of two cores from station 84, collected in 1985 and 1988, were analysed for concentrations of ferrous and ferric ions by Mössbauer spectrometry (Manning *et al.* 1985). Ferric:ferrous ratios were then used as measures of enrichment in hydrated ferric oxides. Most of the ferrous iron in Great Lakes sediments is in clay minerals, whereas ferric iron is distributed between clay minerals and oxides (Manning *et al.* 1985). The ferric : ferrous ratio within the clay structure is assumed to be constant.

RESULTS

Chronological dating yielded mass sedimentation rates of $0.062 \text{ g cm}^{-2} \text{ yr}^{-1}$ at station 84 and of $0.21 \text{ g cm}^{-2} \text{ yr}^{-1}$ at station 351, in reasonable agreement with the values of Kemp *et al.* (1977) and Robbins *et al.* (1978). The important 16 to 17 cm section in a core from station 84 (Fig. 2) is dated to approximately 1940 (56 years BP); the contaminant layer at 17 to 18 cm in a core from station 351 (Fig. 3) corresponds to deposition in 1973.

Cores from stations 349 and 350, in the shallow western basin, show minor accumulation of NAIP and organic phosphorus; most of the phosphorus is in the form of apatite. Fine-grained sediment, which is the main compartment for hydrated oxides and adsorbed contaminants, does not accumulate heavily at these stations.

Concentrations of apatite phosphorus in all central and eastern basin cores show a gradual increase of approximately 10% with increasing depth of burial; concentrations of organically bonded phosphorus decrease gradually with burial. Neither set of profiles shows significant peaks. For stations 84 and 351, for example, apatite concentrations increase with depth from 0.030 to 0.037 wt % and 0.040 to 0.048 wt %, respectively. The trends in organic phosphorus are 0.030 to 0.01 wt % for both stations. Apatite is highly insoluble and biologically unavailable. Organically bonded phosphorus is less available than is NAIP (Williams *et al.* 1980).

The NAIP sediment profiles for station 84 covering several years in the period 1984 to 1996 show clear evidence of sharply-defined layering, particularly in the top 20 cm of sediment (Fig. 4). Most of the profiles depict multiple layering. NAIP concentrations at peak maxima exceed those at the sediment-water interface (Fig. 4). The profiles for the years 1995 and 1996 indicate that the NAIP content of depositing particulate matter is approximately 0.03 wt %, in agreement with the content of depositing matter in Lake Ontario (Manning 1987). Higher concentrations in the surface sediments sampled in 1984, 1993 and 1994 probably reflect the precipitation of porewater phosphate ions at the interface.

The September 1996 sampling of station 84 yields significant coincidences in the concentration maxima for NAIP, Fe, Pb, Zn, and Mn (Fig. 3), primarily at approximately 17 cm sediment depth and with a secondary maximum at approximately 11 cm. The primary peaks are dated to approximately 1940 (Turner 1994). Metal concentrations begin to rise in approximately 1900 (Fig. 2), a few decades following

colonial settlement. Core 352 also displays layering of contaminants (Fig. 5).

Coincidental maxima occur in the concentration profiles for the station 351 sampling in September 1996 (Fig. 4), primarily at approximately 18 cm depth of burial, which is dated to approximately 1973 (Turner 1996). Secondary maxima occur at 6 cm and 12 cm. The October 1996 sampling of station 351 shows additional peaks in contaminant profiles at approximately 30 cm depth of burial (Fig. 5), dating to the mid-1950s.

The Mössbauer spectra of two cores collected in 1983 and 1985 show clear evidence for ferric iron enrichment in sections of the top 20 cm of the sediment column (Fig. 6). Assuming a constant ferric:ferrous ratio within the structure of clay minerals over the top 20 cm of sediment, it is reasonable to ascribe the peaks to the precipitation of oxides. No Mössbauer peaks of vivianite, a ferrous phosphate, are observed. Hydrated ferric oxides are particularly abundant in the top cm (Fig. 6), corresponding to the visible brown oxidized surface layer.

DISCUSSION

Origin of sediment layers

The different dates for the primary maxima in profiles for the stations 84 and 351 (Figs. 2, 3) argue against the profiles being direct reflections of contaminant loadings to the lake. The primary maximum for NAIP in station 84 sediments predates by several decades phosphorus controls on sewage effluents, and 1940 is not a significant date in terms of metal controls. Phosphorus controls were initiated in 1972, and total municipal loadings of phosphorus to Lake Erie declined from 14,000 tonnes in 1972 to 5,800 tonnes in 1982 (Dolan 1993). Total loadings of phosphorus declined similarly (Great Lakes Water Qual. Board 1981). A major NAIP peak in station 351 sediment profiles (Figs. 3, 5) is dated to approximately 1973. However, other layers were formed in sediment laid down after 1973 (Figs. 3, 5) even though loadings declined steadily. Furthermore, the widths of the peaks correspond in many instances to just 2 to 3 years of deposition, which for a large lake is too short a time for any massive change in lake dynamics. The peaks and valleys in the Erie concentration-depth profiles (Figs. 2-5) would be accentuated if sectioning were to be guided by colour laminations in the sediment. The smearing of layers contributes to the differences in shapes and positions of the peaks from one profile to another, for example, note the differences between the September and October sampling at stations 84 and 351 (Figs. 2-5). The coincidences in the maxima for metals, including the redox sensitive iron and manganese ions, is suggestive of an oxidative precipitation process.

The origin of the NAIP-enriched layers in the subsurface sediment of the central basin needs necessarily to be compared to the origin of the reddish-brown NAIP-enriched layer present at approximately 8 cm depth of burial in the sediments of the western basin of Lake Ontario. The Lake Ontario layer was attributed to the precipitation, at an oxidizing horizon, of ferrous and manganese ions diffusing upward

in the porewater. Phosphate ion is then adsorbed on hydrated oxides of iron and manganese (Manning *et al.* 1982). The deeper edge, of lower redox potential, is continually dissolving in response to increasing depth of burial, and the iron, manganese and phosphate ions diffuse upward in the porewater. Precipitation occurs on meeting oxygen diffusing downward. The layer is maintained at a constant depth of burial.

The Fe-enriched layers in the Lake Erie sediments are at similar depths of burial (3 to 15 cm, Figs. 2-5) to the single layer in Lake Ontario sediments (5 to 8 cm, Manning *et al.* 1985). The marked reddish-brown Fe-oxide layer in Lake Ontario sediments (Manning *et al.* 1985), which is overlain by a 0.1 to 0.2 cm thick black Mn-oxide layer, has no visible counterpart in the Lake Erie sediments. This is probably a reflection of lower concentrations of oxides: concentrations of hydrated ferric oxide and hence, of NAIP in the Lake Ontario sediment layer (8 wt % of Fe^{3+} and 1 wt % of NAIP) greatly exceed those in the Erie layers (2 wt % of Fe^{3+} and 0.1 wt % NAIP, Figs. 2-6).

Metal oxide enriched zones are formed in lakes with low rates of sediments and with redox gradients within the sediment. Reduction-diffusion-oxidation cycles are prominent in such lakes (Cornwell 1987, Robbins & Callender 1975). Multiple layers are present in the sediments of an arctic lake (Cornwell 1987). The layers may maintain a constant depth beneath the sediment water interface.

The presence of sub-surface sediment layers describes a healthy sediment column in which molecular oxygen diffuses to significant depth. The retention capacity of the sediments for phosphorus and trace metal contaminants is therefore high. Note that on several occasions, concentrations of NAIP at the sediment-water interface in central and eastern basins are very low (Fig. 3), due probably to the interception of phosphate ions in the porewater by the oxidizing layers.

According to Kemp *et al.* (1977), 14.3×10^9 kg of sediment are being deposited annually. Assuming a 0.03 wt% NAIP in depositing material, approximately 4.3×10^6 kg NAIP are deposited in Lake Erie annually. Similar amounts of organic P and apatite P are also deposited, yielding a total P deposition of approximately 13×10^6 kg or 13000 metric tons annually. Kemp *et al.* (1977) estimated 18×10^6 metric tons annually. The NAIP and total P profiles for central basin sediments collected in 1970 (Williams *et al.* 1976b, Kemp *et al.* 1976) show no significant enhancement in the 10-20 cm depth intervals. Certainly, enrichments of the order of the 0.09 wt% measured currently would be obvious, if present, in their profiles. Their station G-16 is within 5 km of station 84. Although it is possible that 1970 was not a representative year, it is nevertheless likely that the depth of penetration of oxygen into the sediments has increased since that time. The early 1970s mark a time of relatively poor water quality in Lake Erie.

What is the fate of the contaminant layers during summer hypolimnion anoxia? The absence of layers in the May 1970 sampling of the central basin sediments (Williams *et al.* 1976b) suggests that the layers are subject to dissolution under extended periods of anoxia. A layer of decomposing algae covered the surficial sediments in 1970 (Burns and Ross 1972). Anoxia has been rarely attained in recent years, consequently the layers seem stable. The contaminant layers are well

developed in the September 1996 samplings of the central and eastern basin sediments (Figs. 2, 3)

The filtering action of zebra mussels serves to increase the rate of sedimentation of phosphorus and other contaminants in the nearshore area of Lake Erie. This has resulted in clearer water in the shallower western basin in particular. Lower rates of sedimentation of organic matter to the offshore sediments would permit the diffusion of oxygen to greater depth of sediment. The fate of the phosphorus deposited in the pseudofaeces is not known. How rapidly is this NAIP transferred to the offshore sediments or released to the overlying water? These questions need an answer. However, ferric iron and NAIP enriched layers were well developed by 1984 (Fig. 4), immediately prior to the introduction of zebra mussels. It is likely that zebra mussels have not played a significant role in the layering of the offshore sediments. The layers should remain as permanent features, provided there is no significant deterioration in trophic status.

ACKNOWLEDGEMENTS

We thank Technical Operations for core retrieval, and M.N. Charlton and F. Rosa and G. Sardella for assistance.

CAPTIONS FOR FIGURES

- FIG. 1. Shown are the locations of the five sampling stations in the three basins of Lake Erie.
- FIG. 2. Elemental profiles in a core retrieved from station 84 in the central basin of Lake Erie in September 1996. The main concentration peak is at 17 cm depth corresponding to deposition in 1940. A secondary peak occurs at approximately 11 cm.
- FIG. 3. Elemental profiles in a core retrieved from station 351 in the eastern basin of Lake Erie in September 1996. The main concentration peak is at 18 cm depth, marking sediment deposited in 1973.
- FIG. 4. Concentration-depth profiles, covering several years, for NAIP ions in a sediment core from station 84 in the central basin of Lake Erie.
- FIG. 5. Some elemental profiles for sediment collected from stations 351 (October 1996) and 352, in the eastern and central basins, respectively. The 30 cm peaks in station 351 sediments pre-date controls on contaminant loadings.
- FIG. 6. Ferric : ferrous iron profiles as a function of sediment depth in two cores from the central basin in 1985 and 1988. The ferric enriched layers pre-date zebra mussel infestation.
- FIG. 7. Hg and NAIP profiles in a sediment core retrieved from station 84 in April 1997.

REFERENCES

- BURNS, N.M. & ROSS, C. (1972): Oxygen-nutrient relationships within the central basin of Lake Erie. In Project Hypo: An Intensive Study of the Lake Erie Central Basin. Information Canada, Ottawa.
- CORNWELL, J.C. (1987): Phosphorus cycling in arctic lake sediment: adsorption and authigenic minerals. *Arch. Hydrobiol.* 109, 161-179.
- DOLAN, D.M. (1993) : Point source loadings to Lake Erie. *J. Great Lakes Res.* 19, 212-223.
- GREAT LAKES WATER QUALITY BOARD (1981): 1981 Report on Great Lakes Water Quality. International Joint Commission, Windsor Ontario.
- KEMP, A.L.W., MACINNES, G.A. & HARPER, N. (1977): Sedimentation rates and a revised budget for Lake Erie. *J. Great Lakes Res.* 3, 221-233.
- MANNING, P.G., LUM, K.R., WONG, H.K.T. & BIRCHALL, T. (1985): Origin and age of ferrihydrite layers in Lake Ontario sediments. *Can. Mineral.* 23, 103-110.
- MANNING, P.G. (1987): Phosphate ion interaction at the sediment-water interface: relationship to sediment adsorption capacities. *Can. J. Fish. Aquat. Sci.* 44, 2204-2211.
- MANNING, P.G., MURPHY, T.P. & PREPAS, E.E. (1991): Intensive formation of vivianite in the bottom sediments of mesotrophic Narrow Lake, Alberta. *Can. Mineral.* 29, 77-85.
- NEMBRINI, G.P., CAPOBIANCO, J.A., VIEL, M. & WILLIAMS, A.F. (1983): A Mössbauer and chemical study of the formation of vivianite in sediments from Lago Maggiore (Italy). *Geochim. Cosmochim. Acta* 47, 1459-1464.
- ROBBINS, J.A. & CALLENDER, E. (1975): Diagenesis of manganese in Lake Michigan sediments. *Am. J. Sci.* 275, 512-533.
- ROBBINS, J.A., EDGINGTON, D.N. & KEMP, A.L.W. (1978): Comparative ^{210}Pb , ^{137}Cs , and pollen chronologies of sediments from Lakes Ontario and Erie. *Quaternary Res.* 10, 256-278.
- TURNER, L.J. (1994): ^{210}Pb dating of lacustrine sediments from Lake Erie (Core 055, Station 84-1), Ontario. NWRI Contribution 94-116.

TURNER, L.J. (1996): ^{210}Pb dating of lacustrine sediments from Lake Erie (Core 083, Station 351), Ontario. NWRI Contribution 96-02.

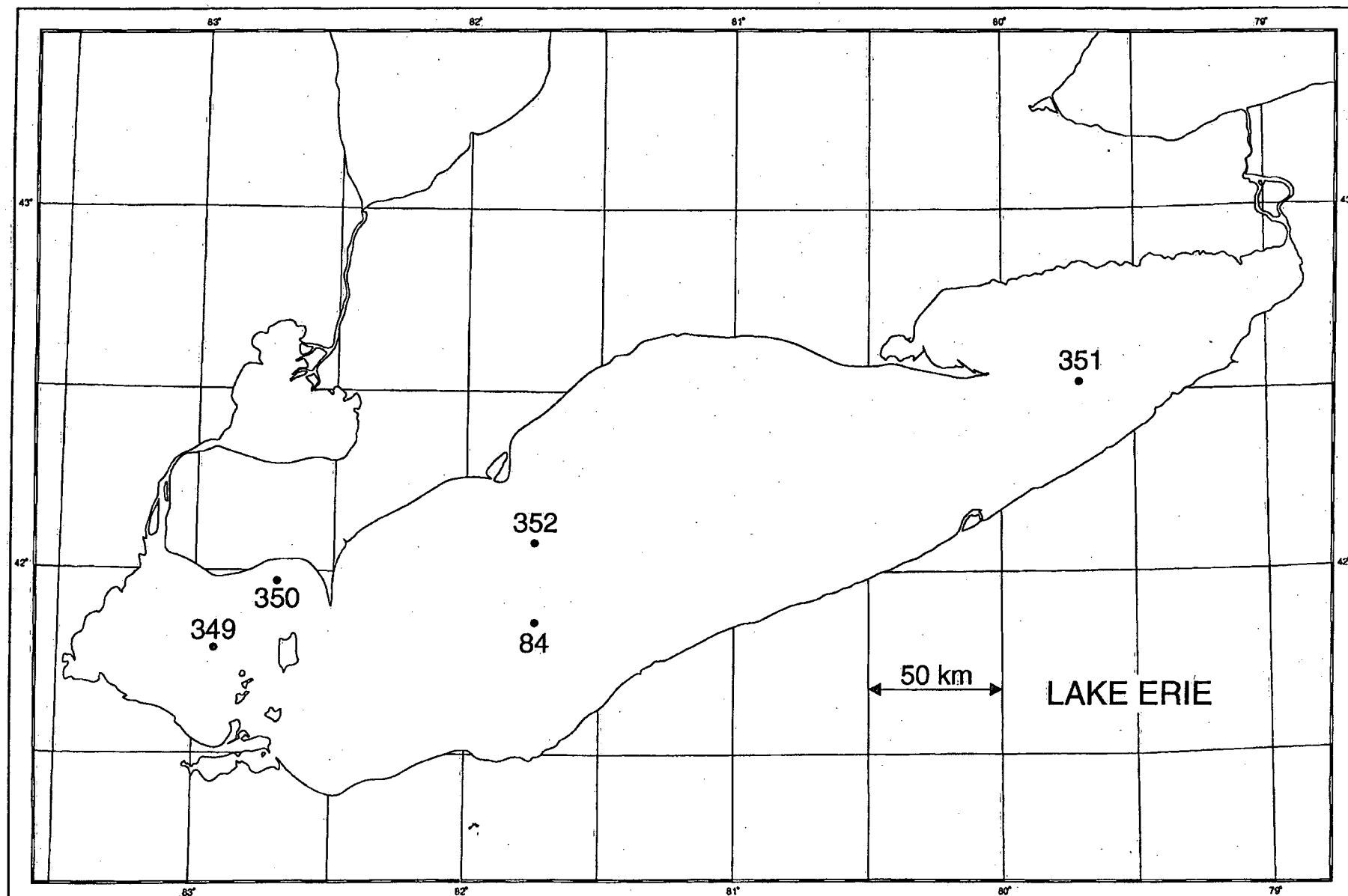
WILLIAMS, J.D.H., JAQUET, J.-M. & THOMAS, R.L. (1976a): Forms of phosphorus in the surficial sediments of Lake Erie. J. Fish. Res. Board Can. 33, 413-429.

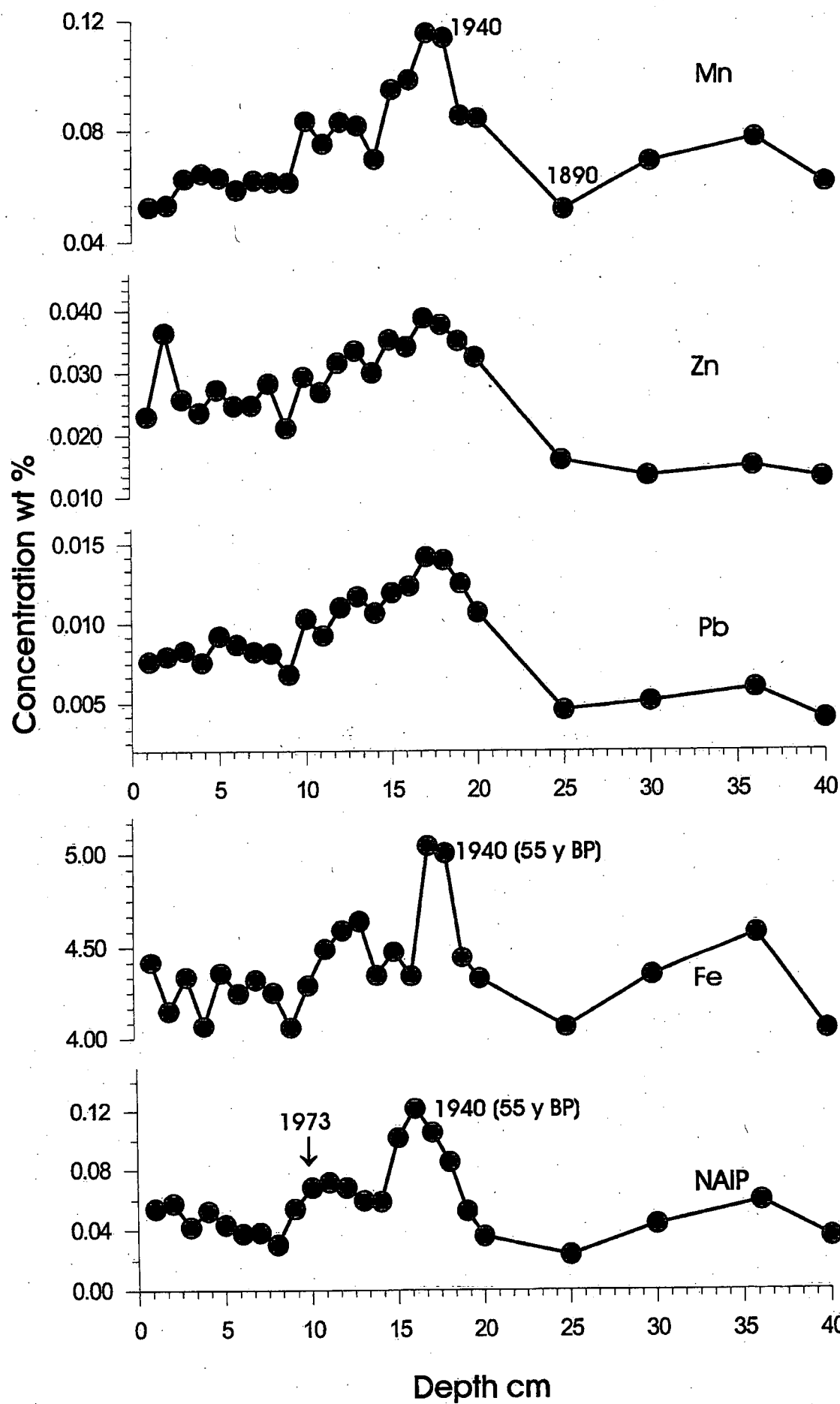
WILLIAMS, J.D.H., MURPHY, T.P. & SHEAR, H. (1976b): Rate of accumulation of phosphorus forms in Lake Erie sediments. Can. J. Fish. Res. Board Can. 33, 430-439.

WILLIAMS, J.D.H., SHEAR, H. & THOMAS, R.L. (1980): Availability to *Scenedesmus quadricauda* of different forms of phosphorus in sedimentary materials from the Great Lakes. Limnol. Oceanogr. 25, 1-11.

ADD ENDUM

Following completion of this work, analyses were received for mercury and NAIP ions in a sediment core retrieved from station 84 in April 1997. The profiles (Fig. 7) as a function of sediment depth, demonstrate clearly an enhancement in the concentration of Hg, and concentration of NAIP, 8-12cm beneath the sediment-water interface. It seems the Hg ions are also subjected to the reduction (of Fe, Mn)-diffusion-oxidation cycle.





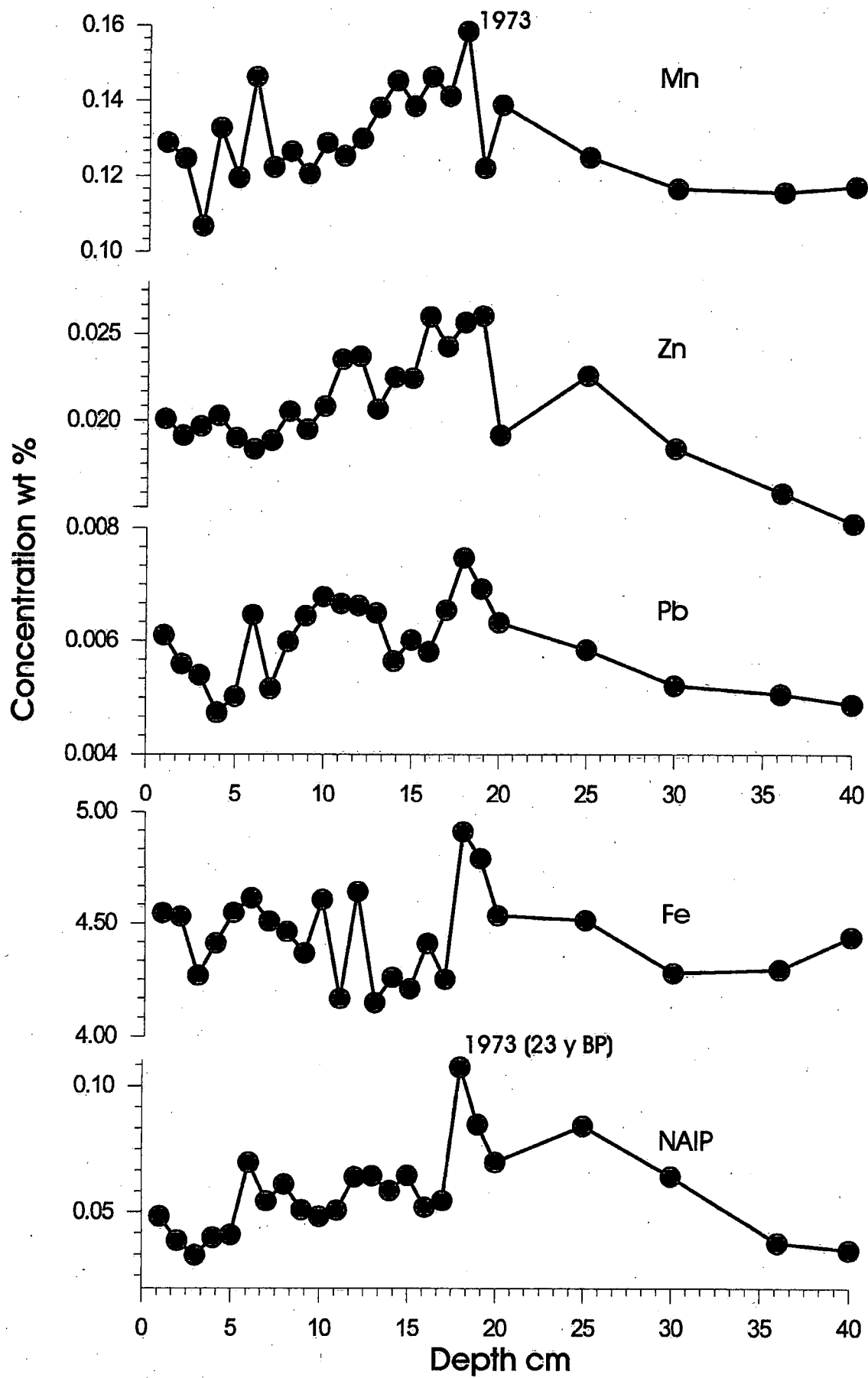
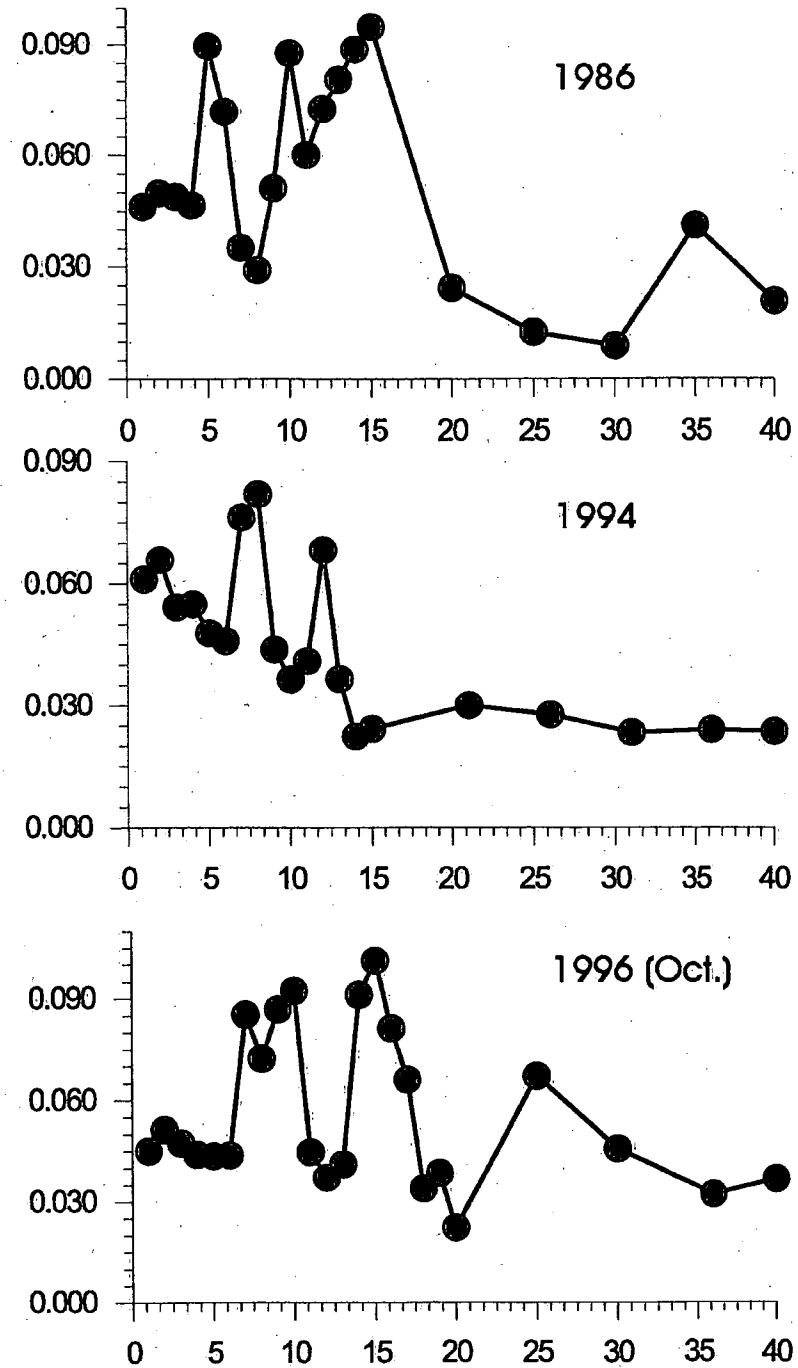
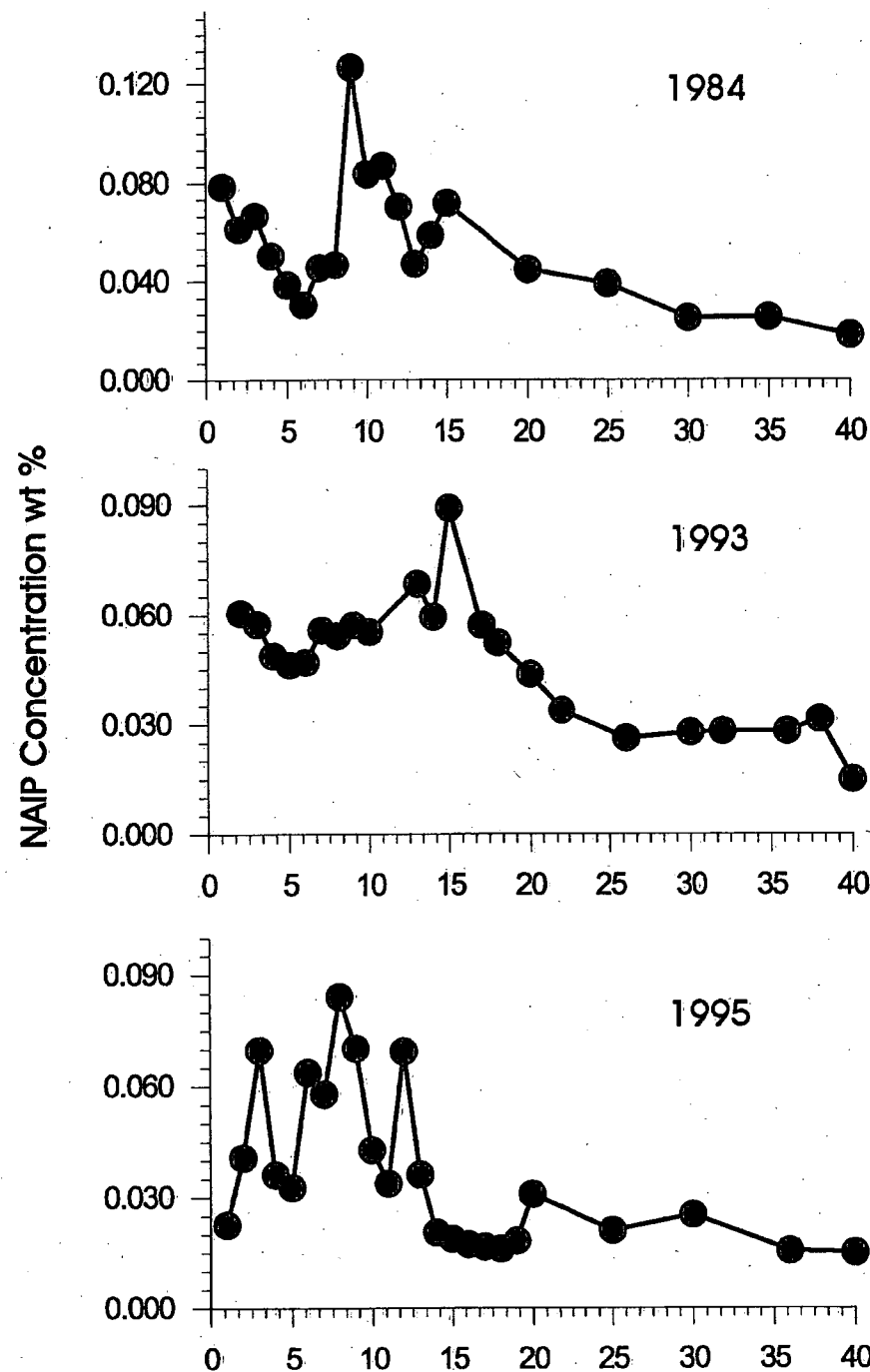


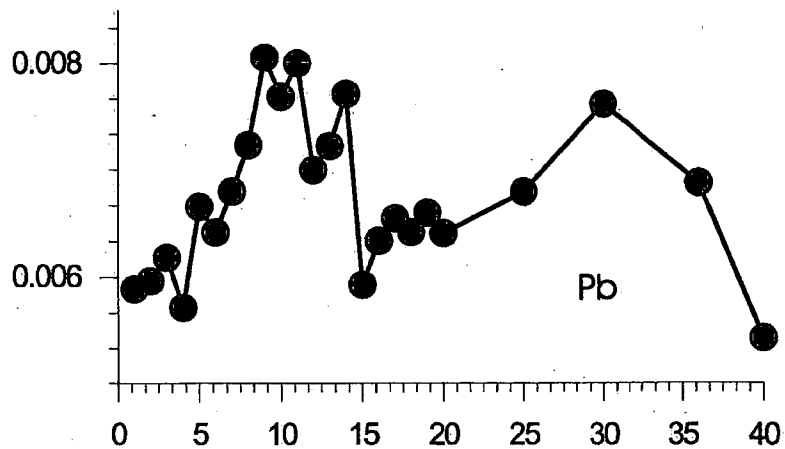
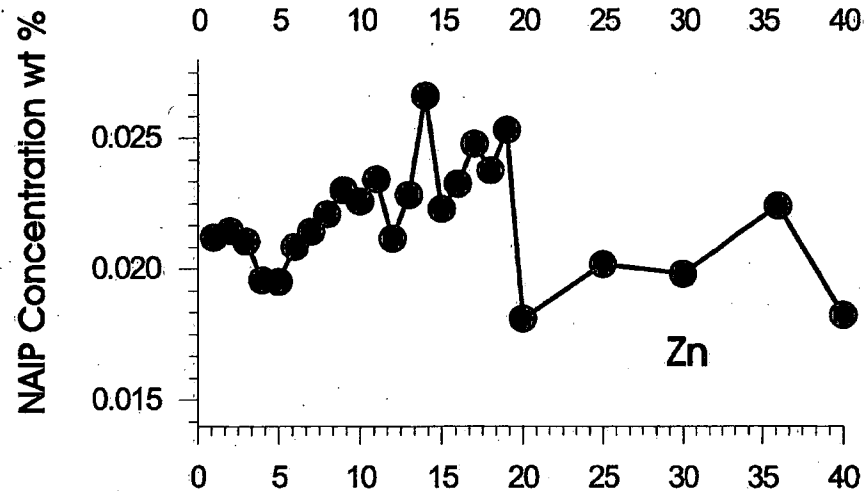
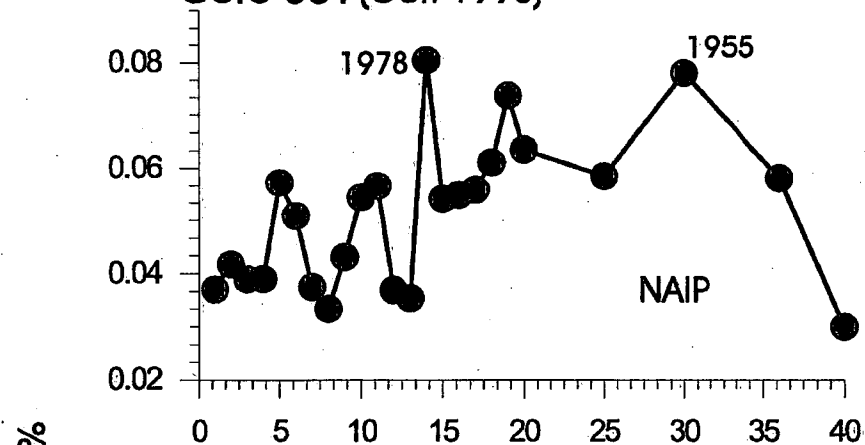
Fig 7



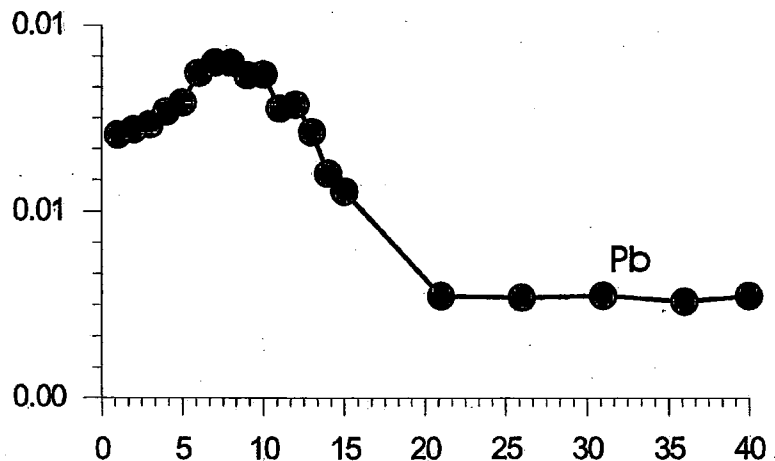
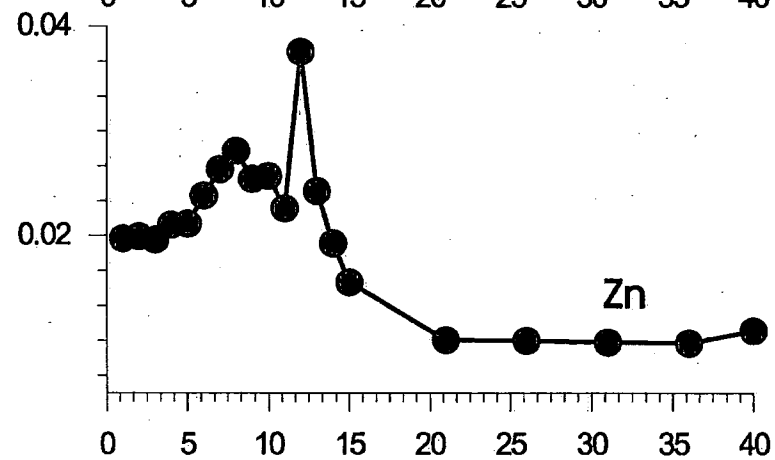
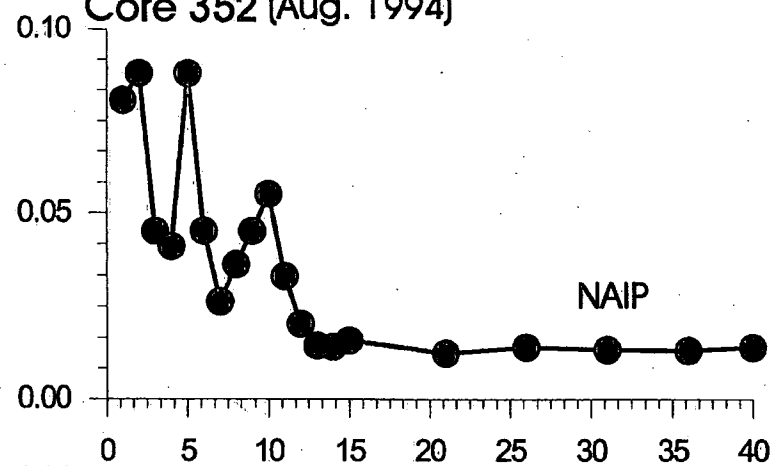
Depth cm

FIG 4

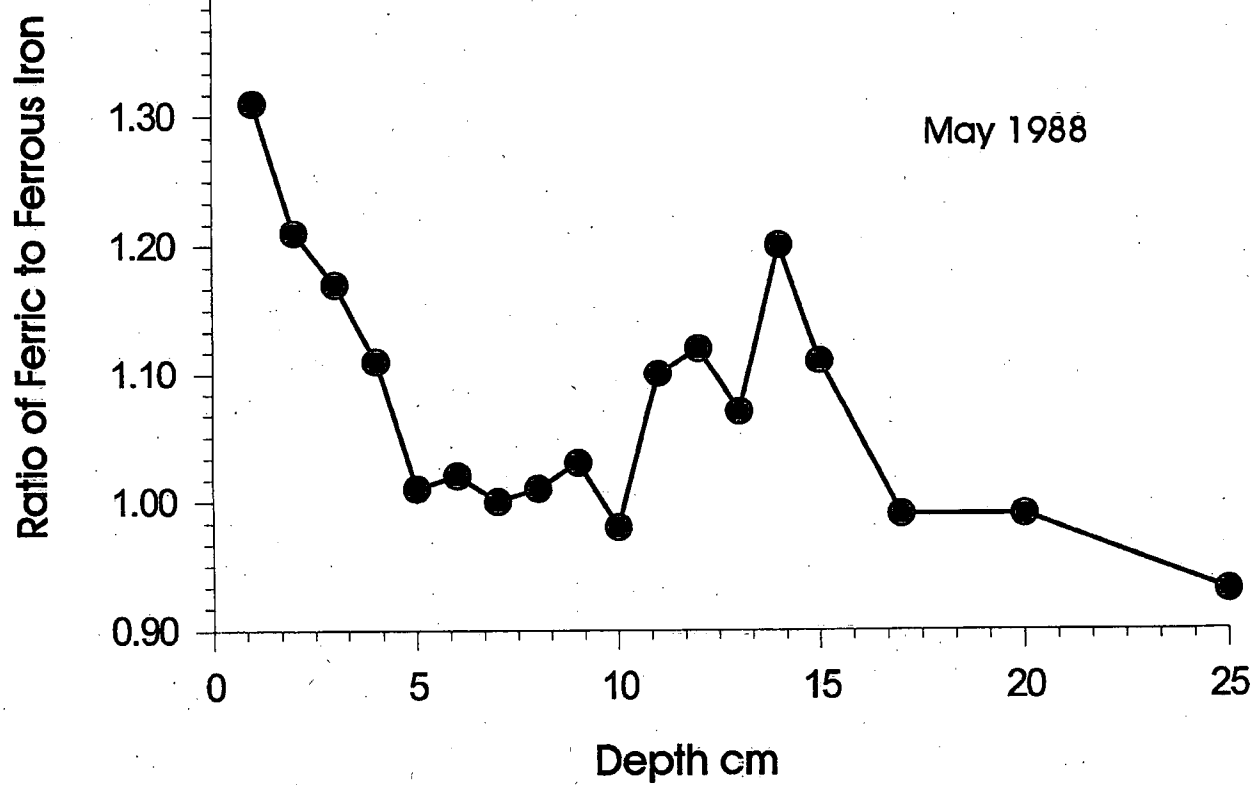
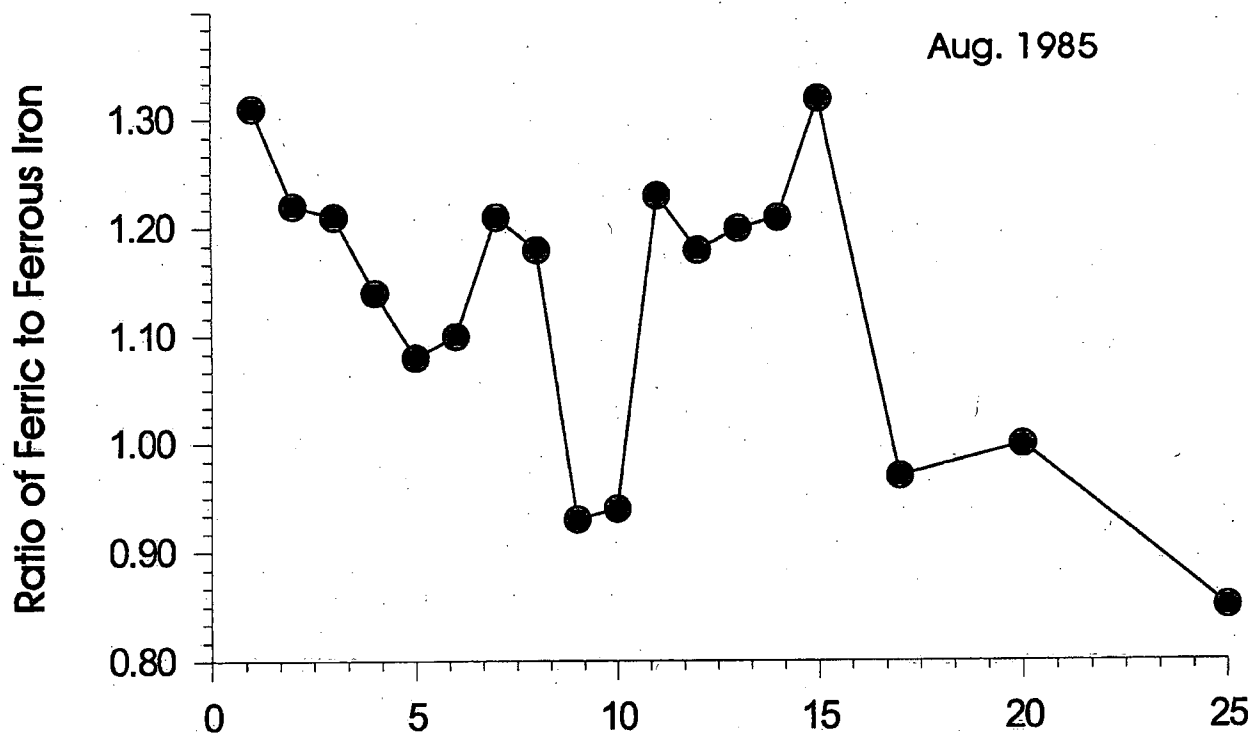
Core 351 (Oct. 1996)

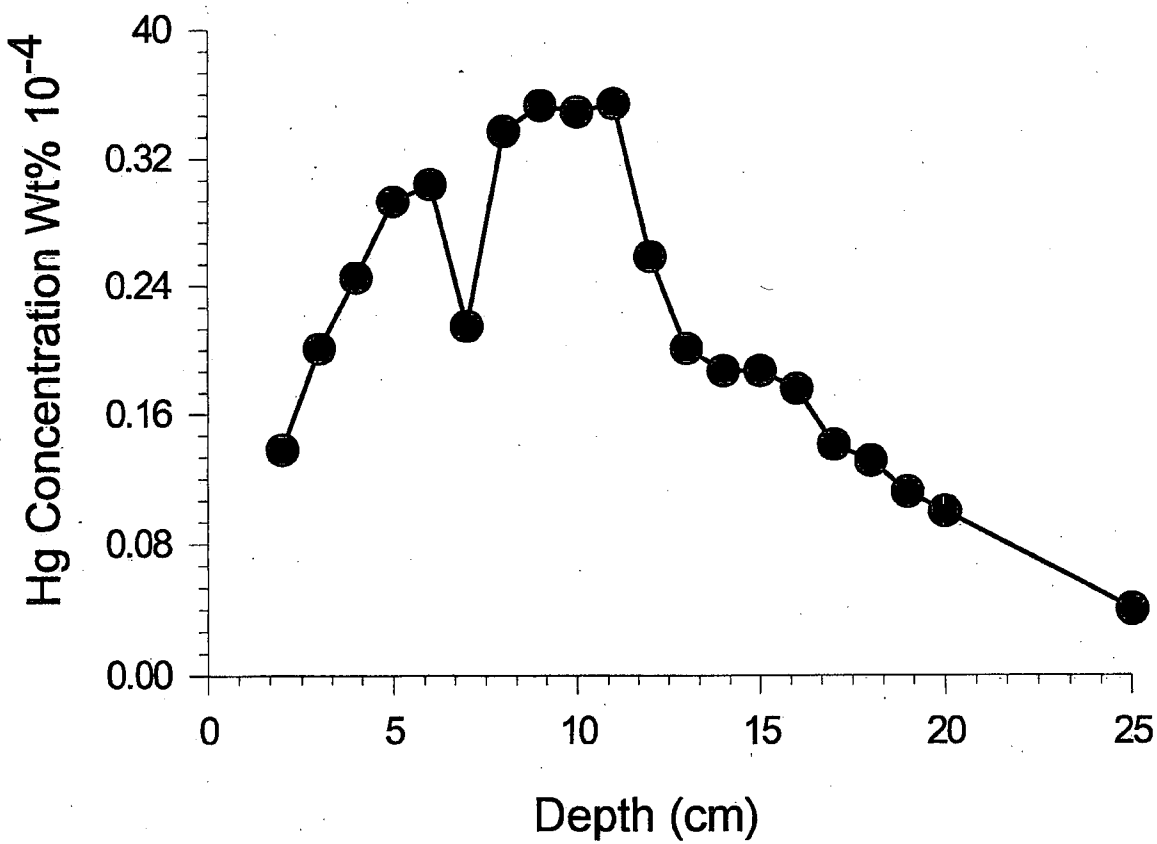
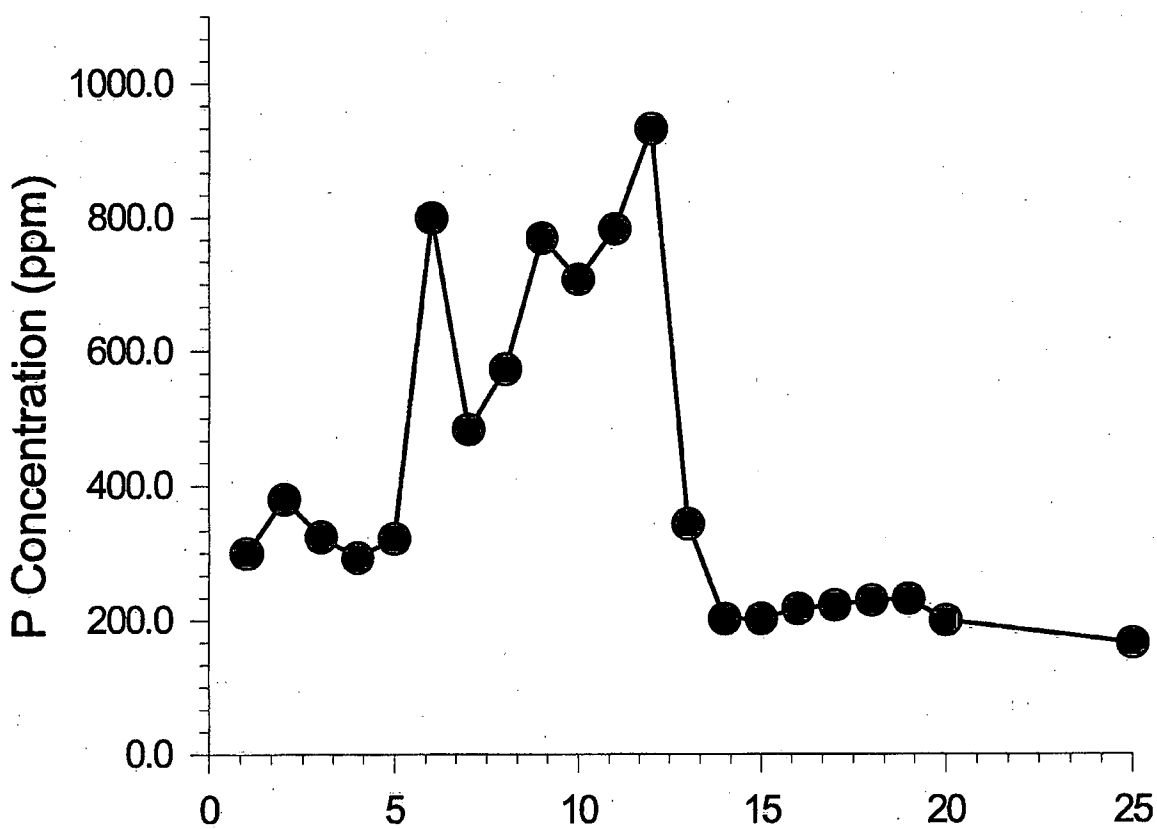


Core 352 (Aug. 1994)



Depth cm







3 9055 1017 7234 0

PRINTED IN CANADA
IMPRIMÉ AU CANADA



ON RECYCLED PAPER
SUR DU PAPIER RECYCLÉ

National Water Research Institute
Environment Canada
Canada Centre for Inland Waters
P.O. Box 5050
867 Lakeshore Road
Burlington, Ontario
L7R 4A6 Canada



**NATIONAL WATER
RESEARCH INSTITUTE**
**INSTITUT NATIONAL DE
RECHERCHE SUR LES EAUX**

National Hydrology Research Centre
11 Innovation Boulevard
Saskatoon, Saskatchewan
S7N 3H5 Canada

Institut national de recherche sur les eaux
Environnement Canada
Centre canadien des eaux intérieures
Case postale 5050
867, chemin Lakeshore
Burlington, Ontario
L7R 4A6 Canada

Centre national de recherche en hydrologie
11, boul. Innovation
Saskatoon, Saskatchewan
S7N 3H5 Canada



Environment
Canada

Environnement
Canada

Canada