

Sediment Record of Biogeochemical Responses to Anthropogenic Perturbations of Nutrient Cycles in Lake Ontario¹

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Two sediment cores collected from the Rochester basin of Lake Ontario were dated with ²¹⁰Pb and stratigraphic correlation and analyzed to determine whether nutrient accumulation with time was consistent with previous computer-simulated total phosphorus (TP) loadings. Relative increases in TP and nonapatite inorganic phosphorus (NAIP) accumulation were less than the fivefold increase in TP loading from 1800 to 1950 predicted independently from Chapra's simulation model. In addition, increases in TP accumulation occurred mainly after 1940 and the proportion of NAIP relative to TP increased in one core and decreased in the other. Of the nutrients studied, only increases in organic carbon (OC) paralleled the increases in modelled TP loadings. The relative increase in inorganic carbon (IC) was greatest, with accumulation increasing an order of magnitude after 1940 in one core. This large increase in IC, amounting to 20% calcite in recent sediments, was attributed to biologically induced calcite precipitation, a secondary consequence of increased planktonic photosynthetic removal of carbon dioxide that resulted from accelerated eutrophication after 1940 when modelled TP concentrations increased rapidly. Biogenic silica (BSi) accumulation, an indicator of increased diatom production, peaked between 1850 and 1870 when increases in TP and NAIP fluxes were minimal. Results provide evidence that historic biogeochemical responses inferred from OC, IC, and BSi accumulation in the sediment record provide stronger signals of phosphorus enrichment effects than can be inferred directly from changes in accumulation of different forms of phosphorus in the sediment record.

Deux carottes de sédiments prélevées dans le bassin Rochester du lac Ontario ont été datées au ²¹⁰Pb et par corrélation stratigraphique et analysées afin de déterminer si l'accumulation de matières nutritives en fonction du temps correspondait aux charges de phosphore total (PT) déjà déterminées par simulation informatique. Les augmentations relatives de PT et l'accumulation de phosphore inorganique à l'exclusion de l'apatite (PIEA) étaient inférieures à l'augmentation par un facteur de 5 de la charge de PT prévue de façon indépendante par le modèle de simulation de Chapra pour la période allant de 1800 à 1950. De plus, l'accroissement du taux d'accumulation de PT était surtout noté après 1940 et la proportion de PIEA par rapport au PT augmentait dans l'une des carottes mais diminuait dans l'autre. Des matières nutritives étudiées, seul l'accroissement du carbone organique (CO) présentait un parallèle avec l'accroissement des charges de PT du modèle. L'accroissement relatif du carbone inorganique (CI) était le plus important, son taux d'accumulation augmentant d'un ordre de grandeur après 1940 dans l'une des carottes. Cette importante augmentation du CI, qui représentait jusqu'à 20 % de calcite dans les sédiments récents, a été attribuée à une précipitation de calcite de cause biologique, une conséquence secondaire d'une plus grande disparition du dioxyde de carbone par photosynthèse planctonique qui résultait d'une eutrophisation accélérée des eaux après 1940, moment où les concentrations de PT du modèle augmentaient rapidement. L'accumulation de silice biogène (SiB), qui est un indicateur d'une plus grande production de diatomées, a atteint son maximum entre 1850 et 1870, lorsque les accroissements des flux de PT et de PIEA étaient les moins importants. Les résultats obtenus montrent que les réponses biogéochimiques du passé déduites à partir de l'accumulation de CO, de CI et de SiB dans les sédiments sont de meilleurs indicateurs des effets de l'enrichissement en phosphore que ceux qui peuvent être directement déduits à partir des modifications de l'accumulation des diverses formes de phosphore dans les sédiments.

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Historic total phosphorus (TP) concentrations and loads (from 1800 to 1975) are known only from computer simulations (Chapra 1977). Simulations show bimodal increases in TP amounting to sixfold or sevenfold in Lake Erie, fivefold in Lake Ontario, but only about 75% in Lake Huron. The first inflection in loading is associated with forest clearance and settlement by Europeans in the early 1800s. The second increase began in the 1940s in association with urban sprawl and introduction of phosphate detergents. Management programs instituted in the 1970s to improve sewage treatment and reduce phosphorus inputs reversed a 100-yr trend of increasing TP loads and initiated a period of decreasing TP concentration in Lake Ontario (Kwiatkowski 1982; Dobson 1984).

Historic water quality data are lacking for most of the period of interest; however, the sediment record should reflect historic changes in phosphorus loading. Indeed, based on analysis of one core per lake, Kemp et al. (1972) found postsettlement TP increases in concentration of about 60 or 70% for Lake Huron. However, they found only twofold increases for Lake Erie and Lake Ontario. Analysis of Lake Erie cores (Williams et al. 1976) showed greater postsettlement increases in TP as well as increases in organic phosphorus and nonapatite inorganic phosphorus (NAIP) but increases were still smaller than might be expected from Chapra's simulations.

Only the record of organic carbon (OC) in the sediments appears to correspond closely to the historic TP loads reported by Chapra (1977). Although the temporal pattern of OC increase was similar to that for TP loads, the increase in OC concentration was no more than threefold in Lake Erie or Lake Ontario (Kemp et al. 1972) or about half that expected based on the assumption of a constant stoichiometric relationship between computer-simulated TP loads and OC accumulation in the sediments.

Other sedimentary elements that might vary in response to changing TP load are inorganic carbon (IC) and biogenic silica (BSi). Photosynthetically induced precipitation of calcite which increases with nutrient enrichment (McKenzie 1985) has been reported during summer stratification (Strong and Eadie 1978). An increase in calcium and calcite concentrations in sediments was attributed in part to eutrophication (Mudroch 1983). Pre-

vious studies of Lake Erie and Lake Ontario including the Bay of Quinte indicate that increases in BSi concentration occurred early in the sediment record (Schelske et al. 1983, 1985, 1986a), or soon after European settlement. However, the record of BSi accumulation in cores cannot be used to assess historic changes in TP loads. Increased diatom production can deplete soluble silica reserves in the water mass which in turn uncouples diatom production and BSi sedimentation from phosphorus enrichment (Schelske et al. 1983).

We argue here that historic biological effects of phosphorus enrichment in the water column, manifested through increased primary productivity, have affected the biogeochemistry of carbon and silica and hypothesize that the sediment record of IC, OC, and BSi provides insight about historical water chemistry changes not available from other data. Our results show that biogeochemistry of silica and carbon in the Lake Ontario system changed markedly several times since the mid-1800s and that the record of these changes can be resolved in the sediment stratigraphy even though such marked changes would not be predicted from the relatively small changes seen in phosphorus accumulation in the sediment.

Methods

Two box cores and one gravity core (7.5-cm diameter, benthos) were obtained in 1981 from the Rochester basin of Lake Ontario at Stations E30 and G32 at depths of 223 and 158 m, respectively (Fig. 1). Subcores (7.5-cm diameter) obtained from the box corer at both stations were dated with ^{210}Pb . The box core collected at G32 could not be used for early historical comparisons because the sedimentation rate was higher than at E30 and the ^{210}Pb date for the bottom interval of this 40-cm subcore was approximately 1820. Therefore, gravity core G32 (G32-BEN-81) and box core E30 (E30-RNB-81) were the primary cores analyzed for BSi, OC, IC, and different forms of phosphorus.

Cores were extruded and sectioned onboard ship. E30 and G32 box cores were sectioned at 1-cm intervals to 20 cm and at 2-cm intervals to 40 cm. G32-BEN was also sectioned at 1-cm intervals to 20 cm, but at 2-cm intervals to 50 cm and then

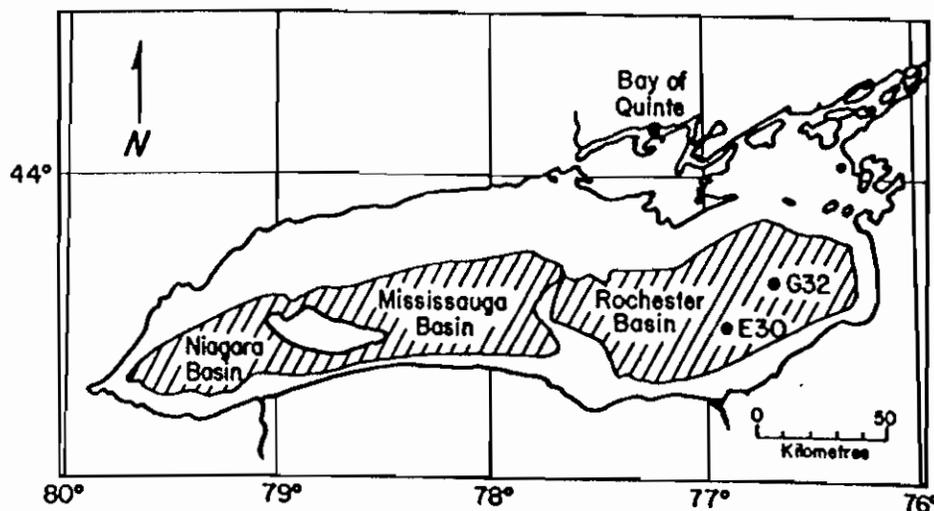


FIG. 1. Depositional basins and station locations in the Rochester basin, Lake Ontario.

at 5-cm intervals to 150 cm. Sections were frozen, weighed, freeze-dried, and weighed again to obtain dry weights and porosities.

Sedimentation rates for E30 and G32 were determined by a combination of ^{210}Pb dating and stratigraphic correlation.

The activity of ^{210}Pb was determined in box cores E30 and G32 by a modified version of a method described by Flynn (1968). Portions of freeze-dried sediment from each interval were spiked with a standard solution of ^{209}Po ($t_{1/2} = 103$ yr) and extracted for 96 h at 85°C in 10% HCl (v/v) with periodic additions of 30% hydrogen peroxide to oxidize organic matter. For comparison, additional subsamples of material from each section of core G32 were also extracted for 96 h in hot aqua regia. In the aqua regia extraction, the mixture was evaporated to dryness to remove residual nitric acid (which interferes with spontaneous plating) and then reconstituted in 10% HCl (v/v). The activity of the standard ^{209}Po solution (122.2 ± 1.2 dpm·mL⁻¹ as of September 17, 1982) was determined by inter-comparison with a ^{209}Po reference supplied by the National Bureau of Standards. Each extract was filtered through a 0.45- μm membrane filter and adjusted to a volume of 50 mL with 10% HCl (v/v) to which was added 1.0 g of hydroxylamine hydrochloride to remove the interference of iron with polonium plating. Extracts were adjusted to a final pH of 1.5 ± 0.1 with small additions of concentrated ammonium hydroxide. Polonium isotopes were plated from the extracted solutions for 24 h at 85°C onto polished copper disks backed on one side with Mylar tape.

Activities of ^{209}Po and ^{210}Po were determined by conventional alpha spectroscopy with surface barrier detectors and corrected for radioactive decay of the isotopes, particularly ^{210}Po ($t_{1/2} = 138.4$ d), between the time of plating and counting of the disk. Uncertainties in the activities of ^{210}Po are under 10%. No significant differences were found between the 10% HCl and aqua regia extractions.

The activity of ^{210}Pb should be indistinguishable from that of ^{210}Po because secular equilibrium prevails in most core sections initially and, in addition, several half lives elapsed between collection and extraction of sediment samples.

Average mass sedimentation rates were determined by stratigraphic correlation of the postsettlement BSi peak. The BSi peak was assumed to occur at 1850, or at the date expected for the *Ambrosia* horizon (Kemp and Harper 1976). Because this major peak in BSi concentration was not sharply defined by one sampling interval, the average cumulative dry weight of the two sampling intervals with the largest BSi concentration was used to estimate the average mass sedimentation rate since 1850. The BSi peak was also used to model mass sedimentation rate and nutrient flux in core G32 which was not dated with ^{210}Pb . For this purpose, the peak was set at 1865 which was the date obtained for E30 by ^{210}Pb dating.

Samples for BSi were leached with 1.0% Na_2CO_3 at 85°C and analyzed using previously described procedures (Schelske et al. 1985) including a correction for silicate mineral dissolution (DeMaster 1981).

TP was determined after samples (20–40 mg) were digested in a sulfuric acid/potassium sulfate solution (200 mL of 6 N H_2SO_4 , 65 g of K_2SO_4 , and 25 mL of 8% HgO diluted to 1000 mL). Two millilitres of this solution, the sediment sample, and 20 mL of double-distilled water were mixed in 50-mL glass digestion tubes, evaporated at 150–200°C for about 1 h, and then digested at 360°C for 22 min. Samples were cooled for approximately 3 min and mixed with 20 mL of distilled water.

A portion of each sample was transferred to a 7-mL sample tube, centrifuged, and then analyzed for soluble reactive phosphorus. Extracted phosphorus or NAIP was determined by extracting 0.7–2.0 mg of sample with 10 mL of 0.1 N NaOH in 20-mL plastic vials. The loaded vials were placed on a shaker table and mixed (175 rpm) for approximately 20 h at room temperature, centrifuged, and then analyzed for soluble reactive phosphorus. Soluble reactive phosphorus for both analyses was measured with a Technicon AutoAnalyzer II system (J. M. Malczyk, Great Lakes Environmental Research Laboratory, NOAA).

OC and IC were determined by dry combustion on a Leco model IR 12 carbon determinator. The method uses cupric oxide and an oxygen atmosphere for combustion and infrared detection of the carbon dioxide produced. Total carbon was determined on aliquots of ground dry sediment and OC was determined on separate aliquots that had been treated with concentrated sulfuric acid to remove carbonates by volatilization. IC was determined by difference between results from the two analyses. The system was standardized daily using Lake Ontario sediment of known carbon content. The precision of replicate analyses routinely had a standard error of 3.0%.

All data were converted to units of milligrams per gram of dry sediment or to millimoles per gram of sediment for calculations of atomic ratios. The cumulative inventory of nutrients with core depth was calculated by multiplying the nutrient concentration times the dry sediment weight expressed as grams per square centimetre in each sediment interval and summing the results over the depth of the core.

Results

Mass Sedimentation Rate

Results of models used to interpret ^{210}Pb profiles (Fig. 2) and to obtain age–depth relationships (Fig. 3) and mass sedimentation rates (Fig. 4) are presented in the Discussion along with the assumptions and rationale used to develop the models.

Estimates of average mass sedimentation rate obtained from BSi correlation agreed closely with rates obtained from ^{210}Pb dating and the *Ambrosia* pollen horizon (Table 1). Differences in rates for the two cores from G32 obtained from correlation of the postsettlement BSi peak probably reflect real differences because station location was not fixed accurately for the gravity core (i.e. vessel drifted between sites for box and benthos coring) and point to the need to obtain independent estimates of mass sedimentation rate for every core.

Nutrient Concentration

Both cores showed a major peak in BSi concentration at depth with a less obvious minor peak in more recent sediments (Fig. 5). The major peaks occurred at approximately 1840–1860 in both cores but were deeper in G32 which had a higher sedimentation rate than E30. The maximum concentration was fivefold greater than the minimum concentration in E30 but only about threefold greater than the minimum concentration in G32. Similar major peaks were also present in three cores collected in 1984 in eastern Lake Ontario (Schelske et al. 1986a).

Relative ranges in TP concentration were generally less than those for BSi in both cores (Fig. 5). In both cores, TP concentrations were greater in near-surface sediments than at depth

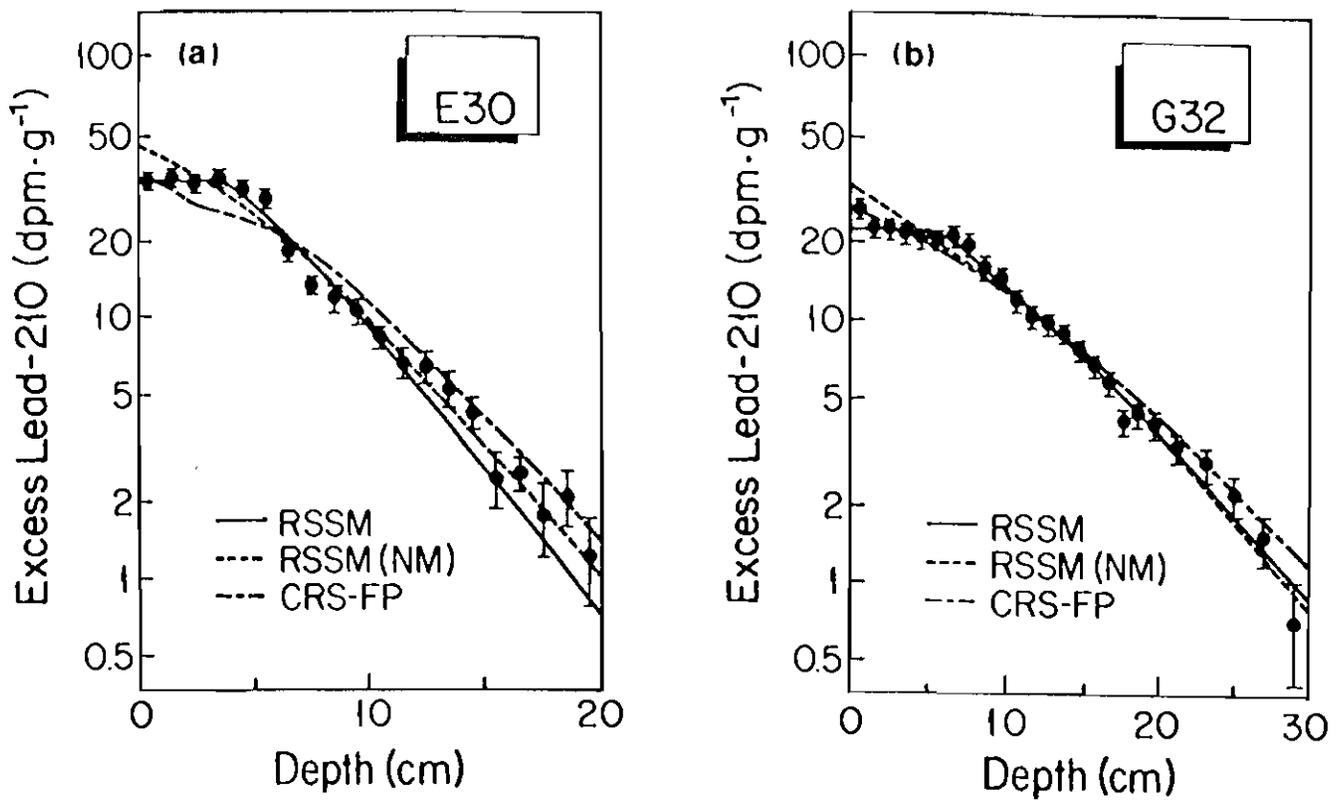


FIG. 2. Excess ^{210}Pb activity with depth for cores (a) E30-RNB-81 and (b) G32-RNB-81. Solid circles with error bars represent excess ^{210}Pb activity. Curves were fitted to excess ^{210}Pb activity using three models: RSSM (rapid steady-state mixing), RSSM-NM (rapid steady-state mixing with effects of mixing removed), and CRS-FP (constant rate of supply – fixed parameter).

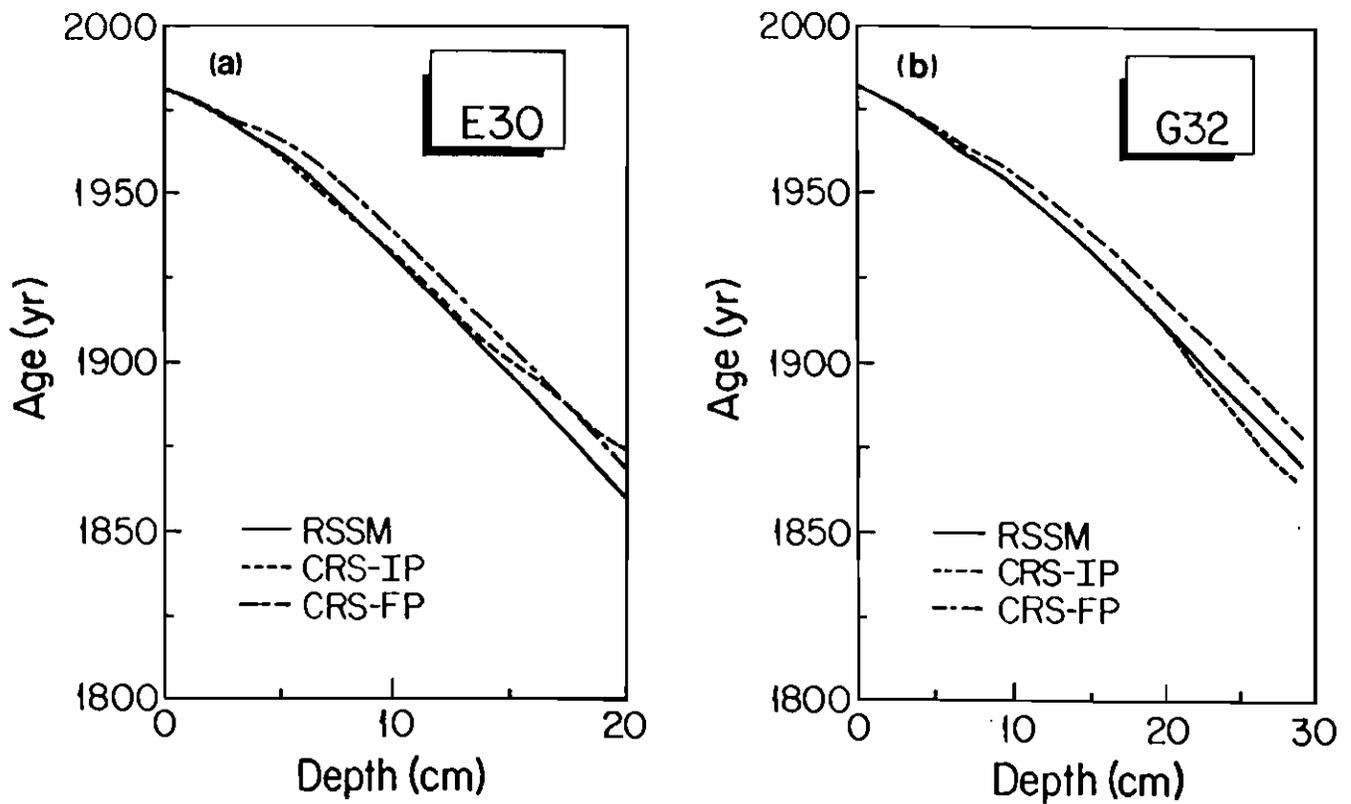


FIG. 3. Depth-time relationships for cores (a) E30-RNB-81 and (b) G32-RNB-81. Curves represent results using RSSM and infinite and fixed parameter CRS models (see text and Fig. 2).

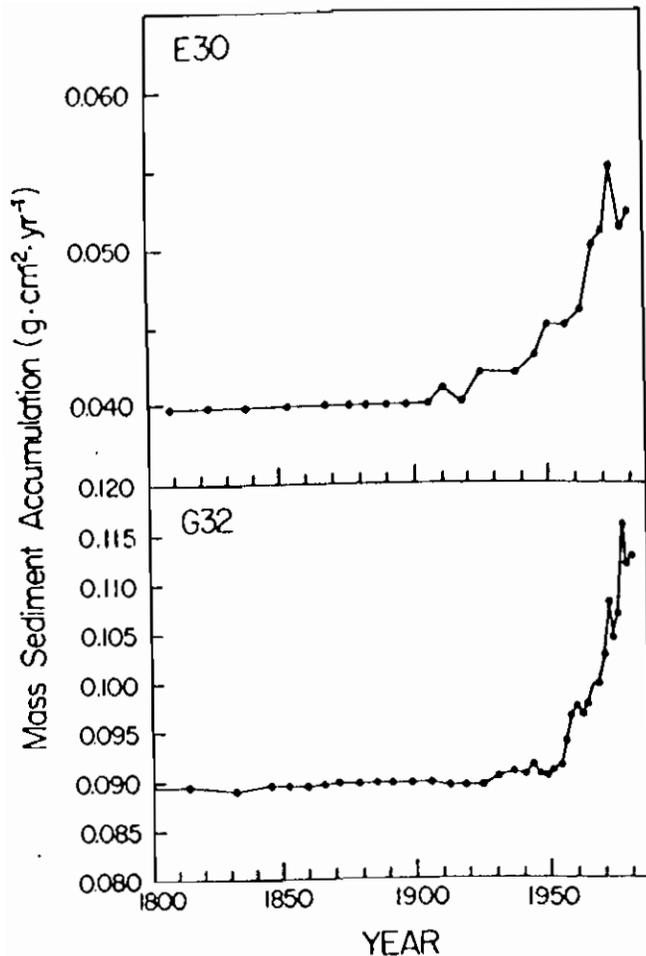


FIG. 4. Mass sedimentation rates in Lake Ontario cores E30-RNB-81 and G32-BEN-81.

TABLE 1. Comparison of mass sedimentation rates ($\text{mg}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$) obtained by ^{210}Pb dating, postsettlement BSi peak, and *Ambrosia* pollen horizon. Data in parentheses for the biogenic silica peak are the two estimates used to obtain the average. It was assumed that the biogenic silica peak occurred at 1850, or at the date of the *Ambrosia* horizon obtained from cores collected from 1969-1971 by Kemp and Harper (1976). Mass sedimentation rates for the biogenic silica peaks would be increased by a factor of 1.13 if the date of the peak is assumed to be 1865 as indicated by ^{210}Pb dating.

Station	Core	^{210}Pb	Postsettlement BSi peak	<i>Ambrosia</i> horizon
E30	E30-RNB-81	39.1	37.8 (35.6-40.1)	—
	22	—	—	35.5
G32	G32-RNB-81	81	71.0 (68.1-73.9)	—
	G32-BEN-81	—	84.7 (82.4-87.0)	—
	27	—	—	81.5

with the exception of the 24-26 cm interval in E30. NAIP profiles for each core were similar to the TP profiles. Similar results were obtained for a core from the Bay of Quinte (Schelske et al. 1985) and for cores from Lake Erie and Lake Michigan (Schelske et al. 1986a).

Of the nutrients studied, the chronology of OC concentration (Fig. 5) was most consistent generally with the expected temporal responses of phytoplankton to patterns of phosphorus enrichment obtained from computer simulations (Chapra 1977). In E30, OC concentrations were relatively constant at the bot-

tom of the core and then showed periods of rapid increase after 1850 and 1940. A similar pattern is evident in G32 but analyses were not run on samples deep enough to obtain data for the relatively low and constant concentrations found below 18 cm in E30. Like OC, concentrations of IC also increased in recent sediments.

Atomic Nutrient Ratios

BSi:TP profiles for both cores show initial major peaks at 18-22 cm for E30 and 40-44 cm for G32 (Fig. 6) which correspond to the major peaks in BSi concentration. In sediments deposited after the major peaks, ratios of BSi:TP and BSi:NAIP decrease. This result is expected if diatom production was silica limited and if rates of diatom dissolution did not change prior to permanent burial to compensate for the reduced flux of diatoms to the sediments.

The largest ratios of NAIP:TP were found in the deepest sediments of one core and in the most recent sediments in the other (Fig. 6). In E30, the only obvious pattern with depth was a tendency for smaller ratios above 19 cm (approximately 1865) with an average ratio of 0.47 below 19 cm or 50% more than the average of 0.31 above 19 cm. In G32, the pattern was reversed. Ratios above 28 cm were >0.36 whereas below that depth, ratios were more variable, with most values being less than the range of values above 28 cm.

Ratios of OC and IC with BSi were greater in near-surface sediments than at depth (Fig. 7). These results may indicate that increased deposition of OC in near-surface sediments resulted from increases in nonsiliceous algal production, provided the bulk of OC was derived from algae.

Nutrient Fluxes

The temporal pattern of TP and BSi flux was similar for cores E30 and G32. BSi accumulation peaked from 1860 to 1870 at 2.5 and 5.5 $\text{mg}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$, respectively, for E30 and G32 (Fig. 8). After the peak period, flux in both cores from 1930 to 1940 decreased to half that of the peak period and then increased to a secondary maximum about 1970. Relatively large fluxes for the uppermost interval likely represent input of recently deposited BSi in the zone of active dissolution (Schelske et al. 1983). An increase in TP flux for the two cores (Fig. 9) corresponding with the increased flux of BSi in 1860-1870 was not obvious. An increase in TP flux about 1890 represented by one sample in each core only weakly indicated increased TP fluxes before 1900.

Patterns in NAIP fluxes were different for the two cores. Pre-1850 fluxes at E30 were among the largest fluxes obtained whereas at G32, pre-1850 fluxes were among the smallest (Fig. 10). Like TP fluxes, patterns in NAIP flux were inconsistent with increases expected from modelled TP concentration.

The temporal pattern of increases in OC and IC fluxes was similar for cores E30 and G32. OC flux increased gradually beginning about 1880 until about 1950 when it increased rapidly until about 1970 (Fig. 11). This pattern corresponds closely with that for modelled TP concentration. OC flux after 1970 was relatively constant. Obvious increases in IC flux in both cores were not found until 1920 (Fig. 12). In core E30, IC increased 10-fold by 1950 relative to the early 1800s and 30-fold at the peak in 1970 whereas the historic increase in IC flux at G32 was only about 10-fold. The maximum IC flux at G32

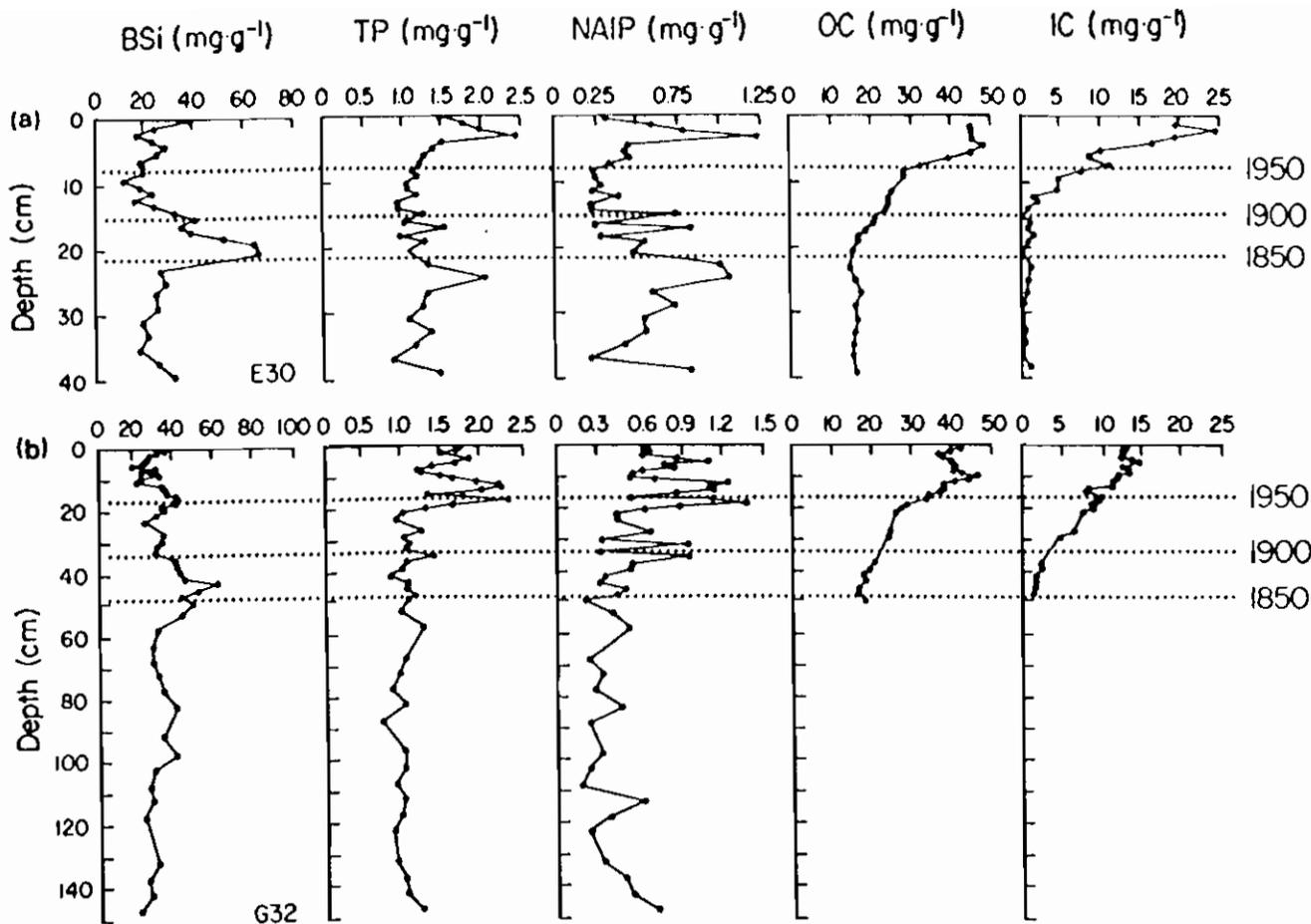


FIG. 5. Concentrations of biogenic silica, total phosphorus, nonapatite inorganic phosphorus, organic carbon, and inorganic carbon in Lake Ontario cores. (a) Box core E30-RNB-81; (b) benthos core G32-BEN-81.

was less than that at E30, a pattern that was not found for any of the other nutrients.

Discussion

²¹⁰Pb Dating

Profiles of excess ²¹⁰Pb for E30 and G32 (Fig. 2) were calculated as the difference between total ²¹⁰Pb and a supported activity which is small and assumed to be constant over the length of the core (E30, 2.45 ± 0.25 dpm·g⁻¹; G32, 2.66 ± 0.25 dpm·g⁻¹). Errors associated with the estimate of unsupported ²¹⁰Pb are the standard deviations about the mean value over a range of depths at the bottom of the core where the activity of total ²¹⁰Pb is essentially constant. Error bars in Fig. 2 indicate the uncertainty in the estimate of excess ²¹⁰Pb which is a combination of analytical and counting errors in the determination of total ²¹⁰Pb and the uncertainty in estimating unsupported ²¹⁰Pb. The uncertainty is small in the upper portions of the core but increases significantly toward the bottom as excess ²¹⁰Pb approaches background levels.

Profiles of excess ²¹⁰Pb exhibit features encountered elsewhere in the Great Lakes: a zone of nearly constant activity extending down from the sediment-water interface. Below this zone (4 cm for E30; 5 cm for G32), activities decrease exponentially with depth (Fig. 2). Previous studies (cf. Robbins 1982) have shown that the depth of this zone is directly related to the range of penetration of macrobenthos in sediments. Tubificid worms were the dominant species (1450 and

3200·m⁻² in E30 and G32, respectively). These animals redistribute sediments through a conveyor belt feeding mode which introduces both advective and diffusive mixing processes (cf. Robbins 1986). Another important organism present in these sediments was the amphipod *Pontoporeia hoyii*. It appears to mix sediments in a random (eddy diffusive) way over a shallow range of 1–2 cm (cf. Robbins et al. 1979).

Because organisms were present in sufficient densities to cause significant mixing (Robbins 1986), distributions of ²¹⁰Pb could be interpreted in terms of the rapid steady-state mixing (RSSM) model developed previously. It is important to point out that all models which have been developed to interpret ²¹⁰Pb profiles (Robbins and Edgington 1975; Robbins et al. 1977, 1978) assume a constant rate of supply (CRS) of excess ²¹⁰Pb. In large lakes with long hydraulic residence times, this is the most reasonable assumption. The RSSM model assumes that the sedimentation rate is constant and that ²¹⁰Pb is delivered at a constant rate into a mixed layer of fixed extent which moves upward as sediments are added (Robbins et al. 1979). To apply the RSSM model to the data, a weighted least squares fit was made to determine optimum values of the mixed depth and sedimentation rate. The fit to the excess ²¹⁰Pb profile is shown in Fig. 2 as a fit to the profile using the RSSM sedimentation rate with the effect of mixing removed (RSSM-NM). The resulting age–depth relationship for RSSM is given in Fig. 3.

Alternatively, effects of mixing could be disregarded and the flattening of the ²¹⁰Pb profile ascribed solely to a changing sedimentation rate (Fig. 2). If the ²¹⁰Pb flux remains constant,

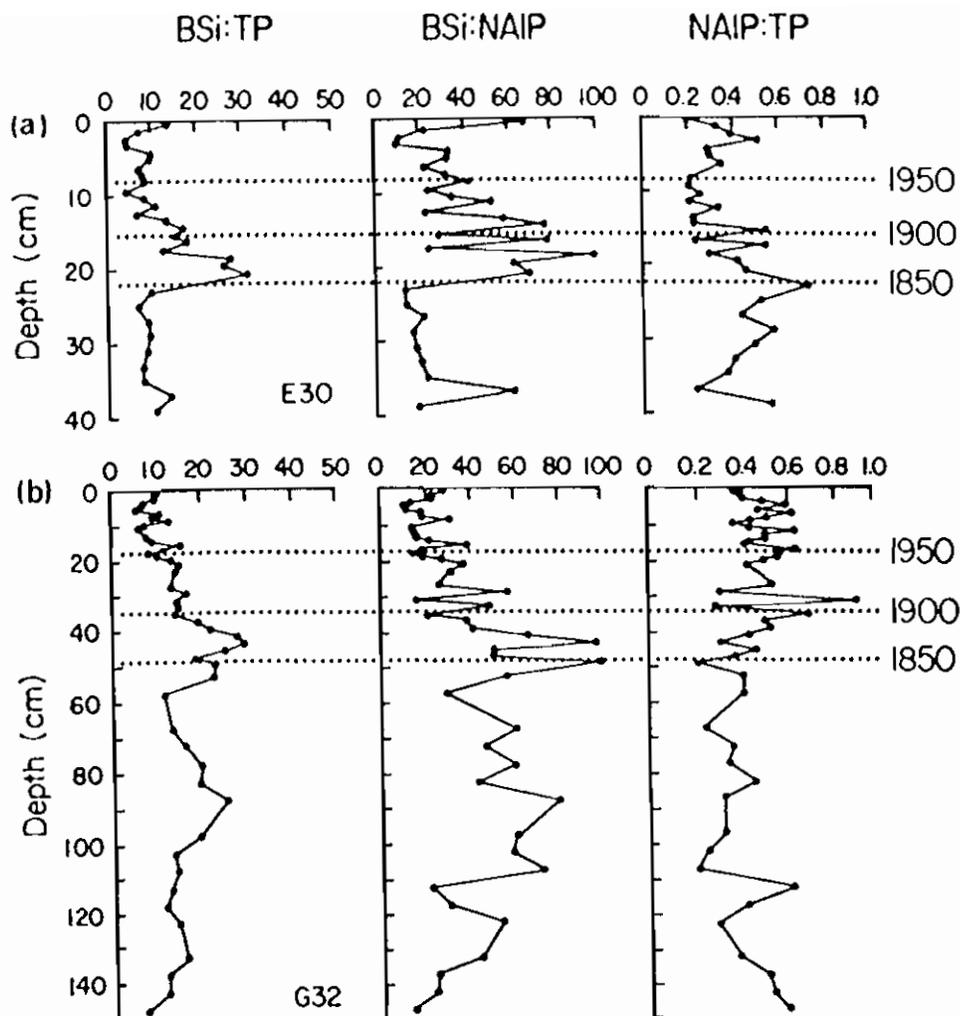


FIG. 6. Atomic ratios of biogenic silica to total phosphorus, biogenic silica to nonapatite inorganic phosphorus, and nonapatite inorganic phosphorus to total phosphorus. (a) Box core E30-RNB-81; (b) benthos core G32-BEN-81.

the relationship between age and depth is given by a straightforward relation described by Goldberg (1963) and later referred to as a constant flux (CF) (Robbins 1978) or CRS model (Appleby and Oldfield 1978). With either of these models, the predicted distribution of excess ^{210}Pb will coincide exactly with the data points because every variation in ^{210}Pb activity is converted into a change in sedimentation rate. Since the CRS model is an infinite parameter (IP) model, processes other than variable sedimentation which contribute to deviations from exponential profiles are conveniently ignored. Moreover, a strictly flat portion on an excess ^{210}Pb profile occurs only for the very special and unlikely circumstance of compensation (see Robbins 1978) where the change of sedimentation rate with sediment depth is exactly matched by radioactive decay. Nevertheless, the result of applying the infinite parameter CRS model (CRS-IP) represents one extreme in the range of assumptions about the nature of the sedimentation process. The age-depth relationship is shown in Fig. 3.

An intermediate treatment, finite parameter CRS model (CRS-FP), attributes some but not all of the flattening to a change in the sedimentation rate (Fig. 2). A correct model would incorporate variable sedimentation and depth-dependent mixing into a single diagenetic equation such as that described by Berner (1980) and modified by Robbins (1986) to include

conveyor belt transport processes. For the present purposes, a simpler calculation suffices. Mixing is considered to have a minimal effect on rapidly varying signals such as OC and IC so that profiles of these constituents can be used to reconstruct the time dependence of the net sediment accumulation rate. Other constituents, primarily clay and clay-sized minerals plus a small amount of quartz, are assumed to be supplied at a constant rate, R_s .

To correct for varying concentrations of IC and OC under these conditions the sedimentation rate, $R(g)$, was calculated by

$$(1) \quad R(g) = R_s + R_{IC}(g) + R_{OC}(g)$$

where R_s is the constant base sedimentation rate equal to the RSSM model value, or essentially the sedimentation rate based on the linear portion of the log excess ^{210}Pb curve, and R_{IC} and R_{OC} are the mass sedimentation rates of IC and OC, respectively. All terms are in units of grams per square centimetre per year. The sediment "depth" g is expressed in units of cumulative weight of dry sediment (grams per square centimetre) to remove small compaction effects. The above relationship implicitly assumes that both IC and OC are not subject to diagenesis. If IC and OC have the approximate formulae of CaCO_3 and CH_2O , respectively, then

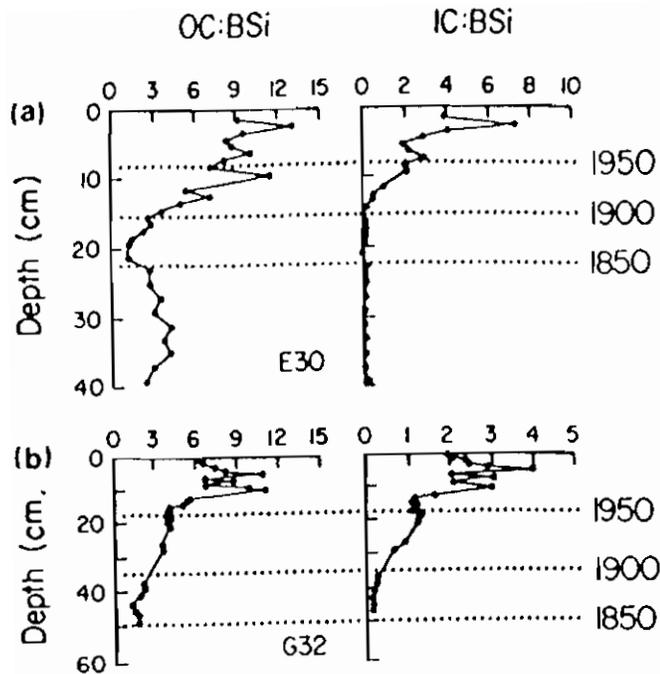


FIG. 7. Atomic ratios of organic carbon to biogenic silica and inorganic carbon to biogenic silica. (a) Box core E30-RNB-81; (b) benthos core G32-BEN-81.

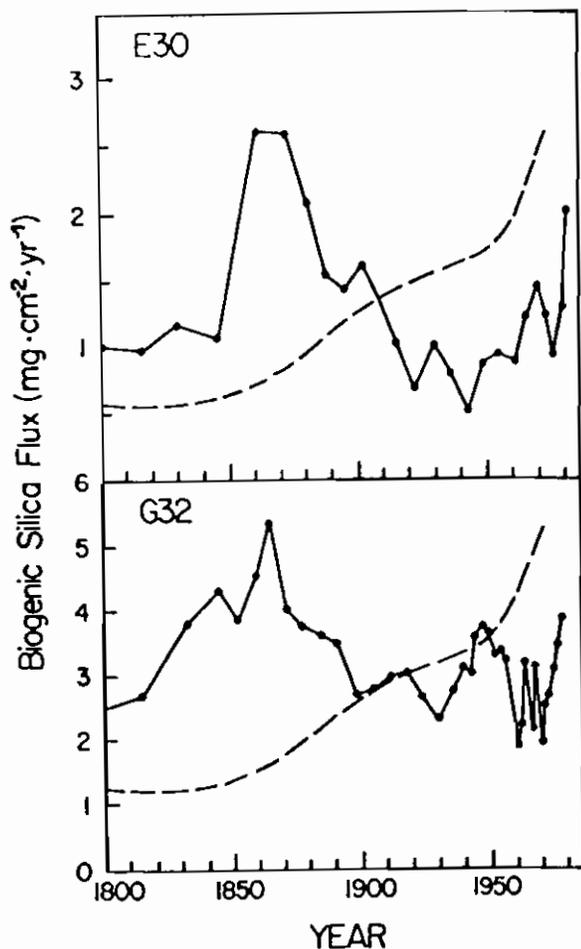


FIG. 8. Flux of biogenic silica in Lake Ontario cores E30-RNB-81 and G32-BEN-81. Broken line is modelled total phosphorus concentration (see Fig. 9).

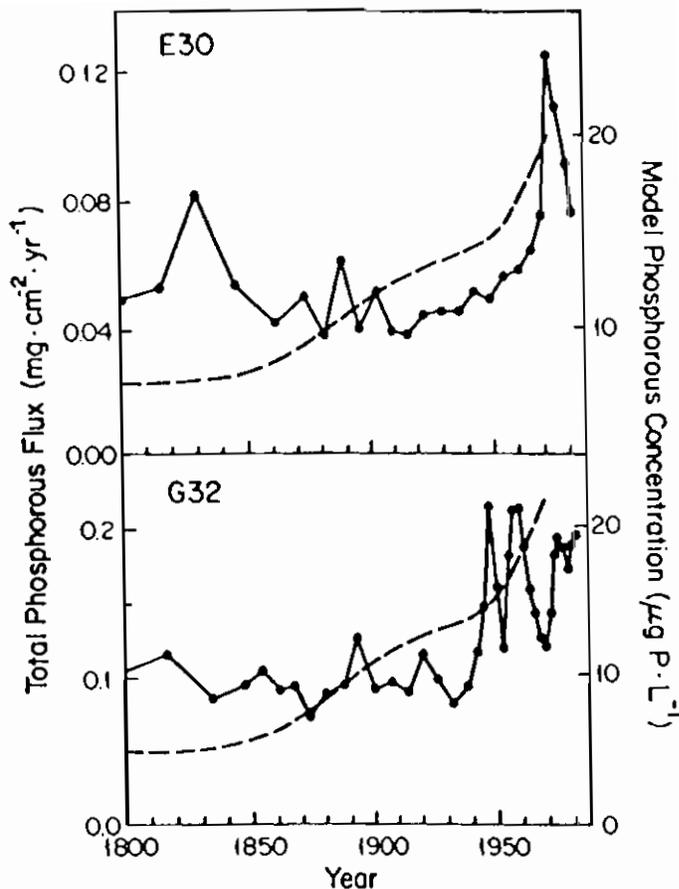


FIG. 9. Flux of total phosphorus in Lake Ontario cores E30-RNB-81 and G32-BEN-81 and computer-simulated total phosphorus concentrations in Lake Ontario from 1850 to 1970 (from Chapra 1977).

$$(2) \quad R_i(g) = 100 C_i R / 12$$

$$R_o(g) = 30 C_o R / 12$$

where C_i and C_o are the measured IC and OC concentrations in grams per gram of dry sediment, respectively. From Equations 1 and 2 it follows that

$$(3) \quad R(g) = R_i / (1 - 100 C_i / 12 - 30 C_o / 12)$$

and the distribution of excess ^{210}Pb is given by

$$(4) \quad A(g) = F e^{-\lambda t} / R(g)$$

where F is the constant ^{210}Pb flux, t is the time before present, and $\lambda = 0.0311 \cdot \text{yr}^{-1}$. Since R varies with sediment "depth," the age-depth relationship is given by

$$(5) \quad t = \int_0^z dg / R(g).$$

The value of F was chosen to reproduce the measured standing crop of excess ^{210}Pb in each core. Either the RSSM or the CRS-IP model approximates the data better than the RSSM-NM model in which no mixing is included (Fig. 2). The age-depth relationship (Fig. 3) indicates that the age associated with a given interval of sediment is not strongly model dependent for these cores. The largest differences among estimates occur toward the end of the excess ^{210}Pb profiles where they are within about 7 yr of each other.

The mass flux or net sediment accumulation rate ($R(g)$ vs. t) was based on the CRS-FP model (Fig. 4). For E30 the base sedimentation rate was $0.040 \text{ g} \cdot \text{cm}^{-2} \cdot \text{yr}^{-1}$ and remained essentially constant until 1900 after which it increased to a

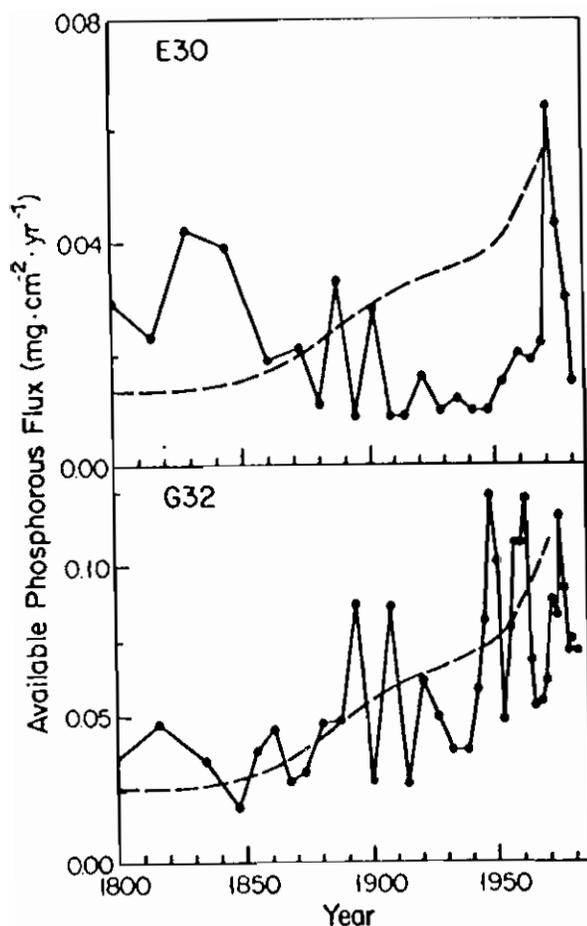


FIG. 10. Flux of nonapatite inorganic phosphorus in Lake Ontario cores E30-RNB-81 and G32-BEN-81. Broken line is modelled total phosphorus concentration (see Fig. 9).

maximum of about $0.055 \text{ g}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$. For G32, the base sedimentation rate was about $0.090 \text{ g}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$ and also remained constant until about the turn of the century. Thereafter it increased to a maximum of about $0.115 \text{ g}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$. Therefore, to the extent that mixing can be ignored, flux of a constituent with concentration C at "depth" g is given by

$$(6) F_c = CR(g)$$

using Equations 1 and 5 above.

Sediment Accumulation and Focusing

Sedimentation rates were obtained using excess ^{210}Pb activity with the CRS-FP model corrected for changes in amount of OC and IC with depth. This correction in ^{210}Pb activity was necessary because carbon-bearing materials constituted a significant portion of the sediment bulk and decreased in concentration over the depth of sediments used for dating (Fig. 5). In lakes with large hydraulic residence times in comparison with ^{210}Pb removal times, the flux of the radionuclide tends to be constant in the presence of changing sedimentation rates (CF model, Robbins 1978; CRS model, Oldfield and Appleby 1984). Thus the effect of increased deposition of carbon-bearing constituents may be to dilute the activity of ^{210}Pb . Alternatively, the observed distributions of OC and IC could be wholly or partly the result of postdepositional processes such as the oxidation of organic materials or dissolution of carbonates. Such diagenetic processes do not affect the dating method

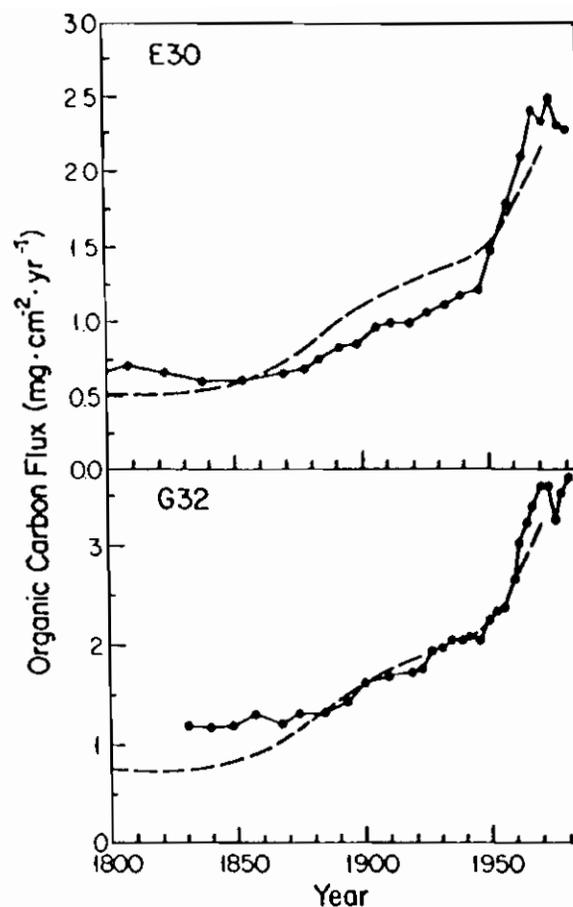


FIG. 11. Flux of organic carbon in Lake Ontario cores E30-RNB-81 and G32-BEN-81. Broken line is modelled total phosphorus concentration (see Fig. 9).

if the isotope remains immobilized. The variable sedimentation rates obtained were approximately 17 and 38% greater at G32 and E30, respectively, in the near-surface sediments than at depth (Fig. 4).

Several independent methods are available to make estimates of mass sedimentation rates. The *Ambrosia* horizon along with ^{210}Pb and ^{137}Cs dating can be used independently to date sediments (Robbins et al. 1978), but establishing the *Ambrosia* horizon only provides information for an average postsettlement mass sedimentation rate. Although a direct comparison has not been made, our results (Table 1) suggest that the major BSi peak could be used to define the period of nutrient enrichment resulting from European settlement beginning about 1850. The BSi peak could prove to be a better biostratigraphic marker of the settlement horizon in some cores than the *Ambrosia* horizon because it provides a sharper peak with better time resolution.

As might be expected intuitively, accumulation of nutrients in sediments was related generally to mass sedimentation rate or degree of sediment focusing. This conclusion is supported by the relationship between nutrient accumulation and average mass sedimentation rate. Cumulative inventories of BSi, OC, IC, and TP to the depth of the settlement horizon were 2.24–2.53 times greater in core G32 than in core E30. This is consistent with a 2.23 times greater average mass sedimentation rate in G32 (Table 1). The cumulative inventory of NAIP, however, differed from the other nutrients in that it was 3.33 times greater in G32 than in E30.

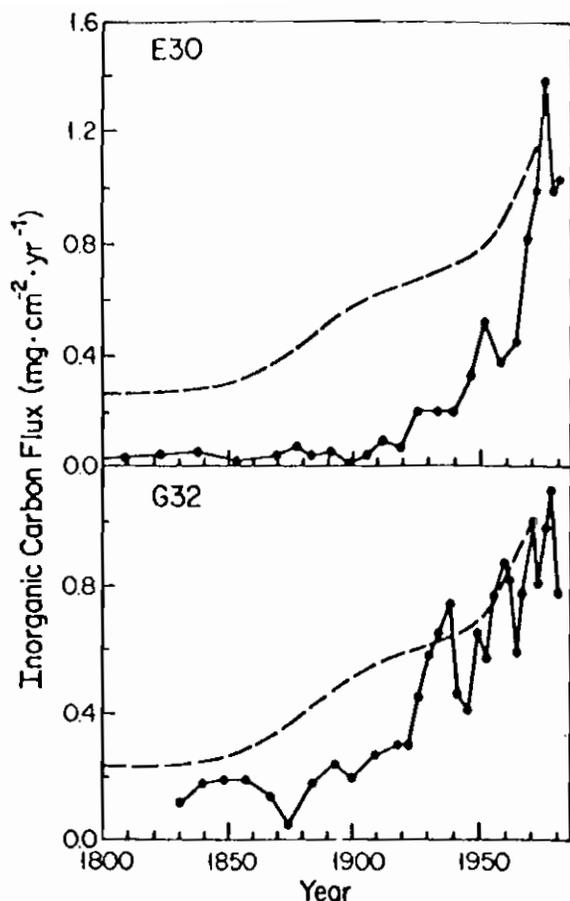


FIG. 12. Flux of inorganic carbon in Lake Ontario cores E30-RNB-81 and G32-BEN-81. Broken line is modelled total phosphorus concentration (see Fig. 9).

Phosphorus and Biogenic Silica Accumulation

The greater relative NAIP accumulation at G32 in combination with the different chronology of NAIP flux at G32 and E30 (Fig. 10) suggests a more complex relationship than simple differences related to sedimentation rate. In G32, NAIP flux and proportion of NAIP increased with time, but these trends were not apparent in the data for E30. The fraction of NAIP relative to TP in the upper 10 cm averaged 46% at G32, about 50% greater than the average of 28% at E30. Williams et al. (1976) and Vernet and Favarger (1982) reported that the proportion of NAIP decreased with sediment depth and attributed this change to an increased proportion of NAIP from anthropogenic sources in recent sediments. In Lake Michigan, large quantities of NAIP are resuspended yearly, primarily during the winter-spring period of thermal mixing (Eadie et al. 1984). In Lake Ontario the NAIP fraction (31–46%) of phosphorus collected in sediment traps (Charlton 1983) was similar to that for NAIP in recent sediments (top 10 cm) at E30 and G32. Williams et al. (1976) concluded that the rate of sedimentation of organic phosphorus and NAIP "was greatest where the most fine-grained sediments were accumulating." One possible explanation, then, for greater NAIP accumulation at G32 is that NAIP is resuspended and deposited with the major part of the fine-grained sediment load in high sedimentation areas in relatively shallow areas of the Rochester basin (Kemp and Harper 1976).

Changes in flux of TP and NAIP for E30 and G32 were not consistent with the fivefold increase in TP inputs from 1800 to

1975 calculated by Chapra (1977). Maximum and minimum yearly fluxes of TP ranged about threefold for both E30 and G32, but twofold increases for both cores occurred between 1940 and 1981 (Fig. 9) when TP loads from sewage inputs increased rapidly (Chapra 1977). Thus, actual loads of phosphorus may have increased less than fivefold or, alternatively, NAIP loads rather than TP loads should have been modelled. Our data for NAIP fluxes do not provide a clear indication of increased flux with time because pre-1850 fluxes were relatively large at E30 and because there was no clear pattern of increasing fluxes between 1850 and 1940 (Fig. 10). Comparison of data for available phosphorus from some Lake Erie cores provided better agreement with computer-simulated TP loads (Williams et al. 1976), but relative increases were still less than those obtained from computer simulations.

By contrast, post-1960 rates of TP sedimentation (Fig. 9) were larger than the average TP sedimentation loss for the lake basin of $0.0250 \text{ mg}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$ for the mid-1970s calculated from computer simulation by Chapra and Sonzogni (1979). If 47.7% of the lake bottom is assumed to be in the three major depositional basins (Thomas et al. 1972), then the average rate of TP sedimentation over the depositional area would be $0.0524 \text{ mg}\cdot\text{cm}^{-2}\cdot\text{yr}^{-1}$. This rate is much smaller than measured TP fluxes in recent sediments, especially at G32 (Fig. 9), and intermediate between the recent NAIP fluxes at G32 and E30 (Fig. 10). It is not surprising that the TP loss at G32 with a high sedimentation rate and TP flux was larger than that predicted by the model. In addition, if TP accumulation is related to mass sedimentation rate, greater than average accumulation rates for TP might be expected in the Rochester basin where from 65% (Kemp and Harper 1976) to 80% (Thomas et al. 1972) of the fine-grained sediments are deposited. Data from these two cores therefore indicate better agreement between TP sedimentation losses in the 1970s calculated by Chapra and Sonzogni (1979) and NAIP flux than with TP flux. The twofold or threefold range in rates for the two cores, however, points to the need to analyze cores from additional stations to obtain a better basin-wide average and to analyze cores from other basins to obtain a lake-wide average.

Peaks in BSi accumulation after European settlement have been attributed to depletion of the epilimnetic silica reserve by increased diatom production that resulted from increased phosphorus inputs from the drainage basin of Lake Ontario (Schelske et al. 1983). Increased rates of BSi and siliceous microfossil accumulation (Fig. 8; Stoermer et al. 1985b) indicate that phosphorus limitation for diatom production must have been relaxed after settlement. These results and increased BSi and siliceous microfossil accumulation in the sediments of Lake Superior (Stoermer et al. 1985a) where TP concentrations have not exceeded $5 \mu\text{g P}\cdot\text{L}^{-1}$ indicate that diatom production can be increased measurably with relatively small phosphorus enrichments. The sensitive response of diatom assemblages to phosphorus enrichment and its relationship to rapid changes in the geochemistry of silica have been addressed previously (Schelske et al. 1986b).

Inorganic Carbon Accumulation

Historic increases in IC accumulation of an order of magnitude or more, however, can be explained only if a combination of biological, physical, and chemical processes changed as the lake became more eutrophic. The most probable cause for the increased flux of IC (Fig. 12) was increased photosyn-

thetic removal of carbon dioxide after 1940 in response to increased TP or NAIP loading (Fig. 9, 10) and an associated increase in pH during summer stratification (Schelske and Callender 1970). In Lake Ontario during the 1970s, epilimnetic calcium concentrations were $40 \text{ mg}\cdot\text{L}^{-1}$ and summer epilimnetic pH exceeded 8.5 (Dobson 1984). These conditions cause the calcium carbonate saturation product to be exceeded and result in biologically induced precipitation of calcite.

Sediments apparently are nearly saturated with respect to calcium carbonate because near-surface interstitial calcium (0–5 cm) ranged from 50 to $54 \text{ mg}\cdot\text{L}^{-1}$, larger than concentrations that ranged from 41 to $42 \text{ mg}\cdot\text{L}^{-1}$ in the overlying water (Weiler 1973). The calcium flux from sediments was estimated to be only $6.25 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ (Weiler 1973), equivalent to only about 0.05% of the calculated calcite flux to the sediments (Fig. 12). These results provide strong evidence that diagenesis of calcium carbonate would not appreciably affect calculated rates of calcite loss to the sediments except possibly in the surface layer of sediments.

In Lake Ontario, calcite precipitation occurs on a lake-wide scale (Strong and Eadie 1978), and calcium and carbonate carbon were highly correlated ($r = 0.985$) in a sediment core (Kemp et al. 1972). Calcium and calcite increased by an order of magnitude in the last 50 yr to more than 20% calcite in cores from the Niagara basin (Mudroch 1983). Also, the downward flux of carbonate during summer stratification is very high ($>2.0 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, Rosa 1985). This summer flux of carbonate (probably calcite) is commensurate with a calcite flux of 56 and $85 \text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, respectively, calculated for recent sediments of E30 and G32.

Other workers have attributed increased calcite concentration in recent sediments of Lake Ontario partly to consequences of eutrophication (Mudroch 1983) or only indirectly to eutrophication through increased carbon dioxide production resulting from decomposition of an increasing load of organic matter which is then preserved as calcite in the sediments (Kemp et al. 1972). Increased dissolution of calcite in the hypolimnetic waters of Lake Erie as the result of eutrophication could have provided a new source of reactants for calcite production in downstream Lake Ontario (Mudroch 1983). If calcite sedimentation of the magnitude we have found is extrapolated over the depositional area of the lake, it is equivalent roughly to the calcium input from the Niagara River (Weiler 1973). The specific mechanism we propose for the 10- to 20-fold increase in IC carbon flux since presettlement is biologically induced precipitation of calcite caused by increased phytoplankton productivity and photosynthetic removal of carbon dioxide that resulted from phosphorus enrichment. Although the proposed mechanism is not unique and was proposed by Minder in 1920 (see Kelts and Hsu 1978; McKenzie 1985), we believe that increased IC flux represents a sediment signal of historic phosphorus enrichment of Lake Ontario waters.

Patterns of Nutrient Accumulation

Four different patterns (signals) of nutrient accumulation in the sediment stratigraphy can thus be used to trace historic responses of phytoplankton communities in Lake Ontario to phosphorus enrichment. The earliest signal, the major BSi peak, occurred between 1850 and 1870. The other three signals occurred much later. An increase in OC flux was evident by 1900 but was most pronounced after 1940. The major increase in IC flux and a secondary peak in BSi accumulation also

occurred after 1940. If the phasing of these signals is compared with TP or NAIP flux to the sediments, it is apparent that the first BSi signal reflecting epilimnetic silica depletion was a response to levels of phosphorus enrichment so small that only relatively weak signals of phosphorus flux were found in the sediments. Epilimnetic silica depletion, where mixed layer diatom populations were silica limited in the summer, probably occurred soon after 1850 when open-lake waters contained $<10 \text{ }\mu\text{g TP}\cdot\text{L}^{-1}$. This conclusion is supported by previous results from Lake Michigan (Schelske et al. 1983). Increases in OC flux only resulted from additional phosphorus loading beginning about 1900, and the greatest increase in OC and IC flux occurred after 1940 when simulated TP concentration increased rapidly from a level of about 12 – $14 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ (Fig. 9). These changes in carbon geochemistry, including an increase of calcite flux to the sediments by at least an order of magnitude, can be attributed to increased phytoplankton productivity. The secondary peak in BSi accumulation could have resulted from the rapid increase in phosphorus loading after 1940 when phosphorus enrichment of lake waters, to levels exceeding $20 \text{ }\mu\text{g TP}\cdot\text{L}^{-1}$, is thought to have produced water column silica depletion (Schelske et al. 1986b; Stoermer et al. 1985b). After water column silica depletion developed, when silica is $<0.4 \text{ mg SiO}_2\cdot\text{L}^{-1}$ during the winter–spring convective mixing period, most diatom populations would have been silica limited throughout the year (Tilman et al. 1982). These general trends in nutrient accumulation also provide evidence for dramatic changes in the biogeochemistry of silica and carbon as a result of phytoplankton responses to increased phosphorus loading.

Historic changes in TP concentration in the water column (Chapra 1977) were modelled from assumptions about phosphorus loading from different sources using a term for sediment loss that was linearly proportional to TP concentration in the water. Lack of correspondence between modelled TP concentration and measured TP or NAIP accumulation in sediments can be attributed generally to three factors. First, appropriate parameters could not be modelled because only TP, and not NAIP, data can be obtained from the literature. Because refractory forms of phosphorus are measured as TP, it is not known how much the inputs of biologically available phosphorus increased historically. Second, sediment loss may not be linearly proportional to water column TP concentration (P_w) but may depend on sediment adsorption characteristics (A) which are controlled by $A\cdot P_w^{1/3}$ (Golterman 1980, 1984). Third, historic sediment losses of phosphorus, as discussed below, were probably controlled by a varying combination of physical, chemical, and biological processes.

A major discrepancy between computer-simulated TP concentration and our TP and NAIP fluxes is in the 50-yr period after European settlement beginning about 1850. Simulated TP concentration increased and did not decrease after settlement whereas neither TP nor NAIP accumulation in cores indicates similar trends (Fig. 9, 10). We can only speculate about this discrepancy because we only analyzed two cores and obtained different patterns of NAIP accumulation. Accumulation of phosphorus in sediments then would indicate that P_w concentration was stable or actually decreased after 1850. By contrast, NAIP and TP accumulation increased after 1940 at a faster rate than indicated by modelled TP concentration. Such an increase could be attributed to increased losses associated with increased precipitation of calcite (see Murphy et al. 1983; Koschel et al. 1983), changes in biological turnover rates (Lean et al. 1983) that would be expected to accompany nutrient enrichment, or

both. NAIP and TP fluxes therefore strongly indicate that historic changes in TP concentration cannot be modelled using the assumption that sediment losses are proportional to phosphorus concentration in the water mass.

Both TP and NAIP fluxes were highly variable between some sampling intervals, especially in the period after 1940 (Fig. 9, 10). Variability in TP flux has been noted in a Bay of Quinte core (Warwick 1980; Schelske et al. 1985) and in other Great Lakes cores where the variability results from differences in NAIP concentration among samples (Schelske et al. 1986a). Peaks in phosphorus fluxes after forest clearance might be expected if a major source of loading associated with forest clearance is phosphorus released by the destruction of debris dams in pristine streams (Bilby 1981). Other possible explanations for variability might be postdepositional mobilization of phosphorus, year-to-year differences in patterns of resuspension or deposition of particulate material during the winter-spring period of thermal mixing, and year-to-year differences in patterns of calcite precipitation. These factors could be influenced by annual fluctuations in weather. In fact, greater than average ice cover and associated reduction in winter-spring thermal mixing in Lake Michigan has been postulated as the mechanism for a short-term decrease in water column TP concentration (Rodgers and Salisbury 1983).

Modelled TP concentration in the water column (Chapra 1977) provides a useful framework on which historic ecosystem changes can be compared. Although assumptions used in obtaining modelled TP concentrations have been questioned, the pattern simulated for Lake Ontario appears to be consistent with the record of organic carbon accumulation in sediments (Fig. 11). Golterman (1984) also found a linear relationship between TP concentration in the water and organic carbon and organic nitrogen accumulation in sediments of Lake Constance. Thus, one of the expected consequences of eutrophication, an increase in production and sedimentation of organic matter, is consistent with the pattern of simulated TP concentration.

In summary, a record of changing biogeochemistry in Lake Ontario during the last 130 yr can be obtained from the stratigraphic analysis of several nutrients in sediment cores. BSi accumulation peaked between 1850 and 1870 in response to hypothesized small increases in phosphorus inputs resulting during early European settlement. The most obvious record of postsettlement change was increased deposition of OC and also increased deposition of IC in the form of calcite, a secondary effect of increased nutrient loading and phytoplankton production. The sediment record for OC and IC corresponds temporally with increased deposition of TP because major changes occurred since 1940 when the major increases in TP deposition were found. Relative changes in TP or NAIP accumulation, however, were less than those for OC, IC, or BSi and, unlike the other nutrients, differed between cores, suggesting that system responses to increased P loading cannot be predicted entirely on stoichiometric relationships between phosphorus and other nutrients. The relationship is complicated because rate constants of phosphorus recycling by organisms (Lean et al. 1983), co-precipitation of phosphorus with calcite (Murphy et al. 1983), or sorption of phosphorus to particles that remain suspended in the water column (Eadie et al. 1984) may have been modified during the changing trophic history of Lake Ontario.

Even though our results confirm that the trophic history can be inferred from the sediment record, discrepancies in ratios of NAIP:TP and differences in NAIP storage and recent IC flux

between cores point to a lack of complete understanding about the factors that interact to produce the sedimentary record. Additional cores should be analyzed to determine how patterns of nutrient sedimentation and accumulation vary over depositional environments and to test hypotheses suggested by our results.

Acknowledgments

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