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Cultural Impact on the Geochemistry of the Sediments of Lakes Ontario, Erie and Huron

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Abstract

The concentration of organic matter, major elements and trace elements were determined in 14 cores from Lakes Ontario, Erie and Huron. The chemistry of the cores was related to the sediment particle size, Eh, pH, chronology and location. Surface elemental concentrations were normalized to the baseline Al concentration at each location to correct for surface enrichments of organic matter and carbonates.

Concentrations of Si, Al, K, Na and Mg, which represent the major mineral species in the sediments, are generally uniform in each core. Surface enrichments of Hg, Pb, Zn, Cd, Cu, organic-C, N and P are observed at most locations; their concentrations are generally much greater above the *Ambrosia* horizon (ca. 120 BP), irrespective of the depth of the horizon. The enrichment of these elements is attributed mainly to the increasing anthropogenic loading to the sediments in recent years. Increasing carbonate concentrations at some of the locations is believed to be due to present-day calcite precipitation. Concentration profiles for Mn, Fe and S are related to the sediment Eh and may be accounted for by diagenetic-mobilization mechanisms.

Anthropogenic inputs of the heavy metals and nutrient elements are up to 100 times those of the natural inputs. Natural loadings parallel the sedimentation rates and anthropogenic loadings parallel the population and degree of industrialization of each drainage basin. Evidence is presented that atmospheric inputs are significant.

Résumé

La teneur en les éléments majeurs, mineurs, et en traces et la matière organique ont été déterminés de 14 carottes prélevées dans les lacs Ontario, Erie et Huron. La chimie des carottes a été liée à la granulométrie du sédiment, l'Eh, le pH, la chronologie et l'endroit des échantillons. La teneur en les éléments dans le cm supérieur de sédiment ont a été normalisée à la teneur de Al dans le sédiment, qui a été déposé avant 1850 A.D., pour corriger de l'enrichissement de la surface en C organique et C carbonate.

Les teneurs en Si, Al, K, Na et Mg, qui représentant les principaux minéraux du sédiment, sont uniformes en général dans chaque carotte. L'enrichissement de la surface en Hg, Pb, Zn, Cd, Cu, C organique, N et P a été observé à la majorité des endroits, ainsi que les teneurs les plus hautes situées au-dessus de l'horizon de *Ambrosia* (ca. 1850 A.D.), indépendant de la taille de l'horizon. L'enrichissement de ces éléments est causé en grand mesure par un apport anthropogénique croissant dans les sédiments depuis ca. 1850. L'enrichissement des carbonates à quelques endroits est causé par la précipitation récente de la calcite. Les profils de teneur en Mn, Fe et S sont liés à l'Eh du sédiment et sont le résultat de la mobilisation de ces éléments dans l'eau des pores.

Les apports naturels et anthropogénique de substances nutritives et de métaux lourds ont été calculés. Les apports naturels sont pareil à les taux récents de sédimentation et les apports anthropogénique sont pareil à la quantité des habitants et des industries dans les bassins drainages de chaque lac. Les apports atmosphérique représentent une source importante de métaux lourds.

Introduction

During the last 60 years, changes in the biota and environment have taken place in each of the Great Lakes. The increases in aqueous chemical concentrations and plankton together with changing fish and benthic faunal populations in the lakes can be attributed directly or indirectly to man's activities in the drainage basin of each lake (Beeton, 1965; 1969). The relative changes in the environment of Lakes Ontario, Erie and Huron can be seen from the increases in dissolved solids over the last 60 years. Total dissolved solids have increased 43 per cent in Lakes Ontario and Erie as compared with only a nine per cent increase in Lake Huron (Beeton, 1969).

Sediment studies have also demonstrated the changing environments of Lakes Ontario, Erie and Huron. Enrichment of organic carbon, nitrogen and phosphorus in the surface sediments of Lakes Ontario and Erie are attributed mainly to increasing nutrient inputs to the lake since around 1900 (Kemp, 1971; Kemp *et al.*, 1972, 1974). Mercury enrichment in the surface sediments of Lakes Ontario and Erie is also attributed to increasing mercury inputs to the lakes (Thomas, 1972, 1973; Walters *et al.*, 1972; Kovacik and Walters, 1973; Kemp *et al.*, 1974; Wolery and Walters, 1974). The major increases in mercury and nutrient loadings to the sediments of Lakes Ontario and Erie are estimated to have taken place since 1950. On the other hand, nutrient and mercury loadings to the surface sediments of Lake Huron are much less than to Lakes Ontario and Erie (Kemp *et al.*, 1974). In particular, loadings to northern Lake Huron are very small relative to the Lower Lakes. Thus, the sediments of the three lakes are well-suited for a comparative geochemistry study, where the impact of man's activities in the drainage basin can be superimposed on the natural geochemical processes.

In order to interpret the geochemistry of the recent sediments of Lakes Ontario, Erie and Huron, it is necessary to establish a time-scale for sediment deposition. The increase in *Ambrosia* pollen (120 years BP) and the decline in *Castanea* pollen (ca. 35-40 years BP) provide the chronologic framework necessary for the sediment studies (Anderson, 1974; Kemp *et al.*, 1974). The

high sedimentation rates found at these sediment locations and the probable absence of reworking of the sediments below three cm at the deeper locations (Kemp *et al.*, 1972) allows preservation of the anthropogenic record at these sediment locations. It is thus possible to relate present-day levels of geochemical elements with the natural pre-cultural levels and also to compare sediment profiles from Lake Huron, where man's activities in the drainage basin are small, with those from Lakes Ontario and Erie. For this symposium we describe the results of exploratory studies on the distribution of organic matter, major elements and trace elements in 14 cores from Lakes Ontario, Erie and Huron. Elemental concentrations are evaluated statistically and related to the sediment particle size, redox potential, pH, chronology and location of sampling site. The objectives of our present studies are threefold: 1) To ascertain the extent of man's activities in the drainage basins of the lakes by determining the changes in sediment chemical composition with time; 2) To estimate the present-day anthropogenic and natural inputs of organic matter, major elements and trace elements to the sediments of the three lakes; 3) To attempt to evaluate the chemical composition of the sediments in terms of sedimentary geochemical processes. Part of these studies has been published previously, particularly with reference to Lake Erie (Kemp *et al.*, 1976; Kemp and Thomas, 1976).

The distribution, composition and characteristics of the surface sediments of Lakes Ontario, Erie and Huron have been described previously (Lewis, 1966; Thomas *et al.*, 1972, 1973, 1976). Sedimentation rates were found to be variable at the 14 core locations ranging from high values in Lake Erie to intermediate in Lake Ontario to low in Lake Huron (Kemp *et al.*, 1974). Trace metals were determined in sediment cores at eight Lake Erie locations recently (Walters *et al.*, 1974). The authors found significant enrichments in Cr, Cd, Zn, Ni, Sb, As, Hg and Cu in each of the cores.

Sediment cores were used to determine the accumulation of major, minor and trace constituents in southern Lake Michigan sediments (Shimp *et al.*, 1970, 1971; Leland *et al.*, 1973). Surface

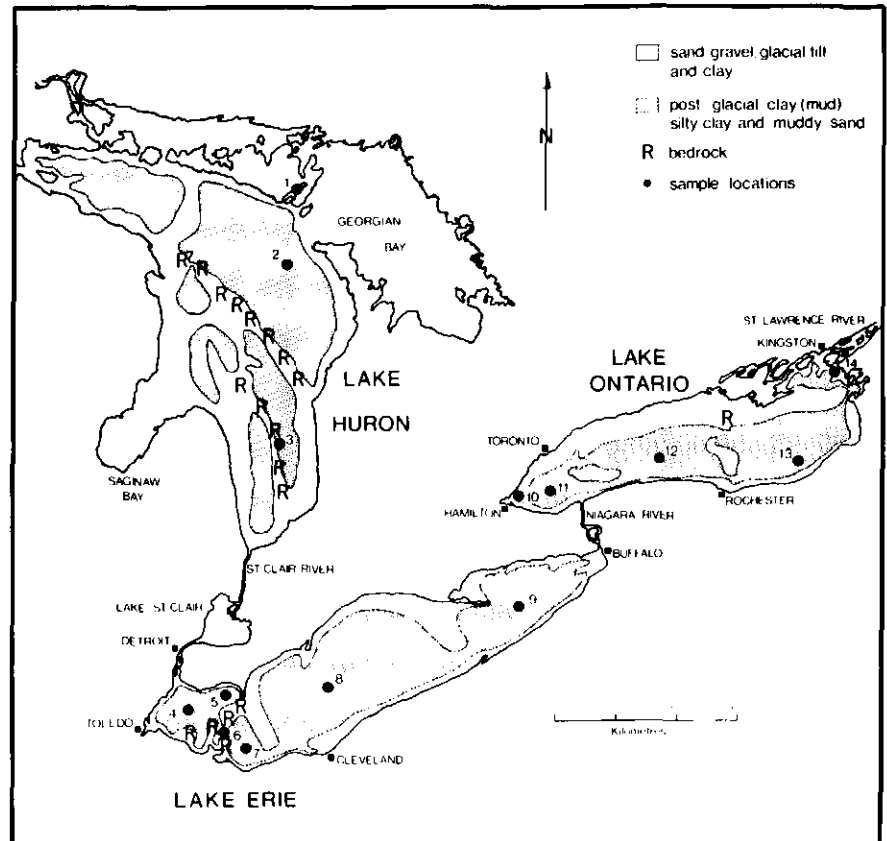


Figure 1
Station locations and surficial sediment distribution in Lakes Ontario, Erie and Huron.

Table I
Sample locations and present-day sedimentation rates at the 14 coring stations.

Station Number	Sample Location		Water Depth (m)	Present-day Sedimentation Rate ($\text{gm}^{-2}\text{yr}^{-1}$)	Mean Annual Accumulation of Sediment (mm)
	Lat. N.	Long. W.			
Lake Huron					
1	45° 37.5'	81° 52.73'	56	147	0.7
2	45° 0.1'	82° 3.1'	245	157	0.9
3	43° 47.95'	82° 07.15'	91	325	1.4
Lake Erie					
4	41° 45.7'	82° 59.2'	11	3580	7.6
5	41° 56.78'	82° 49.90'	12	3465	6.7
6	41° 41.8'	82° 44.2'	11	847	1.1
7	41° 32.6'	82° 33.3'	14	1109	2.7
8	42° 0.2'	81° 36.2'	24	1190	5.1
9	42° 32.19'	79° 39.63'	58	5049	13.4
Lake Ontario					
10	43° 19.96'	79° 43.64'	33	452	1.0
11	43° 24.10'	79° 26.66'	101	420	2.0
12	43° 33.0'	78° 10.4'	186	423	2.1
13	44° 30.7'	76° 54.0'	225	366	2.0
14	44° 04.71'	76° 24.72'	26	1156	5.4

enrichments of Cu, Hg, Pb and Zn were found in the Lake Michigan sediments. Apparently these trace elements are sorbed onto suspended particles which are transported by water and deposited in the regions of active sedimentation (Leland *et al.*, 1973). Regression analyses indicated a relationship between trace element concentrations and quantities of organic matter and iron oxide in the Michigan sediments. Enrichment of Cu and Ni in sediment cores in the Wanapitei River were related to industrial inputs from Sudbury, Ontario (Hutchinson *et al.*, 1976).

Methods

Surficial sediment samples were collected at 14 sample locations in Lakes Ontario, Erie and Huron (Fig. 1 and Table I). The samples were obtained with a modified Benthos gravity triple corer (Kemp *et al.*, 1971). Eh and pH values were measured within two hours of retrieval of the triple corer, on one of the cores. Sediment from the same core and a second core was then immediately freeze dried and stored for geochemical analysis. The remaining core was stored at 4°C and sub-sampled later for analysis of sediment particle size and *Ambrosia* and *Castanea* pollen content. Sub-sampling of the cores, sample preparation, Eh and pH measurements, determination of water content, pollen counts, organic carbon, carbonate carbon, total nitrogen, mercury and sediment particle size have been previously described (Kemp *et al.*, 1972; 1974).

Total major element analysis for Na, K, Ca, Mg, Fe, Mn, P, S, Ti, Al and Si was carried out by X-ray fluorescence, using a Philips PW 12200 semi-automatic X-Ray fluorescence spectrometer on pelletized samples. Calibration was based on lake sediment standards of similar matrix with correction for inter-element interference. Trace elements, extractable in concentrated HCl, were determined on a Techtron AA-5 atomic absorption spectrophotometer. The freeze-dried samples were extracted in hot concentrated HCl (ca. 90°C) for 20 minutes and the leachate analysed for Pb, Cu, Zn, Cd, Be and V. The extraction method was tested against other extraction methods (e.g., aqua regia, conc. nitric acid) and found to yield consistent results. The method extracts the same quantity of the trace metals

from the Great Lakes sediment as aqua regia.

Surface Sediment Distribution in Lakes Ontario, Erie and Huron

A recent overview of the glacial and post-glacial evolution of the Great Lakes has been given by Sly and Thomas (1974). The recent sediment distribution is intimately related to past events and a very general sequence as a background to the discussion of the surficial materials in the lakes may be taken as follows: 1) Deposition of last glacial tills during final northward ablation of Wisconsin Ice. 2) Formation of high level glacial lakes ponded to the north by the retreating ice mass, with southerly outflow drainage. 3) Continuation of northward ice retreat freeing the northern exits from Lake Erie to Ontario, Lake Ontario to the St. Lawrence River and Lake Huron to the Ottawa Valley. Lake levels dropped to a low level stage. 4) Isostatic uplift, closed drainage of Lake Huron to the Ottawa Valley and raised the outlet sills at the Niagara River and the St. Lawrence resulting in a continuing deepening of the lakes to the present levels.

In terms of lake sediments, the following general correlations can be made against the above enumeration:

- Deposition of the last glacial tills with ice ablation forming tills varying in colour from medium grey to brown, and composed of boulders, cobbles and pebbles in a stiff, sand, silt, clay matrix. Where tills are exposed to sub-aqueous erosion, winnowing of the finer components has resulted in the formation of lag or residual gravel deposits.
- Deposition of glaciolacustrine sequences, often varved clays, with occasional ice-rafted erratics; mostly composed of clay materials derived from the reworking of exposed glacial tills. These clays are generally medium to light grey in colour, red at some locations and low in organic materials. Where glaciolacustrine clays are exposed on the lake bed to erosional energy, the deposits are capped with a lag sand ranging from two to six cms in thickness.
- Continued deposition of fine clayey sediments (rarely varved) in the more central and deepest parts of the lake basins. Ameliorating climate conditions, resulting in increasing lake productivity produced higher levels of organic matter

with associated dark grey sediment colouration.

- Continued deposition of fine clayey sediments increasing in thickness with outward transgression of these sediments over older deposits (glaciolacustrine clays, tills and glacial features).

The distribution of surficial materials in Lakes Huron, Erie and Ontario is shown in Figure 2. The distribution maps were compiled from echosounding records (Kelvin Hughes, M.S.-26 operating at 14.25 kilohertz) with surface sediment grab samples as control (Thomas *et al.*, 1972, 1973). General similarities in the distribution of materials can be observed due to the recent geologic evolution discussed above and lake bathymetry. Glacial till and bedrock were not differentiated in the interpretation of the echograms though in general it can be stated that surface bedrock occurrence is relatively restricted in the Great Lakes.

Till occurs predominantly in the shallow water nearshore zone around the periphery of the lakes (Fig. 2) and in shallow water areas in the offshore regions of Lake Huron. The tills are overlain by glacio-lacustrine clays which are exposed immediately offshore of the tills and on the flanks of the offshore till occurrences in Lake Huron (Fig. 2). In Lakes Erie and Ontario offshore occurrences of glacio-lacustrine clays occur as low amplitude bathymetric highs exposed as cross-lake sills perpendicular to the main axis of the lakes. These glacio-lacustrine cross lake sills have been used as natural partitions subdividing the offshore regions of the lakes into discrete depositional basins (Thomas *et al.*, 1972; Thomas *et al.*, 1976) A similar cross lake sill occurs in the northwestern part of Lake Huron (Fig. 2) again effectively subdividing the northern part of the lake into two major basins (Thomas *et al.*, 1973). The offshore deep, or deeper water regions of all three lakes are characterized by the accumulation of modern muds which texturally consist of silty clays and clays. These modern mud deposits overlie glacio-lacustrine clays conformably in the deep water areas and are transgressing the older deposits at the individual basin margins. This transgressive modern sequence is related to basin infilling under conditions of rising water levels (Sly and Thomas, 1974).

The core sample locations are chosen to be representative of the various sub-basins of fine-grained postglacial sediment accumulation in the three lakes (Fig. 2). Station 1, in South Bay, Lake Huron is selected to represent a Great Lakes sediment location unaffected by cultural influences (Kemp *et al.*, 1972). As the core profiles are similar at a number of the locations, the results for only six of the sample locations are shown (Figs. 3 to 8). The profiles for each Ontario core are very similar to each other and station 13 is chosen as being typical for the lake. In Lake Erie, where the sedimentation rate is more variable, profiles are shown for stations 4, 8 and 9. The profiles at station 1 are similar to those for station 2 and cores from stations 2 and 3 are shown for Lake Huron. The core results

are presented and discussed under three separate headings: 1) the physical characteristics of the sediments, 2) the chemical composition and enrichment of the sediment, and 3) natural and anthropogenic accumulation of the elements in the sediments.

Physical Characteristics and General Description of the Sediments

The fine-grained sediments in each of the three lakes are generally similar in their physical characteristics. This is mainly due to the more or less uniform source of inorganic sediment materials from the drainage basins and to the similar environments of deposition. The sediments at each location consist characteristically of a reddish-brown floc from zero to a few mm thickness at the sediment-water interface overlying a

soft gray to dark gray ooze. The sediment which is soft in the top few cm becomes increasingly firmer with depth of burial. The colour and firmness of the sediments are reflected by the water contents and redox potentials observed (Figs. 3 to 8). The water contents decrease from surface values of around 90 per cent water by weight in the sediment to around 50 to 60 per cent water at a depth of one meter. Additionally variations in water content in each core parallel the sediment particle size distribution with the coarser sediments having lower water contents. The decrease in water content from the interface reflects the increasing compaction of the sediment with depth of burial.

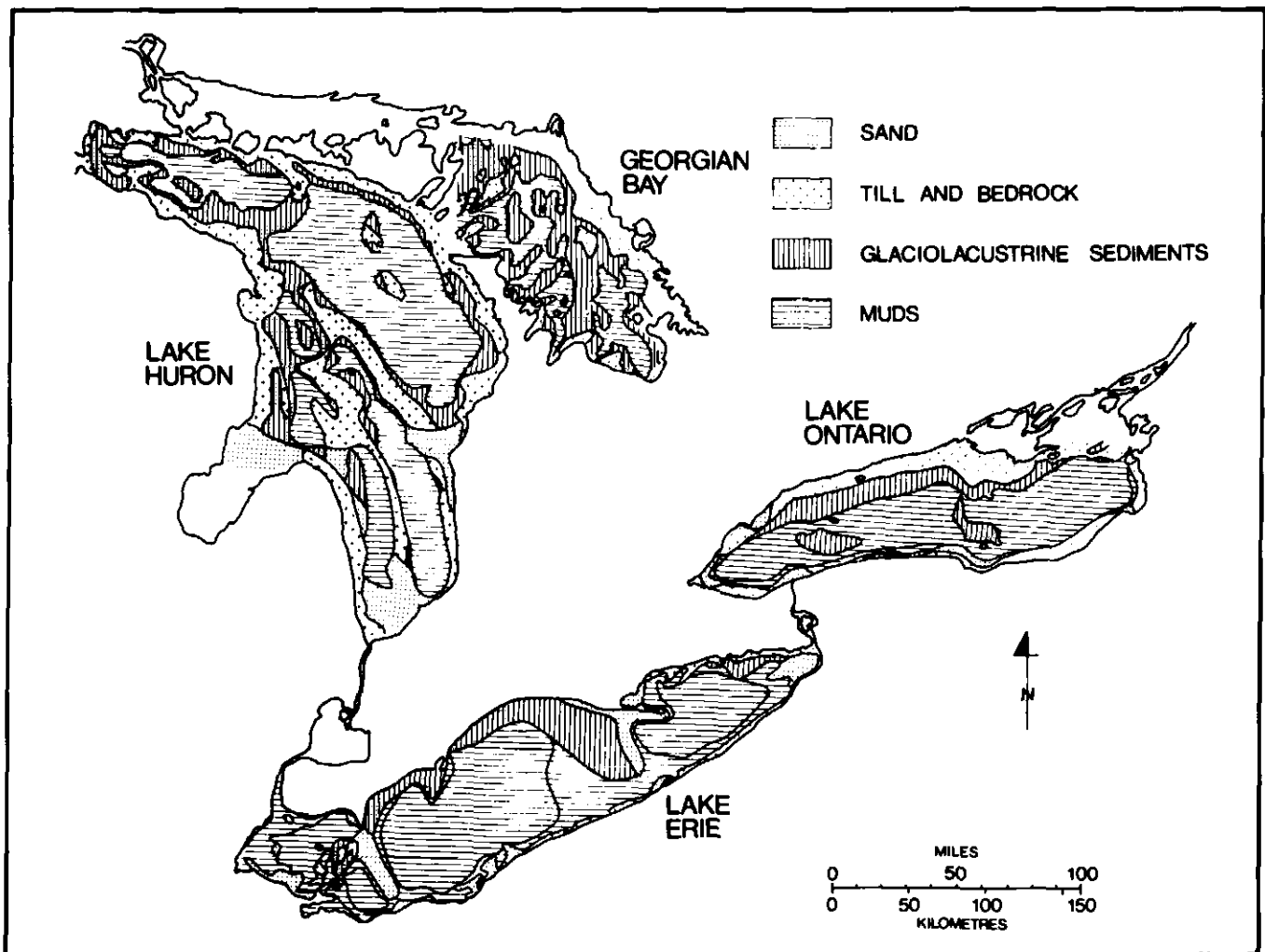


Figure 2
Surficial sediment distribution in Lakes Ontario, Erie and Huron.

The Eh decreases from around 0.100 to 0.200 volts in the reddish-brown surface layer to around zero volts at 20 cm at each of the locations, with the exception of station 8. The most negative values are found in the Lake Ontario cores where values of around -0.200 volts occur between five and 15 cm (Fig. 8). These negative zones have a dark gray colour and smell of H₂S. The sediment colour and Eh indicate that the positive surface zone contains hydrated iron oxides with the black reduced zones containing iron sulphides (Hough, 1958). Exposure of the dark gray reduced sediment to air oxidizes the dark gray sediment to a brown colour. The hypolimnion water of the central basin of Lake Erie was anoxic at the time of collection of the core at station 8 in August 1970. It can be seen that the Eh is negative at the sediment-water interface and is most reduced between one and three cm (Fig. 6). A core collected at the same location in May 1971, when the hypolimnion waters were saturated with oxygen, yielded an Eh profile similar to that of station 13 (Fig. 8), demonstrating the seasonal variations possible in sediment Eh near the water-interface. Oxygen depletion of the hypolimnion waters only occurs to any extent in the western and central basins of Lake Erie (Beeton, 1965) affecting the chemical composition of the sediments at stations 4, 5, 6, 7 and 8. Mobilization of Mn and Fe is particularly important under reducing conditions (Mackereth, 1966) and is discussed in the next section. More extensive discussions of redox potential in the Great Lakes surface sediments may be found in Mortimer (1971), Vanderpost (1972) and Kemp *et al.* (1972).

The sediment pH is variable. In most cases the sediment pH tends to decrease from values around 7.0 to 7.5 at the sediment-water interface to uniform values between 6.7 and 7.0 at 1 m (Figs. 3 to 8). The decrease in pH in the cores is presumably due to decomposition of sediment organic matter and release of CH₄, CO₂ and NH₄⁺ to the interstitial waters (Kemp *et al.*, 1972).

The sediment particle size distribution is generally uniform in each core and varies only slightly from location to location (Figs. 3 to 8). The sediments consist of 50 to 75 per cent clay size materials with silt size sediment

comprising most of the remainder. The sediments are more silty at stations 4, 5, 6, 10 and 14. These locations are in regions of shallow water or are close to the edge of sub-basins of fine-grained sediment and are thus subject to greater depositional energies (Fig. 1, Table I). The high clay-size contents suggest that deposition of sediment occurs under low energy conditions at most of the locations.

Mineralogical examination of the surface sediments (0-1 cm) at each location shows that the sediments consist mainly of quartz, feldspars,

carbonates, organic matter and clay minerals. Thomas (1969) demonstrated a high degree of correlation between the clay size fraction and clay mineral contents of fine-grained Great Lakes sediments and it is believed that a similar situation exists at these locations. The clay minerals consist of around 70 to 80 per cent illite and 20 to 30 per cent chlorite and kaolinite. Calcite and dolomite are the dominant carbonates in the surface sediments of Lakes Huron and Erie with calcite, only, being present in Lake Ontario. The latter observation will be discussed in the next section. In

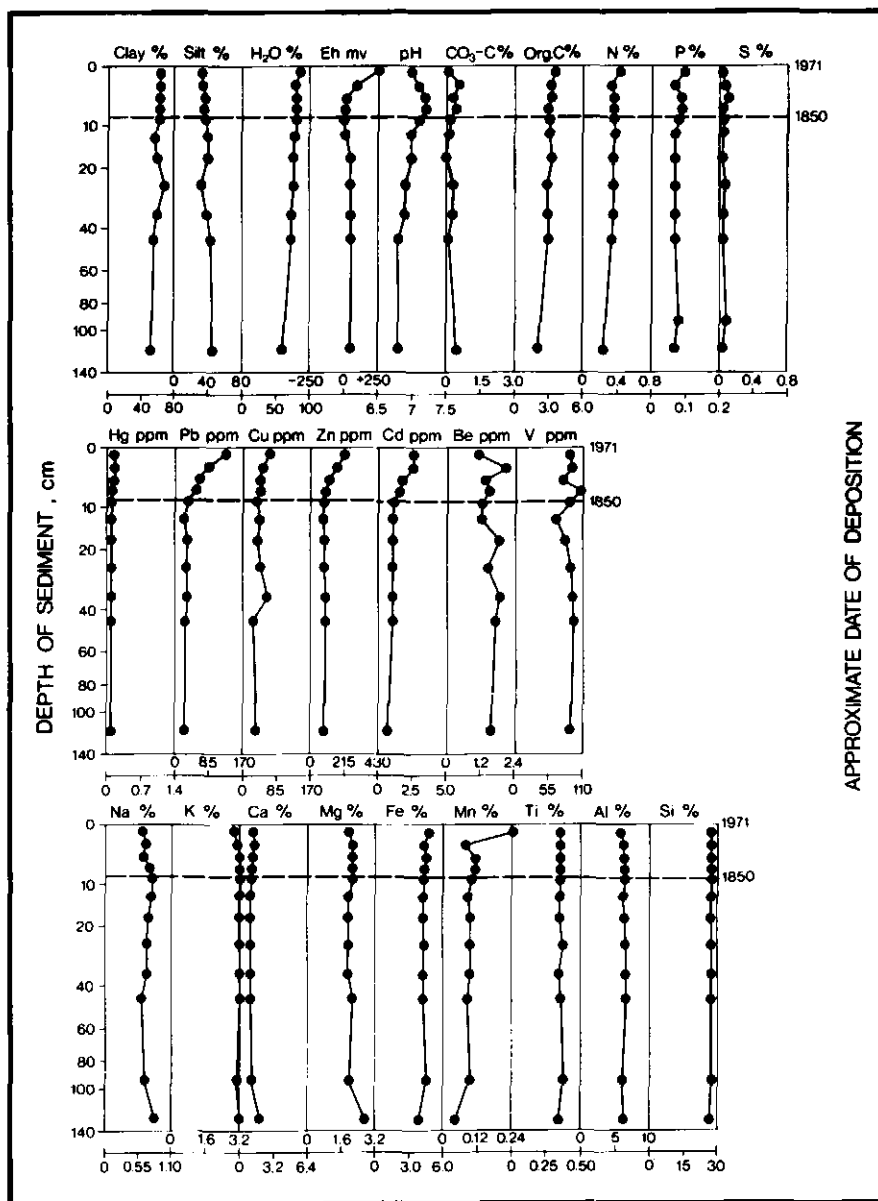


Figure 3
Concentration vs depth profiles for sediment composition at station 2, Lake Huron.

general, the mineralogy of the surface sediments is similar at each location.

Microscopic examination of the surface sediments (0-1 cm) also shows that fly ash is also present in varying amounts at each location. The fly ash is derived from local industrial sources and from the extensive shipping traffic on the lakes. Although fly ash concentrations were not determined quantitatively, a qualitative examination indicates that concentrations are greatest in Lakes Erie and Ontario, which are closer to the major industrial centres. Examination of sections of core at the *Ambrosia* horizon (ca. 120 years BP) in Ontario and Erie cores show only trace amounts of fly ash presumably due to the early shipping traffic in the lakes. These latter findings require further examination.

Chemical Composition and Enrichment of the Sediment

Although the physical characteristics of the sediment in the three lakes are generally similar, the chemical composition of the cores is variable from lake to lake (Figs. 3 to 8). A number of patterns emerge on examination of the chemical profiles. These patterns are most obvious in the Lake Ontario profiles, where concentration differences are more extreme (Fig. 8). A number of elements show marked enrichments at the sediment-water interface relative to their concentrations at the *Ambrosia* horizon. Hg, Pb, Zn, organic-C, N, Mn and P show this trend most noticeably. Si, Al, K, Na, Mg and Fe concentrations are relatively constant except near the sediment-water interface where variations compensate for the increases and/or decreases in organic matter and carbonates.

Sediment enrichment factors (SEF) have been calculated for each element in the 14 cores (Kemp *et al.*, 1976) and the values are shown in Table II. For comparative purposes the elements are arranged into six separate groupings, each having similar SEF trends. The groupings are designated: conservative (Si, K, Ti, Na and Mg); enriched (Hg, Pb, Zn, Cd and Cu); nutrient (organic-C, N and P); carbonate ($\text{CO}_3\text{-C}$, Ca); mobile (Fe, Mn and S); and miscellaneous (Be and V); as previously described by Kemp *et al.* (1976).

The core data, consisting of 31 variables measured on 156 samples, was split into the following seven groups:

- All samples
- Each lake separately
- Recent samples, early-colonial samples and pre-colonial samples for all the lakes.

Mean, standard deviation and correlation coefficient matrices were computed for each group, and the most significant correlations are discussed. *Conservative elements.* As defined previously, (Kemp *et al.*, 1976) Si, Al, K, Na and Mg have been assigned to this grouping of elements. Their zero SEF values indicate that the concentration of these elements in the sediments has

remained essentially constant. In the case of Na, Mg and possibly Ti some positive SEF values can be seen, particularly in Lake Ontario (Table II). This implies that these elements are not wholly conservative in nature and have been enriched in Lake Ontario to some extent. However, in general terms and from the statistical analysis discussed subsequently, these elements fit the requirements for inclusion in the Conservative element grouping. With the exception of carbon, iron and calcium, these elements are the most abundant in the sediment materials and

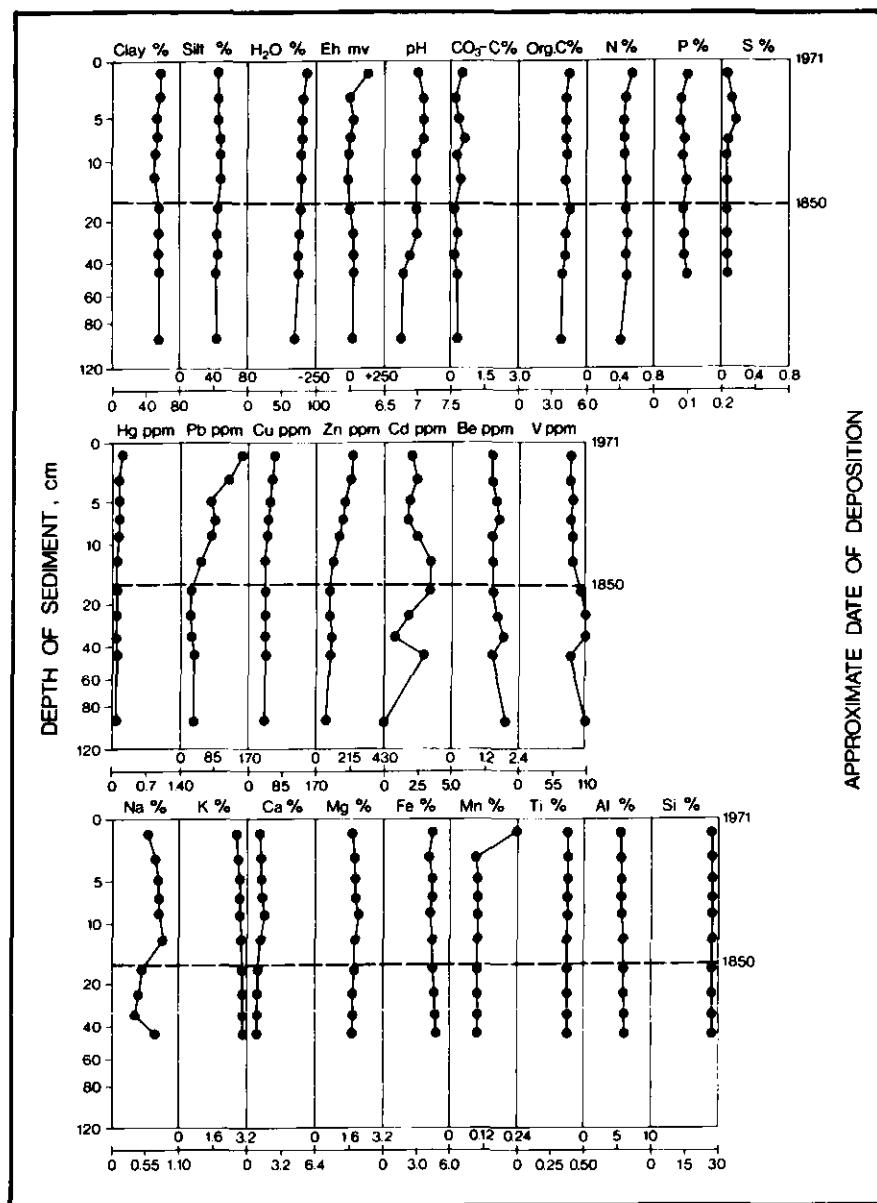


Figure 4
Concentration vs depth profiles for sediment composition at station 3, Lake Huron.

Table II
Sediment enrichment factors (SEF) for the elements at the 14 coring stations. Values between -0.2 and +0.2 are designated as zero in the table.

Element	Huron			Erie						Ontario				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Conservative Elements														
Si	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ti	0	0	0	0	0	0	0	0	0	0	0.3	0.3	0.3	0
Na	0	0	0.7	0	0	0	-0.3	0	0	0	3.0	0.7	0	0.5
Mg	0	0	0	0	0	0	0	0	0	0	0	0	0.4	0.3
Enriched Elements														
Hg	0	0.9	2.3	22.8	4.3	13.2	9.7	11.4	7.3	6.7	6.4	131.5	64.8	13.1
Pb	1.1	3.1	6.2	3.2	0.9	3.4	2.6	6.7	3.7	6.7	8.4	7.3	8.7	14.0
Zn	0.5	1.7	3.4	2.6	0.8	1.4	1.4	3.2	2.2	3.1	4.5	6.2	6.2	4.5
Cd	0	1.9	0.4	1.4	1.9	4.0	0.8	4.6	2.7	1.1	3.6	8.3	6.8	11.3
Cu	0.4	0.8	1.9	1.4	0.7	1.3	1.1	1.2	0.8	2.2	1.7	1.7	2.1	1.9
Nutrient Elements														
Org-C	0.4	0.3	0	0.8	0.5	1.1	1.3	2.8	1.7	1.0	2.5	2.3	2.7	2.0
N	0.5	0.3	0.3	1.3	1.1	1.2	2.1	3.0	2.0	0.6	2.4	2.8	3.1	2.3
P	0.8	0.4	0.4	0.4	0	0.5	0.3	0.7	0.8	0.7	1.4	2.2	0.8	1.8
Carbonate Elements														
CO ₃ -C	0	0.3	0.8	-0.5	0	-0.4	-0.4	58.0	0	1.7	4.7	18.7	14.4	55.7
Ca	0	0.5	0.4	0	0	-0.3	-0.4	4.3	-0.3	1.2	10.8	10.7	13.3	7.9
Mobile Elements														
Fe	0	0	0	0	0.3	0	0.3	0.3	0	0	0	0	0.3	0
Mn	2.3	2.5	1.8	0.4	0	0.4	0.4	2.7	1.1	0.4	4.5	4.2	9.3	1.0
S	-0.6	0	0	0.3	0.7	0.3	0	8.2	1.0	0.6	0.5	1.7	0.8	2.3
Miscellaneous Elements														
Be	0.3	0	0	0.4	0.5	1.0	0.5	0.6	0.3	0	0	0	0	0
V	0.6	0	0	0	1.1	1.5	0.7	0.3	0.7	0.3	0	0	0.5	0.5

reflect the major mineralogical species derived from terrigenous sources.

A linear correlation matrix, based on all samples, for the conservative elements and including silt and clay size fractions is given in Table III. It can be seen that Al shows strong positive relationships to K and clay and a lesser positive relationship to Ti. This is in agreement with the earlier observation that Al is indicative of the clay mineral content with the relationship of Al to K confirming the dominance of illite as determined by X-ray diffraction (Lewis, 1966; Thomas *et al.*, 1972, 1973). The relationship of Al to Ti suggests that titanium is clay-lattice-bound, probably in illite as discussed by Dolcater *et al.* (1970).

Both Si and Na show a poor relationship with the other Conservative elements and no positive interpretation can be made with respect to these elements. Mg shows a good positive

Table III
Correlation coefficient matrix for all 156 samples.

	Al	K	Ti	Na	Mg	Silt-Size Fraction	Clay-Size Fraction
Si	.043	-.083	-.198	.022	.154	.281	-.419
Al		.704	.403	-.113	-.659	-.494	.626
K			.152	-.103	.335	.421	.586
Ti				.183	.022	-.104	.243
Na					-.057	.141	.202
Mg						.413	.423

relationship with silt and a negative relationship with clay (Table III). On the basis of the SEF values (Table II) it appears that Mg is behaving as a Conservative element and is hence included in this grouping. However, the relationship of Mg to silt, suggests that Mg represents a detrital dolomite contribution and is discussed subsequently under the section on Carbonate elements.

Enriched elements. These elements (Hg, Pb, etc.) form the smallest group in the sediment accounting for less than 0.1 per cent of the sediment materials. However, they are a most significant group as most of the metals are toxic in high concentrations and it is important to understand their geochemical cycles in the surface sediments (Wood, 1974). The Enriched elements are characterized by small concentrations

below the *Ambrosia* horizon and generally much higher concentrations above the horizon (Figs. 3 to 8).

Enrichment of a chemical element at the interface may be due to two possible factors: 1) Anthropogenic loading of the sediments in recent years, 2) Diagenesis and/or upward migration of chemical species in the pore waters (Thomas, 1972; Kemp *et al.*, 1972). As the Hg profiles in these lakes (Kemp *et al.*, 1974) and the trace element profiles in Lake Erie (Walters *et al.*, 1974), the enrichments are believed to be mainly due to the first factor. Similar conclusions have been drawn recently for the increases in Hg, Pb, Zn, Cu and Cr in Lake Michigan (Leland *et al.*, 1973), Pb, Zn, Cu, Cd, Ni and Cr in the Wisconsin lakes (Iskandar and Keeney, 1974), Cd, Pb, Zn and Cu in the Baltic Sea (Erlenkeuser *et al.*, 1974) and for Pb, Cr, Cd, Zn, Cu, Ag, V and Mo in the southern California coastal sediments (Bruland *et al.*, 1974).

The increase in elemental concentrations appears to commence at the *Ambrosia* horizon at most of the locations, lending primary support to this argument. For example, it can be seen that the Pb concentration increases at 8, 17, 25, 27, 75 and 19 cm at stations 2, 3, 4, 8, 9 and 13 respectively (Figs. 3 to 8). With the exception of station 4, the rises coincide with the *Ambrosia* horizon. As the physical characteristics are generally similar at each station, the observed Pb enrichment is unlikely to have resulted from upward migration of the element. Further support is given by the steady increase in Hg and Pb SEF values from the north to the south in Lake Huron (stations 1 to 3), together with the larger Hg and Pb SEF values found in Lakes Ontario and Erie (Table II).

Diagenetic-mobilization mechanisms have been proposed by a number of authors to explain exponential elemental concentration curves such as are observed for Pb in these cores (e.g., Manheim, 1970; Berner, 1971; Lasaga and Holland, 1976). These mechanisms assume steady-state conditions, which cannot be applied at most of our locations. The accelerating sedimentation rates (Kemp *et al.*, 1974) and the exponential increase in anthropogenic loading to the lakes (Beeton, 1969) preclude steady-state conditions. Also, a close examination of the concentration curves of the

Enriched elements, shows that they are rarely exponential but that they fluctuate or even decrease near the interface (Figs. 3 to 8). This is presumably a result of the fluctuating anthropogenic inputs of materials to the sediments, bioturbation and physical mixing.

Surface enrichment of trace elements could also be related to organic matter increases in the sediment, whereby trace elements are concentrated in the organic fraction. This possibility is discussed later. It is not possible to determine the extent of trace element enrichment due to any particular

mechanism on the basis of this study. Until the cycles of the trace elements in the Great Lakes sediment are better understood, it is proposed that the enrichments of Hg, Pb, Zn, Cd and Cu are mainly a result of increasing anthropogenic inputs in recent years, although it is recognized that surface enrichment may also be modified by mixing of the uppermost layers of sediment.

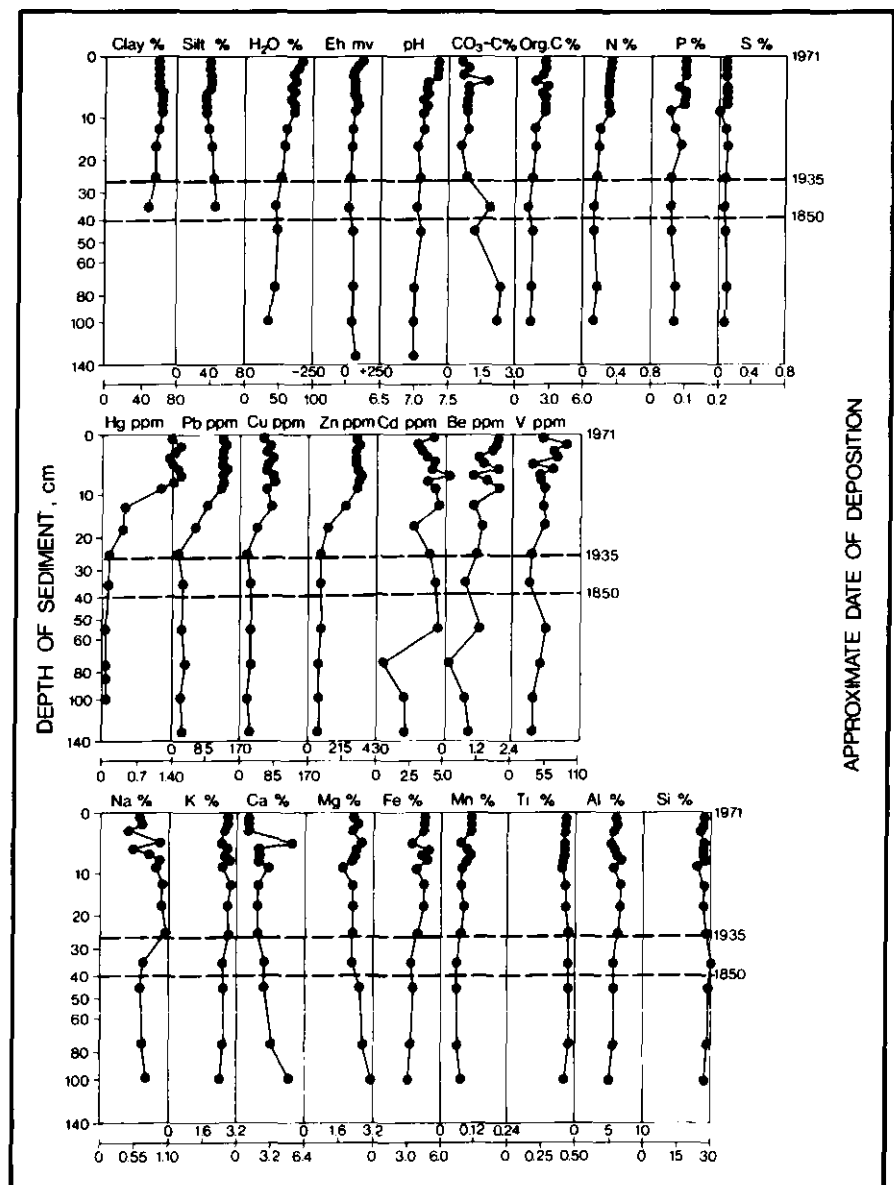


Figure 5
Concentration vs depth profiles for sediment composition at station 4, Lake Erie.

Table IV

Average concentrations of the Enriched elements in the recent and pre-colonial sediments, suspended particulate matter and bluffs (Concentrations are expressed with respect to the dry weight of sediment.)

Element	Lake Huron Sediments		Lake Erie Sediments		Lake Ontario Sediments		All rivers (28)	Niagara River (1)	Bluffs (16)
	Recent (3)	Pre-colonial (3)	Recent (6)	Pre-colonial (6)	Recent (5)	Pre-colonial (5)			
Hg (ppb)	210	150	855	78	2350	78	285	560	44
Pb (ppm)	129	39	106	28	220	29	192	110	28
Zn (ppm)	197	94	279	98	475	104	411	317	39
Cd (ppm)	2	1	4	1	5	1	3	6	1
Cu (ppm)	58	38	57	29	98	44	118	309	24

Table IV provides a summary of mean concentrations for the recent sediments (0-1 cm) and the precolonial sediments (sub-samples below the *Ambrosia* horizon) for the three lakes. The recent sediments of Lake Ontario show the highest mean concentrations for all the Enriched elements. The high Ontario values parallel the higher organic concentrations in the lake (Kemp, 1971).

Studies were initiated in 1974 on suspended particulate matter and bluff samples from the drainage basins of the lakes. Some preliminary results for Lake Ontario are shown in Table IV. Suspended particulate samples were collected near the mouths of all rivers entering the Canadian shore of Lake Ontario (Thomas, unpublished data). As the Niagara River contributes 80 per cent of the inflowing river water to the lake, these results are shown separately. Results are also shown for the mean of 16 bluff locations around the lake, where silt-size bluff material is eroding rapidly into the lake (Kemp, unpublished data).

The pre-colonial or natural background levels of Hg, Pb and Cd in Lake Ontario are similar to those found in the bluffs (Table IV), indicating that these elements are sedimented without any further alteration taking place. The concentrations of Zn and Cu however are enriched in the pre-colonial sediments relative to the bluffs indicating that these elements have been concentrated in the lake sediment by natural lacustrine processes. With the exception of Hg, the concentrations of the suspended sediment samples are all in the same range as the surface sediments. This would suggest that the present-day riverborne particulates have a similar composition to the surface sediments of Lake Ontario as has been shown previously for Lake Michigan (Leland *et al.*, 1973). In the

case of Hg, the sediment samples were collected in 1971 and the particulate samples in 1974, and it is possible that these results reflect a diminishing anthropogenic input of Hg to Lake Ontario due to recent controls curtailing Hg inputs to the Great Lakes.

Statistically, a high degree of correlation can be demonstrated between the individual elements in this grouping (Table V). These elements in turn co-vary with organic-C, listed as a Nutrient element. The relationship of the Enriched elements to the organic matter may well be indicative of complexing and/or adsorption by organic matter as suggested for southern Lake Michigan by Shimp *et al.*, (1971) or may reflect increased anthropogenic loading with time paralleled by increasing organic detritus inputs due to increased nutrient supply and associated primary productivity in the lakes.

Nutrient elements. Included under this category are organic-C, N and P. The Nutrient elements, as organic matter category are organic-C, N and P. The Nutrient elements, as organic matter and phosphorus make up the third largest group of materials in the recent sediments, accounting for up to 10 per cent of the sediment by weight. Examination of the SEF values (Table II) and the individual core profiles for these elements (Figs. 3 to 8) show surface enrichment throughout the three lakes. This enrichment has been ascribed mainly to anthropogenic loading of P with the ensuing increase in the productivity of the lakes (Kemp *et al.*, 1974).

The small SEF values for organic-C in Lake Huron reflect mainly the natural decomposition of organic matter at the sediment-water interface, as nutrient inputs have not increased significantly

(Glooschenko *et al.*, 1973). It can be seen from the profiles that organic-C increases only very slightly from the base of the core to the water interface in Lake Huron (Figs. 3 and 4). This small increase is presumably due mainly to natural diagenesis at the sediment-water interface. A comparison of the Huron profiles and SEF values with those from Lakes Ontario and Erie indicates that natural decomposition is likely to account for only a small part of the surface organic enrichments in the latter lakes.

The statistical relationships observed between the nutrient elements (organic-C, N and P), Fe, Mn, Al, K and the clay size fraction are summarized in the correlation matrix given in Table V. As described by previous authors (e.g., Stangenberg, 1949; Hutchinson and Vallentyne, 1955; Tadajewski, 1966; Kemp, 1971), organic-C and N show an almost perfect relationship. The previously reported relationship of organic-C to clay (e.g., Trask 1932; Van Straaten, 1954; Bordovski, 1965; Thomas *et al.*, 1972, 1973) is not seen. This lack of a clay, organic-C relationship is attributed to the increasing organic carbon loading to the sediment with time under conditions of increasing trophic level and, as such, is independent of a proportionately constant deposition of clay.

Table V

Correlation coefficient matrix for all 156 samples.

	Hg	Pb	Zn	Cd	Cu
Org-C	.497	.687	.614	.530	.547
Hg		.747	.781	.661	.675
Pb			.929	.805	.837
Zn				.799	.845
Cd					.740

Table VI

Correlation coefficient matrix for all 156 samples.

	N	P	Fe	Mn	Al	K	Clay-Size Fraction
Org-C	.960	.561	.311	.390	-.036	-.024	.192
N		.614	.361	.486	.040	.032	.296
P			.393	.545	.506	.043	.420
Fe				.265	.634	.721	.762
Mn					.019	-.059	.423

The relationships of P with the other elements is not entirely clear (Table VI). The high degree of correlation between Fe and P noted by many previous authors (e.g., Williams *et al.*, 1971) is not seen. Here the P appears to be partitioned with Fe, Mn, Al and clay suggesting that P uptake is occurring in the finer sediment fraction due to adsorption by the hydrated oxides of Fe, Mn and possibly Al.

Carbonate elements. The Carbonate grouping of elements, which includes Ca and CO₃-C and, as discussed previously, Mg, make up the second largest group in the sediments, accounting for up to 15 per cent of the materials. The SEF values (Table II) for these elements show firstly, that Mg remains constant with time, confirmed by the individual core profiles (Figs. 3 to 8), and secondly, that the remaining three elements show surface enrichment in Lakes Huron, Ontario and the central basin of Lake Erie with a loss in the western and eastern basins of Lake Erie. These SEF patterns are best illustrated by the core profiles for Ca and CO₃-C in the three lakes. Ca and CO₃-C concentrations are fairly uniform and low in Lake Huron and central Lake Erie (Figs. 3, 4, 6), decrease towards the surface in western and eastern Lake Erie (Figs. 5, 7) and increase to very high surface concentrations above the *Ambrosia* horizon in Lake Ontario (Fig. 8).

The carbonate element distribution in the cores is poorly understood at the present time. The very high surface concentrations of carbonates in Lake Ontario are difficult to explain and the limited evidence we have to date is contradictory. X-ray diffraction examination of the surface sediments of Lake Ontario shows a well-defined calcite peak. However, examination with an optical microscope of the sand and coarse-silt fraction of these sediments does not disclose the presence of detrital calcite even though it would be expected in these fractions. It appears that the calcite is limited to the finer size fraction - an anomalous situation that suggests that it may be present as fine-grained authigenic calcite. High concentrations of Ca and Mg in the Ontario pore waters have been attributed to dissolution of detrital

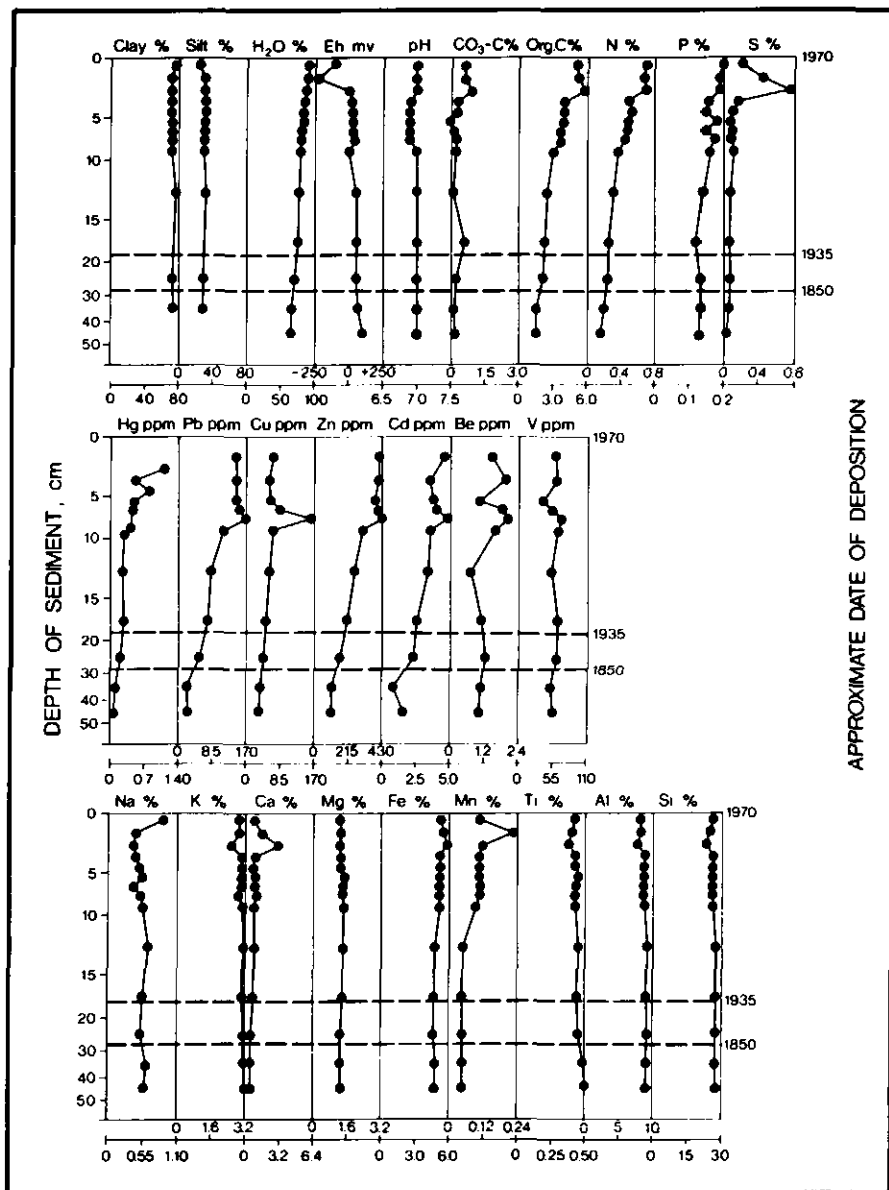


Figure 6
Concentration vs depth profiles for sediment composition at station 8, Lake Erie.

carbonates (Weiler, 1973). However, Weiler also found that the interstitial waters were saturated with respect to calcite and conditions favoured calcite precipitation. At this stage, it would appear that detrital carbonates are dissolving in Lake Ontario and that calcite is being precipitated in large quantities either in the lake or at the sediment-water interface.

The generally low surface concentrations of Ca and CO₃-C in Lakes Huron and Erie also require explanation. In Lake Huron, low surface carbonate concentrations could be due to the generally low sedimentation rates and dissolution of detrital carbonate as proposed for Lake Superior (Dell, 1973). In Lake Erie, where sedimentation rates are rapid, low surface carbonate concentrations may be due to the high organic loading to the sediments at our locations in recent years (see next section). It is possible that both detrital and precipitated carbonates are dissolved under the acidic conditions which follow *in situ* decomposition of organic matter at the sediment-water interface.

The linear correlation matrix for the Carbonate elements and the silt size fraction is given in Table VII. The coefficients indicate the presence of calcite (CO₃-C to Ca) and subsidiary dolomite (CO₃-C to Mg), both showing a moderate degree of relationship to the silt size fraction. The relationship between carbonates and silt has been previously found for the surface sediments of Lakes Ontario and Huron (Thomas *et al.*, 1972, 1973). The correlation matrices would thus suggest that calcite and dolomite are present in the sediments and are associated with the silt size fraction. The carbonate cycle in these lakes appears to be very interesting and, as is obvious from this discussion, requires much more detailed investigation; in particular, studies on carbon and oxygen isotopes

should be used to clarify the mechanisms controlling the carbonate sources, distribution, precipitation and dissolution.

Mobile elements. On the basis of the SEF values relative to the observed core profiles S, Mn and Fe have been assigned to the Mobile group of elements. The term mobile, herein, is used to designate those elements which, due to variation in the physical-chemical properties of the core, are subject to dissolution, and migration in

the interstitial waters. These elements account for five per cent of the total sediment by weight. Because of their mobility they can substantially influence the bottom waters of the lakes.

The vertical profiles of Mn in the cores can be broken down into two distinct groups: those that show a large increase at the sediment-water interface from a background level of around 0.1 per cent and those that remain uniform with depth. Upward migration of soluble Mn under reducing conditions in sediment pore waters with surface precipitation is

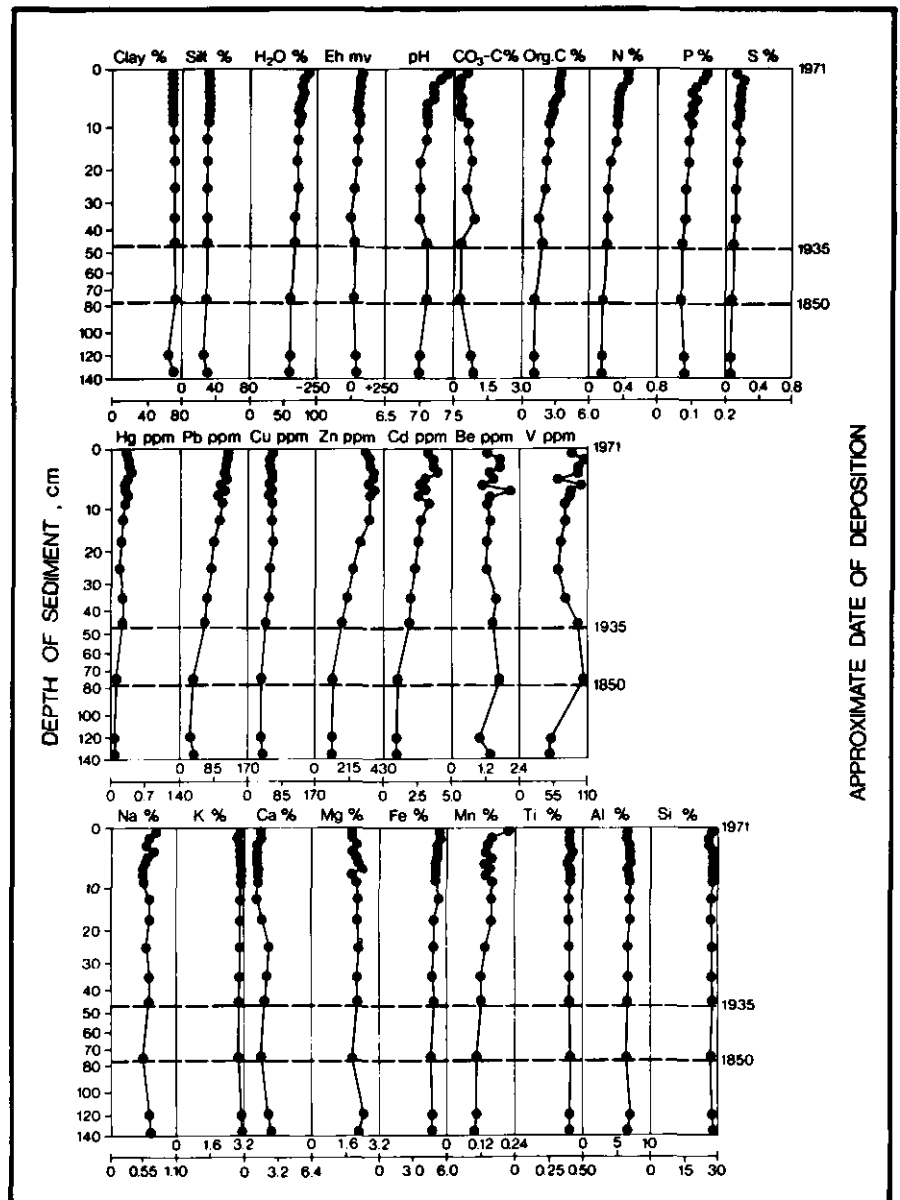


Figure 7
Concentration vs depth profiles for sediment composition at station 9, Lake Erie.

Table VII
Correlation coefficient matrix for all 156 samples.

	Ca	Mg	Silt-Size Fraction
CO ₃ -C	.807	.452	.367
Ca		.264	.249
Mg			.413

well known (e.g., Mackereth, 1966; Weiler, 1973). This condition is best illustrated by the core profiles for Lake Huron (Figs. 3, 4), eastern Lake Erie (Fig. 7) and Lake Ontario (Fig. 8). At these deep water locations, where the hypolimnion waters are well oxygenated at all times, Mn tends to be concentrated in the surface oxidized sediments. Similar profiles are also found at stations 1 in Lake Huron and 11 and 12 in Lake Ontario.

Surface enrichment of Mn is not found in western and central Lake Erie (stations 4, 5, 6 and 7) and Lake Ontario (stations 10 and 14). At these locations, the seasonal redox conditions (oxygen depletion in summer months, accompanied by negative redox potentials) are such that overall precipitation of upward migrating Mn is not occurring and the bulk of the Mn is being lost to the overlying waters. This situation is well illustrated by station 4 in western Lake Erie (Fig. 5). Anoxic conditions in the hypolimnion waters of western and central Lake Erie (Beeton, 1965) account for the loss of Mn from the sediment interface at these locations. Presumably seasonal anoxic conditions must also exist at stations 10 and 14 in Lake Ontario to yield the linear Mn profiles found at these locations. A more general account of Mn in the sediments of the Great Lakes has been presented by Sly and Thomas (1974) who noted the sensitivity of both Mn and Fe to the trophic levels of individual lakes within the system.

The studies of Burns and Ross (1972) have demonstrated the significance of the regeneration of soluble Fe from the sediments of central Lake Erie under anoxic hypolimnion conditions indicative of the mobile nature of this element. The SEF values for total Fe (Table II) and the core profiles (Figs. 3 to 8) suggest that this element may be better placed with the Conservative elements with the exception of stations 5, 7 and 8 from Lake Erie. As the levels of total Fe in the sediments average 4.3 per cent for all of the core samples, when compared to the mean of 0.15 per cent for Mn, it can be seen that only a small percentage release of the total Fe concentration is highly significant.

The upward migration and precipitation of Fe, to some extent, can be seen in the SEF values at stations 5, 7 and 8 (Table II). In these cores the Eh

values at the surface range from 0 to approximately 100 millivolts. These conditions appear to be such that upward migrating iron has been partially retained in the surface sediment. For example, at station 8 (Fig. 6) in the central basin of Lake Erie there is a decrease in the surface Mn paralleled by a minor decrease in Fe which, when normalized for Al, gives rise to an SEF value of 0.3. At station 4 (Fig. 5) in the seasonally anoxic western basin of Lake Erie, the profiles for Fe and Mn are very similar and this core is

representative of a situation in which soluble Fe had been released subsequent to Mn to the overlying bottom waters as described by Burns and Ross (1972). In other cores, for example, station 2 (Fig. 3), under oxic conditions, Mn has been precipitated in the surficial sediment. Immediately below the rise in Mn a minor increase in the Fe profile can be seen. This implies upward migration of both Fe and Mn with sequential precipitation firstly of Fe and then Mn relative to the increasing redox potential in the uppermost part of the

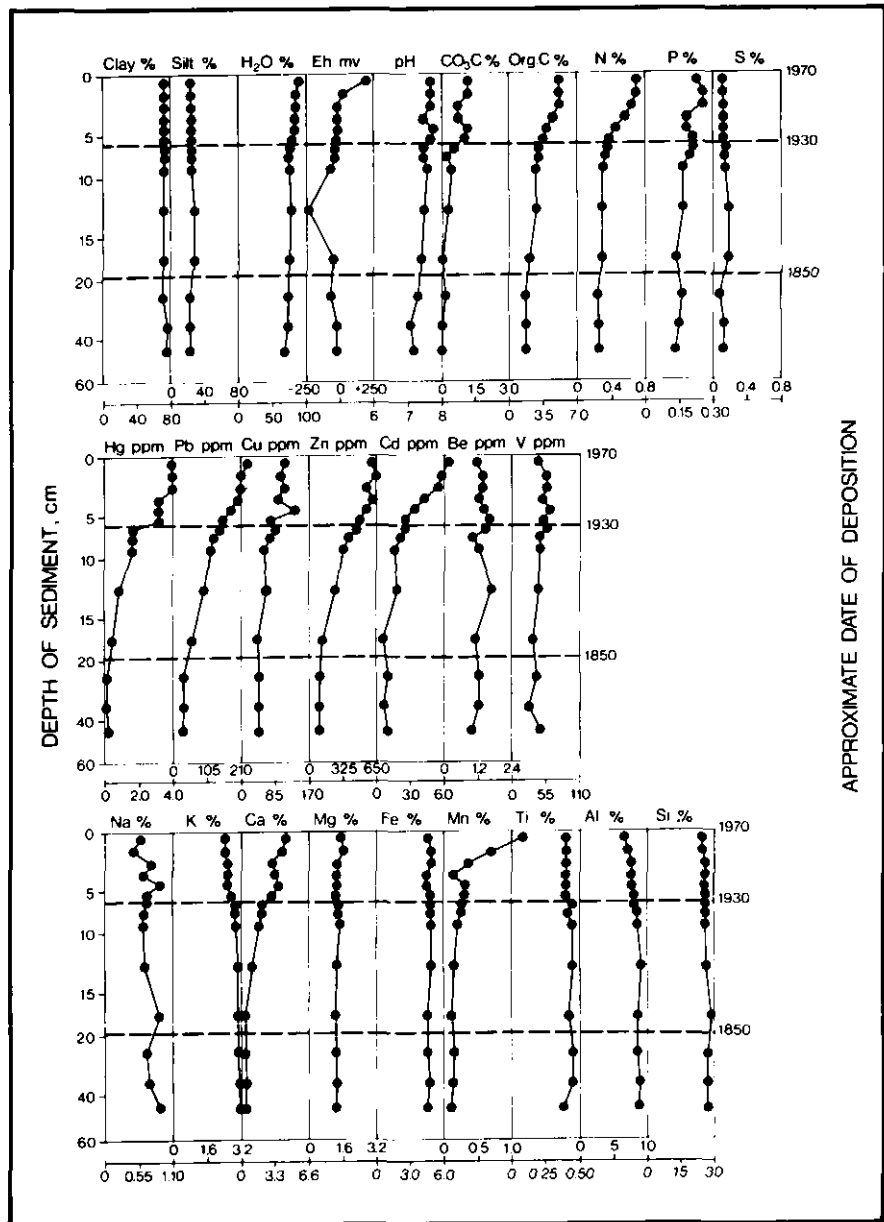


Figure 8
Concentration vs depth profiles for sediment composition at station 13, Lake Ontario.

core. More detailed studies are required, particularly in determining the forms and valence state of the Fe in order to make a more definite interpretation of the Fe mobilization.

Total S generally increases with depth relative to a decreasing redox potential in the cores (Figs. 3 to 8). Statistically, S shows a significant inverse correlation with Eh ($r=0.522$) and with organic-C ($r=0.531$). These correlations suggest that the classic relationship exists whereby decreasing redox potential induced by the bacterial oxidation of organic matter results in the reduction of Fe^{3+} and SO_4^{2-} with the formation of iron sulphides (Zobel, 1946). Reduction of SO_4^{2-} has been observed in the surface sediments of Lake Erie, after sedimentation of an algal bloom (Menon *et al.*, 1971) and SO_4^{2-} concentrations were found to decrease from the surface in a number of cores from Lake Ontario (Weiler, 1973) and Lake Erie (Nriagu, 1975). These findings, together with the colour changes mentioned previously, indicate that fresh organic matter is being decomposed at the water interface with the formation of iron sulphides in the reduced zone of sediment. A more specific account of the sulphur cycle and diagenetic changes in S near the sediment-water interface in Lake Erie has been presented recently by Nriagu (1975).

Miscellaneous elements. Be and V have been included under this category primarily due to the variability of their concentration profiles (Fig. 3 to 8). The concentration of these elements in the Great Lakes sediments does not appear to provide a clear trend in enrichment. The SEF values would indicate however that there is a small enrichment of these elements in Lakes Ontario and Erie (Table II). The enrichment of V would be in agreement with observations of V enrichment in the California coastal sediments (Bruland *et al.*, 1974).

It is possible, however, that these elements may occur as accessory elements in the clay minerals and are of detrital origin. As the enrichments are small, the elements are maintained as Miscellaneous pending a more detailed assessment of the surficial sediment geochemistry.

Natural and Anthropogenic Accumulation of Elements in the Sediments

By utilizing the SEF values, we have been able to determine the degree of enrichment of the heavy metals and nutrients. These values, however, do not fully reflect the changes that have taken place at each location as variations in sedimentation rate have not been taken into account. In order to compare each sample on an equal basis, the chemical data is combined with the sedimentation rate data previously reported (Kemp *et al.*, 1974). The sediment loading is broken down into a natural sediment input and an anthropogenic input.

The present-day sedimentation rates (Table I) were calculated assuming a constant rate above the *Castanea* horizon in Lakes Ontario and Erie and the *Ambrosia* horizon in Lake Huron. Sedimentation rates are expressed as $\text{g}/\text{m}^2/\text{yr}$ and are calculated by dividing the dry weight of sediment per square metre of column, between time horizons by the estimated time interval (Kemp *et al.*, 1974). The specific gravity of the sediment is assumed to be 2.6 for these calculations (Lewis, 1966). The natural sediment inputs have been calculated by multiplying the present-day sedimentation rate by the normalized surface (0-1 cm) elemental concentrations. This assumes that the natural elemental input has the same ratio to Al as the baseline ratio below the *Ambrosia* horizon and is therefore independent of the sedimentation. The anthropogenic input is then calculated by multiplying the difference between the total and normalized elemental concentrations at the surface by the sedimentation rate. For these calculations, it is assumed that the high surface concentrations of the enriched and nutrient elements are solely due to anthropogenic inputs. Anthropogenic and natural inputs of the Enriched and Nutrient elements are shown in Table VIII. The Great Lakes' results are compared with those found in the California coastal basin sediments (Bruland *et al.*, 1974) and the average annual atmospheric precipitation over Lake Ontario for 1970-71 (Shiomi and Kuntz, 1973). Although there is probably a large natural and anthropogenic contribution of Fe, Mn and S to the lakes, the Mobile elements are not included in the calculations as their surface

concentrations mainly represent diagenetic-mobilization changes, as has been discussed previously.

The breakdown of the heavy metal and nutrient loading into natural and anthropogenic inputs demonstrates the large differences between the 14 sample locations and the three lakes (Table VIII). It can be seen that the anthropogenic loading of heavy metals and nutrients is low in Lake Huron, very high in Lake Erie and intermediate in Lake Ontario, paralleling the populations of the respective drainage basins. As with the SEF values, discussed previously, the Enriched and Nutrient elements are accumulating at much higher anthropogenic levels in Lakes Erie and Ontario than for Lake Huron. Fluxes of Hg, Pb, Zn, Cd and Cu show an increase from station 1 in Lake Huron, which is far removed from urban influences, to station 3 in the southern portion of the lake, which is under the influence of inputs from Saginaw Bay. Organic carbon shows a similar trend at the 3 locations, correlating with the lakewide chlorophyll determinations, where primary productivity was shown to be greatest in southern Lake Huron (Glooschenko *et al.*, 1973). A comparison of station 3 in Lake Huron with stations 10-13 in Lake Ontario, where sedimentation rates are similar, demonstrates the much greater anthropogenic input to the Ontario sediments.

The natural sediment loadings parallel the varying sedimentation rates at each of the 14 sample locations. It can be seen that natural inputs of trace nutrient elements at station 3 in Lake Huron are similar to those of the main basin of Lake Ontario (Table VIII). The natural loading of Pb, Zn, Cd and Cu in southern Lake Huron and Lake Ontario is similar to that found in the California coastal basin sediments, where sedimentation rates are of the same order of magnitude (Table VIII). However, the anthropogenic inputs of these heavy metals are far greater in the Lake Ontario sediments. Anthropogenic inputs of 8.0, 2.2, 1.2 and $0.058 \mu\text{g}/\text{cm}^2/\text{yr}$, for Zn, Pb, Cu and Cd respectively, have recently been estimated for Baltic Sea sediments (Erlenkeuser *et al.*, 1974). The latter values are intermediate between the California sediments and those from Lake Ontario. The Lake Erie anthropogenic inputs are much larger

Table VIII

Present-day natural and anthropogenic inputs of the Enriched and Nutrient elements at the 14 sample locations.

Lake	Huron			Erie					Ontario					California Coastal Basins (Bruland <i>et al.</i> , 1974)	Lake Ontario Rainfall (Shiomi and Kuntz, 1973)		
	1	2	3	4	5	6	7	8	9	10	11	12	13			14	
Elements	Input	(Inputs in $\mu\text{g cm}^{-2}\text{yr}^{-1}$)															
Enriched Elements																	
Hg	A	0	0.001 [†]	0.005	0.49	0.28	0.056	0.068	0.11	0.147	0.022	0.144	0.111	0.142	0.122	-	-
	N	0.004	0.001	0.002	0.02	0.07	0.004	0.007	0.01	0.02	0.003	0.002	0.001	0.002	0.009	-	-
Pb	A	0.8	1.5	4.2	34.4	14.3	5.4	6.8	15.1	44.3	6.9	8.1	7.4	7.4	30.7	1.6	1.4
	N	0.8	0.5	0.7	10.7	16.4	1.6	2.7	2.3	12.1	1.0	1.0	1.0	0.8	2.2	0.5	-
Zn	A	0.7	2.0	5.7	81.2	30.6	10.9	12.4	38.1	113.1	10.9	16.9	20.3	22.1	39.6	2.1	5.3
	N	1.6	1.2	1.7	31.8	43.1	6.5	8.9	11.8	52.6	3.5	3.7	3.3	3.6	8.8	5.2	-
Cd	A	0	0.03	0.02	0.9	0.9	0.2	0.1	0.4	1.2	0.09	0.2	0.2	0.2	0.5	0.07	0.09
	N	0.02	0.01	0.05	0.6	0.5	0.04	0.2	0.1	0.5	0.08	0.05	0.03	0.03	0.05	0.14	-
Cu	A	0.2	0.4	1.4	13.0	6.9	2.6	2.9	4.3	12.6	3.1	2.9	2.6	2.7	6.0	1.3	0.4
	N	0.4	0.6	0.8	9.4	11.5	1.9	2.6	3.6	16.3	1.4	1.7	1.5	1.3	3.1	1.6	-
Nutrient Elements																	
Org-C	A	145	115	295	4455	2870	1025	1830	4495	10445	715	1450	1440	1415	4830	-	-
	N	410	445	1220	5710	5410	925	1375	1610	6215	745	570	620	515	2430	-	-
N	A	25	20	40	645	450	115	290	635	1515	50	175	205	195	615	-	100
	N	45	55	165	500	415	95	135	210	755	80	70	70	60	265	-	-
P	A	13	5	6	105	30	25	25	100	305	25	40	45	35	105	-	4
	N	16	11	27	250	320	50	90	140	405	30	30	25	45	55	-	-

A indicates Anthropogenic inputs, N indicates Natural inputs.

than the Lake Ontario and marine inputs. The larger anthropogenic loadings in Lakes Erie and Ontario are presumably a function of their proximity to large centres of population and the restriction of a lacustrine system, where the sediments within a limited area act as a sink for the contaminants entering the lake.

For a geochemical model of the lakes, it is necessary to have information on the sources, dispersion and sinks of the chemical elements entering the drainage basins. At the present time, information is fragmentary on the sources and dispersion pathways of the anthropogenic heavy metal and nutrient loads to the lake sediments.

The source of the sediment materials can only be inferred at the present time. As was mentioned previously, the natural sediment input is primarily derived from the till cover in the drainage basins of the lake while the anthropogenic inputs are mainly derived from urban and industrial sources. In a study of Lake Michigan, Winchester and Nifong (1971) estimated that the atmospheric contribution of Cu to the lake equalled that of all river inputs and that for Zn, the atmospheric input was eight times that of all rivers. The source of these contaminants was mainly from the Chicago urban and industrial

complex. Bruland *et al.*, (1974) also concluded that atmospheric sources could account for the anthropogenic loading of Pb, Zn and Cu to the California coastal sediments. Similarly, atmospheric sources, derived from fossil fuel consumption, were considered to be the major source of heavy metal pollution in the Baltic Sea sediments (Erlenkeuser *et al.*, 1974). The large cities of Detroit, Cleveland, Buffalo and Toronto can provide similar atmospheric sources for Lakes Erie and Ontario.

Primary productivity is low at the two northern locations in Lake Huron (station 1 and 2). These locations are a considerable distance from industrial and urban sources and the anthropogenic inputs must primarily originate from atmospheric loading. Rainfall data are not available for Lake Huron. However, utilizing the average rainfall data for Lake Ontario it can be seen that the anthropogenic sediment inputs of Pb, Zn, Cd, Cu, N and P for stations 1 and 2 are in the same range as the Ontario atmospheric precipitation data (Table VIII). Shiomi and Kuntz (1973) found that atmospheric precipitation values were high at their sample location near Kingston, which is far removed from the major industrial and urban areas of the Lake Ontario

basin. It is thus assumed that the Ontario precipitation values would be probably similar to those for northern Lake Huron. It would then appear that the anthropogenic inputs of Pb, Zn, Cd, Cu, N and P in northern Lake Huron could correspond to a baseline sediment loading that could be expected in the Great Lakes region originating from atmospheric sources. Superimposed on these baseline values one would expect larger atmospheric inputs closer to industrial or urban sources. It is also noted that the Ontario precipitation data are very similar to the atmospheric fluxes estimated for the California coastal sediments (Bruland *et al.*, 1974).

A comparison of the Lake Ontario rainfall data with the anthropogenic inputs to southern Lake Huron, Lake Erie and Lake Ontario, indicates that the baseline atmospheric inputs are likely to contribute only a minor portion of the heavy metal loading to Lake Erie, but a more substantial portion to the southern Lake Huron and Lake Ontario sediments. The difference between the baseline atmospheric inputs and the total anthropogenic inputs, originates from river inputs and local atmospheric sources. The presence of fly ash in the sediments also indicates that atmospheric inputs of dry particulate matter could contribute substantially to

the heavy metal loading. At this stage it is not possible to pin-point the sources of the anthropogenic heavy metals and nutrients to these lakes more precisely. The present evidence suggests that atmospheric inputs are an important source of trace elements to the Great Lakes. Much more detailed studies will be required to determine the individual sources of the metals.

The dispersion pathways of the anthropogenic materials in these lakes are also poorly understood. Substances that enter the lake are subjected to physical transportation processes and may be dispersed over wide areas before being transferred out of the water mass into the sediments. Mercury distributions in these lakes have shown that the Hg in the sediments is related to general surface water circulation and that it is mainly deposited at the downstream locations in each lake (Thomas, 1974).

Examination of the data for Lakes Ontario and Erie shows that the largest anthropogenic inputs are at stations 4, 5 and 9 in Lake Erie and 14 in Lake Ontario (Table VIII). Stations 9 and 14 are both a considerable distance from the major source areas of Detroit and Cleveland for Lake Erie and Buffalo and Toronto for Lake Ontario. However, proximity to source does not apparently influence the anthropogenic loading to these offshore locations. The uniformity of the anthropogenic inputs in the deep offshore locations of Lake Ontario (stations 11, 12 and 13) show no apparent relationship to source.

Water quality and primary productivity data for the two lakes show that the highest concentrations of nutrients and heavy metals and the highest primary productivity occurs in the western basin of Lake Erie, along the south shore of the central basin of Lake Erie and in the western end of Lake Ontario (Weiler and Chawla, 1968; Chau *et al.*, 1970; Gachter *et al.*, 1974; Glooschenko *et al.*, 1974). The highest values are usually in the nearshore zones. These zones are all closest to the major population areas. Surface sediment data show that Organic-C, N and Hg have their highest concentrations in association with the fine-grained offshore sediments of Lake Ontario and Erie (Kemp, 1971 and Thomas, 1974). This study indicates that the anthropogenic inputs to the sediments are greatest where the

sedimentation rate is highest and are not dependent on proximity to the source areas. The high sedimentation rates in the eastern basin of Lake Erie and the Kingston basin of Lake Ontario are presumably a function of their easterly locations. The prevailing westerly winds and the west to east flow of the lake systems towards the Atlantic Ocean enables the most easterly basins to act as sinks for the fine-grained suspended material.

Chau *et al.*, (1970) found a correlation between trace element concentrations and chlorophyll *a* in Lake Ontario waters suggesting that the biological food chain is concentrating part of the heavy metal input to the lake. It is not certain from this study to what extent the anthropogenic heavy metal inputs are associated with the autochthonous organic matter, fine-grained clay particles or with fly ash particles. The fly ash in the sediments, the demonstration of atmospheric loading to the lakes and the downstream location of heavy metal inputs indicates that the dispersion pathways are complex and require careful study.

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