Historic low-level phosphorus enrichment in the Great Lakes inferred from biogenic silica accumulation in sediments

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Abstract

Sedimentary biogenic silica (BSi) accumulation was used in conjunction with a hypothetical model of BSi accumulation to show that BSi is a sensitive proxy for low-level phosphorus enrichment in the Great Lakes. We hypothesize that historic nutrient-driven changes in diatom production altered silica biogeochemistry and induced biologically mediated silica depletion (BMSD) and that a record of the underlying mechanism, enhanced diatom production and BSi sedimentation stimulated by anthropogenic phosphorus enrichment, is preserved in the sediment record. Paleolimnological results support three hypotheses based on this model. First, BSi accumulation increased in Lake Superior and Lake Huron at total phosphorus (TP) concentrations (4 and 5 μg TP L^{-1} or 0.13 and 0.16 μmol L^{-1}, respectively) too small to induce BMSD and with changes in TP concentration too small to be detected by routine water-column sampling. Second, a peak in BSi accumulation in Lake Michigan resulted from epilimnetic silica depletion that developed rapidly in the 1950s and 1960s when TP averaged 8 μg L^{-1} (0.26 μmol L^{-1}). In addition, epilimnetic silica depletion in the late 1800s was inferred from BSi accumulation in Lake Erie and Lake Ontario when the TP concentration was <10 μg L^{-1} (0.32 μmol L^{-1}). Third, a secondary peak in BSi accumulation in the 1950s and 1960s signaled water-column silica depletion in Lake Ontario and the eastern basin of Lake Erie that developed as TP concentration increased to 27 μg L^{-1} (0.87 μmol L^{-1}). Ratios of NAIP:TP, BSi:TP, and BSi:NAIP also provide sensitive proxies for phosphorus enrichment. BSi accumulation is a sensitive proxy for phosphorus enrichment because BSi production by diatoms integrates silica utilization over an annual cycle, silica is recycled slowly (on annual time scales) compared with phosphorus, and sedimented BSi is focused into depositional zones.

Cultural eutrophication of the Great Lakes became a major issue in the 1950s and 1960s, when impaired water quality in Lake Erie was evident to the general public. Before then, these lakes were considered too large to be affected by nutrient enrichment (Hasler 1969) or affected only in nearshore areas and harbors (Beeton and Edmondson 1972). Signals of

eutrophication were overlooked in early surveys (Beeton and Edmondson 1972), partly because cultural nutrient enrichment was thought to benefit fisheries in the Great Lakes and other freshwater bodies (Hasler 1969). Documenting environmental change was difficult because of sparse data, particularly from lake-wide sampling, and a paucity of systematic data collection in these large lakes. Consequences of eutrophication in Lake Erie were documented from long-term sampling of phytoplankton using collections from nearshore municipal water intakes at Cleveland, Ohio (Davis 1964). Such long-term records from other water intakes also showed increases in conservative ions that are associated with eutrophication (Beeton 1965). A major effort to reverse cultural eutrophication by reducing phosphorus inputs was initiated in 1972 through a water-quality agreement between the United States and Canada (Schelske 1979). This effort successfully reduced inputs from phosphate-based detergents and sewage treatment plants and lowered total phosphorus (TP) in lake water. Filtering activities of exotic zebra mussels have been credited with additional lowering of TP (Nalepa and Fahnenstiel 1995; Makarewicz et al. 2000).

Nutrient-driven changes in diatom production altered the biogeochemical cycle of silica in the Great Lakes (Schelske

Table 1. Comparison of seasonal changes in major nutrient concentrations in the Great Lakes for 1969–1971 and 1990s. Units in first line for each year grouping are silica (mg SiO_2 L^{-1}), nitrate (mg NO_3-N L^{-1}), and total P (μg TP L^{-1}). Units in second line are μmol L^{-1} for silica, nitrate, and total P. Sources of data: ranges for 1969–1971 for Lake Michigan are summer minima and winter maxima (Rousar 1973) and other ranges are from Dobson et al. (1974). Ranges for 1998 are from spring and summer samples (Barbiero and Tuchman 2001). Total P data (1993–1995) are from Fahnenstiel et al. (1998).

	Superior	Huron	Michigan	Eastern Lake Erie	Ontario
Silica (1969–1971)	2.06–2.26	0.73–1.01	0.15–1.40	0.03–0.30	0.10–0.67
	34.3–37.6	12.2–16.8	2.5–23.3	0.5–5.0	1.7–11.2
Silica (1998)	2.27–2.51	1.16–1.65	0.43–1.54		0.18–0.62
	37.8–41.8	19.3–27.5	7.2–25.7		3.0–10.3
Nitrate (1969–1971)	0.23–0.28	0.19–.26	0.10–0.27	0.02–0.18	0.05–0.28
	16.4–20.0	13.6–18.6	7.1–19.3	1.4–12.9	3.6–20.0
Nitrate (1998)	0.30–0.34	0.27–0.34	0.17–0.32		0.23–0.38
	21.4–24.3	19.3–24.3	12.1–22.9		16.4–27.1
Total P (1969–1971)	4.2	5.0	8.3	25	27
	0.14	0.16	0.27	0.81	0.87
Total P (1993–1995)	4.8	5.0	6.3	6.5	9.3
	0.15	0.16	0.20	0.21	0.30

and Stoermer 1971; Schelske et al. 1983, 1986*a*). Such nutrient-driven changes led to biologically mediated silica depletion (BMSD), defined as a consequence of cultural eutrophication manifested at the ecosystem level. The underlying mechanism is enhanced diatom growth stimulated by anthropogenic phosphorus enrichment (Schelske and Stoermer 1971). The resulting increased biogenic silica (BSi) production and sedimentation decrease silica reserves in the water column, eventually leading to silica depletion and silica-limited diatom growth (Schelske et al. 1983, 1986*a*). In mass balance terms, BMSD occurs over a period of years when BSi accumulation in sediments, the result of increased diatom production, exceeds silica inputs to the ecosystem (Schelske 1985*a*).

Long-term data sets from chemical measurements of water in the Great Lakes are inadequate to trace historic phosphorus enrichment (cultural eutrophication). Computer simulations for the Great Lakes drainage basin provide historic TP loading and TP concentrations from 1800 to 1970 for all the Great Lakes (Chapra 1977). In the early 1800s, simulated TP concentrations were relatively low for all of the Great Lakes, ranging from approximately 3 μg L^{-1} (0.1 μmol L^{-1}) in Lake Superior to 6 μg L^{-1} (0.2 μmol L^{-1}) in Lake Ontario and the eastern basin of Lake Erie. Reliable data for water quality are available beginning in the 1960s. Paleolimnological data are used for inferences about water quality during periods for which no direct measurements of water quality are available (Smol 2002).

Chemical proxies in Great Lakes sediment cores for ecosystems responses to nutrient enrichment include BSi (Schelske et al. 1983, 1986*b*, 1988), biologically induced precipitation of calcite (Schelske et al. 1988; Schelske and Hodell 1991; Hodell and Schleske 1998), TP and nonapatite inorganic phosphorus (NAIP) (Schelske and Hodell 1995; Schelske et al. 1986*b*), organic carbon (Schelske et al. 1988; Schelske and Hodell 1991; Hodell and Schelske 1998), and stable carbon isotopes of calcite and organic carbon (Schelske and Hodell 1991; Hodell and Schelske 1998; Hodell et al. 1998). Microfossil diatom communities also provide records of progressive, historic phosphorus enrichment (Stoermer 1998). In addition to being a proxy for diatom abundance (Conley 1988), BSi is also found in freshwater sponge spicules (Kenney et al. 2002) and phytoliths (Bootsma et al. 2003; Gaiser et al. 2004). BSi has been employed as a proxy for recent silica depletion in Lake Victoria (Verschuren et al. 2002) and on longer time scales for paleoproductivity in Lake Ontario (McFadden et al. 2004) and other lakes (Johnson et al. 2002; Bradbury et al. 2004). BSi has been utilized as a paleolimnological proxy for varied purposes in lacustrine and marine systems (Conley and Schelske 2001). In this article, we use BSi in sediments as a proxy for diatom production.

Three lines of evidence demonstrate that BMSD results from low-level phosphorus enrichment in the Great Lakes. First, nutrient-enrichment experiments with natural phytoplankton assemblages show that diatoms respond to phosphorus enrichment through increased growth and silica utilization and that silica depletion (secondary nutrient limitation) can be induced experimentally by phosphorus enrichment (Schelske 1984; Schelske et al. 1986*a*). Second, although sparse, water-column data show that epilimnetic silica depletion developed in Lake Michigan between 1955 and 1969, when the mean TP concentration was 8 μg L^{-1} (0.26 μmol L^{-1}) (Schelske 1988). Water-column silica depletion developed by the early 1970s in Lake Erie and Lake Ontario (Table 1) (Schelske et al. 1986*a*). Finally, sediments provide continuous records that can be used to infer the history of cultural eutrophication (Schelske et al. 1983; Schelske 1999).

A hypothetical model relating BSi accumulation in sediments and phosphorus enrichment of the water column (Schelske et al. 1983) can be used to test three hypotheses on historic effects of low-level phosphorus enrichment in the Great Lakes: (1) historic phosphorus enrichment increased diatom production that can be inferred from increased BSi accumulation in sediments; (2) historic phosphorus enrichment induced epilimnetic silica-limited diatom growth, leading to a signal of BMSD in sediments; (3) historic phosphorus enrichment induced water-column silica depletion, leading to a secondary signal of BMSD in sediments. We
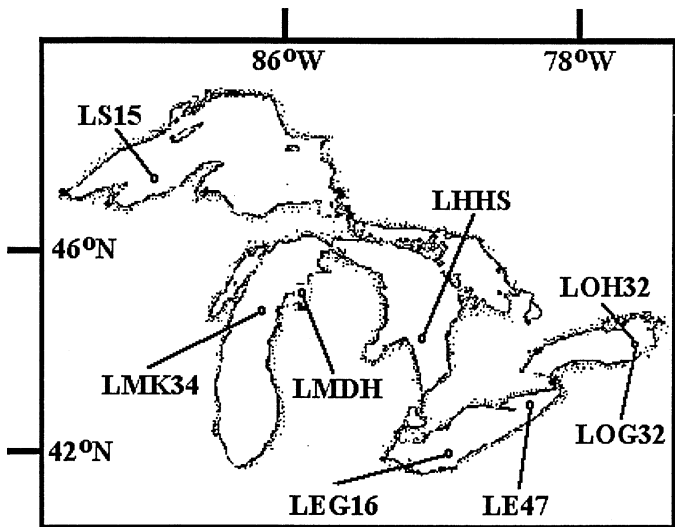
Fig. 1.   Map with coring stations in the Great Lakes. Cores are identified with an alpha numeric code. The first two letters are codes for the lake; these codes are followed by station identification. In the text, the two numbers following the hyphen represent year of collection.

also used a simple model to confirm that diatom production and BSi accumulation in sediments respond to phosphorus enrichment too small to be detected with routine water-column sampling. Finally, we evaluated NAIP:TP, BSi:NAIP, and BSi:TP mass ratios as proxies for nutrient enrichment.

Materials and methods

The Laurentian Great Lakes are interconnected hydrologically with water flow beginning in the two headwater lakes, Lake Superior and Lake Michigan (Fig. 1). Inputs from the upstream lakes form a major fraction of the outflow to the downstream lakes, Lake Huron, Lake Erie, and Lake Ontario (Table 2). The two upper lakes are deeper with larger volumes and longer hydraulic residence times than the other lakes. Large volumes and long residence times provide rather stable chemical conditions on short time scales, which are important characteristics in studying chemical mass balances (Schelske 1985a).

Obtaining sediment cores from the Great Lakes is complicated by their large size and depth (Table 2). However,

good coring sites are found in depositional zones where soft sediments accumulate (Thomas 1981). Cores were obtained with a Soutar box corer from eight stations located in depositional zones (Fig. 1) and processed according to methods described in Schelske and Hodell (1991). Cores were sectioned at fine intervals, generally at 1.0 cm, but also at 0.5 cm for the upper 20 cm in LOG32-93 and LOH32-94. Core identifications with year of collection and latitude and longitude are Lake Superior (LS15-94, 47°00.00′N, 90°00.00′W), Lake Huron (LHHS-94, 43°59.90′N, 81°59.90′W), Lake Michigan (LMK34-94, 44°36.88′N, 86°37.32′W; and LMDH-94, 44°56.40′N, 85°27.00′W), Lake Erie (LEG16-93, 42°00.10′N, 81°36.20′W; and LE47-87, 42°32.80′N, 79°44.90′W), and Lake Ontario (LOG32-93, 43°38.60′N, 76°42.00′W; and LOH32-94, 43°42.90′N, 76°42.00′W). LE47-93 was collected in 1993 at the same location as LE47-87.

Sediment cores were dated with ^{210}Pb using the constant rate of supply (CRS) model (Schelske et al. 1994). To obtain sediment ages using unsupported ^{210}Pb activity, gamma activity was measured with a low-background well-type intrinsic gamma detector (EG&G Ortec). The CRS model allows calculation of variation in mass sedimentation rate (MSR) with age. This model was evaluated and compared with alternate models for ^{210}Pb dating (Schelske et al. 1988). An inherent characteristic of CRS ages is increased uncertainty with sediment age. These uncertainties translate into greater uncertainty in MSR with sediment age. For the Lake Superior core, age uncertainty is 17 yr for the 1855 section, but only 1 yr for the two top sections. MSR uncertainty in the oldest sediments is approximately 100%. A detailed analysis of errors in dating is beyond the scope of our article. Ages are used as approximations, primarily to determine whether increased phosphorus loading after early European settlement in the mid- to late-1800s and urban development beginning in the 1940s affected BSi accumulation in sediments. Core LE47-93 was not dated because the core was too short to obtain the complete inventory of unsupported [210]Pb. Age resolution in LE47-87 is poor below 47 cm (1908) because deeper sediment samples were combined and ^{210}Pb activity was measured at 4-cm intervals. Ages for LOH32-94 were derived by correlating percent carbonate variations to a detailed chronology for LOG32-93 (Hodell et al. 1998).

The BSi method is described in Conley and Schelske

Table 2. Morphometric and hydrologic data on the Laurentian Great Lakes.*

	Superior	Michigan	Huron	Erie	Ontario	Total
Area, water suface (10^3 km²)	82.4	58.0	59.6	25.7	19.7	245
Area, drainage basin† (10^3 km²)	207	176	188	87.4	90.1	745
Maximum depth (m)	406	281	228	60	244	
Mean depth (m)	148	84	53	17	86	
Volume (10^{12} m³)	12.2	4.87	3.53	0.458	1.64	22.7
Outflow (10^9 m³ yr⁻¹)	65.2	49	159	175	208	
Renewal time (years)‡	190	100	22	3	8	

* From Schelske (1975).
† Includes water suface.
‡ Volume divided by outflow.

Table 3. Summary of sediment proxies: biogenic silica (BSi) concentration, biogenic silica accumulation rate (BSiAR), total phosphorus (TP), nonapatite inorganic phosphorus (NAIP).

Proxy	Proxy for
BSi	Diatom production and sedimentation (mg g^{-1} dry sediment)
BSiAR	Diatom production and sedimentation rate (mg cm^{-2} yr^{-1})
TP	TP loading or water-column enrichment of TP (mg g^{-1} dry sediment)
NAIP	NAIP loading or water-column enrichment of NAIP (mg g^{-1} dry sediment)
NAIP : TP	Proportion of TP that is biologically available P; also increase in relative contribution from anthropogenic sources
BSi : TP	Diatom assemblage composition, planktonic/benthic ratio, diatom silicification, quality of nutrient enrichment, silica depletion, or some combination of these factors
BSi : NAIP	Same proxies as those for BSi : TP except these are based on the relative contribution to measured NAIP component of TP

(2001). It utilizes time-course extraction of amorphous silica (1% NaCO$_3$ at 85°C). Linear regression is then used to correct for mineral dissolution and, if necessary, to estimate components with different extraction rates. BSi accumulation was inferred from BSi concentration and BSi accumulation rate (BSiAR), the product of BSi concentration and MSR. BSi concentration is reported in mass units as SiO$_2$ per unit dry weight (mg g^{-1}). Methods for TP and NAIP, a biologically available phosphorus form, are described in Schelske and Hodell (1995). Different samples were used for measurements of TP and NAIP, so results are indepen-

Biogenic silica accumulation

Fig. 2. Hypothetical model of BSi accumulation in the sediment record (from Schelske et al. 1983).

dent. Data for TP, NAIP, and BSi and mass ratios of BSi : NAIP, BSi : TP, and NAIP : TP are used as sediment proxies (Table 3). These data are smoothed as 3-point running means. Consequently, the top sample in cores sectioned at 1.0-cm intervals is plotted at 2 cm as the average of the top three samples. Phosphorus data for LE47-87 and LE47-93 were presented earlier (Schelske and Hodell 1995). These cores are used here because they provide clear signals of historic phosphorus loading.

Effects of water-column phosphorus enrichment on diatom production and BSi accumulation in sediments are shown in a hypothetical model (Fig. 2). The hypothetical model is based on relatively simple premises. We assume that BSi accumulation is a proxy for diatom production and sedimentation. Similar to other paleolimnological models of diatom sedimentation, it is assumed that the dissolution rate of diatoms is relatively constant. The model predicts that, in a phosphorus-limited system, BSi accumulation will increase with phosphorus enrichment from a dynamic steady state for P-limited diatom production until diatom production is limited by silica supplies. Silica supplies become limited when the water-column reservoir of silica is depleted seasonally to levels that limit diatom production. Diatom production then becomes silica-limited and is no longer phosphorus-limited. With this shift from phosphorus-limited diatom production to silica-limited diatom production, BSi accumulation begins to decrease. Therefore, a transient peak in BSi accumulation is predicted to be the signal of BMSD in the sedimentary record. A new dynamic steady state is then established based on external silica supplies, primarily tributary inputs, and internal recycling (Schelske 1985a). Initially, silica depletion occurs seasonally in the epilimnetic mixed layer but can develop year round in the entire water mass with increased phosphorus enrichment (Schelske et al. 1986a).

We developed a new model to demonstrate the sensitivity of sediment BSi accumulation to nutrient-driven changes in silica utilization and production by diatoms. Only areal silica utilization during the winter–spring isothermal period is used (Schelske et al. 1986a). It represents the major fraction of silica utilization in Lake Superior because the mean depth is 148 m and the isothermal period extends into the summer. Thermal stratification in the main body of the lake occurs in July or later (Bennett 1978). This fraction of annual silica utilization is important in all of the Great Lakes (Schelske
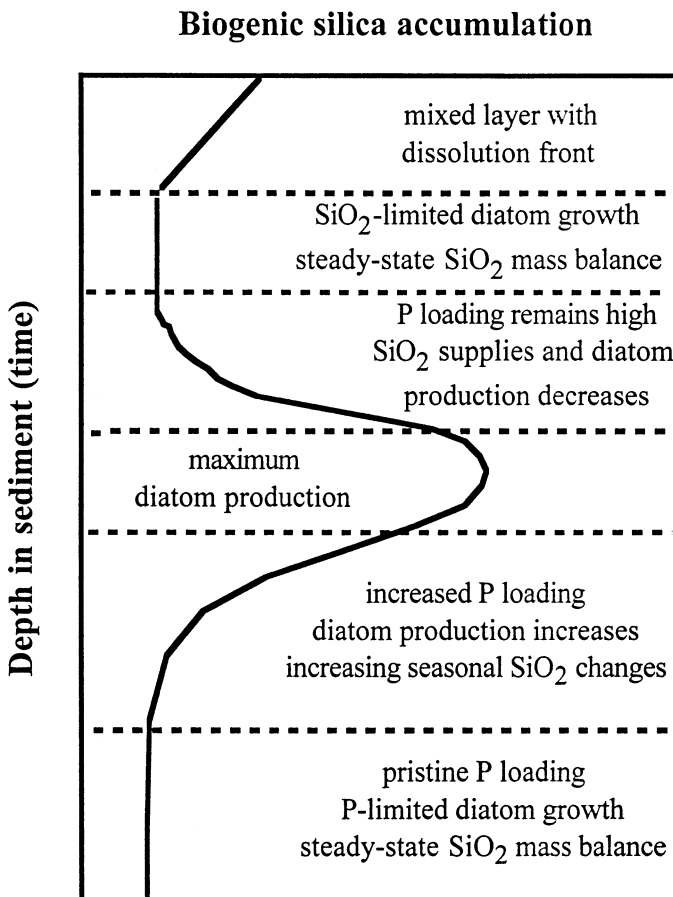
1999) and is an indirect measure of BSi production. The model calculated BSi accumulation is

$$BSi \ (mg \ g^{-1}) = Z \times VU \times RF \times FF/MSR$$

where Z is mean depth, VU is volumetric silica utilization, RF is a recycling factor, and FF is a focusing factor. We assumed that 95% of this BSi production is recycled annually (Schelske 1985*a*) and that BSi is sedimented uniformly in depositional areas that occupy 40% of a lake basin (Thomas 1981). Finally, an average MSR for the depositional area must be assumed for each lake so that areal utilization in g SiO_2 m^{-2} yr^{-1} can be converted to BSi accumulation in mg g^{-1}. These MSRs were 40, 60, and 80 mg cm^{-2} yr^{-1} for Lake Superior, Lake Huron, and Lake Michigan, respectively.

Chapra (1977) simulated historic TP concentrations in the Great Lakes based on phosphorus loading from four sources: atmospheric inputs, land runoff, sewage, and phosphate-based detergents (Fig. 3A). Two inflections are apparent for the lower lakes. The first inflection, attributed to increased loading from land runoff, occurred in the mid-1800s. This increased loading is associated with early European settlement and forest clearance in the drainage basin, as shown by data for Lake Ontario (Fig. 3B). The second inflection, beginning in the 1940s, resulted from sewage inputs due to increased population growth and sewer construction and to introduction of phosphate-based detergents. In the early 1800s, only land runoff and atmospheric fallout were important phosphorus sources. In Lake Ontario and the eastern basin of Lake Erie, TP concentration doubled by the late 1800s to more than 10 μg L^{-1} with increased land runoff. With increased loading from urban sources, it more than doubled again between the early 1940s and early 1970s to approximately 25 μg L^{-1}. For comparison, the TP concentration in the western basin of Lake Erie increased much more, to nearly 50 μg L^{-1}. In Lake Michigan, the two inflections are apparent, but the simulated TP concentration in the 1970s was much lower, approximately 10 μg L^{-1}. Inflections are even smaller in Lake Huron and Lake Superior, the lakes with the smallest TP concentrations.

A simple input–output mass balance was used to estimate diatom production and BSi sedimentation in Lake Erie. In the 1970s, Lake Erie was highly enriched with phosphorus from anthropogenic sources, and hydraulic loading from Lake Huron provided a continuous silica supply to maintain high diatom production (Tables 1, 2). Lake Erie, therefore, can be viewed as a natural chemostat with a short residence time (2.5 yr) that provides real-time results of a nutrient-enrichment experiment (Schelske 1999).

Results

Sediment chemistry—In LS15-94, BSi more than doubled from 12 cm to 6 cm, increasing to 44 mg g^{-1} at 6 cm (Fig. 4). This period of increase began before 1854 (10 cm). Peaks in TP and NAIP at 8 cm (1886) coincided with the period of increase in BSi. Several other peaks in TP and NAIP were found earlier in the core, but none of these affected BSi markedly. BSi was relatively constant from 52 to 12 cm.
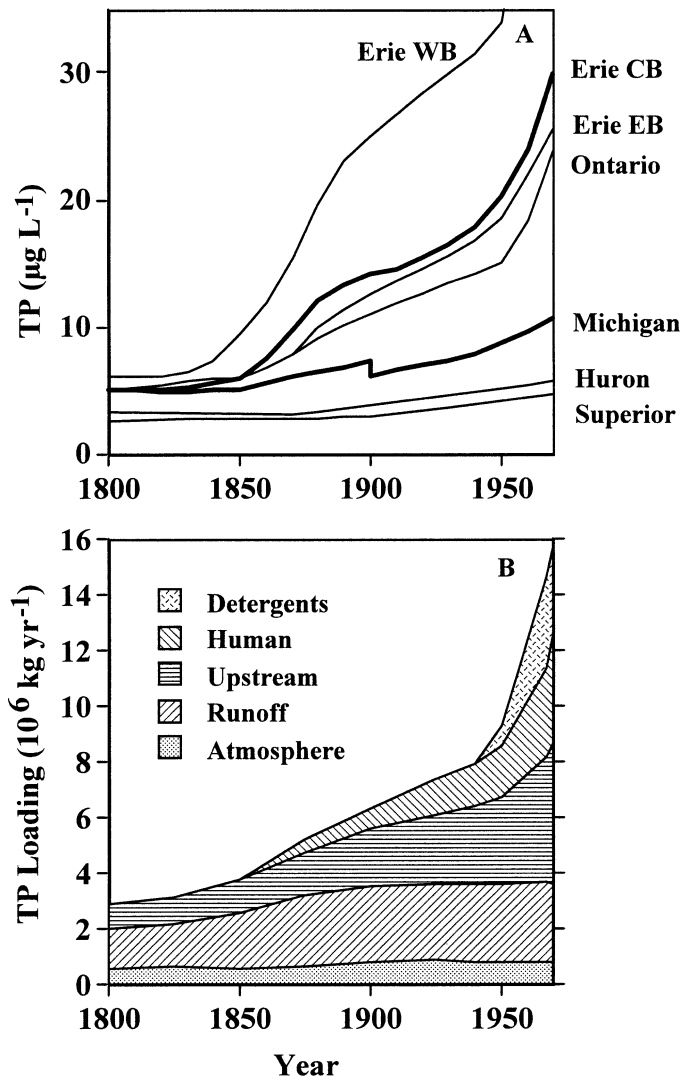

Fig. 3. Historic total phosphorus (TP) concentrations in the Great Lakes (A) and TP loading by source for Lake Ontario (B) (from computer-simulations, Chapra 1977). Western, central and eastern basins of Lake Erie are designated by WB, CB, and EB, respectively.

Both BSi and TP decreased to low levels from 55 cm to the bottom of the core.

Peaks in NAIP and TP at 8 cm affected the BSi:NAIP and BSi:TP stoichiometry in LS15-94 (Fig. 4). This resulted in maxima in BSi:NAIP and BSi:TP in the upper 5 cm and minima at 8 cm in the core. A peak in NAIP:TP also occurred at 8 cm. Peaks in NAIP and TP at deeper depths also produced minima in the BSi:NAIP and BSi:TP stoichiometry. The NAIP fraction was variable over the core, ranging from <0.2 at 31 cm to nearly 0.8 at 7–9 cm.

In LHHS-94, BSi was relatively constant, from 61 cm to 27 cm (1876), and then increased from 7.6 mg g^{-1} at 28 cm to 33 mg g^{-1} in the top sample (Fig. 4). BSi was relatively constant from 17 cm (1944) to 11 cm (1970) and then increased sharply to the top of the core, a section that may include the dissolution front (Fig. 2). TP increased slightly upcore to 11 cm (1970) and then increased sharply to the
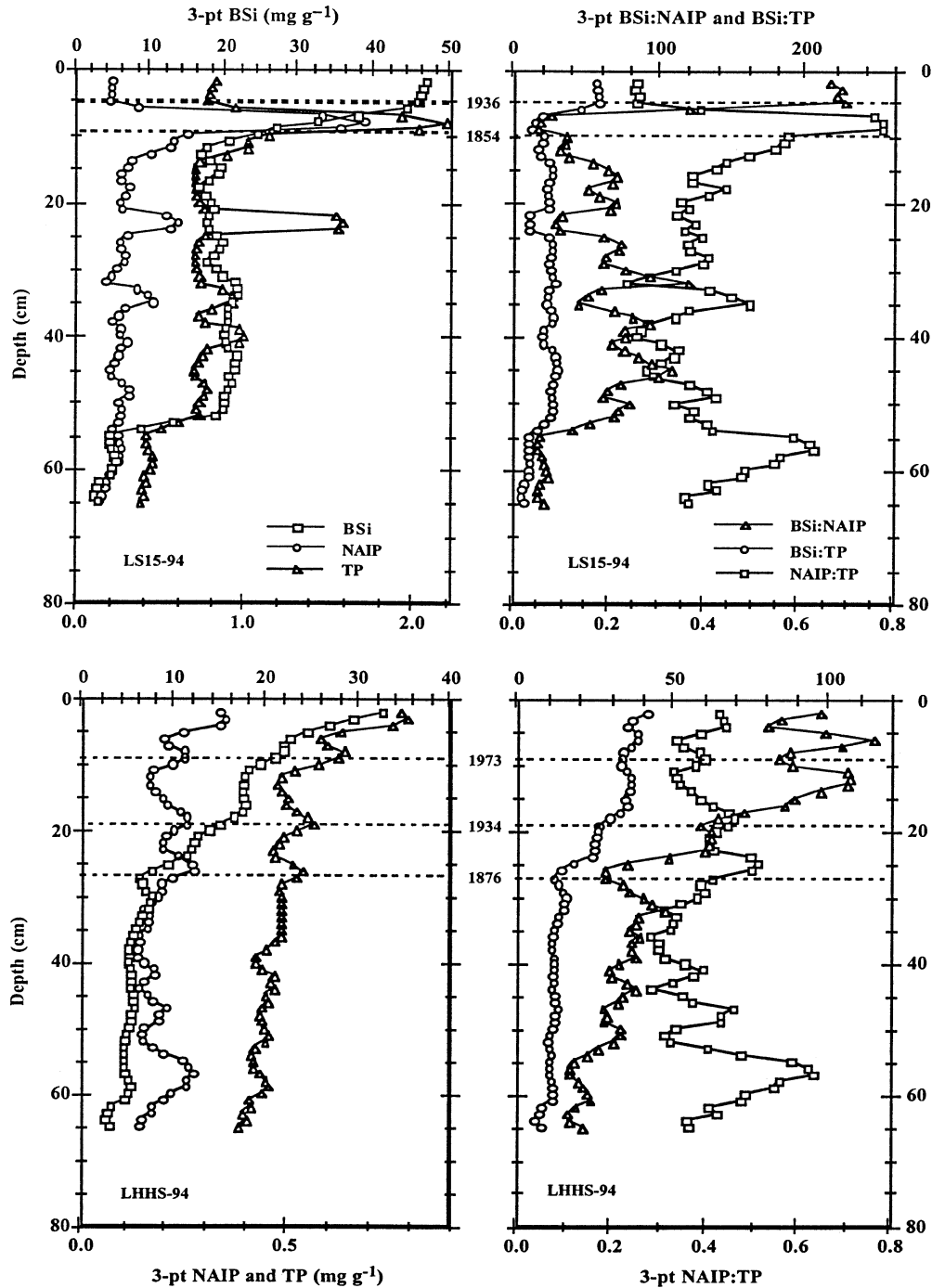
Fig. 4. Depth profiles of biogenic silica (BSi), total phosphorus (TP), and nonapatite inorganic phosphorus (NAIP) and their stoichiometry in sediment cores from Lake Superior and Lake Huron.

surface. NAIP displayed a similar pattern except the peak concentration at 57 cm was nearly as large as that for samples near the core top. Peaks in NAIP and TP were found at 19 cm (1934) and 9 or 8 cm (1973 or 1976) and at other depths in sediments too old for ^{210}Pb dating.

Peaks in NAIP and TP also affected BSi:NAIP and BSi:TP stoichiometry in LHHS-94, producing minima at 9, 19, and 26 cm (Fig. 4). Largest ratios for BSi:NAIP and BSi:TP were found in the dated portion of the core, begin-

ning at 26 cm (1888). Ratios generally increased upcore above this depth and were greater than those in older sediments below this depth. The NAIP:TP ratio varied over the core, with the largest ratios at depth. A peak in ratios at 25 cm (1897) coincided with the rise in BSi and BSi:NAIP and BSi:TP ratios.

In LMK34-94, BSi increased sharply from 60 mg g^{-1} at 11 cm (1945) to >140 mg g^{-1} at 8 cm (1964) (Fig. 5). BSi also increased from 33 mg g^{-1} at 27 cm to 58 mg g^{-1} at 22
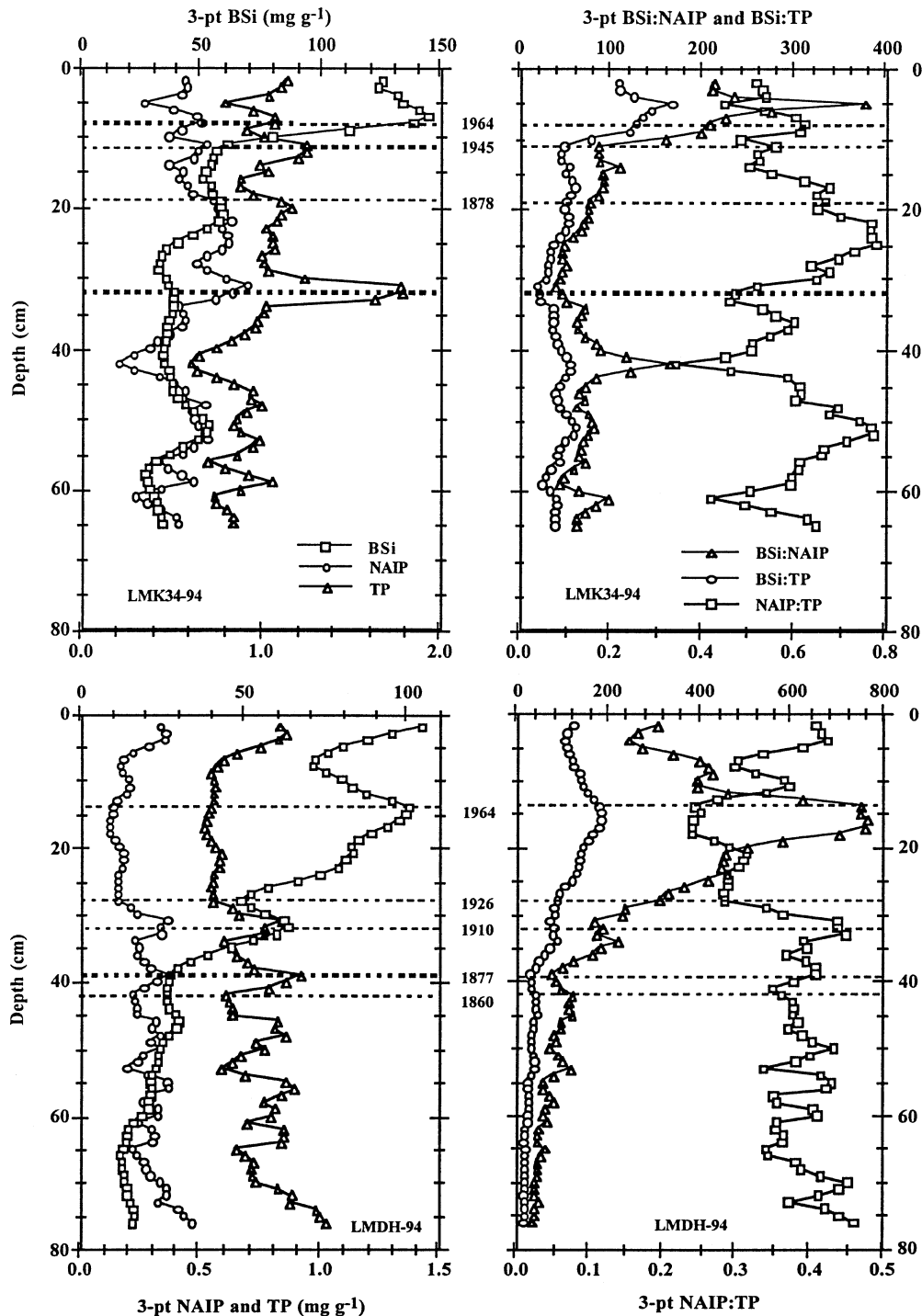
Fig. 5. Depth profiles of biogenic silica (BSi), total phosphorus (TP), and nonapatite inorganic phosphorus (NAIP) and their stoichiometry in sediment cores from Lake Michigan.

cm in sediments older than those dated with [210]Pb (1878 at 19 cm). NAIP and TP were relatively constant over the core, with the exception of peaks at 32 cm and minima at 42 cm. A peak in TP at 11–13 cm (1933–1950) preceded the rise in BSi beginning at 10 cm.

Both BSi : NAIP and BSi : TP increased sharply at 10 cm (1950) in LMK34-94 and both peaked at 5 cm (1980) as the

result of minima in NAIP and TP (Fig. 5). Both also peaked at 42 cm, where NAIP and TP were at minima. The NAIP fraction was variable over the core, reaching maxima at 22–25 cm and 51–52 cm. Except for a peak at 7–9 cm, NAIP : TP was relatively low in the ^{210}Pb-dated portion of the core.

The core from LMDH-94 preserved a long record of

[210]Pb-dated sediments, extending to 1842 at 44 cm (Fig. 5). Pronounced peaks in BSi at 32 cm (1910) and 14 cm (1964) are superimposed on a trend of increased BSi accumulation beginning at 38 cm (1882). The apparent increase in BSi in the upper 6 cm is attributed at least in part to an increase in concentration expected in a dissolution front (Fig. 2). Small peaks in BSi, TP, and NAIP at 45–46 cm provide evidence for increased BSi accumulation earlier in the record. The peak in BSi at 1910 coincided with peaks in TP and NAIP, but the large peak at 1964 was associated with a long, relatively flat record of TP and NAIP. Both TP and NAIP were variable over the core, with some of the largest values being at the base and top of the core.

The BSi : NAIP stoichiometry in LMDH-94 was unusual in that the ratio increased upcore, generally with a sharp increase extending from 38 cm (1882) to peak values from 19 to 14 cm (1954 to 1966) (Fig. 5). These values occurred at the same depths as the lowest NAIP fraction and the largest ratios for BSi : TP. The NAIP fraction varied over the core, with a pronounced record of low values from 28 cm to 13 cm (1926–1968).

The greatest increase in NAIP and TP in LE47-87 began in the 1940s and continued until the early 1970s (Fig. 6). Although there was little or no change in NAIP and TP, a peak in BSi occurred at 64 cm (1894) in a region with poor age resolution. After 1900, BSi accumulation was relatively constant over the remainder of the core. A small increase in BSi beginning in the 1950s was maintained into the 1970s.

The BSi : NAIP and BSi : TP ratios peaked about 1890 in LE47-87 (Fig. 6). High ratios of BSi : TP began below the zone of ^{210}Pb-dated sediments. BSi : TP was high between 58 and 72 cm, with three distinct peaks. Both ratios decreased from the 1950s to the 1970s, during a period when NAIP and TP increased and NAIP fraction was greatest. After the early 1970s, NAIP, TP, and NAIP : TP decreased as the result of phosphorus-abatement strategies (Schelske and Hodell 1995).

In LEG16-93, BSi at 29 cm increased above a baseline beginning below the zone of ^{210}Pb-dated sediments (Fig. 6). BSi increased sharply from 25 cm (1865) to a peak at 18–16 cm (1907–1922). The largest values for BSi were found above 12 cm in sediments deposited after 1948. A noticeable increase in NAIP above the baseline occurred at 25 cm (1865), earlier than the increase in TP at 20 cm (1896) but later than the increase in BSi at 31 cm (too old to date). Both TP and NAIP decreased above 9 and 8 cm (1966 and 1971, respectively).

The BSi : NAIP stoichiometry in LEG16-93 was similar to LMDH-94 in that the ratio increased upcore to a peak; however, the peak period in the Lake Erie core was older, extending from 1878 to 1914 (22–18 cm) (Fig. 6). Increases in BSi : NAIP and BSi : TP began at 29 cm, a few centimeters deeper than the zone of ^{210}Pb-dated sediments. The NAIP fraction increased from 26 cm to a peak at 8 cm (1966), where BSi : TP mirrored the NAIP : TP peak.

Both Lake Ontario cores are characterized by BSi peaks at depths corresponding to the late 1800s (Fig. 7). In LOH32-94, early BSi peaks were found at 73 cm (1867) and 59 cm (1889). In LOG32-93, one early peak was found at 44 cm (1873). Correlation of the BSi peaks in the two cores shows that the average MSR in LOG32-93 is smaller because the peak at 44 cm is shallower than peaks in LOH32-94. During the peak periods, BSi begins to decrease at 42 cm in LOG32-93 and at 50 cm in LOH32-94, indicating an approximately 8-cm offset between cores. BSi also peaked at 15 cm (1971) in LOH32-94 and at 15 cm (1964) in LOG32-93. A pronounced peak in TP coincided with the early BSi peak in LOG32-93. An early TP peak in LOH32-94 was not as pronounced, but NAIP peaked at 59 cm in this core. In both cores, TP and NAIP varied upcore to 19 cm in LOG32-93 (1953) and 26 cm in LOH32 (1950), with essentially no increase in concentration. After 1950, peaks in TP and NAIP in both cores coincided with increases in BSi.

Patterns in BSi : NAIP and BSi : TP stoichiometry were similar in LOG32-93 and LOH32-94 (Fig. 7). Ratios were high and varied in the older portions of the core. After 1970, BSi : NAIP and BSi : TP ratios were lower and varied less, particularly in LOH32-94. Peaks in NAIP fraction were associated with early BSi peaks in the late 1800s. Peaks also occurred at 1964 (LOG32-93) and 1971 (LOH32-94). The NAIP fraction decreased in the upper few centimeters of both cores.

Correlation between NAIP and TP was highly significant in all cores. Correlation coefficients ranged from 0.690 to 0.801 in cores from the upper Great Lakes, except for a coefficient of 0.943 for LMDH-94, and from 0.942 to 0.978 in cores from Lake Erie and Lake Ontario, except for a relatively low value of 0.862 in LOH32-94. Outliers omitted in this analysis were 32 cm from LMK34-94 and 7 cm and 23 cm from LS15-94.

Model results demonstrate the sensitivity of BSi accumulation in sediments to nutrient-driven silica utilization by diatoms in the water column (Fig. 8). Two variables in the model, mean depth and MSR, control output. Therefore, BSi accumulation in Lake Superior was largest because the mean depth (148 m) is greater than in Lake Michigan (84 m) or Lake Huron (53 m) and because modeled MSR was least.

An input/output model shows that 16×10^7 kg SiO_2 yr^{-1} was retained in Lake Erie sediments in the 1970s (Fig. 9). Retention results from diatom production and subsequent BSi sedimentation.

Discussion

Background on eutrophication—Because the Great Lakes are so large, spatial heterogeneity is characterized by inshore–offshore differences in parameters associated with cultural eutrophication (Beeton and Edmondson 1972; Schelske 1988). Sources of phosphorus loading to the lakes with the exception of atmospheric inputs are associated with tributary inputs or point sources along the shoreline (Fig. 3B). From the standpoint of environmental effects, diffuse sources collected in a tributary basin and discharged by the receiving stream are effectively point sources to the lake. Because nutrients in tributaries are discharged at relatively high concentrations, TP concentrations are much greater in shallower nearshore waters (depth <40 m) than in offshore waters (Rousar 1973; Schelske 1988). Problems associated with nearshore nutrient enrichment therefore are apparent when
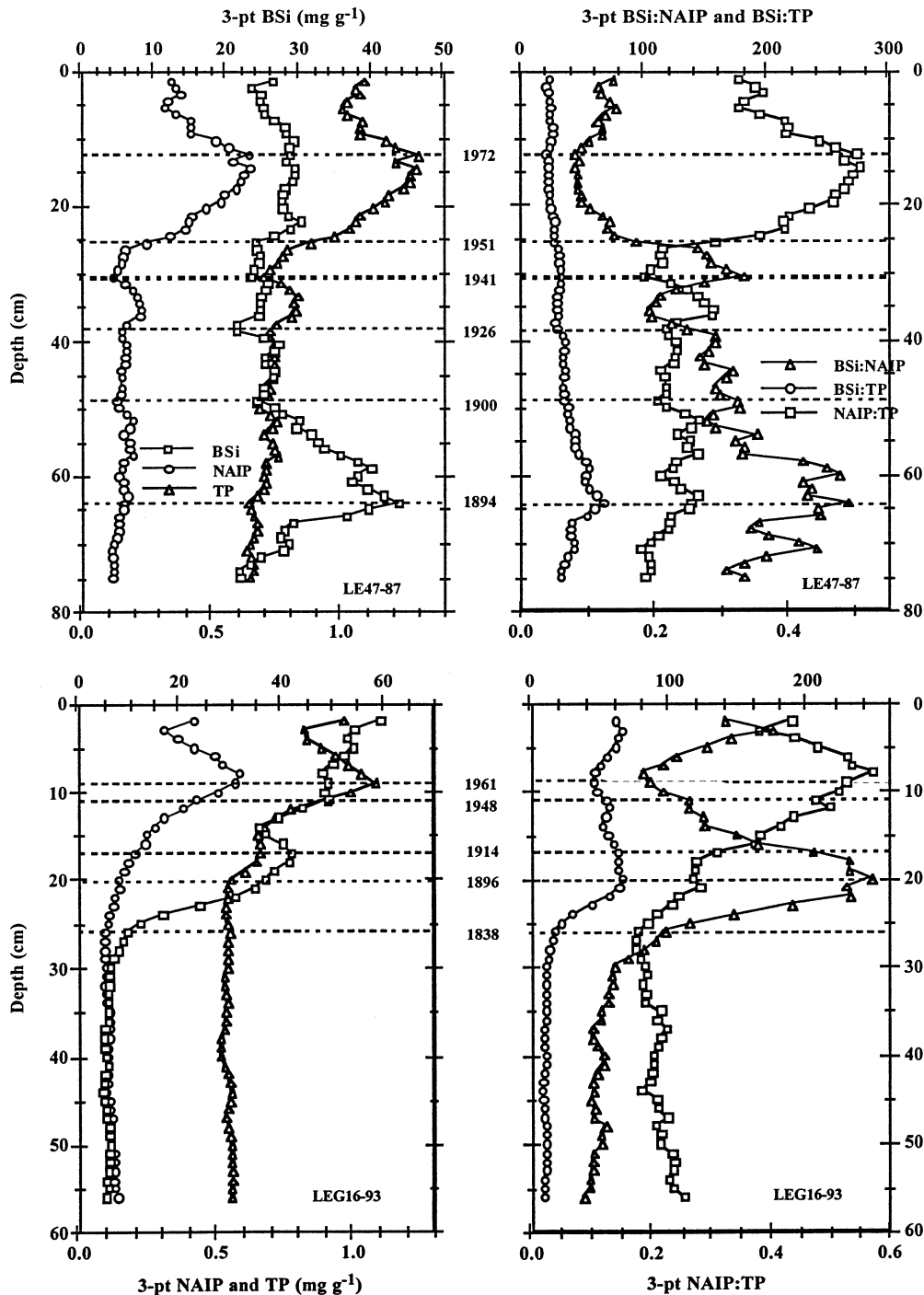
Fig. 6. Depth profiles of biogenic silica (BSi), total phosphorus (TP), and nonapatite inorganic phosphorus (NAIP) and their stoichiometry in sediment cores from Lake Erie.

offshore waters appear not to be affected. Beeton and Edmondson (1972) reported that early studies of the Great Lakes concluded that eutrophication was not a problem and that water-quality problems were restricted to localized nearshore areas and harbors. It later became evident that the symptoms of eutrophication in nearshore areas and harbors were the forerunners of lake-wide water-quality problems.

Eutrophication of the Great Lakes was initially attributed

to enrichment of waters with nitrogen and phosphorus (Schelske 1979), but these lakes are similar to most lakes in that phosphorus is the major nutrient limiting phytoplankton growth (Schelske and Stoermer 1972; Schindler 1977; Hecky and Kilham 1988). That nitrogen is not a cause of eutrophication in the Great Lakes can be supported by comparing chemical data from Lake Superior, the most oligotrophic of the five lakes, with the other Great Lakes (Table 1).
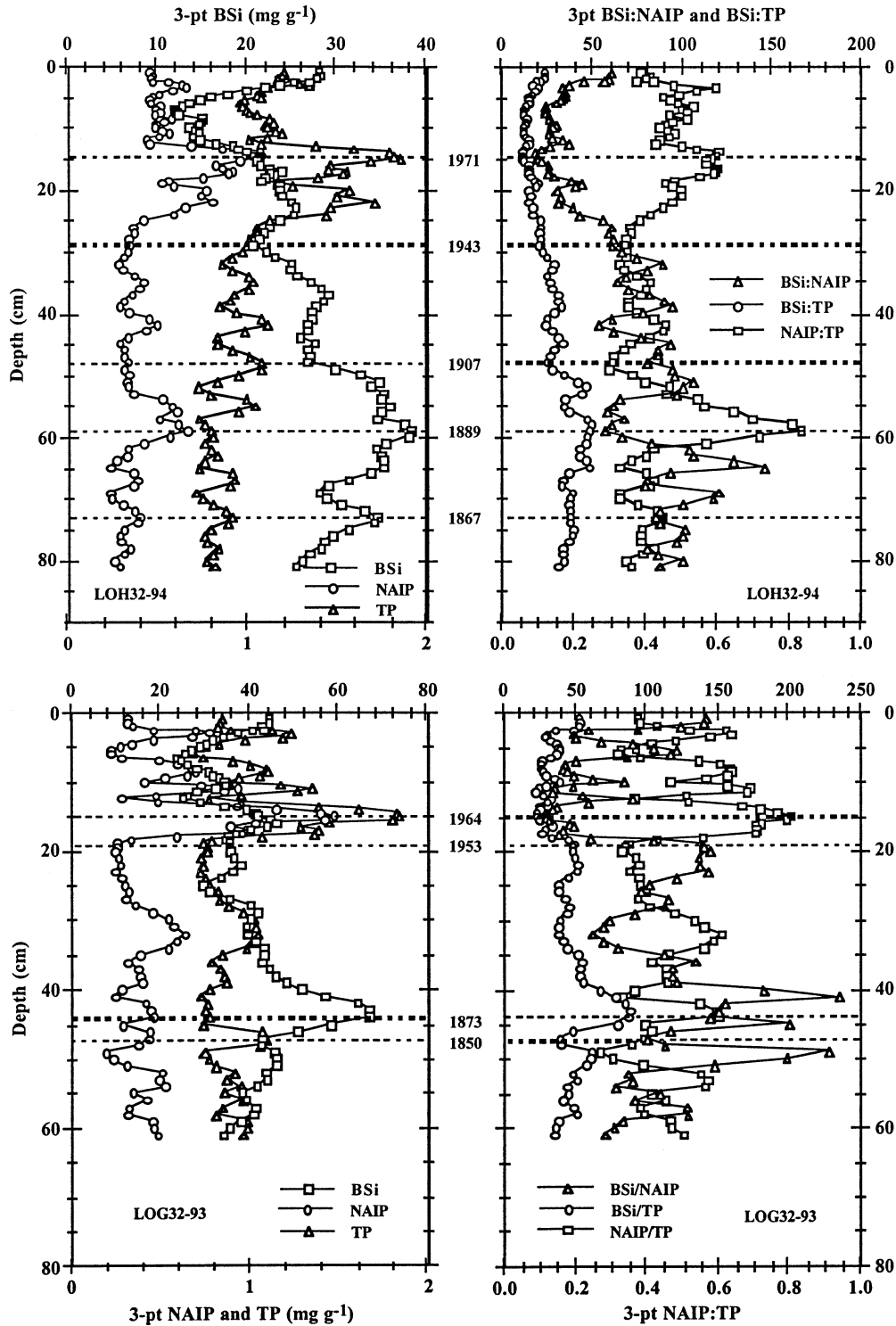
Fig. 7. Depth profiles of biogenic silica (BSi), total phosphorus (TP), and nonapatite inorganic phosphorus (NAIP) and their stoichiometry in sediment cores from Lake Ontario.

Nitrate is the primary form of dissolved inorganic nitrogen in the Great Lakes. The winter maximum concentration in the 1970s was 280 μg L^{-1} (20 μmol L^{-1}) in Lake Superior, nearly as large as in the other Great Lakes during winter–spring isothermal circulation (Table 1). Nitrogen increased

in all lakes after 1970, with the maximum concentration 380 μg L^{-1} (27 μmol L^{-1}) in Lake Ontario in 1998. Part of this increase, as shown by data for Lake Superior, resulted from acid rain (Bennett 1986) and part, as shown by data for Lake Ontario, was due to increased anthropogenic enrichment. In
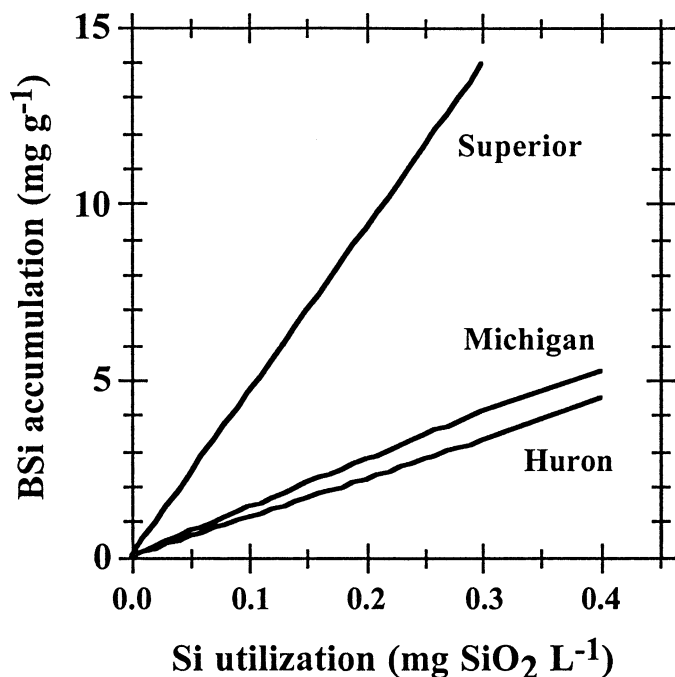
Fig. 8. Sensitivity test of biogenic silica (BSi) accumulation in sediments to nutrient-driven changes in water-column silica utilization (BSi production by diatoms) in Lake Superior, Lake Michigan, and Lake Huron. See text for additional explanation.
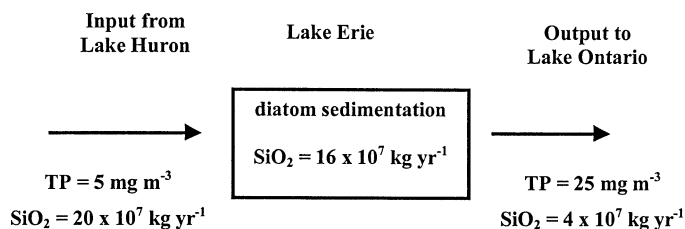

Fig. 9. Using Lake Erie as a natural chemostat in an input/output model of silica dynamics to calculate diatom (biogenic silica) sedimentation in the 1970s. Input and output data for TP and SiO_2 are presented as concentrations. Data from Schelske (1999).

addition, an increase in nitrate since the 1970s can be attributed to a smaller demand for phytoplankton production as the result of smaller phosphorus supplies (Schelske 1975). Phosphorus concentrations in all the lakes except Lake Superior decreased measurably after phosphorus-management strategies were initiated in the early 1970s. Seasonal uptake of nitrate in the lakes in 1998 was smaller than in the 1970s (Table 1), supporting the hypothesis that decreased phosphorus supplies lowered nitrogen demand for phytoplankton production. Pronounced seasonal cycles in nitrate concentration for all the lakes except Lake Superior provide additional evidence that phosphorus supplies regulate phytoplankton production and nitrate utilization in the Great Lakes.

Seasonal changes in epilimnetic nitrate and silica can be used to assess secondary nutrient limitation by either of these nutrients (Schelske 1984). Such seasonal limitation, where it occurs, is one of the consequences of phosphorus enrichment of lake waters (Schelske 1975). Comparison of nitrate data across lakes reveals that secondary nitrate limitation occurred historically only in Lake Ontario and Lake Erie and possibly in some other phosphorus-enriched areas, such as inner Saginaw Bay and lower Green Bay (Schelske 1975). In these systems, nitrogen limitation developed in the 1970s, when TP concentrations were 27 μg L^{-1} (0.87 μmol L^{-1}) in Lake Ontario (Table 1). Secondary silica limitation also results from excessive phosphorus enrichment, but compared with nitrogen limitation, it develops at relatively low phosphorus concentrations in the Great Lakes (Schelske 1975). Seasonal epilimnetic silica limitation in the late 1960s was evident from water-column data for Lake Michigan, when TP concentrations averaged 8.3 μg L^{-1} (0.27 μmol

L^{-1}) (Schelske 1988). Seasonal epilimnetic silica limitation in the 19th century was inferred from paleolimnogical records in Lake Erie and Lake Ontario (Schelske et al. 1983). Water-column silica limitation or severe silica limitation characterized Lake Ontario and Lake Erie in the 1970s, when TP concentrations reached 25 μg L^{-1} (Schelske et al. 1986a). Under severe silica limitation, diatom growth is silica limited throughout the year in the entire water column, not only seasonally in epilimnetic waters. Thus, both nitrate and silica became secondary limiting nutrients in response to excessive phosphorus enrichment and represent consequences of cultural eutrophication.

Seasonal and severe silica limitation can be inferred from data on areal silica utilization in the water column (Fig. 10). Although areal silica utilization in Lake Michigan is greatest, epilimnetic diatom production is limited seasonally by silica supplies during summer stratification. By contrast, large reservoirs of silica are not utilized for diatom production in Lake Superior and Lake Huron, lakes with the smallest mean TP concentrations. Because of severe silica limitation, diatom production in Lake Ontario and the eastern basin of Lake Erie occurs mainly during winter–spring isothermal mixing. Experimental studies show that diatom production is important under low light and nutrient conditions associated with isothermal mixing (Fahnenstiel et al. 2000), leading to BMSD during winter–spring isothermal mixing (Schelske et al. 1986a).

Effects of BMSD are reflected in structural modifications of some diatom species and changes in assemblage composition. Specimens from pre-European settlement assemblages are generally more robust and more silicified than their more recent counterparts (Stoermer et al. 1985b) and some populations exhibit systematic changes in morphology and silicification as BMSD becomes more pronounced (Stoermer et al. 1985c). As BMSD intensifies, members of the so-called oligotrophic *Cyclotella* association (Hutchinson 1967), which usually occupy the summer deep chlorophyll maximum (Moll and Stoermer 1982; Fahnenstiel and Glime 1983), are replaced as water transparency decreases. Importance of the interplay between BMSD and transparency is demonstrated by the fact that these populations return to Lake Erie almost immediately after zebra mussel (*Dreissena polymorpha*) and quagga mussel (*D. bugensis*) filtering increased water transparency (Stoermer et al. 1996). First replacements are species with low temperature requirement (Stoermer and Ladewski 1976; Stoermer et al. 1985b) that can exploit hypolimnetic silica stores during winter–spring
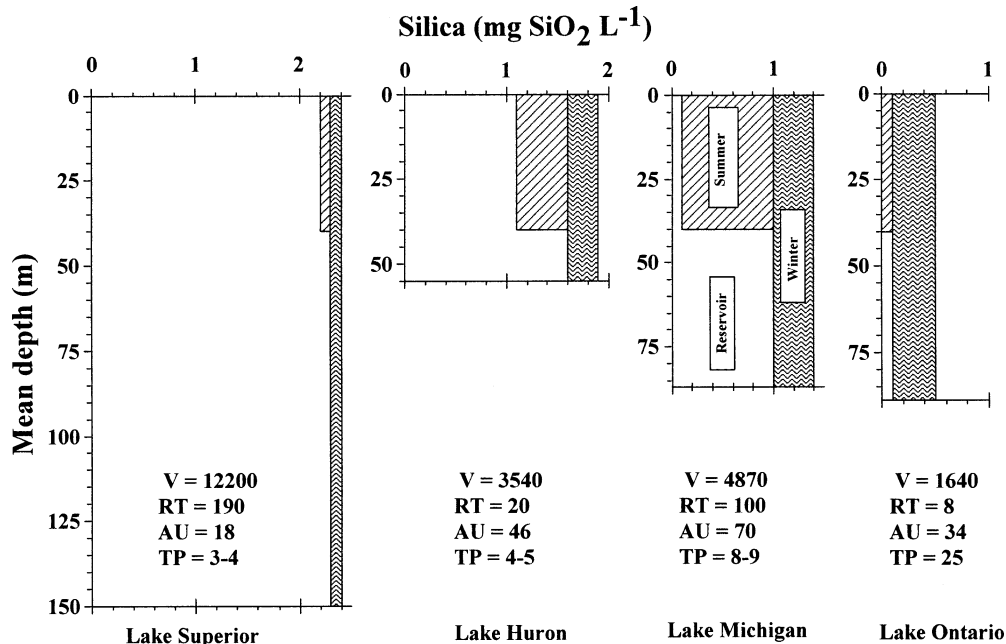
Fig. 10. Annual silica utilization and silica reservoirs by mean depth in Lake Superior, Lake Huron, Lake Michigan, and Lake Ontario in the early 1970s (from Schelske 1999). Annual utilization (AU) in g SiO_2 m^{-2} yr^{-1} is the sum of summer epilimnetic utilization and winter–spring isothermal utilization. Units for lake volume (*V*), hydraulic renewal time (*RT*), and total phosphorus (*TP*) are 10^3 m^3, 10^9 m^3 yr^{-1}, and μg L^{-1}, respectively. See text for additional explanation.

isothermal circulation. These species usually persist in modern assemblages, but some have been eliminated from Lake Ontario (Stoermer et al. 1989). Terminal replacements are species with prolonged vegetative survival capability as meroplankton (Sicko-Goad et al. 1989), the growth of which is effectively decoupled from nutrient concentrations in the water column (Schelske et al. 1995). These species can assimilate nutrients at the sediment–water interface and readily occupy upwelling regions during summer (Stoermer et al. 1981). Several of these species are probably invasive but became biomass dominants in relatively shallow areas of the Great Lakes during maximum eutrophication (Hohn 1969).

Computer simulations provide historic TP concentrations in the Great Lakes from 1800 to 1970 (Fig. 3). Reliable TP data from water-column sampling of Lake Ontario overlap the computer-simulated concentrations. These data show that the concentration peaked in the early 1970s and then decreased sharply later in the decade (Schelske and Hodell 1991). The decrease was the direct result of phosphorus abatement measures instituted by the 1972 Water Quality Agreement between the United States and Canada. In Lake Ontario, TP concentration decreased from a mean of 25 μg L^{-1} to about 12 μg L^{-1} by 1990. An additional decline in TP in the 1990s was attributed to the zebra mussel invasion and population explosion beginning in 1991 (Makarewicz et al. 2000). These filter-feeding mollusks remove particulate materials from the water—this process apparently contributed to the decline in TP concentration. By 1994, summer TP concentrations in all the Great Lakes, with the exception of the western basin of Lake Erie, were <10 μg L^{-1} (Table

1), levels near those simulated by Chapra (1977) for the mid-1800s (Fig. 3).

The best historic record of silica depletion is from Lake Michigan because historic decreases have been verified with independent approaches (Schelske 1988). Comparing water-column data collected in 1954–1955 with data from 1969–1970 clearly demonstrates that summer minimum and winter maximum silica concentrations decreased rapidly in 15 yr. The summer epilimnetic minimum decreased from 2.2 to <0.2 mg L^{-1}, or about 2.0 mg L^{-1}. The winter maximum decreased even more from 4.5 to 1.4 mg L^{-1}. If this decrease in the entire water mass were 3.0 mg SiO_2 L^{-1}, it represented a silica loss of 15×10^9 kg in a short period. The pattern of silica depletion in Lake Michigan between 1954 and 1969 provides evidence for a catastrophic change in silica concentration and a dramatic diatom response to low-level phosphorus loading at the ecosystem level.

Data needed to establish historic trends in silica concentrations in the other Great Lakes are either limited or not available. Reliable data for all the lakes became available in the late 1960s and early 1970s, but by this time, silica concentrations had decreased markedly in all of the lakes except Lake Superior (Table 1). Silica concentrations in all the lakes except Lake Superior undoubtedly were greater in the early 1800s before land clearance and early settlement. The rapid decrease in silica in the 1950s and 1960s lowered the output concentration from Lake Michigan and reduced silica input and concentration in Lake Huron (Schelske 1985*b*). This, combined with increased silica demand for diatom production, would have lowered concentrations in the lower lakes.
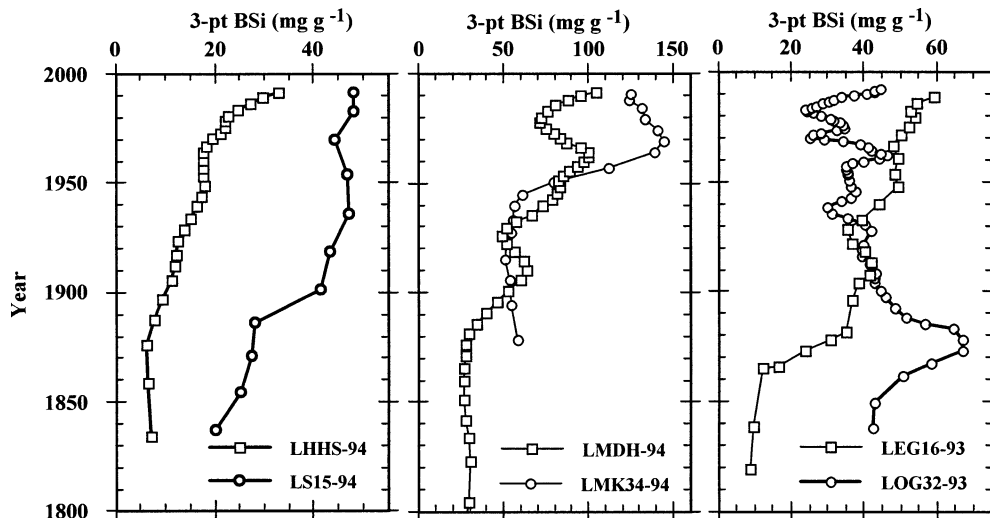
Schelske et al.

Fig. 11.   Biogenic silica (BSi) accumulation versus date in Great Lakes sediment cores.

We can infer, therefore, that silica concentrations in the lower lakes were higher historically than those measured in the 1970s.

Comparing water-column silica data with simulated TP loading by source shows that BMSD in Lake Michigan developed coincidentally with the large increase in TP loading from sewage and phosphate-based detergents beginning in the late 1940s (Schelske et al. 1986*b*). Historic data on water-column TP concentrations are not adequate to investigate time course or its magnitude. Reliable data are available for the 1970s when offshore TP concentrations averaged 8.3 μg L^{-1} (Rousar 1973). This TP concentration represents a relatively small increase compared with the computer-simulated TP concentration in the 1950s and 1960s (Fig. 3). Detecting such a small change is complicated by the large area and volume, nearshore–offshore differences, spatial and seasonal variability, and sampling errors inherent in such a complex system (Schelske 1988). It is questionable, therefore, whether the relatively small change in TP concentration associated with silica depletion could be detected on decadal scales in such large lakes using routine techniques.

BMSD by contrast is defined as a readily measurable ecosystem response to phosphorus enrichment that affects not only nearshore waters but also the entire water mass (Schelske 1988). For example, epilimnetic silica concentrations in southern Lake Michigan in the summer of 1955 were reduced compared with those in deeper offshore waters in the northern part of the lake. This pattern, which represents a clear signal of eutrophication, was attributed to increased silica utilization by diatoms (Lund 1965). A signal of lake-wide response, however, was not observed until 1969 (Schelske 1988). This distinction is important because the nearshore zone in Lake Michigan represents 25% of the lake surface area (approximately 14,500 km^2), but only 5% of the lake volume. Therefore, changes in the nearshore are not necessarily indicators of whole-lake or ecosystem changes (Schelske 1988).

Sediment BSi accumulation—Sediment records of BSi accumulation for each of the Great Lakes (Fig. 11) can be evaluated relative to the hypothetical model relating BSi accumulation and phosphorus enrichment (Fig. 2) and water-chemistry data for each lake (Table 1). Lake Superior and Lake Huron, with the lowest mean TP concentrations, are also lakes in which diatom growth is not limited by silica supplies in the water column. Consequently, diatom growth in these lakes is phosphorus limited (Schelske et al. 1986*a*). In the sediment record, BSi accumulation has increased historically with no indication of a peak. Therefore, the record supports the first hypothesis based on the hypothetical model and is evidence that historic phosphorus supplies have increased in both Lake Superior and Lake Huron. Profiles of BSi and changes in microfossil community structure in other cores from these lakes confirm the conclusion about the effect of low-level phosphorus enrichment on diatom production (Stoermer et al. 1985*a*; Wolin et al. 1988). Findings are particularly significant in that these results show that Lake Superior is not pristine because the lake has been affected by phosphorus enrichment not detected by water-column chemical measurements.

Lake Michigan also has a relatively low TP concentration compared with the lower lakes (Table 1), but BMSD developed rapidly in this lake, beginning in the 1950s, as the result of low-level phosphorus enrichment (Schelske 1988). Sediment records show BSi accumulation increased after 1950 in LMK34-94 and LMDH-94 and clearly decreased after 1970 in LMDH-94 (Fig. 11). These peaks support the second hypothesis based on the hypothetical model that predicts silica limitation in response to phosphorus enrichment (Fig. 2). Increased phosphorus loading from human sources (sewage and phosphate-based detergents), beginning in the late 1940s, provided phosphorus supplies required for the silica-limited diatom response (Schelske et al. 1986*b*). Resolution of the peak in BSi accumulation compared with other cores collected in 1983 at the same sites (Schelske et al. 1986*b*) is improved with additional sediment accumulation over the 11-yr interim. That the peak is deeper in LMDH-94 than in LMDH-83 provides evidence the inferred signal of epilimnetic silica depletion at depth is being buried per-

manently as part of the historic record. A dissolution front (Fig. 2) is present in the upper few centimeters of both cores. Lake Michigan records (LMDH-94 and LMDH-83) also show an increase in BSi accumulation in the late 1800s, a response that is inferred to represent increased phosphorus loading from early settlement and land clearance. The peak in BSi accumulation in 1910 mirrored a pulse in TP that is inferred to represent a pulse in TP loading. We infer that this pulse in TP loading increased diatom production and BSi accumulation in an event that was too brief to induce silica limitation.

Compared with the upper lakes, Lake Ontario and the eastern basin of Lake Erie had relatively high TP concentrations and water-column silica depletion in the 1970s (Table 1). Because long-term water-quality data are not available, the time course of silica depletion must be inferred from BSi accumulation in the sediment record. A peak in BSi accumulation in the mid- to late 1800s in both lakes was found previously (Schelske et al. 1983) and in LE47-87, LOG32-93, and LOH32-94 (Figs. 6, 7, 11). Thus, the second hypothesis of the hypothetical model is supported during the period when early settlement and land clearance by Europeans increased phosphorus loading to the lake. It also can be inferred from the time course of simulated TP loading (Fig. 3) that epilimnetic silica depletion developed at a relatively low TP concentration (<10 μg L^{-1}). Similar to the peak in BSi accumulation in Lake Michigan, these peaks in the lower lakes also developed over a relatively short time of a decade or two. Small peaks or increases in BSi accumulation beginning in the 1940s in LOG32-93 and LOH32-94 (Fig. 11) that are inferred to reflect water-column silica depletion (Schelske et al. 1986a) support the third hypothesis based on the hypothetical model. Combining data from nutrient-enrichment experiments (Schelske et al. 1986a) and diatom microfossils and BSi accumulation in the sediment record (Stoermer et al. 1985b; Schelske et al. 1988) leads to the conclusion that water-column silica depletion developed after the 1940s as a consequence of increased urban phosphorus loading, primarily from sewage and phosphate-based detergents (Fig. 3).

The BSi accumulation record in LEG16-93 in the central basin of Lake Erie differs from other cores from Lake Erie and Lake Ontario in that BSi accumulation generally increased after 1870 in this core (Fig. 11) and in a 1983 core from this station (Schelske et al. 1986b). Inferred diatom production that generally increased since the 1870s depends on high silica loading from Lake Huron that provides a continuous silica supply and maintains high diatom production in nutrient-enriched waters of Lake Erie (Fig. 9). A simple input/output model shows that at least 0.16×10^9 kg SiO$_2$ yr^{-1} is retained in Lake Erie. Calculated retention is 0.11×10^9 kg SiO$_2$ yr^{-1} if mean SiO$_2$ concentrations from Table 1 are used. Large inferred BSi retention results from diatom production stimulated by anthropogenic phosphorus loading to the lake. Calculated BSi sedimentation in Lake Erie is conservative because silica loading from tributaries is not included. Although large, it is less than the average rate of loss (1.0×10^9 kg SiO$_2$ yr^{-1}) during the 15-yr period of rapid silica depletion in Lake Michigan (Schelske 1985a). The rate in Lake Michigan is greater because a larger silica
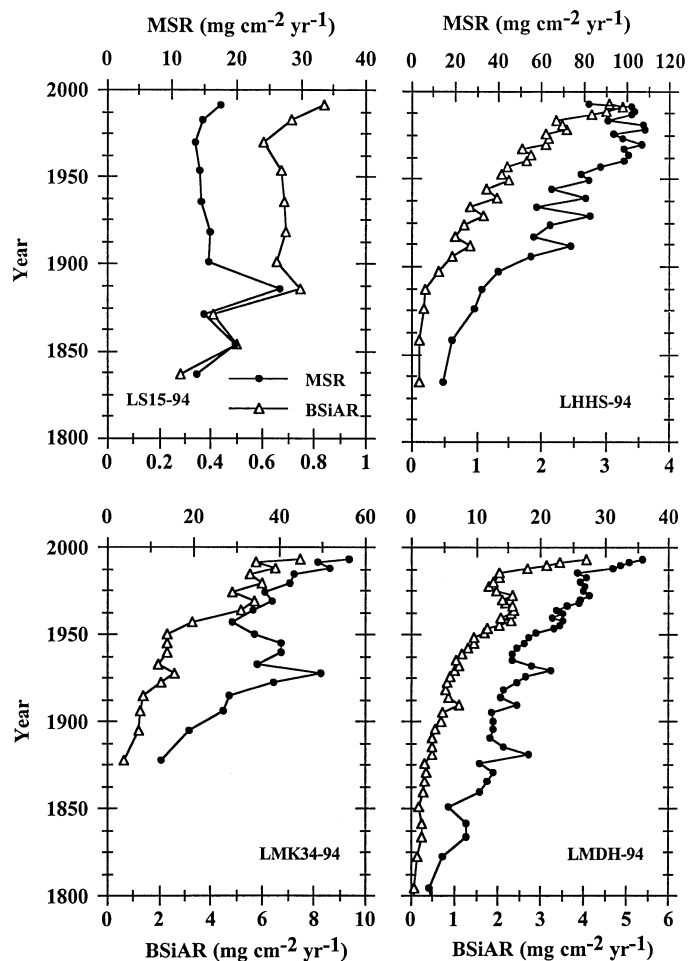

Fig. 12. Mass sedimentation rate (MSR) and biogenic silica accumulation rate (BSiAR) versus date for Lake Superior, Lake Huron, and Lake Michigan sediment cores.

reservoir could be utilized for diatom production in the larger and deeper water mass. Thus, diatom production fueled by continuous silica loading and anthropogenic phosphorus enrichment explains an apparently anomalous record of continued high BSi accumulation in the central basin of Lake Erie.

Data on BSi accumulation are based on BSi concentrations in sediments (Figs. 4–7, 11). Such data do not account for variability in MSR that determines BSiAR. If we assume a constant fraction of diatom production is sedimented, BSiAR can be used as a proxy for diatom production. To evaluate this rate as a proxy, we calculated BSiAR and plotted these data for comparison with MSR (Figs. 12, 13). In cores from the upper Great Lakes, BSiAR increased historically at about the same or at a greater rate than MSR. Two cores from the lower lakes (LE47-87 and LOG32-93) have different patterns of MSR and BSiAR. In these cores, BSiAR peaked during early European settlement in the late 1800s and then decreased as a response to silica-limited diatom growth as predicted by the hypothetical model (Fig. 2). In a third core from the lower lakes (LEG16-93), BSiAR in-
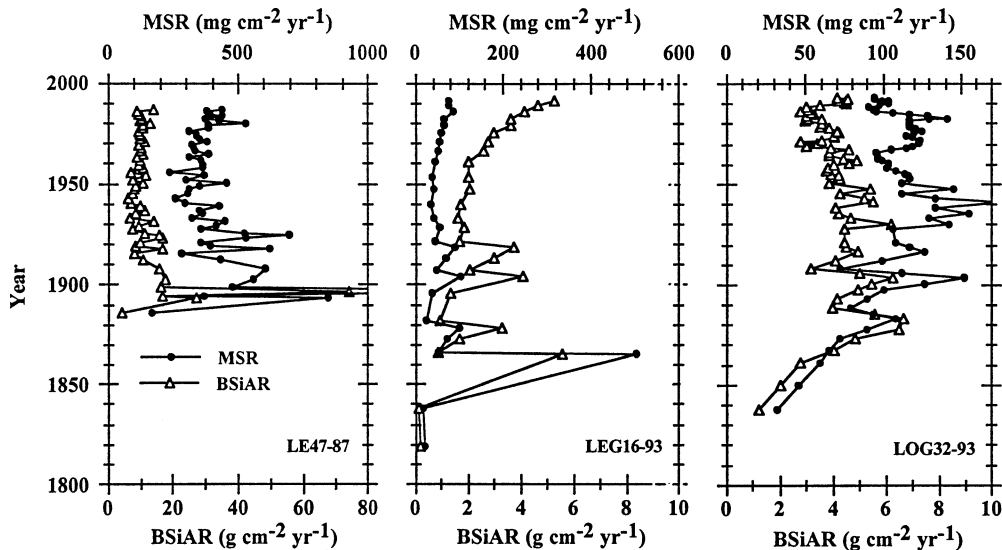
Fig. 13. Mass sedimentation rate (MSR) and biogenic silica accumulation rate (BSiAR) versus date for Lake Erie and Lake Ontario sediment cores.

creased sharply after European settlement and then, after 1920, increased moderately but at a greater rate than MSR.

In cores from the upper Great Lakes, BSiAR provides a proxy for the historic response of the diatom community to increased phosphorus loading (Fig. 12). For the Lake Superior core, this proxy indicates diatom production approximately doubled in the late 1800s and remained relatively constant over the remainder of the record, a pattern similar to that for BSi concentration (Fig. 11). Increased diatom production inferred from either proxy, therefore, is not affected by MSR. For the Lake Huron core, increased diatom production also is inferred from either proxy, although MSR increases over a large portion of the core.

Patterns for the two proxies differ for the two Lake Michigan cores (Fig. 12). For LMK34-94, diatom production inferred from BSiAR increased from the late 1800s to 1950, then increased rapidly for about 15 yr until the 1960s, and then increased more slowly over the remainder of the record. This last period of increase includes sediments in the zone of diagenesis. By contrast, diatom production inferred from BSi concentration increased sharply after 1950, peaked about 1970, and then decreased. For LMDH-94, diatom production inferred from BSiAR appeared to increase exponentially until about 1960, peaked from about 1955 to 1970, and then decreased, with the exception of a zone of diagenesis represented by the upper 4 or 5 cm. The peak in BSi concentration at about 1910 corresponds to a smaller peak in the BSiAR profile. Increased diatom production after 1950 can be inferred from either proxy in both Lake Michigan cores. However, only LMDH-94 shows peaks in both proxies for silica depletion that occurred between 1954 and 1969. Thus, BSiAR is a valid proxy for epilimnetic silica depletion in LMDH-94 but not in LMK34-94.

A model tested the sensitivity of BSi accumulation in Lake Superior sediments to nutrient-driven silica utilization in the water column (Fig. 8). The output shows that BSi accumulation increases 10 mg g^{-1} when annual silica utili-

zation in the water column is 0.21 mg SiO$_2$ L^{-1} (3.5 μmol L^{-1}). This annual silica utilization is essentially the same as the annual change in water-mass silica concentration (Table 1; Fig. 10). Because 95% of the silica is recycled, calculated BSi accumulation would result in only a small net change in water-mass silica concentration (0.01 mg SiO$_2$ L^{-1}, 0.17 μmol L^{-1}). The amount of P required to utilize 3.5 μmol L^{-1} Si for diatom production can be calculated using the Si:P ratio in diatoms and the Redfield atomic ratio (106 C:16 N:16 Si:1 P). Dry weight Si:C atomic ratios for freshwater diatoms, which are larger than those for marine forms (Conley et al. 1989), ranged from 0.26 to 1.52 (Sicko-Goad et al. 1984). Using these limits, Redfield atomic ratios range from 106:16:28:1 to 106:16:162:1. If the Si:P ratio in diatoms was 95:1, the average of the two estimates, then P enrichment necessary to utilize 3.5 μmol L Si is only 0.037 μmol L^{-1} (1.1 μg P L^{-1}). This P enrichment is less than the modeled historic increase in TP (Fig. 3), and the modeled increase in BSi accumulation is roughly equivalent to the historic increase in BSi accumulation found in LS15-94 (Fig. 11). MSR for the Lake Superior core averaged <20 mg cm^{-2} yr^{-1} (Fig. 12), less than half the input value. Therefore, this model input parameter (average MSR of 40 mg cm^{-2} yr^{-1}) is conservative.

BSi accumulation in the model also is very sensitive to the BSi recycling rate because it has a large effect on BSi sedimentation (Schelske 1985a). If the rate were 97.5% instead of 95%, BSi accumulation decreases by half, and if the rate were 90%, BSi accumulation doubles. A 95% recycling rate was used for silica mass balances in Lake Michigan (Schelske 1985a). Recycling in Lake Superior, however, may be smaller because the water temperature is colder than the other lakes and alkalinity and pH are lower. The model provides strong evidence that, contrary to other models (Johnson and Eisenreich 1979), diatom assemblages in Lake Superior respond to low-level phosphorus enrichment. Despite uncertainties in input parameters and possible outcomes

given different assumptions, the model clearly demonstrates that BSi accumulation in sediments can be affected by environmentally undetectable changes in water-column silica concentrations driven by environmentally undetectable changes in nutrient enrichment of this large, relatively pristine lake.

We used BSi accumulation in the sediment record to infer how environmental consequences of low-level phosphorus enrichment were mediated historically by diatom assemblages in the Great Lakes (Fig 11). Diatom assemblages responded with BSi accumulation that increased in Lake Superior and Lake Huron, with mean TP concentrations of 4 μg TP L^{-1} and 5 μg TP L^{-1}, respectively (Table 1). Phosphorus enrichment in these large lakes with small TP concentrations may not be detectable on short time scales with routine water-column sampling. Consequently, inferred historical phosphorus enrichment in these lakes has not been reported from water-column measurements, but has been inferred from analysis of microfossil diatom assemblages (Stoermer et al. 1985*a*; Wolin et al. 1988). In Lake Michigan (8.3 μg TP L^{-1}), a peak in diatom production and BSi accumulation in the sediments was inferred to represent epilimnetic silica depletion that developed over a 15-yr period in the 1950s and 1960s. Inferred phosphorus enrichment for this signal coincided with a period of increased loading from urban sources. Epilimnetic silica depletion was also inferred from sediment records in Lake Erie and Lake Ontario, but this inferred consequence of phosphorus enrichment occurred in the late 1800s, when TP concentrations were <10 μg TP L^{-1} (Schelske et al. 1983). A secondary peak in BSi accumulation in these lakes in the 1950s and 1960s was inferred to represent severe silica depletion (Schelske et al. 1986*a*), a result of additional phosphorus enrichment (25 μg TP L^{-1}). These results support three hypotheses based on the hypothetical model of BSi accumulation in the sediments (Fig. 2).

Sediment nutrient stoichiometry—To account for recalcitrant phosphorus, the NAIP fraction of sedimentary phosphorus has been proposed as an index of phosphorus availability in Great Lakes sediments (Williams et al. 1980). We investigated relative changes in the NAIP fraction using the NAIP:TP ratio. In Lake Erie and Lake Ontario cores, ratios are large after the 1940s, when phosphorus loading from urban sources increased exponentially (Fig. 3) and then decreased in response to phosphorus remediation in the 1970s. Examples are LE47-87, LEG16-93, LOG32-93, and LOH32-94 (Figs. 6, 7) and other Lake Erie cores (Schelske and Hodell 1995). A high ratio of biologically available phosphorus would be expected in anthropogenic sources affected most by remediation measures.

Compared with the two lower Great Lakes, profiles of the NAIP fraction differ in cores from the upper lakes. Peaks in NAIP:TP were found over the sediment record in LS15-94, LHHS-94, and LMK34-94 (Figs. 4, 5). The NAIP:TP ratio ranged from 0.4 to 0.8 in LMK34-94 and peaked at 0.45 in LMDH-94. Because many of these peaks occur in sediments too old for ^{210}Pb dating, we believe they may be related to stochastic events. One possibility is atmospheric and tributary inputs of ash and other debris from forest fires (Stoermer et al. 1990*b*). The variable record of NAIP:TP in the
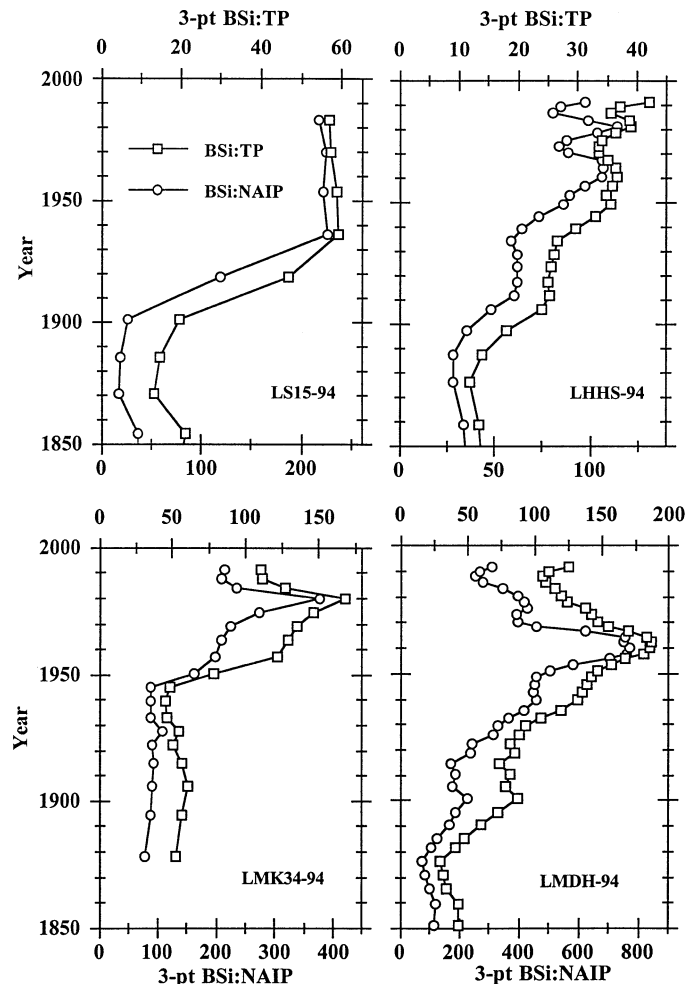

Fig. 14. Biogenic silica:total phosphorus (BSi:TP) and biogenic silica:nonapatite inorganic phosphorus (BSi:NAIP) versus date in Lake Superior, Lake Huron, and Lake Michigan sediment cores.

older sediments of LMDH-94, a station in Grand Traverse Bay, may be related to its proximity to a forested landscape. The ratio at this station was markedly lower during the period from 1926 after the forests were cleared to the early 1960s and then was relatively large after 1970. We infer that sources of urban and agricultural phosphorus were relatively small until the 1960s. We hypothesize that accelerated population growth and agriculture in the shoreline counties of Grand Traverse Bay provided an increased supply of NAIP in the 1960s and 1970s. In summary, the NAIP fraction was affected mainly by anthropogenic activities associated with urban growth in the lower Great Lakes and by anthropogenic as well as stochastic events in the upper Great Lakes.

The stoichiometry of BSi:NAIP and BSi:TP can be related to the history of phosphorus loading in the Great Lakes (Fig. 3). Profiles of BSi:NAIP and BSi:TP in Lake Superior and Lake Huron, the two lakes that have not experienced silica depletion, follow similar patterns with time (Fig. 14). Both increase after 1900 and reach maximum levels after 1950, with no clear indication of a decrease that would be indicative of BMSD. They differ in that ratios in LHHS-94
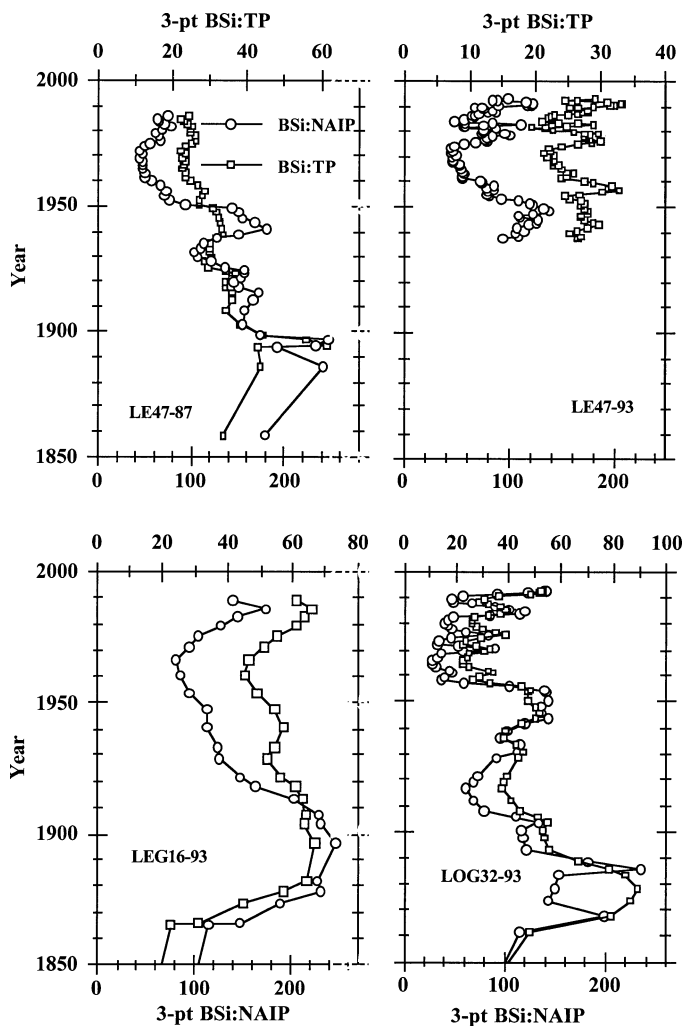
Fig. 15. Biogenic silica:total phosphorus (BSi:TP) and biogenic silica:nonapatite inorganic phosphorus (BSi:NAIP) versus date in Lake Erie and Lake Ontario sediment cores. Note: different time scale for LEG16-93, a core too short for ^{210}Pb dating.

appear to increase in two steps. The first increase occurred after 1900, when land runoff associated with forest clearance was an important source of TP, and the second after 1940, when urban sources of phosphorus loading increased. In LHHS-94, BSi:NAIP varied after 1950 due to changes in the NAIP fraction that are inferred to represent increased urban phosphorus loading. In Lake Michigan cores, profiles of BSi:NAIP and BSi:TP stoichiometry have similar patterns, but peaks in both cores occur after 1950. The peaks are inferred to represent a signal of epilimnetic silica depletion that developed lake wide by 1969 (Schelske 1988).

Profiles of BSi:NAIP and BSi:TP stoichiometry in Lake Erie and Lake Ontario, the two lakes with severe silica depletion, differ from those in the upper lakes in that the ratios peaked before 1900 (Fig. 15). This pattern in LE47-87 and LOG32-93 is inferred to represent development of epilimnetic silica depletion in the two lakes in response to early European settlement (Schelske et al. 1983). The profile in LEG16-93 must be interpreted differently because silica sup-

plies in Lake Erie were maintained by loading from Lake Huron (Fig. 9). Consequently, BSi accumulation increased upcore after 1870 because diatom production was not limited by silica supplies (Fig. 11). BSi:NAIP and BSi:TP ratios increased after 1870 and remained high until about 1910. The decrease in ratios after the peak period is inferred to represent increased phosphorus loading, particularly NAIP from urban sources. We hypothesize that low ratios in the 1950s and 1960s represent a period when TP and NAIP enrichment was high and when silica loading may not have been adequate to supply demands for diatom growth at the elevated phosphorus levels. Ratios of BSi:NAIP and BSi:TP increased beginning in the 1980s in response to reduced urban phosphorus loading that began in the 1970s.

We can only speculate about sources of variability in BSi:NAIP and BSi:TP ratios (Figs. 14, 15) in the absence of specific information about species composition and BSi content of microfossil diatoms. Cellular silica content among naturally occurring diatom populations from the Great Lakes ranged from 39% to 79% SiO_2 dry weight (Sicko-Goad et al. 1984). Cellular silica content of diatom populations also varies in response to silica availability (Stoermer et al. 1985b; 1989). Therefore, BSi:NAIP and BSi:TP would decrease in response to the development of environmental silica depletion. Benthic species with the greatest cellular silica content tend to be more important in sediments deposited before land clearance (Stoermer et al. 1998) and are sensitive to nutrient enrichment (Carrick and Lowe 1988). The areal extent of the benthic photic zone was greater before phosphorus loading associated with early settlement and forest clearance stimulated phytoplankton growth and reduced water transparency. The largest ratios were found in LMDH-94 from Grand Traverse Bay. In this core, BSi:NAIP was nearly 800:1 and BSi:TP was nearly 200:1 (Fig. 5). BSi:NAIP and BSi:TP in the core from northern Lake Michigan (LMK34-94) also were relatively large, with maxima of 380:1 and 170:1, respectively. No other cores displayed ratios as large. These BSi:TP are within the range of SiO_2:P weight ratios (54:1–314:1) calculated from published data on naturally occurring populations of diatoms (Sicko-Goad et al. 1984). Larger ratios in sediments are expected because of differential cycling of the two nutrients in the water column (Conley et al. 1988). Efficient phosphorus recycling (on time scales of days or less) maintains phosphorus supplies in the photic zone, while BSi is sedimented and recycled annually (Schelske 1985a). Differential loss of BSi and phosphorus during diagenesis in the zone of dissolution also may affect ratios. In the next section, we present hypotheses that address the large variability in BSi:TP and BSi:NAIP ratios.

Implications for future research—In this section, we examine how findings from research on the Great Lakes might apply in other aquatic systems. We have shown that BSi accumulation and BSiAR in sediments are sensitive proxies of phosphorus enrichment in the water column. We also have shown that nutrient stoichiometry of BSi:NAIP and BSi:TP changes markedly in the sediment record, possibly reflecting changes in silicification and species composition of historic diatom assemblages. Differences between cores

and within cores are so large, however, that no one ratio would adequately describe stoichiometric profiles. Variability in NAIP:TP in the sediment record is an inference for sources of phosphorus loading to the lakes. The NAIP fraction increases, beginning in the 1940s, when human wastes and phosphate detergents became major sources of urban phosphorus loading. Causes for high ratios in older sediments of the upper lakes, however, can only be hypothesized at present. Variability in proxies among cores and among lakes provides opportunities for future research in aquatic systems.

Results of our model show that BSi accumulation is a function of areal BSi production and MSR. Areal production likewise is dependent on water-column depth during winter–spring isothermal mixing and photic zone depth during the remainder of the year in the Great Lakes. In systems with shallower photic depths, BSi accumulation also may be a proxy for diatom production. If MSR is constant, volumetric production must be larger in systems with shallower photic depths to obtain the same magnitude of areal BSi production. Utilization of this proxy in aquatic systems is dependent on identifying and sampling stations with MSR large enough to preserve an identifiable chronological record.

Patterns in BSi accumulation (Fig. 11) and BSiAR (Fig. 13) differ among cores from the lower Great Lakes. Peak diatom production in the late 1800s was driven by increased phosphorus loading during early European settlement. Three different patterns are present after this period of peak production. In LEG16-93, diatom production inferred from BSiAR peaked about 1870, varied until about 1920, and then increased upcore. This inference differs from that obtained for the profile of BSi concentration, in which inferred diatom production increased sharply after 1870 and then increased upcore. In the Lake Ontario core, peaks in BSiAR occurred about 1870 and 1900, whereas only the 1870 peak was present in the profile of BSi concentration. The Lake Ontario core differs from the other cores from the lower lakes in that BSiAR decreased upcore after 1900. We interpret this to represent severe silica limitation that resulted in part from decreased silica inputs to the lake from Lake Erie. Increased diatom production during this time that is inferred from LG16-93 in the central basin provides evidence of increased silica utilization in Lake Erie and consequently less silica input from the upstream lake that provides approximately 80% of the hydraulic loading to Lake Ontario (Table 2). In LE47-87, diatom production inferred from BSiAR is larger compared with the other cores and is relatively constant. Inferred high diatom production is a consequence of high MSR at this station, located in a high depositional zone off Long Point. We believe that high rates of inferred diatom production result from large quantities of materials focused at this site, partly from the central basin.

In the upper Great Lakes, increased diatom production is inferred from both proxies for Lake Superior and Lake Huron (Figs. 11, 12). Likewise, increased diatom production beginning in the 1940s can be inferred from the two Lake Michigan cores. Epilimnetic silica depletion, however, can be inferred only from BSiAR in LMDH-94 and not from LMK34-94, where inferred decreased diatom production may be masked in the zone of dissolution at the top of the

core or by the relatively short sediment record. Additional research is needed to address discrepancies in inferences obtained from the two proxies.

To utilize BSi accumulation or BSiAR as proxies for ecosystem silica depletion, the reservoir of silica in the water mass must be reduced to limiting levels on time scales of years or longer. Dynamics of silica associated with silica utilization and BSi production annually result in BMSD only if the silica reservoir is reduced in the lake's mass balance. In some lakes, a combination of internal recycling, short residence time, small silica demand for diatom production, and external loading can supply adequate silica so that diatom production is not limited by silica supplies. External loading can maintain replete silica supplies in large lakes with relatively high diatom production (Bootsma et al. 2003). In fact, our results from a central Lake Erie core show that diatom production increased historically because silica was supplied continually from Lake Huron, the upstream lake (Figs. 9, 11). However, as shown by silica concentrations in the eastern basin (Barbiero and Tuchman 2001), silica demand for diatom production exceeds supplies and silica becomes limiting as water is transported through Lake Erie.

Stoichiometric relationships are useful in assessing the effects of cultural eutrophication because they are not affected by variations in MSR. Such ratios are important to analyze because MSR varied more than an order of magnitude across our study cores. MSR ranged from a high of >800 mg cm^{-2} yr^{-1} in LE47-87 (Fig. 13) to a low of approximately 20 mg cm^{-2} yr^{-1} in LS15-94. In addition, nutrient stoichiometry is a valid tool in undated sediments.

BSi stoichiometry provides additional information about diatom assemblage response to phosphorus enrichment (Figs. 14, 15). Intuitively, one might expect ratios would be relatively constant and would not be affected greatly by nutrient enrichment. BSi:TP and BS:NAIP, however, increase in response to relatively small increases in phosphorus loads and then decrease if diatom growth becomes silica limited or if phosphorus loading is excessive. We propose several hypotheses to explain the greater-than-expected proportional changes in BSi in these stoichiometric relationships. First, sources of increased phosphorus loading include a higher proportion of NAIP, increasing the ratio of BSi:TP. Such a scenario increases the proportion of TP that is utilized in diatom production. Second, historic loads include nutrients other than phosphorus that act synergistically to stimulate diatom production and increase BSi:NAIP and BSi:TP. Standing crops of phytoplankton and silica utilization by diatoms in natural phytoplankton assemblages were enhanced by combined nutrient treatments relative to enrichments with phosphorus alone (Schelske 1984; Schelske et al. 1986*a*). Third, benthic forms utilize nutrients regenerated from the sediments, a process that enhances silica utilization and BSi production. Fourth, heavily silicified benthic forms, an important component of diatom assemblages, increase in abundance in the early stages of cultural eutrophication. Although the planktonic:benthic (P:B) ratio of diatoms also increases, heavily silicified benthic forms can affect the ratio. Eventually, increased planktonic abundance and higher standing crops mask this effect. Fifth, the increase in BSi:TP and

BSi:NAIP is reversed by development of silica-limited diatom growth, excessive phosphorus enrichment, increase in P:B, or some combination of these factors.

We believe that proxies reported here will be important in inferring diatom assemblage responses to future changes in phosphorus levels in the Great Lakes. In response to decreased TP, we hypothesize that diatom production and its environmental proxy, BSi accumulation, will reach a new, dynamic steady-state equilibrium in each of the Great Lakes, similar to that predicted for pristine conditions in the hypothetical model (Fig. 2). This equilibrium will be attained when external silica loading is adequate to supply the silica demand for diatom production and create an unused silica reservoir in the water mass. The time required to establish this equilibrium will be long in Lake Michigan because external loading is relatively small compared with the water-column silica reservoir (Schelske 1985a) and the hydraulic residence time is long (Table 2). In Lake Erie and Lake Ontario, the time scale will be shorter because of shorter residence times. Evidence exists that silica is being replenished in Lake Michigan (Barbiero et al. 2002), Lake Erie (Makarewicz et al. 2000), and Lake Ontario (Johengen et al. 1994). How diatoms respond to reversal of the silica depletion legacy is complicated by community structure, structural modification of populations, and factors other than nutrient enrichment (Stoermer 1998). How diatom populations, BSi accumulation, BSiAR, BSi:TP, and BSi:NAIP are affected as silica limitation is relaxed will be important in assessing ecosystem responses in the future.

Why are BSi accumulation and BSiAR such sensitive indicators of cultural eutrophication (P enrichment) in the Great Lakes? Several factors contribute to this sensitivity. First, areal silica utilization is an integrative measure of the response of diatom assemblages to nutrient enrichment (Schelske 1975). Silica utilization during an annual cycle integrates seasonal uptake over the depth scales of interest (Fig. 10). During the winter–spring isothermal period, diatoms utilize silica over the entire water column and, after stratification, silica utilization is restricted to the photic depth, which may be deeper than the mixed layer (Schelske 1985a; Schelske et al. 1986a). Thus, seasonal and depth integration of diatom production enhances sensitivity. Second, sedimentation of diatom microfossils also represents integration of seasonal and spatial (depth and areal) production of BSi (Hecky and Kilham 1973). Focusing of sedimented materials delivers BSi to depositional zones that represent less than half of the lake basin (Thomas 1981). BSi accumulation in depositional zones is not uniform and varies among stations (Schelske et al. 1988). It also varies greatly among systems with reported BSi concentrations as large as 50% of sediment dry weight in Lake Baikal (Stoermer et al. 1995). Third, phosphorus supplies in the water column are maintained by recycling on short time scales (days or less), whereas silica is recycled on yearly time scales (Schelske 1985a; Conley et al. 1988). Thus, dynamic processes of BSi production and diagenesis associated with permanent sedimentation yield a net gain in BSi accumulation relative to phosphorus accumulation.

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