Changes in polyphosphate sedimentation: a response to excessive phosphorus enrichment in a hypereutrophic lake

William F. Kenney, Claire L. Schelske, and Andrew D. Chapman

Abstract: Historic changes in lake phosphorus (P) loading are often determined in paleolimnological investigations by assessing stratigraphic changes in sediment total P. Polyphosphate (poly-P) in sediments may provide additional information on historic lake trophic status, because phytoplankton store surplus P intracellularly as poly-P when supplies exceed growth requirements. We hypothesize that phytoplankton (i.e., cyanobacteria and diatoms) with stored poly-P can remain intact and viable for many decades after sedimentation and that sedimented poly-P is not geochemically reactive. We tested our hypotheses with sediment cores from Lake Apopka, Fla., U.S.A., where P loading has increased ~7-fold since the 1920s and phytoplankton biomass is nitrogen limited owing to excessive P enrichment. We show that sedimented poly-P is mobilized by sample drying (i.e., becomes water soluble, geochemically reactive, and bioavailable); that anthropogenic P enrichment is expressed in the sediment record as increasing concentrations of poly-P; and that, consequently, sedimentary poly-P is a sensitive indicator of historic excessive P enrichment. Sedimentary poly-P is not geochemically reactive; thus, it represents biological attenuation that may partially ameliorate the effects of excessive P loading.

Résumé : Les changements stratigraphiques de la quantité totale de phosphore (P) dans les sédiments sert souvent à déterminer les changements historiques de la charge de P dans les lacs lors d'études paléolimnologiques. Les concentrations de polyphosphates (poly-P) dans les sédiments apportent des informations supplémentaires sur le statut trophique du lac au cours des années parce que le phytoplancton accumule dans son milieu intracellulaire l'excédent de P sous forme de poly-P lorsque les quantités disponibles dépassent les besoins requis pour la croissance. Nous posons en hypothèse que le phytoplancton (i.e., les cyanobactéries et les diatomées) contenant des réserves de poly-P peuvent rester intactes et viables pendant plusieurs dizaines d'années après leur sédimentation et que le poly-P sédimenté n'est pas impliqué dans les réactions géochimiques. Nous avons testé notre hypothèse à l'aide de carottes de sédiments provenant du lac Apopka, Fla., U.S.A., où la charge de P a augmenté d'environ 7 fois depuis les années 1920 et où la biomasse du phytoplancton est limitée par pénurie d'azote en présence d'un enrichissement excessif en P. La mobilisation du poly-P sédimentée se fait lors du séchage des échantillons (i.e., il devient hydrosoluble, il réagit aux facteurs géochimiques et il est biodisponible); l'enrichissement en P d'origine humaine se traduit dans les sédiments par des augmentations de poly-P; en conséquence, les concentrations de poly-P dans les sédiments sont un indicateur sensible de l'enrichissement historique excessif en P. Puisque le poly-P des sédiments n'est pas impliqué dans les réactions géochimiques, il s'agit là d'une atténuation biologique qui peut compenser en partie les effets d'une charge excessive de P.

[Traduit par la Rédaction]

Introduction

Understanding the relationship between anthropogenic disturbance and water-quality problems requires research on phosphorus (P), because this nutrient is the factor most likely to limit algal growth in fresh waters (Schindler 1977). Applied studies have addressed the empirical relationships between total P (TP) and chlorophyll, without examining the components of TP (see Chapra and Auer 1999). These relationships are based on the implicit assumption that changes in chlorophyll concentration are directly proportional to changes in TP concentration, but such inferences are confounded by variable proportions of soluble reactive P (SRP), surplus P stored by algae, and refractory P (Schelske et al. 1999*a*). Although forms of P can be measured, little attention has been given to determining what TP fractions are biologically available (see Hecky and Kilham 1988; Chapra and Auer 1999). Partitioning forms of P has been advanced as a means of refining models that assess the algal-growth potential of waters (Schelske et al. 1999*a*).

In the water column, 2 common forms of biologically available P are SRP, which by definition has not been assimilated by algae, and polyphosphate (poly-P), which represents surplus storage that has been assimilated but not utilized for algal growth (Schelske et al. 1999*a*). Biological availability of sedimentary P can be determined with chemical measurements or algal bioassays. Algal bioassay (bioassay-P) is generally con-

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sidered to be the ultimate test for the bioavailability of P in water and sediments (Golterman 1988; Williams et al. 1980). Sodium hydroxide extractable P (NaOH-P; Williams et al. 1980) and nitrilo triacetic acid extractable P (NTA-P; Golterman 1977) have been shown to be bioavailable by comparison with algal bioassays. NaOH-P is a large fraction of the TP (~40%) in dried Lake Apopka sediments (Schelske 1997) but NaOH-P overestimated bioassay-P by severalfold for recent sediments in this lake (Kenney 1997). It was shown previously that sample handling affects partitioning among P forms in chemical analysis (Twinch 1986). We show here that bioassay-P and water-soluble P (H_2O-P) were greater in dried sediments than in wet sediments from Lake Apopka.

We studied Lake Apopka, a large shallow hypereutrophic lake in central Florida, U.S.A., because P loading increased as much as 7-fold in the past 100 years (Battoe et al. 1999). In Lake Apopka, phytoplankton store poly-P (Newman et al. 1994; Schelske et al. 1999*a*) and are nitrogen (N) limited as a result of excessive P enrichment (Aldridge et al. 1993). Kenney (1997) found an upcore increase in sedimentary poly-P. We contend that this pattern results from surplus P stored as poly-P in phytoplankton, because resting cells of diatoms are sedimented and remain viable for decades or longer (Sicko-Goad et al. 1989) and because, in Lake Apopka, many algal species remain viable decades after sedimentation (A. Chapman, unpublished data).

Herein we show that sedimented poly-P is mobilized and becomes water-soluble and bioavailable by sample drying; that anthropogenic P-enrichment is expressed in the sediment record as increasing concentrations of poly-P; and that, consequently, sedimentary poly-P is a sensitive indicator of historic excessive P enrichment.

Materials and methods

Study site

Lake Apopka is a shallow (mean depth = 1.7 m) polymictic hypereutrophic lake (mean ± SD = 0.203 ± 0.062 mg $P \cdot L^{-1}$) that has been significantly impacted by anthropogenic nutrient loads (Battoe et al. 1999; Schelske et al. 2000). This subtropical lake is located ~20 km northwest of Orlando, Fla., U.S.A. Historically, the lake was macrophyte dominated with clear water (Schelske and Brezonik 1992). In the 1920s, effluent from citrus processing and municipal sewerage increased P loading to the lake (Schelske and Brezonik 1992). In the early 1940s, the lake area was reduced from 210 to 125 km^2 as "muck" farms were created on diked and drained littoral and marsh areas (Battoe et al. 1999). In the late 1940s, large standing crops of phytoplankton replaced macrophyte beds in the lake, creating a planktonic system with turbid water (Battoe et al. 1999).

Increased P loading is a major forcing factor in the development of phytoplankton dominance in Lake Apopka. In several papers, the shift to phytoplankton dominance was attributed to the effects of a hurricane, but this has not been supported by recent studies (see Battoe et al. 1999; Schelske et al. 2000). Periodic pumping of the drainage water from the P-rich and heavily fertilized farm lands was responsible for 0.42 g $P \cdot m^{-2} \cdot year^{-1}$ or 85% of the average P loading from 1989 to 1994 (Battoe et al. 1999). Since the late 1940s, basin-wide sedimentary TP accumulation has increased as much as 4-fold (Schelske 1997) and phytoplankton biomass has become N limited (Aldridge et al. 1993). A considerable amount of water column TP is poly-P stored in phytoplankton (~18%; mean = 0.036 ± 0.005 mg $P \cdot L^{-1}$); however, a much smaller amount of TP is SRP (~3%; mean = 0.007 ± 0.009 mg $P \cdot L^{-1}$; Schelske et al. 1999*a*).

Highly organic sediments deposited in Lake Apopka during the 20th century reflect 2 source materials (Olila et al. 1995). Deeper sediments (referred to as macrophyte sediments) represent the period of macrophyte dominance, and overlying sediments (referred to as phytoplankton sediments) represent the period of phytoplankton dominance (Schelske et al. 1999*b*). Macrophyte sediments are highly organic (mean loss on ignition (LOI) = 55%), with intermixed snail shells and low TP concentrations (<0.75 mg·g^{-1}). Phytoplankton sediments have a mean LOI of 64% and a range in TP concentrations (~1.0 to ~2.0 mg·g^{-1}) typical of many Florida lake sediments (Brenner and Binford 1988). The accumulation of phytoplankton sediments averages 47 ± 32 cm (n = 46) or 1.77 ± 1.56 g·cm^{-2} (n = 46; Schelske 1997). Phytoplankton sediments did not accumulate uniformly in the lake basin. Half the TP accumulated on only 20% of the lake bottom and ~70% of the TP accumulated on ~40% of the lake bottom (Schelske 1997).

Because of high organic matter content and a disproportionate accumulation of refractory materials in sediments, many Florida lakes, including Lake Apopka, form a subset of lakes with respect to sediment dynamics. In Lake Apopka, high rates of primary production (Schelske et al. 2000) and polymixis influence the sediment composition. Primary production by phytoplankton is sufficient to account for the organic matter sedimentation rate (Schelske et al. 2000), and total carbon to total nitrogen ratios identify its source as phytoplankton (Schelske et al. 1999*b*). The large size (125 km^2), shallow mean depth (1.7 m), and large fetch in all directions promote frequent resuspension of surface sediments (Carrick et al. 1993; Reddy et al. 1996). Frequent wind resuspension increases the time that organic particles are exposed to aerobic conditions; therefore, the material that accumulates as permanent sediment is largely refractory (<10% of the organic carbon is labile under anoxic conditions; Gale et al. 1992). Compared with Lake Okeechobee, Lake Apopka sediments have lower concentrations of extractable cations (Olila et al. 1995). In these highly organic sediments from Lake Apopka, P is not bound to Fe, Al, or Mn, and P release is not redox dependent (Olila and Reddy 1997).

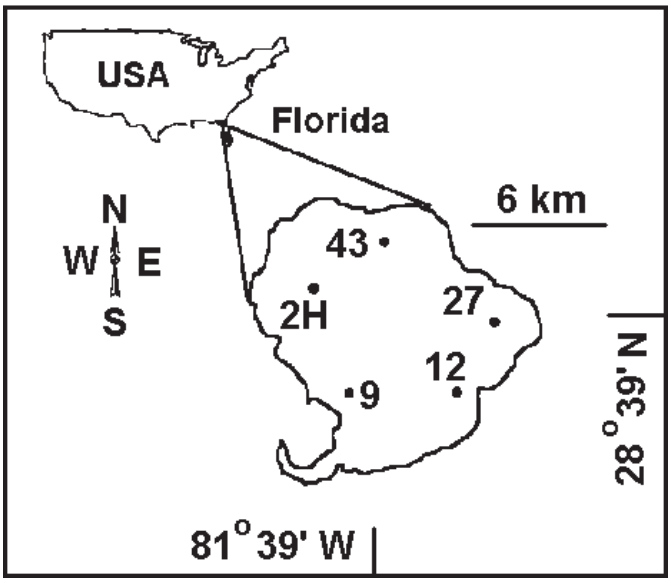
Field and laboratory methods

Six sediment cores were collected with a piston corer (Fisher et al. 1992), and the depth to the sediment–water interface was determined with an infrared nephelometer (Meyers and Schelske 2000). Five core stations (LA-2H, LA-9, LA-12, LA-27, LA-43) were distributed at depositional sites over the lake basin (Fig. 1). Results from the chemical analyses and bioassays of wet sediments from these 5 locations led us to investigate the effects of freeze-drying on P fractionation and bioavailability in 20 contiguous samples from one of these locations, LA-9 (core LA-9-97). Among depositional areas, location LA-9 has an average accumulation of sediments (Schelske 1997). Cores were vertically extruded and sectioned in the field, aboard a motor-powered skiff, and samples were stored in Whirl-Pak® bags at ~5°C in ice chests for transport to the laboratory.

In the laboratory, samples were refrigerated at ~5°C. Chemical analyses of wet sediments were completed within 4 days of collection. Bioassays of wet sediments were initiated 5 days after collection. Representative subsamples were freeze-dried and ground to a maximum particle size of 100 μm for chemical analyses and bioassays.

Bioassays to determine bioavailable P were conducted according to Williams et al. (1980), with modifications from Golterman (1988). Sediment (<0.2 g dry mass equivalent·L^{-1}) and associated P (<50 μg $P \cdot L^{-1}$) added were at least an order of magnitude smaller than in other studies (Golterman et al. 1969; Chiou and Boyd 1974). The initial density of algal cells (5000 cells/mL) was an order of magnitude greater than in other studies (Golterman et al.

Fig. 1. Map of Lake Apopka, Fla., U.S.A. Coring locations are plotted by station designation.



1969; Golterman 1977). These modifications minimized bias from viable algal populations in the sediment addition, including those with stored poly-P. Bioassay-P was determined in 500-mL glass flasks, using cultures of *Scenedesmus quadricauda*, obtained from E.J. Phlips, University of Florida (Gainesville, FL 32653, U.S.A). Before determinations of bioassay-P, test cultures were maintained in freshwater medium (Phlips et al. 1989), containing replete available N (>30 mg $N \cdot L^{-1}$, as nitrate) and low available P (<0.005 mg $P \cdot L^{-1}$, as orthophosphate), in 2 identical Percival® incubators. We conducted simultaneous duplicate bioassays in the incubators with samples replicated within each incubator. Growth responses were log-transformed in vivo fluorescence (Turner Brands® fluorometer) data collected every 48 h on diluted (1:20) test cultures. To calculate bioassay-P, growth responses of cultures with sediment as the P source were calibrated to a linear function derived from the growth responses of cultures with small additions of orthophosphate as the P source (a range of known concentrations ≤0.040 mg $P \cdot L^{-1}$). Bioassays were conducted on only 6 samples. Bioassay-P concentrations for the remaining 14 samples were predicted from a linear model comparing H_2O-P with bioassay-P ($R^2 = 0.97$, $n = 6$).

We measured TP (Schelske et al. 1986) and 4 sedimentary P fractions (Table 1). The NaOH-P assay (0.1 M NaOH; Williams et al. 1980) measured sorbed Fe-, Al-, and Mn-bound P. Some organic-P/biogenic-P and possibly poly-P (Olila and Reddy 1997) are also measured by the NaOH assay. In addition, the NaOH assay partially dissolves the siliceous valves of diatoms (20–30% of diatom biogenic silica (BSi) in Lake Apopka sediments; W. Kenney, unpublished data) and releases intracellular P. Some of the organic-P/biogenic-P may be hydrolyzed to reactive P by the NaOH or the colorimetric reagents (pH <2) in the SRP analysis. The NTA-P assay (0.01 M NTA, pH = 7; Golterman 1977) measures P loosely bound to cations (e.g., Fe, Al, Mn, Ca, Mg). Although NTA-P and NaOH-P may be extracted from the same cations (e.g., Fe, Al, Mn), NaOH-P is also extracted from organic–biogenic forms that are not affected by the neutralized NTA assay. Sediment samples were equilibrated in H_2O (18 MΩ) to determine H_2O-P and were then wet-autoclaved to determine heat-extractable P. Heat extraction measures poly-P (Fitzgerald and Nelson 1966) and other intracellular reserves of P (Pettersson 1980) in phytoplankton. Because assays were not conducted sequentially, results presented for NaOH-P, NTA-P, and poly-P were corrected by subtracting the corresponding H_2O-P concentration for each sample.

The dry-mass equivalent of sediment, volume of suspension, duration of extraction, and equipment required for each chemical assay are listed in Table 1. To disperse aggregates, increase surface area, and reduce replicate error, sediment suspensions were sonicated in a Fisher Scientific® FS 110 ultrasonic cleaner. Suspensions were then equilibrated or autoclaved, diluted, neutralized, and analyzed colorimetrically for SRP with ascorbic acid and ammonium molybdate on a Bran+Luebbe® autoanalyzer (APHA 1989). Dried ground sediment samples were analyzed for diatom and sponge BSi as in Conley and Schelske (1993). We used diatom BSi as a proxy for phytoplankton contribution to sediment matter. Because macrophytes are the primary substrate for freshwater sponges in Lake Apopka, sponge BSi was used as a proxy for macrophyte contribution to sediment matter.

Sediment characterization and chronology

The interface between phytoplankton and macrophyte sediments was determined with BSi and bulk-density data. In core LA-9-97, phytoplankton sediments ($n = 12$) had lower bulk density (mean = 29.7 ± 9.5 $mg \cdot cm^{-3}$) and lower concentrations of sponge BSi (mean = 14.3 ± 5.9 mg $SiO_2 \cdot g^{-1}$) than macrophyte sediments ($n = 8$, mean = 63.0 ± 4.5 $mg \cdot cm^{-3}$ and 24.4 ± 5.8 mg $SiO_2 \cdot g^{-1}$, respectively). The mean concentration of diatom BSi was higher in the phytoplankton sediments (38.3 ± 3.6 mg $SiO_2 \cdot g^{-1}$) than in the macrophyte sediments (6.5 ± 6.9 mg $SiO_2 \cdot g^{-1}$). For core LA-9-97, the interface between phytoplankton and macrophyte sediments was at 60 cm (Fig. 2).

Age at depth and mass sedimentation rates (MSR) for LA-9-97 were estimated on the basis of temporal patterns of sediment accumulation determined for a suite of ^{210}Pb-dated cores collected previously. Phytoplankton sediments in Lake Apopka have accumulated since ~1947, and ^{210}Pb activities were used to develop sediment chronologies (Schelske 1997). The dated sequences showed that over the past ~50 years, MSR increased 3- to 4-fold or an average annual increase of 1.0227–1.0287. We applied these end-member rates of increase to the cumulative dry mass (1.78 $g \cdot cm^{-2}$) determined for phytoplankton sediments (upper 60 cm) from LA-9-97. This enabled us to compute dates for the base of each 5-cm core section using 2 rates of increase in sediment accumulation. The 2 modeling approaches yield sediment ages that differ by <3 years at the base of each 5-cm section. Ultimately, we averaged the increase in MSR between 3- and 4-fold to apply dates to depths in the core. This approach generated the age–depth pairs 1995 (10 cm), 1991 (20 cm), 1984 (30 cm), 1975 (40 cm), 1964 (50 cm), and 1947 (60 cm), as the specified initial time. Calculated MSR for the 4-fold increase ranged from 19 to 76 $mg \cdot cm^{-2} \cdot year^{-1}$.

Results

Using linear regression, we tested data from wet-sediment analyses for relationships between H_2O-P, poly-P, NaOH-P, or NTA-P and bioassay-P or TP. Unexpectedly, bioassay-P represented only a small fraction of NaOH-P and TP. Results from the 5 cores indicated that NaOH-P and poly-P were correlated with TP (Fig. 3*a*), while H_2O-P and NTA-P were correlated with bioassay-P (Fig. 3*b*). The relationships between either NaOH-P or poly-P and TP are best described by second- or third-order polynomial models, not linear models. Because similar relationships existed among P measures for LA-9-97 (Figs. 3*c* and 3*d*), we considered this core to be representative of recent Lake Apopka sediments.

That sample preparation affected the fractionation among the measured sedimentary P forms is evident from depth profiles of P fractions for LA-9-97. For phytoplankton sedi-

Table 1. Methods for the analysis of water-soluble phosphorus (H_2O-P), polyphosphate (poly-P), nitrilo triacetic acid extractable P (NTA-P), sodium hydroxide extractable P (NaOH-P), and total P (TP).

Extraction	Dry mass (g)	Volume (L)	Process	Temperature (°C)	Time (h)	Solution
H_2O-P	0.05	0.05	Equilibrate	25	20	18 MΩ water
Poly-P	0.05	0.05	Wet-autoclave	100	0.5	18 MΩ water, sequential to H_2O-P
NTA-P	0.05	0.05	Equilibrate	25	20	0.01 M nitrilo triacetic acid, pH 7
NaOH-P	0.05	0.05	Equilibrate	25	17	0.1 M sodium hydroxide
TP	0.05	0.03	Wet-autoclave	100	0.5	0.53 M sulfuric acid – 0.062 M potassium persulfate

Note: For each method, the dry mass equivalent of sediment and volume of the suspension are presented, together with the process, temperature, and time required for each analysis. All samples were equilibrated at 85 rpm in a shaker bath.

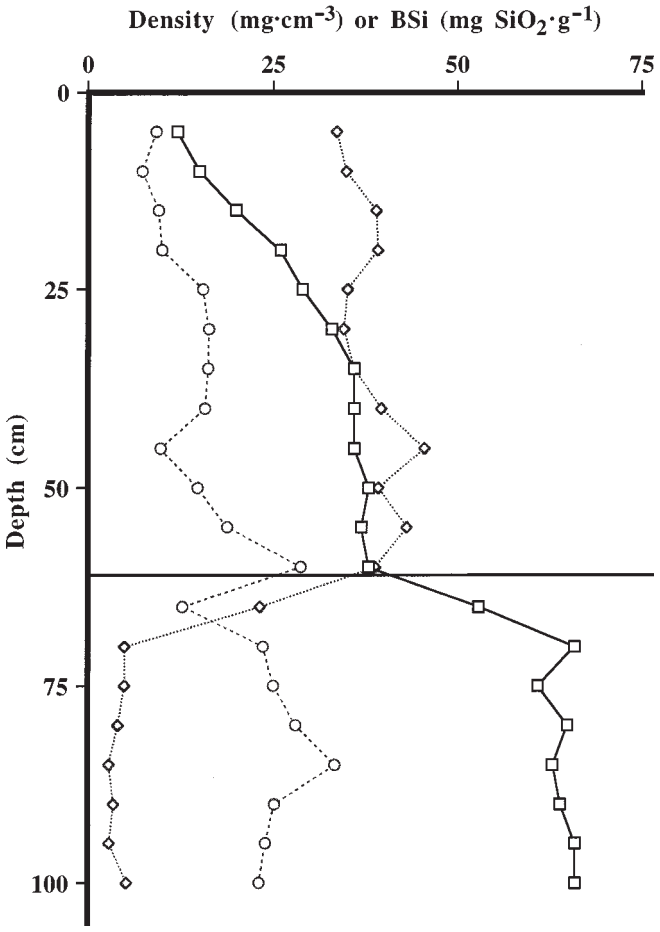


Fig. 2. Diatom biogenic silica (BSi, broken line with open diamonds), sponge-BSi (broken line with open circles), and bulk-density (solid line with open squares) data for core LA-9-97 plotted against depth. The interface between phytoplankton- and macrophyte-sediment types is indicated by the horizontal line at 60 cm.

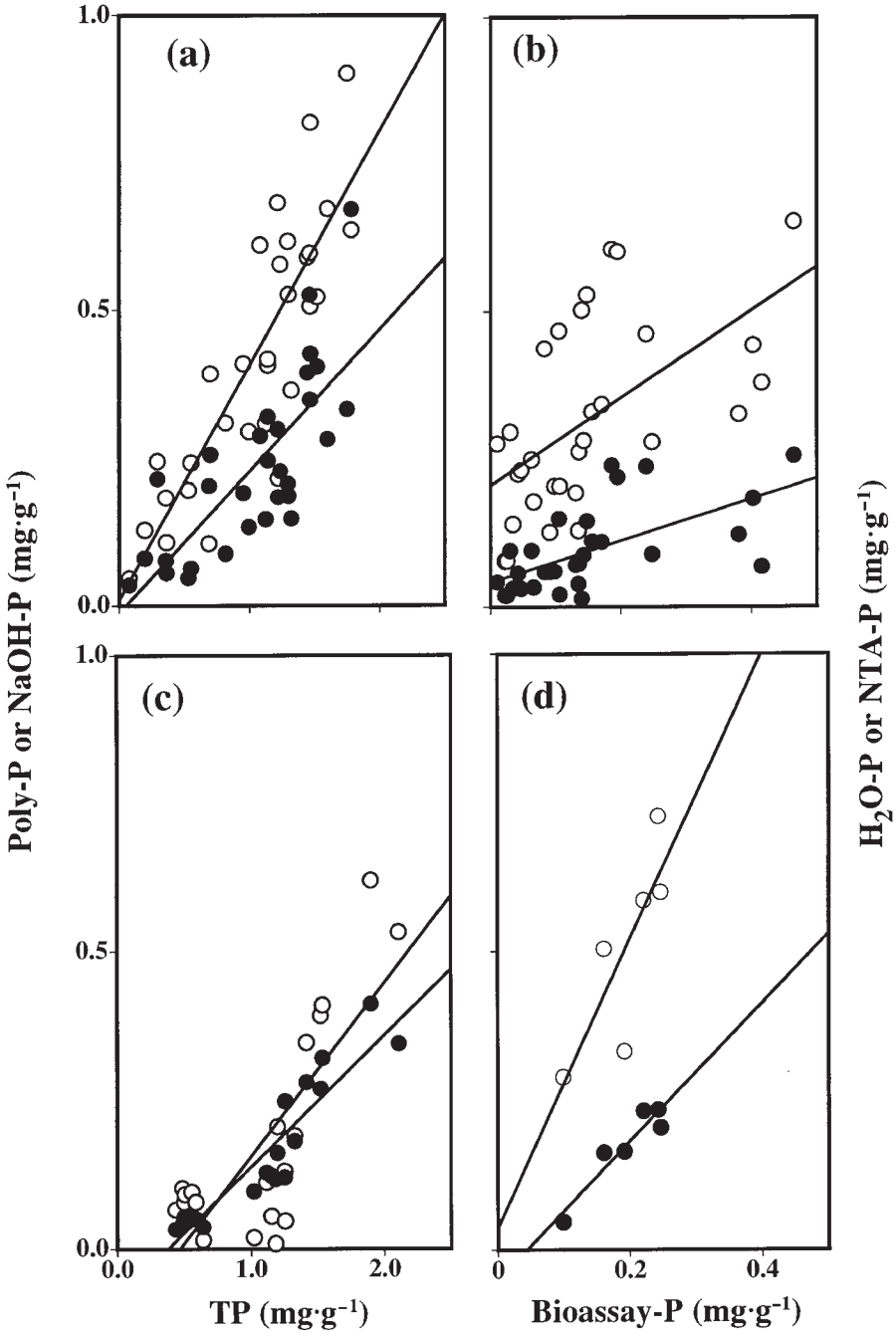
ments, H_2O-P concentrations were greater in dried samples than in wet samples, but dry and wet values were similar for macrophyte sediments (Fig. 4*a*). Poly-P was greatest in phytoplankton sediments and measurable in all wet samples but was not detectable in dried samples below 10 cm (Fig. 4*b*). The profiles of NTA-P differed from those of poly-P (Fig. 4*c*). Similarly to poly-P, concentrations of NaOH-P were greater in wet samples, with the greatest differences between wet and dry NaOH-P in phytoplankton sediments (Fig. 4*d*). Bioassay-P concentrations were larger in dried samples (relative percent difference >20%) than in wet samples in the surface 25 cm of the phytoplankton sediments (Fig. 4*e*). Wet and dry TP values varied on average by 9% (Fig. 4*f*), but the largest differences, 23 and 32%, were in the 10- and 100-cm samples, respectively.

Sediments from LA-9-97 were separated into 3 stratigraphic zones based on differences in poly-P concentration (Fig. 4*b*). Macrophyte-derived sediments below 65 cm were used to represent baseline conditions. Sediments from 40 to 65 cm are termed zone 1, and those above 40 cm are termed zone 2. We compared the changes in biological responses (BSi and poly-P) and forcing factors (TP and other P fractions) relative to baseline conditions (Fig. 5). In zones 1 and 2, diatom BSi concentrations changed more (~9-fold), relative to baseline, than any proxy investigated. In contrast, sponge spicule BSi concentrations decreased in zones 1 and 2 compared with baseline. These results show that a biological response to P enrichment in shallow lakes is an increased contribution of phytoplankton to sediment matter. The relative increase in poly-P concentration was greater than for any other P form measured: 5.6-fold greater than baseline in zone 2 and 2.5-fold greater than baseline in zone 1. The TP concentration was 2.9-fold greater than baseline in zone 2 and 2.2-fold greater than baseline in zone 1. Although the bioassay-P and NTA-P concentrations were ~1.7-fold greater than baseline in zone 1, they were not different from baseline in zone 2. These results show that poly-P was the most sensitive proxy for historic P enrichment.

Discussion

Bioassay-P concentrations determined in our experiments with wet sediments were lower than expected from chemical assays of Lake Apopka sediments. NaOH-P (Williams et al. 1980) extracted from dried sediments averaged 40% of TP in an extensive sediment survey (Schelske 1997) and 43% of TP in the present study. By contrast, bioassay-P averaged only 14% of TP in wet sediments (Kenney 1997). Williams et al. (1980) established NaOH-P as an appropriate chemical assay for estimating bioassay-P in dried sediments from the Laurentian Great Lakes. However, the 0.1 M NaOH employed in this extraction partially destroys the structural integrity of phytoplankton cells, particularly diatoms, and releases intracellular P, including poly-P, that is not externally available under bioassay conditions using wet sediments. As a result, NaOH-P overestimated bioassay-P by severalfold for the highly organic phytoplankton sediments from Lake Apopka. These results are counter-intuitive, because poly-P may support growth in the enriched phytoplankton popula-

Fig. 3. Comparison of the forms of phosphorus (P; TP, total P; bioassay-P, bioavailable P (tested by algal bioassay); poly-P, polyphosphate; NaOH-P, sodium hydroxide extractable P; H_2O-P, water-soluble P; and NTA-P, nitrilo triacetic acid extractable P) in wet sediments from Lake Apopka. (*a*) Plots of poly-P (filled circles) or NaOH-P (open circles) versus TP for the initial 5-core study. Regression equations are poly-P = 0.24 × TP – 0.01, R^2 = 0.58, n = 30 and NaOH-P = 0.40 × TP + 0.01, R^2 = 0.72, n = 30. (*b*) Plots of H_2O-P (filled circles) and NTA-P (open circles) versus bioassay-P for the initial 5-core study. Regression equations are H_2O-P = 0.35 × bioassay-P + 0.04, R^2 = 0.37, n = 30 and NTA-P = 0.74 × bioassay-P + 0.21, R^2 = 0.33, n = 30. (*c*) Plots of poly-P (filled circles) or NaOH-P (open circles) versus TP for core LA-9-97. Regression equations are poly-P = 0.22 × TP – 0.08, R^2 = 0.62, n = 20 and NaOH-P = 0.29 × TP – 0.14, R^2 = 0.86, n = 20. (*d*) Plots of H_2O-P (filled circles) and NTA-P (open circles) versus bioassay-P for core LA-9-97. Regression equations are H_2O-P = 1.16 × bioassay-P – 0.05, R^2 = 0.97, n = 6 and NTA-P = 2.42 × bioassay-P – 0.04, R^2 = 0.67, n = 6.



tion but sedimented poly-P is not externally available to the test population in bioassays conducted on wet sediments.

Bioassay-P concentrations were as much as 3-fold greater in dried than in wet phytoplankton sediments. In wet sediments, concentrations of NaOH-P and poly-P were similar, indicating that these procedures extract P from the same sources. Drying the phytoplankton sediment increased H_2O-P concentrations by an amount comparable with the decrease in poly-P or NaOH-P concentration (as much as 0.6 mg P·g^{-1} dry mass equivalent or ~40% of TP). We con-

Fig. 4. Sediment phosphorus (P) fractions (reported on a dry weight basis) of both wet (filled circles) and dried (solid line) sediments plotted against depth for core LA-9-97. The interface between phytoplankton- and macrophyte-sediment types is indicated by the horizontal line at 60 cm. (*a*) Water soluble P (H_2O-P) concentrations. (*b*) Polyphosphate (poly-P) concentrations. (*c*) Nitrilo triacetic acid extractable P (NTA-P) concentrations. (*d*) Sodium hydroxide extractable P (NaOH-P) concentrations. (*e*) Bioavailable P (bioassay-P (tested by algal bioassay)) concentrations. (*f*) Total P (TP) concentrations.

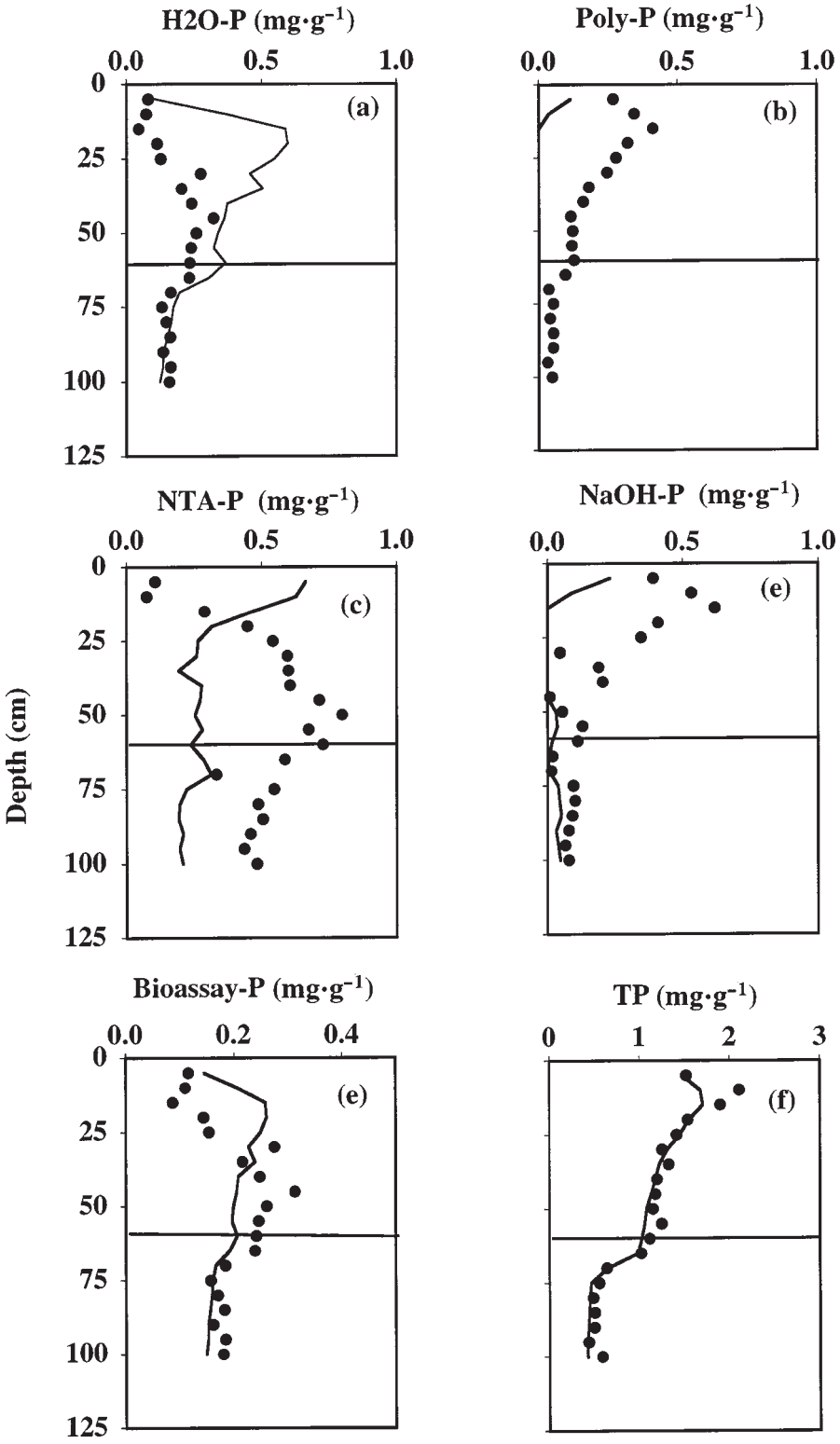
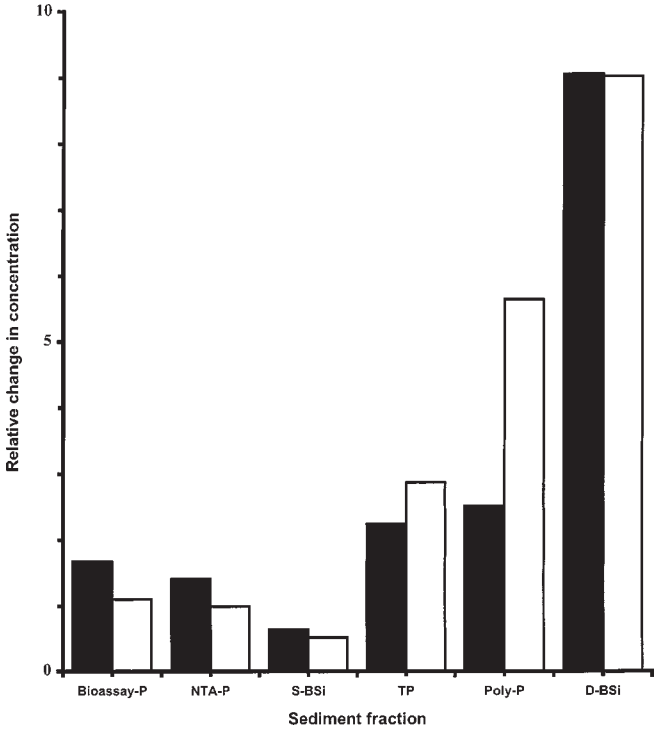


Fig. 5. Relative differences in mean phosphorus (P) and biogenic silica (BSi) concentrations for stratigraphic zones in Lake Apopka sediments. Concentrations of P (wet sediments) and BSi fractions measured on dry sediment samples from zone 1 (40–65 cm; filled bars) and zone 2 (0–40 cm; open bars) are plotted relative to baseline conditions (below 65 cm) for core LA-9-97. P fractions included are bioavailable P as determined through bioassays (bioassay-P), nitrilo triacetic acid extractable P (NTA-P), polyphosphate stored in phytoplankton (poly-P), and total P (TP). Diatom BSi (D-BSi) and sponge BSi (S-BSi) were determined as in Conley and Schelske (1993). See text for further explanation.



tend that poly-P originally sequestered in phytoplankton became water soluble and externally bioavailable by drying the sediment. This indicates that sample preparation (freezing, freeze-drying, and grinding) damaged cells to the extent that intracellular reserves of P became reactive with colorimetric reagents (pH <2). Some of the measured H_2O-P from dried sediments was not bioavailable under bioassay conditions run at higher pH (~8–9). Consequently, bioassay-P was less than H_2O-P for dried-sediment assays, but was roughly equal to H_2O-P for wet-sediment assays.

Our results show that sedimentary poly-P concentrations changed more relative to baseline conditions than any other P form measured. Total P has been used as a proxy for nutrient enrichment (Engstrom and Wright 1984; Schelske et al. 1986), but an increasing fraction of sedimentary poly-P provides direct evidence of historic P enrichment relative to biological demand. Increased storage of poly-P in Lake Apopka sediments corresponded stratigraphically to known increases in P loading and increased sedimentation of diatom BSi. Our data indicate that P loading and diatom sedimentation first increased at 65 cm and increased more above 40 cm. Because 65 cm is below the zone of phytoplankton sediments (60 cm) that were deposited after ~1947, the initial increase in poly-P reflects increased P loading before the onset of phytoplankton dominance. The sediment chronology indicates that the upper 40 cm of sediment in LA-9-97 was deposited since ~1975, during the period of maximum P loading in Lake Apopka. Excessive enrichment since ~1975 is evident from the relative increase in poly-P sedimentation, which was 2-fold greater than the increase in TP sedimentation. These comparisons show that, as TP loading to Lake Apopka increased relative to biological demand, the surplus available P accumulated as poly-P in phytoplankton instead of being processed geochemically. Likewise, in hypereutrophic Kis-Balaton reservoir in Hungary, nutrient uptake by phytoplankton was the dominant mechanism for removing P from the water (Istanovics 1994).

That phytoplankton and their propagules may be sedimented intact and remain viable for extended time periods, up to decades or longer, can be inferred from rejuvenation experiments conducted on sediment-core samples from Lake Apopka (A. Chapman, unpublished data) and other lakes (see Schelske et al. 1995). Resting propagules or sedimented cells were rejuvenated from all depths tested in other cores from Lake Apopka (A. Chapman, unpublished data). Microscopic examination of wet sediment from LA-9-97 confirmed that phytoplankton cells contained intact protoplasts at all depths. The long sedimentary record of poly-P from Newnans Lake, another hypereutrophic Florida lake, shows that poly-P can be permanently sedimented. Poly-P is a significant fraction of TP in the upper 128 cm, >100 years, of sediments from Newnans Lake (W. Kenney, unpublished data).

In lakes in which anthropogenic enrichment is excessive, poly-P synthesis is ecologically significant, because P is stored by phytoplankton without increasing biomass. Poly-P storage by phytoplankton provides a competitive advantage in Lake Apopka, because available inorganic nutrients (both N and P) are at times in short supply relative to the large biological demand from the large algal standing crop (Aldridge et al. 1993). Under experimental conditions, phytoplankton assemblages from Lake Apopka synthesized 83% of added reactive P as poly-P in less than 2 h (Newman et al. 1994). We hypothesize this biological uptake may limit chemical processes in the water column, because poly-P can be synthesized when SRP concentrations are low enough to prevent many inorganic precipitations. Because of excessive P enrichment, phytoplankton in Lake Apopka are sedimented with stored poly-P, thereby removing more P per unit biomass from the water column than if phytoplankton were P limited.

We suggest that burial of intact phytoplankton cells or their resting propagules is a significant contributor to P sedimentation in Lake Apopka. In the upper 40 cm of sediment, <10% of TP was bioassay-P or H_2O-P, indicating that >90% of the TP was not biologically available or chemically reactive under natural conditions. Poly-P averaged 18% of TP in both the water column and surface sediments in Lake Apopka. According to other studies, poly-P accounts for a variable percentage (<75%) of phytoplankton P (Wynne and Berman 1980; Sakamoto and Inoue 1996). These data indicate that, in Lake Apopka, between 25 and 90% of sediment TP may be sequestered in intact phytoplankton. With these data, the contribution of phytoplankton to sediment TP can only be predicted from poly-P data with a large uncertainty

(~3.6-fold range), but the range shows that phytoplankton are an important contributor to sediment TP.

The process of poly-P storage by phytoplankton removes SRP from the water column, and sedimentation of sequestered poly-P that is not geochemically reactive minimizes the potential for internal P loading. Poly-P sedimentation is a possible explanation for the large P-retention coefficient found for recent Lake Apopka sediments (Schelske 1997). Currently, the mass of P sedimented annually equals the TP reservoir in the water column (Schelske 1997) and is at least 65% of the annual P load (see Battoe et al. 1999; Schelske et al. 2000). This biological attenuation may partially ameliorate the effects of increased P loading.

The global relevance of poly-P sedimentation may be limited to eutrophic systems that support large standing crops of phytoplankton, but this will only be determined by future research. In oligotrophic, P-limited, or ephemeral systems, poly-P sedimentation may be of little ecological significance. Oligotrophic lakes not limited by P may lack the phytoplankton biomass required to store increases in available P as poly-P and, therefore, surplus available P is more likely to be processed geochemically in systems that support minimal biomass. Poly-P is not important in P-limited lakes, because it is stored primarily as a result of relaxed P limitation of phytoplankton growth. Although poly-P may be deposited in ephemeral systems, such as wetlands, periodic desiccation may prevent long-term storage in the sediments. Ecological significance in lakes can be evaluated with existing data and routine limnological techniques, even if poly-P has not been measured. If TP is in greater concentration than chlorophyll in water samples or if NaOH-P is a large fraction of TP in sediments, then poly-P sedimentation may have ecological significance. Measurable SRP in water samples may indicate surplus P in the water column and that poly-P is being stored in phytoplankton (Schelske et al. 1999*a*).

Our results demonstrate that poly-P sedimentation is an important P sink that should be considered in lakes with anthropogenic enrichment. Poly-P synthesis by phytoplankton is important in this regard, because P is stored intracellularly without increasing phytoplankton biomass. Intracellular poly-P in both phytoplankton cells and their resting propagules may be preserved in the sediment for decades or longer. This process removes SRP from enriched waters and buries it in a form that cannot diffuse into the water column, thereby providing negative feedback to P enrichment. With data from Lake Apopka, we show that anthropogenic P enrichment is expressed in the sediment record as increasing concentrations of poly-P and, consequently, that sedimentary poly-P is a sensitive indicator of historic, excessive, P enrichment.

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