

Release rates and potential fates of nitrogen and phosphorus from sediments in a eutrophic reservoir

WESTON H. NOWLIN, JENNIFER L. EVARTS AND MICHAEL J. VANNI

Department of Zoology, Miami University, Oxford, OH, U.S.A.

SUMMARY

1. Nutrients released from lake sediments can influence water column nutrient concentrations and planktonic productivity. We examined sediment nutrient release [soluble reactive phosphorus (SRP) and ammonia (NH_4^+)] at two sites in a eutrophic reservoir (Acton Lake, OH, U.S.A.) that differed in physical mixing conditions (a thermally stratified and an unstratified site).
2. Sediment nutrient release rates were estimated with three methods: sediment core incubations, seasonal *in situ* hypolimnetic accumulation and a published regression model that predicted sediment phosphorous (P) release rate from sediment P concentration. All three methods were applied to the deeper stratified site in the reservoir; however, we used only sediment core incubations to estimate SRP and NH_4^+ release rates at the shallow unstratified site because of the lack of thermal stratification. We also compared the total P concentration (TP_S) of sediments and the concentration of P in various sediment fractions at both sites.
3. Anoxic sediments at the stratified site released SRP at rates more than an order of magnitude greater than oxic sediments at the shallow unstratified site. However, P accumulated in the hypolimnion at much lower rates than predicted by sediment core incubations. In contrast, NH_4^+ was released at similar rates at both sites and accumulated in the hypolimnion at close to the expected rate, indicating that P was 'lost' from the hypolimnion through biogeochemical pathways for P, such as precipitation with inorganic material or biological uptake and sedimentation.
4. TP_S was significantly greater at the deeper stratified site and organically bound P accounted for >50% of TP_S at both sites.
5. We examined the magnitude of SRP fluxes into the study reservoir in 1996 by comparing the mean summer daily SRP fluxes from anaerobic sediments, aerobic sediments, stream inflows and gizzard shad excretion. While the SRP release from anaerobic sediments was high, we hypothesise that little of this SRP gained access to the epilimnion in mid-summer. SRP flux to the reservoir from aerobic sediments was less than from gizzard shad excretion and streams. Large interannual variability in thermocline stability, gizzard shad biomass and stream discharge volumes, will affect SRP loading rates from different sources in different years. Therefore, construction of P budgets for different years should account for interannual variation in these parameters.

Keywords: gizzard shad, nutrient release, phosphorus, sediments, thermal stratification

Correspondence: Weston H. Nowlin, Department of Zoology, Miami University, Oxford, OH 45056, U.S.A.

E-mail: nowlinw@muohio.edu

Present address: Jennifer L. Evarts, Science Department, Landon School, 6101 Wilson Lane, Bethesda MD 20817, U.S.A.

Introduction

Sediments are an important source of nutrients to freshwater ecosystems. The release of phosphorus (P) and nitrogen (N) from lake sediments has been

examined for decades (Mortimer, 1941, 1942; Nürnberg, 1987; Andersen & Jensen, 1992; Gardner *et al.*, 2001). Historically, P input from lake sediments has received much more attention from researchers than N input because of the complex nature of N transformations in lake sediments and the fact that P often limits the biomass and productivity of plankton communities (Dillon & Rigler, 1974; Smith, 1979). Sediment P inputs (internal P loading) can be a significant term in the annual P budget of many lakes (Nürnberg, 1984b; Nürnberg *et al.*, 1986; Auer *et al.*, 1993) and attempts at lake restoration through the reduction of external P inputs often fail because of large P inputs from sediments, even after external loads have been substantially reduced (Søndergaard, Jensen & Jeppesen, 1999). Further, in some lakes, sediment nutrient release may represent a more ecologically important process than inputs from external nutrient sources because P released from sediments often contains a larger portion of immediately bioavailable P (Peters, 1981; Nürnberg & Peters, 1984; Nürnberg, 1985; but see Auer *et al.*, 1998). Therefore, it is critical to characterise sources of P, both external and internal, to lakes and reservoirs in order to manage nutrient inputs to freshwater systems.

Processes leading to P release to the water column from underlying sediments are numerous, and include the desorption and dissolution of P bound in precipitates and inorganic material (Mortimer, 1941, 1942; Moore & Reddy, 1994), microbial mineralisation of organic matter (Gächter & Meyer, 1993) and the diffusion of dissolved P from sediment pore waters (Boström *et al.*, 1988; Moore, Reddy & Fisher, 1998; Pettersson, 1998). The environmental variables that appear to regulate the release rate of dissolved P from sediments (mostly as phosphate, PO_4^{3-}) are temperature, dissolved oxygen (DO) concentration, pH, and redox potential (Mortimer, 1941; Kamp-Nielsen, 1974; Boström *et al.*, 1988; Jensen & Andersen, 1992). In productive lakes, after the onset of summer stratification, biological activity in sediments and the hypolimnion decreases hypolimnetic DO concentration and pH, lowering the redox potential at the sediment-water interface. At low redox potentials (<200 mV), Fe (III) in the sediments is reduced to Fe (II), leading to the release of PO_4^{3-} and Fe (II) (Boström *et al.*, 1988). The total P concentration of sediments (TP_s) and the relative concentration of various P

fractions (i.e. Fe-bound P, aluminium-bound P, organic-bound P) in sediments also influence sediment P release rates (Boström, Jansson & Forsberg, 1982; Messer, Ihnat & Wagner, 1984; Boström *et al.*, 1988; Nürnberg, 1988). However, P release from sediments is not strictly a result of abiotic chemical processes mediated by lake physical conditions. For example, under anoxic conditions, high concentrations of nitrate (NO_3^-) in waters overlying sediments can raise the redox potential by providing denitrifying bacteria with an alternate electron acceptor (Andersen, 1974, 1982; Boström *et al.*, 1988), thereby enhancing Fe oxidation and sediment sorption of PO_4^{3-} . In contrast, the growth of Fe-reducing bacteria may be stimulated by high NO_3^- levels, leading to higher decomposition rates of organic matter and enhancement of PO_4^{3-} release from sediments (Boström *et al.*, 1988). Thus, the release of PO_4^{3-} from sediments into overlying water during summer hypolimnetic anoxia is a result of the complex interaction between biotic and abiotic processes in the water column and sediments.

Reservoirs are appropriate systems for studying factors affecting nutrient release from sediments because of the strong longitudinal gradient of physical and chemical conditions. Relatively shallow areas near inflows may lack thermal stratification throughout the year, while deeper regions near the dam may establish summer stratification (Thornton, 1990a). This longitudinal development of thermal stratification can lead to variation in DO concentration in waters above sediments, thus affecting sediment nutrient release rates. The composition of sediments may also vary along the longitudinal axis of a reservoir, with sediments near inflows containing a larger proportion of allochthonous material and sediments near the dam containing a larger proportion of autochthonous material (Goldman & Kimmel, 1978; Vannote *et al.*, 1980; Thornton, 1990b). Various P-containing fractions within sediments may vary with the spatial heterogeneity of sediment characteristics within a reservoir, potentially affecting the P-binding capacity of sediments and sediment P release rates.

In this study we examine P and N release rates from sediments in a eutrophic reservoir. Sediment nutrient release rates from sites within the reservoir that differ in chemical and physical characteristics are compared to examine the influence of within-reservoir variation in physical and chemical conditions on sediment

nutrient release rates. Several methods of estimating sediment nutrient release are compared to investigate and predict sediment nutrient release in the study reservoir: laboratory-based sediment core incubations, measurement of hypolimnetic accumulation of nutrients during summer stratification, and a published regression model (Nürnberg, 1988). We further examine the relative importance of various nutrient sources (sediments, stream inputs and excretion by benthivorous fish) to P loading of the study reservoir.

Methods

Study site and field sampling

Acton Lake is a small (surface area, $A = 253$ ha), hardwater, relatively shallow eutrophic reservoir in south-western Ohio, U.S.A. The mean depth (\bar{z}) of the lake is 4 m, with a maximum depth of 8 m, near the dam. There are several major water inflows to the reservoir (Little Four Mile Creek, Four Mile Creek and Marshall's Branch), which enter a shallow area upstream from the dam (Canfield *et al.*, 1984; Vanni *et al.*, 2001). The only outflow from the reservoir is over the dam spillway. The reservoir discharged only surface (epilimnetic) water during this study. Acton Lake's watershed is approximately 90% agricultural (Medley *et al.*, 1995) with most of the remaining 10% located within forested riparian areas in Hueston Woods State Park. The watershed substrate consists primarily of limestone and shale, typical of south-western Ohio (Martin, 1984). Detailed description of Acton Lake watersheds are provided elsewhere (Vanni *et al.*, 2001).

To examine nutrient release from sediments, we selected two sites within Acton Lake that differed in physical and chemical characteristics. One site is located in the shallow upstream area of the reservoir near the stream inflows (the 'river' site). Maximum water depth at this site is 1.5 m, the water column does not thermally stratify and the sediment-water interface remains oxic throughout summer. Water column pH at the river site is 7.8–8.7 in summer (Green, Canfield & Steinly, 1985). The second site is at the deepest portion of the reservoir near the dam ('dam' site). Maximum depth is 8 m, with surface pH during summer 8.3–8.6, and pH above the sediment water interface 7.0–8.1 (Green *et al.*, 1985). The dam

site stratifies during summer, with hypolimnetic DO dropping to <1 mg DO L⁻¹ shortly after stratification until turnover in the early fall (from early June to mid-September; Winner, Strecker & Ingersoll, 1962).

The deepest point at each site was sampled weekly from early May to mid- to late October, in 1995 and 1996. Water column profiles of temperature and DO concentration were measured with YSI model 58 temperature/DO meter (Yellow Springs Instruments, Yellow Springs, OH, U.S.A.). Water samples were collected at 1 m depth intervals at both sites. Samples were immediately filtered in the laboratory for soluble reactive phosphorus (SRP), ammonia (NH₄⁺), and nitrate (NO₃⁻) analyses [American Public Health Association (APHA), 1992; Crumpton, Isenhardt & Mitchell, 1992]. High levels of H₂S in anoxic hypolimnetic water can potentially lead to unstable SRP analyses and thus underestimates of SRP concentrations (Nürnberg, 1984a). To determine whether this was the case for Acton Lake hypolimnetic water, we conducted a series of 'PO₄³⁻ addition' experiments in which we added PO₄³⁻ to hypolimnetic water samples and then filtered and analysed samples for SRP. We were able to recover all of the added PO₄³⁻ (M.J. Vanni, unpubl. data); therefore, it is unlikely H₂S interference caused us to underestimate hypolimnetic SRP. Unfiltered water samples were frozen for later total phosphorus (TP) analysis (APHA, 1992).

Sediment P concentration and P fractionation

Three replicate sediment cores were taken with a gravity corer from both sites at least once a month from June to October 1996. Sediment cores were divided into 0–1 cm and 1–5 cm sections, individually dried at 60 °C and homogenised. To determine total phosphorus in sediments (TP_S; µg P mg sediment⁻¹), 3–12 mg of dry sediment was weighed, ashed, digested with HCl and analysed for SRP (Stainton, Capel & Armstrong, 1977). A serial extraction procedure adapted from Hieltjes & Lijklema (1980), Nürnberg (1988), Ruttenberg (1992) and Moore, Reddy & Graetz (1991) was used to characterise sediment P fractions in the 0–1 and 1–5 cm sections. Two molar KCl was used to extract loosely sorbed P (loose-P: P loosely absorbed to surfaces of Fe and CaCO₃). To extract P associated with iron compounds (Fe-P), we used a 0.11 M NaHCO₃ and 0.11 M Na-dithionite solution. This extractant was aerated to prevent the dithionite

interference with subsequent SRP analyses (Nürnberg, 1988). One molar NaOH was used to determine the fraction of P associated with aluminium compounds or metallic acids (Al-P). We then extracted calcium-bound P (Ca-P) with 1 M HCl. All extractants at each step were pH balanced and analysed for SRP using the ascorbic acid method (APHA, 1992). The organic-P fraction (Org-P) was measured by subtracting the sum of the inorganic P fractions from TP₅ (Hieltjes & Lijklema, 1980; Ruban *et al.*, 1999).

Estimation of sediment nutrient release rates

In situ hypolimnetic accumulation method. Depth profiles of hypolimnetic nutrient concentrations (TP, SRP and NH₄⁺), temperature profiles and reservoir bathymetry were used to estimate hypolimnetic mass of nutrients (Nürnberg *et al.*, 1986; Nürnberg, 1987). As sediments are likely to be the major source of dissolved nitrogen and phosphorus within the hypolimnion in summer (Nürnberg, 1988), we attributed NH₄⁺ and SRP accumulation after the onset of stratification to sediment release. We calculated sediment release rates ($\mu\text{mol m}^{-2}$ anoxic sediment surface per day) for TP, SRP and NH₄⁺ from anoxic sediments by taking the difference between the 'background' hypolimnetic nutrient mass immediately after the onset of summer stratification (and after early summer storm events; see Results) and the hypolimnetic nutrient mass prior to the downward migration of the thermocline in the fall (Nürnberg *et al.*, 1986). We propose that sediment nutrient release rates determined from *in situ* hypolimnetic nutrient accumulation represent a *net* nutrient flux because rates are calculated from the accumulation of hypolimnetic nutrients after relatively long time periods (weeks to months). As stated previously, the dam site experiences a defined period of thermal stratification and hypolimnetic anoxia, while the river site does not. Therefore, we used the *in situ* hypolimnetic accumulation method at the dam site only.

Sediment core incubation method. Sediment cores were collected from the dam and river sites using a gravity corer during the summer and fall of 1996. Six replicate sediment cores were collected from each site on each sampling date. Cores were collected in Plexiglas core tubes (4.3-cm diameter, 20-cm length) so that there was approximately 10 cm of sediment and 10 cm of

overlying water. Cores were stored vertically in the dark in a cooler and brought back to the laboratory.

Cores from the river site were incubated in the dark at 25 °C, similar to water temperatures at the site. The sediment–water interface at the river site is aerobic, so cores were aerated throughout incubations using an aquarium pump and Tygon tubing, keeping DO concentrations at *in situ* levels. Cores from the dam site were incubated in the dark at 12 °C, similar to hypolimnetic temperature. To ensure the sediment–water interface remained anoxic, cores were immediately stoppered upon collection. We examined pH changes during sediment core incubations in a subset of cores from both sites and found that pH within the water column of the cores did not change from *in situ* conditions during incubations (river pH = 8.1–8.5, dam pH = 7.5–8.0). Sediment core incubations lasted for 2–5 days. Because sediment core incubations were conducted over relatively short periods of time and SRP or NH₄⁺ released from sediments were not subject to the longer term (>1 week) processes which can take place in lakes (such as relatively slow precipitation with some types of inorganic material, diffusion across the thermocline and entrainment into the epilimnion), we consider SRP and NH₄⁺ release rates determined from short-term sediment core incubations to be estimates of *gross* nutrient fluxes from sediments.

During incubations, it was not possible to re-sample the same cores because of limited water volume within tubes. Therefore, three replicate cores were sacrificed for SRP and NH₄⁺ analyses on the first and last days of the incubation time interval. Water samples from cores were analysed for SRP and NH₄⁺. SRP was measured instead of TP because and SRP represents the overwhelmingly dominant fraction of both total dissolved P (TDP) and TP released from sediments (Nürnberg *et al.*, 1986; Nürnberg, 1988; Moore *et al.*, 1991; Auer *et al.*, 1993) and SRP is immediately biologically available to algae and bacteria (Nürnberg & Peters, 1984). In this study, we assume that SRP release during sediment core incubations was equal to TP release, which permits comparison of our sediment core release rates with release rates predicted from Nürnberg's (1988) regression equation.

Sediment core incubation experiments were conducted to determine if relatively high NO₃⁻ concentrations could affect SRP release rates from Acton

Lake sediments. As stated previously, high NO_3^- concentrations in the hypolimnion can suppress or enhance P release from anoxic sediments (Andersen, 1982; Boström *et al.*, 1988). In Acton Lake, epilimnetic NO_3^- concentration is high in the spring and early summer ($>500 \mu\text{mol NO}_3^- \text{-N L}^{-1}$; see Results) and declines to 20–100 $\mu\text{mol NO}_3^- \text{-N L}^{-1}$ by the fall. These relatively high concentrations are because of the large input of NO_3^- from the agriculturally dominated watershed in spring and early summer (Vanni *et al.*, 2001). Seasonal variation of NO_3^- concentrations in Acton Lake and the potential importance of NO_3^- in regulating temporal patterns of P release from sediments in the reservoir led us to explore the role of NO_3^- in Acton Lake. In September 1996, nine sediment cores were collected on two dates from each site (river site = 4 and 11 September, dam site = 18 and 25 September). We collected sediment cores from Acton Lake when NO_3^- levels above the sediment–water interface were low, in order to assess the impact of high nitrate concentrations on SRP release rates. Throughout September 1996, NO_3^- concentration above the sediment–water interface at the dam site were relatively low (11.9 $\mu\text{mol NO}_3^- \text{-N L}^{-1}$), while NO_3^- above the sediment–water interface at the river site was relatively high (September \bar{x} concentration = 167 $\mu\text{mol NO}_3^- \text{-N L}^{-1}$). On each date that NO_3^- addition experiments were conducted for a site, 1 mL of 0.1 M NaNO_3 was added to the overlying water of nine cores from both dam and river sites, to give a final concentration of approximately 500 $\mu\text{mol N L}^{-1}$, similar to *in situ* concentrations observed in early summer. One millilitre of 0.1 M NaCl was added to nine cores from each site in order to serve as controls (i.e. to determine if the addition of Na (as part of NaNO_3) was associated with any changes in sediment core SRP and NH_4^+ release rates). SRP and NH_4^+ release rates were determined at the end of two time intervals: days 0–2, and days 2–5. Three replicate cores were sacrificed at the beginning, after 2 days and after 5 days of incubation for SRP and NH_4^+ analysis. Cores were incubated at conditions described for the standard core incubations.

Nürnberg's (1988) regression method. Anoxic sediment P release rates from the dam site were estimated using a published regression equation, which relates P release and sediment total P (TP_s) concentration of anoxic sediments (Nürnberg, 1988). The following

'world-wide' equation was generated by compiling data from literature values of anoxic sediment P release rates (RR; as TP) and TP_s of 63 lakes (Nürnberg, 1988):

$$\log_{10} \text{RR}(\text{mgTP m}^{-2} \text{ d}^{-1}) = 0.80 + 0.76 \log_{10}(\text{TP}_s).$$

The TP_s of the 0–1 and 1–5 cm sediment core sections from the dam site were pooled because Nürnberg (1988) used TP_s values from the top 5 cm of sediment to generate this equation. We estimated the sediment TP release rate at the dam site on each date we collected sediments in 1996 (12 dates; mid-May to mid-September). It is important to note that this general predictive relationship between P release rate and TP_s was generated from a wide diversity of lakes using numerous methods to estimate both RR and TP_s .

Data analysis

Sediment total phosphorus and individual P fractions (loose-P, Fe-P, Al-P, Ca-P, and Org-P) were compared at each site for both sediment depth intervals with two-way repeated measures ANOVAs. Factors in the analyses were site (river or dam) and sediment depth interval (0–1 cm or 1–5 cm) and the repeated measure was sampling dates ($n = 4$).

It was impossible to resample individual cores during incubations, so we could not obtain a release rate from individual cores. Mean release rates for a site (river or dam site) were calculated as the mean concentration in cores at the end of an incubation interval minus the mean concentration in cores at the beginning of the incubation interval, standardised for time of incubation and surface area of sediments in cores ($\mu\text{mol SRP-P m}^{-2} \text{ day}^{-1}$ or $\text{mmol NH}_4^+ \text{-N m}^{-2} \text{ day}^{-1}$). Because we could not obtain a release rate for individual sediment cores, error estimates were determined via bootstrap simulations (Dixon, 1993). Each bootstrap simulation randomly chose two initial and two final concentrations from replicate cores and averaged their SRP or NH_4^+ concentrations to give new 'bootstrap' initial and final concentrations and a bootstrap release rate (calculated as the bootstrap final minus the bootstrap initial concentration). One thousand simulations were performed. Bootstrap release rates were ranked and bootstrap 95% confidence intervals were taken as the middle 95% of the ranked bootstrap release rates. On a given date,

bootstrap 95% confidence intervals from river and dam sites were compared to determine if overlap between confidence intervals occurred. No overlap of the bootstrap 95% confidence intervals was taken as evidence of a significant difference between the two reservoir sites (Dixon, 1993). The same bootstrapping procedure was used to determine if the addition of NO_3^- had a significant effect on SRP and NH_4^+ release from sediments. The 95% bootstrap confidence intervals for cores receiving NO_3^- and control cores were compared for the two incubation time intervals (days 0–2 and days 2–5).

Results

Stratification patterns and nutrient concentrations

In the summer of 1995, the dam site in Acton Lake was thermally stratified from late May to mid-September (Fig. 1a). Thermocline depth (depth of maximum temperature change) was at approximately 4 m during stratification; however there were two large migration events of the $<1 \text{ mg DO L}^{-1}$ contour during the summer (late May to early June and late July to early August; Fig. 1a). Surface water temperatures did not differ between the dam and river sites on individual sampling dates; however, the river site remained relatively isothermal ($<2 \text{ }^\circ\text{C}$ change in water temperature from surface to sediment–water interface) throughout the summer. DO concentration at the river site exhibited little variation with depth, and concentrations above the sediment–water interface always $>5.3 \text{ mg DO L}^{-1}$. Because of the shallow depth of the river site and the lack of stratification, we do not present isopleth diagrams of temperature and DO concentrations.

Temperature and DO profiles at the dam site in 1996 were different from 1995. Based upon weekly sampling, the thermocline was consistently between 4 and 5 m throughout the summer, and declined as fall turnover approached (Fig. 1b). The anoxic contour ($<1 \text{ mg DO L}^{-1}$) was at 4–5 m for most of the thermal stratification period, and the hypolimnion did not demonstrate the periodic increases in DO observed in 1995. The river site did not thermally stratify during the summer and surface water temperatures were similar to the dam site. DO concentrations at the sediment–water interface at the river site were never $<3.2 \text{ mg L}^{-1}$ through out the summer.

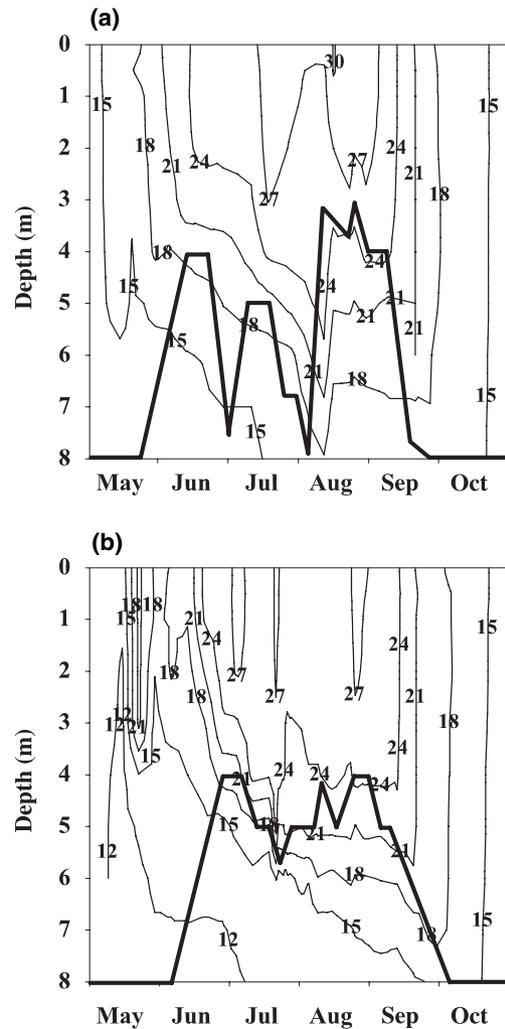


Fig. 1 Temperature ($^\circ\text{C}$) profiles from the Acton Lake dam site from May to October in (a) 1995 and (b) 1996. The $<1 \text{ mg DO L}^{-1}$ contour is indicated by the bold line.

In 1995, summer TP concentration in surface waters of the dam site ranged between 1 and $15 \text{ } \mu\text{mol L}^{-1}$ (mean = $6 \text{ } \mu\text{mol L}^{-1}$), with heavy rains and large stream discharges causing maximum TP concentrations in the early summer (Fig. 2a). In the hypolimnion, TP concentrations increased and reached $>16 \text{ } \mu\text{mol L}^{-1}$ by mid-September. Surface SRP concentrations at the dam site were highest from May to early June declining to $<0.3 \text{ } \mu\text{mol L}^{-1}$ by mid-June (Fig. 2b). There were two periods of hypolimnetic SRP accumulation in 1995, with the first occurring before the late July thermocline migration and the second period occurring after the thermocline re-established at 4 m (Fig. 2b). During the two periods of hypolim-

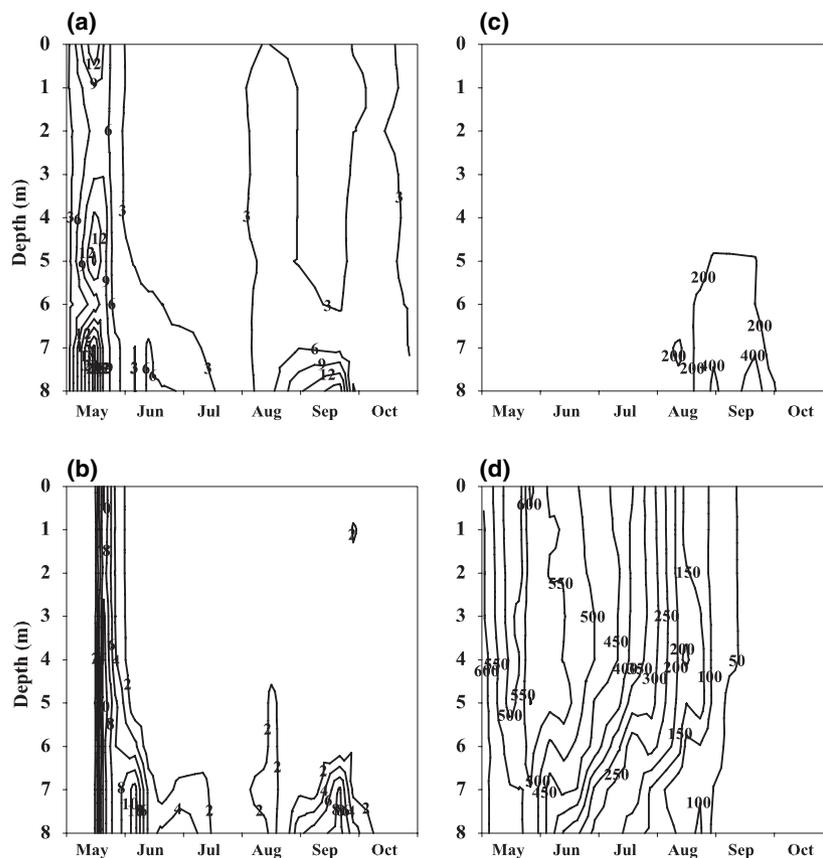


Fig. 2 Nutrient concentration profiles at the Acton Lake dam site May to October, 1995. (a) TP, (b) SRP, (c) NH_4^+ , and (d) NO_3^- . TP and SRP concentrations are in $\mu\text{mol P L}^{-1}$ and NH_4^+ and NO_3^- concentrations are in $\mu\text{mol N L}^{-1}$.

netic SRP accumulation, hypolimnetic SRP concentrations reached $5\text{--}7 \mu\text{mol P L}^{-1}$ near sediments, accounting for 60–70% of the TP pool at that depth. At the river site in 1995, TP and SRP concentrations followed the same seasonal pattern as the surface TP and SRP concentrations at the dam site and were approximately the same concentration. There was little variation in TP and SRP concentration with depth at the river site. Again, because of shallow depth and lack of thermal stratification, we do not graphically present this data for the river site.

At the dam site in 1995, surface NH_4^+ concentrations ranged from 2 to $50 \mu\text{mol NH}_4^+\text{-N L}^{-1}$ (summer $\bar{x} = 14 \mu\text{mol NH}_4^+\text{-N L}^{-1}$), while the hypolimnetic NH_4^+ concentration seasonally increased, reaching a maximum concentration of $430 \mu\text{mol NH}_4^+\text{-N L}^{-1}$ by late September (Fig. 2c). NO_3^- concentration at the dam site was highest at the beginning of the summer (approximately $600 \mu\text{mol NO}_3^-\text{-N L}^{-1}$) and decreased to approximately $100 \mu\text{mol NO}_3^-\text{-N L}^{-1}$ by late summer. Hypolimnetic NO_3^- concentration declined to $<42 \mu\text{mol NO}_3^-\text{-N L}^{-1}$ by September (Fig. 2d). River

site NH_4^+ and NO_3^- concentrations were similar to surface concentrations at the dam site and followed the same temporal patterns.

Dam site surface TP concentrations in 1996 after spring storm events were $<5 \mu\text{mol P L}^{-1}$ for most of the summer, and increased to $13 \mu\text{mol P L}^{-1}$ after fall turnover (Fig. 3a). Hypolimnetic TP increased to approximately $24 \mu\text{mol P L}^{-1}$ by late September, and this concentration quickly declined after fall turnover. Dam site epilimnetic SRP was $>4 \mu\text{mol P L}^{-1}$ in mid-May, but declined by mid-June to $<0.2 \mu\text{mol P L}^{-1}$ for the rest of the summer (Fig. 3b). On several occasions, hypolimnetic SRP concentrations increased to $>1 \mu\text{mol P L}^{-1}$, but then quickly declined. TP and SRP concentration at the river site were highest (12.3 and $8 \mu\text{mol P L}^{-1}$, respectively) in mid-May (coinciding with early summer storm events; see Results for 1995), but quickly declined and remained at concentrations similar to the surface waters at the dam site for most of the summer.

Nitrogen dynamics at the dam site in 1996 followed a similar seasonal trend to the previous year

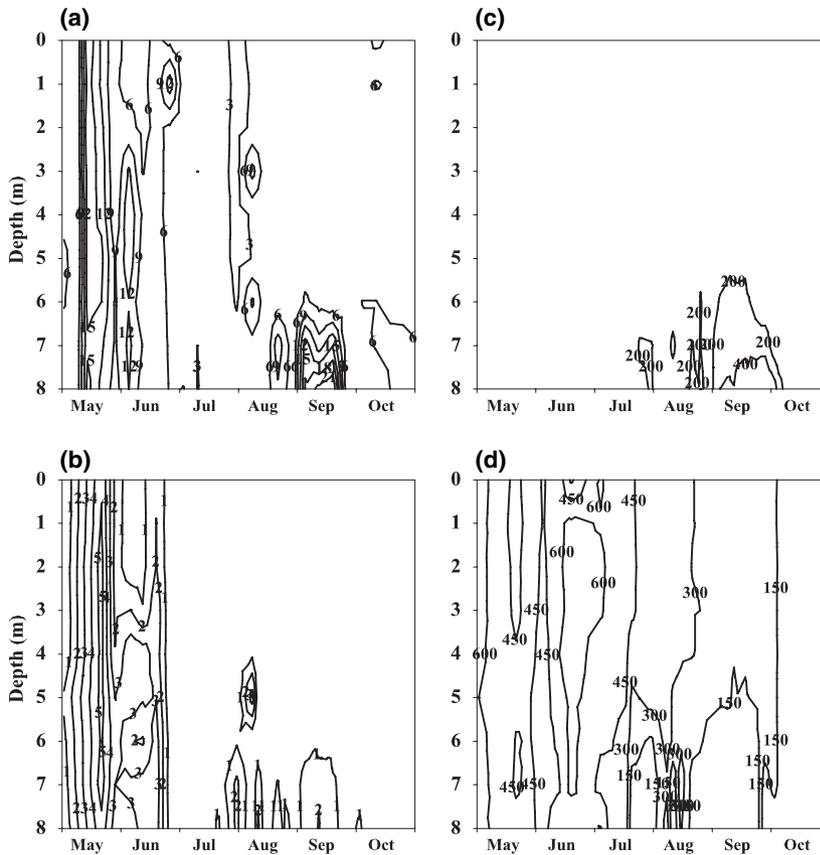


Fig. 3 Nutrient concentration profiles at the Acton Lake dam site May to October, 1996. (a) TP, (b) SRP, (c) NH_4^+ , and (d) NO_3^- . TP and SRP concentrations are in $\mu\text{mol P L}^{-1}$ and NH_4^+ and NO_3^- concentrations are in $\mu\text{mol N L}^{-1}$.

(Fig. 3c,d). Hypolimnetic NH_4^+ increased from mid-July to mid-September, reaching a seasonal maximum above the sediment–water interface of approximately $430 \mu\text{mol NH}_4^+\text{-N L}^{-1}$ (Fig. 3c). Surface NO_3^- concentration declined from $>600 \mu\text{mol NO}_3^-\text{-N L}^{-1}$ in May to approximately $100 \mu\text{mol NO}_3^-\text{-N L}^{-1}$ in the fall, and hypolimnetic NO_3^- declined to $<14 \mu\text{mol NO}_3^-\text{-N L}^{-1}$ in mid-September (Fig. 3d). NH_4^+ and NO_3^- concentrations and temporal dynamics at the river site followed the similar seasonal patterns to the surface waters of the dam site.

Sediment P content and P fractions

The two-way repeated measures ANOVA indicated that there was a significant effect of site (dam versus river) and sediment depth (0–1 versus 1–5 cm) on TP_s , as well as a significant site \times depth interaction (Table 1). TP_s at both sediment depths did not significantly vary with time (Table 1). As there was no significant time effect on TP_s , mean TP_s concentrations at each sediment depth were pooled across all

dates, producing the following seasonal means ($\text{mg P g sediment}^{-1}$; ± 1 SD): dam 0–1 cm = $1.62 (\pm 0.16)$, dam 1–5 cm = $1.51 (\pm 0.2)$, river 0–1 cm = $0.89 (\pm 0.06)$, and river 1–5 cm = $0.88 (\pm 0.06)$. Although, TP_s decreased with depth at both sites, the magnitude

Table 1 Results of two-way repeated measures ANOVA for total phosphorous concentration of sediments (TP_s) at the dam and river sites of Acton Lake in 1996. Data were \log_{10} transformed prior to analysis. Time effect P -values were adjusted with the Greenhouse-Geisser Epsilon value.

	d.f.	F	P -value
Treatment effects			
Site	1	344.6	0.0001
Depth	1	12.7	0.0007
Site \times depth	1	17.6	0.0030
Error (between subjects)	8		
Time effects			
Time	7	2.1	0.1488
Time \times site	7	1.3	0.2921
Time \times depth	7	1.3	0.3136
Time \times site \times depth	7	1.0	0.3855
Error (within subjects)	56		

of the decline was greater at the dam site, causing the significant site \times depth interaction effect.

Results of the two-way repeated measures ANOVA for each of the five sediment P fractions (loose-P, Fe-P, Al-P, Ca-P, and Org-P) indicated that there was a significant difference in concentration between sites for all fractions, with the dam having a larger P concentration in each fraction (Table 2). There was no significant depth effect or significant site \times depth interaction effect for any of the sediment P fractions.

Loose-P and Al-P demonstrated a significant time effect (Table 2), however the overall temporal variation in P concentration for the five P fractions was relatively small (Evarts, 1997). Therefore, we calculated and present the 1996 seasonal means for all sediment P fractions (Fig. 4a,b); temporal trends in P concentration are presented elsewhere (Evarts, 1997). Org-P represented the largest fraction of sediment P, accounting for approximately 50% of TP_S at the river and dam sites at both sediment depths (Fig. 4a,b). Loose-P accounted for the smallest percentage of TP_S, approximately 6% of TP_S at both sites. Fe-P represented 21% of TP_S at the dam, and 16% at the river. Al-P accounted for a higher percentage of TP_S at the dam site (22% of TP_S) than at the river site (8% of TP_S). In contrast, Ca-P was proportionately higher at the river site than at the dam, accounting for 18 and 9% of TP_S, respectively.

Nutrient release from sediments

In situ hypolimnetic accumulation method. We calculated nutrient release rates from sediments in 1996, in

order to facilitate comparison of the different methods of estimating nutrient release from sediments. In 1996, the thermocline and oxycline set up at 4–5 m for most of the summer period. Thus, we used the volume below 4 m and the sediment surface area at this interval to calculate the change in hypolimnetic nutrient mass and the release rate per unit area of anoxic sediments. We used the time interval from 26 June to 9 September to calculate the *in situ* release rate. The start date of this time interval was selected because it was after the early summer storm events (Fig. 3) and thermal stratification had stabilised by this point in the summer (Fig. 1b). The end date of this time interval was used because it was the sampling date that preceded the downward migration of the thermocline in the fall. *In situ* accumulation of TP in 1996 translated into a net sediment release rate of 27.12 $\mu\text{mol P m}^{-2} \text{ day}^{-1}$. SRP release rates calculated from the *in situ* method yielded a release rate of 4.86 $\mu\text{mol SRP-P m}^{-2} \text{ day}^{-1}$. NH_4^+ was released from anoxic sediments in the reservoir at a rate of 2.34 $\text{mmol NH}_4^+\text{-N m}^{-2} \text{ day}^{-1}$.

Sediment core incubations. Sediment core incubations conducted during the summer stratification period of 1996 (July to September) indicated that the dam site exhibited SRP release rates almost an order of magnitude greater than the river site (Fig. 5a; Table 3). The mean SRP release rate for the dam site during thermal stratification was 293.7 $\mu\text{mol SRP-P m}^{-2} \text{ day}^{-1}$, and the river site had a mean release rate of 31.5 $\mu\text{mol SRP-P m}^{-2} \text{ day}^{-1}$ over the same

Table 2 Results of two-way repeated measures ANOVA for sediment phosphorous fractions at the dam and river sites of Acton Lake in 1996. Data were log₁₀ transformed prior to analysis. Time effect *P*-values were adjusted with the Greenhouse-Geisser Epsilon value.

	d.f.	Loose-P		Fe-P		Al-P		Ca-P		Org-P	
		<i>F</i>	<i>P</i> -value								
Treatment effects											
Site	1	105.6	0.0001	476.5	0.0001	5410.9	0.0001	16.2	0.0038	139.5	0.0001
Depth	1	0.6	0.4672	2.4	0.1687	0.5	0.4897	2.0	0.1929	2.3	0.1709
Site \times depth	1	0.4	0.5649	1.1	0.3245	4.1	0.079	1.5	0.2517	0.1	0.8133
Error (between subjects)	8*										
Time effects											
Time	3	6.1	0.0204	0.6	0.6333	8.3	0.004	1.2	0.3324	3.6	0.0691
Time \times site	3	13.6	0.0015	1.7	0.1947	11.2	0.0012	3.6	0.0387	0.9	0.4099
Time \times depth	3	2.1	0.1712	2.3	0.1063	4.6	0.0283	1.1	0.3583	3.2	0.0848
Time \times site \times depth	3	2.7	0.1149	1.0	0.4104	0.6	0.5561	2.0	0.1514	4.0	0.0549
Error (within subjects)	24*										

*Fe-P and Org-P between subjects error = 7 and within subjects error = 21.

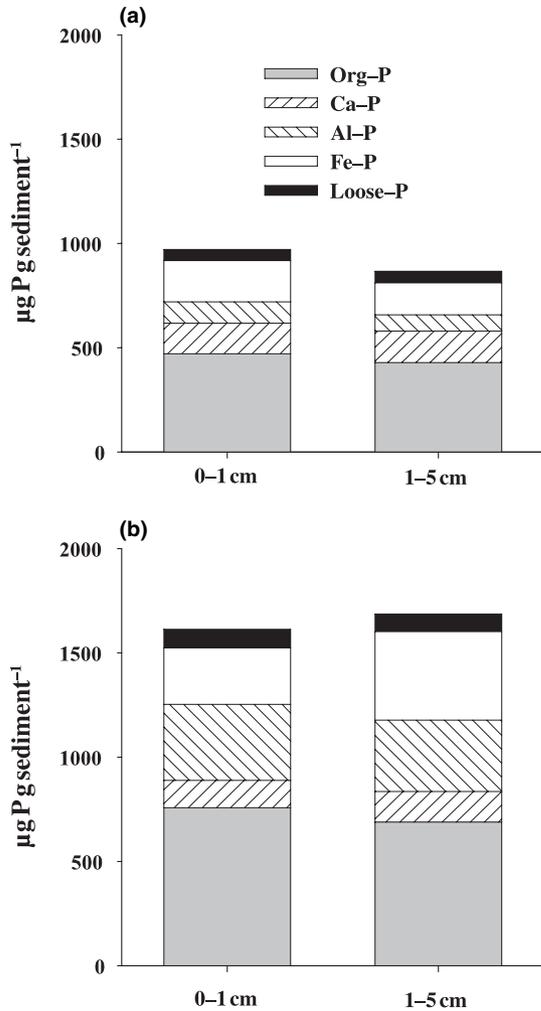


Fig. 4 Mean sediment P concentrations ($\mu\text{g P g sediment}^{-1}$) of each of the five sediment P fractions in the 0–1 cm and the 1–5 cm sediment depth intervals. (a) River site; (b) Dam site.

time interval. When sediment SRP release rates determined from standard sediment core incubations are compared with the SRP release rates obtained from sediment cores used as controls in NO_3^- addition experiments at a given site (cores received that NaCl), the standard incubation sediment core SRP release rates and NaCl 'control' core release rates (for the day 0–2 time interval) were not noticeably different from each other (Table 3). Therefore, we combined the standard incubation core SRP release rates and the NaCl 'control' SRP release rates at a site for analyses. After combining the SRP release rates for standard and NaCl cores for each site, the mean SRP release rate for the river and dam sites did not greatly change and were 16.7 and 299.7 $\mu\text{mol SRP-} \mu\text{m}^{-2} \text{d}^{-1}$, respectively.

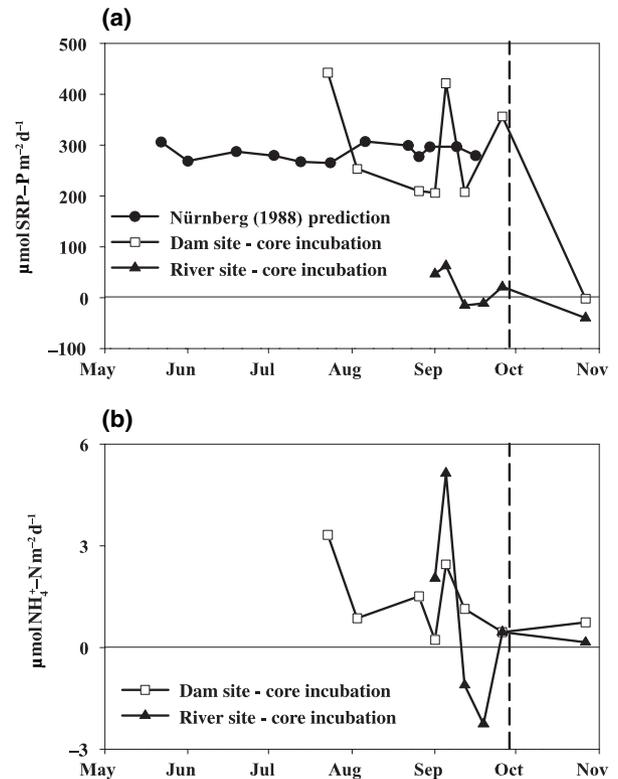


Fig. 5 Temporal variation in estimated nutrient release rates from the river and dam sites in Acton Lake during May to October 1996. (a) SRP release rates obtained from sediment core incubations at the dam and river sites and the predicted release rate from the Nürnberg (1988) regression equation. (b) NH_4^+ release rates from sediment core incubations at the dam and river sites. The vertical line in each panel represents the last date of observed thermal stratification at the dam site.

Comparison of the bootstrap 95% confidence intervals for the dam and river sites on all dates with concurrent incubations (31 August, 4 September, 11 September and 25 September; Table 3) indicated that the SRP release rate bootstrap confidence intervals of the river and dam sites did not overlap on any of these dates. On two dates (11 and 18 September) the river site sediment cores had a net loss of SRP from the overlying water from sediment cores, indicating the possible uptake of SRP by sediments. Considerable variability was observed in dam site sediment core SRP release rates across dates (Fig. 5a; Table 3). This is not unusual, as previous studies have noted variability in P release rates during sediment core incubations (Nürnberg, 1988; James, Barko & Eakin, 1995). Although SRP release rates from dam site sediment cores were dynamic, release rates only appeared to vary season-

Table 3 Soluble reactive phosphorus (SRP) and ammonia (NH_4^+) release rates based on sediment core incubations. Release rates from standard sediment core incubations and NO_3^- addition experiments are given for each date incubations were conducted at the dam and river sites. Observed release rate (Observed RR) is the mean of direct measurements from replicate cores on a given date. Mean release rates predicted from bootstrap simulations (Bootstrap RR) and the 95% bootstrap confidence intervals (95%CI) are also presented. Standard sediment core incubation release rates are presented for the day 0–2 time interval and NO_3^- addition experiment release rates are presented for the day 0–2 and day 2–5 time intervals. Dam site sediments were anoxic on all dates except 27 October and the river site sediments were oxic on all dates.

Sampling date	SRP release ($\mu\text{mol SRP-P m}^{-2}\text{ day}^{-1}$)			NH_4^+ release ($\text{mmol NH}_4^+\text{-N m}^{-2}\text{ day}^{-1}$)		
	Observed RR	Bootstrap RR	95% CI	Observed RR	Bootstrap RR	95% CI
22 July						
Dam site	442.7	445.3	46.7 to 952.3	3.3	3.3	-5.3 to 11.3
2 August						
Dam site	253.4	252.9	54.3 to 422.7	0.9	0.8	-0.9 to 2.3
26 August						
Dam site	209.6	208.7	176.9 to 260.9	1.5	1.5	0.1 to 2.9
31 August						
Dam site	206.2	206.5	170.0 to 238.1	0.2	0.2	-3.1 to 3.5
River site	47.1	47.0	13.6 to 97.0	2.0	2.1	1.3 to 2.8
4 September						
Dam site						
NO_3^- addition (day 0–2)	14.0	15.5	-142.3 to 246.6	6.1	6.0	2.4 to 10.6
NO_3^- addition (day 2–5)	-45.8	-45.9	-194.9 to 51.0	-1.7	-1.7	-3.9 to -0.2
NO_3^- control (day 0–2)	422.0	420.6	300.0 to 521.9	2.5	2.5	1.1 to 4.0
NO_3^- control (day 2–5)	152.5	154.7	69.3 to 247.8	0.1	0.1	-2.7 to 2.1
River site	62.5	63.0	23.3 to 135.3	5.1	5.0	1.1 to 12.5
11 September						
Dam site						
NO_3^- addition (day 0–2)	-86.2	-87.3	-143.3 to -36.1	1.5	1.5	-1.6 to 4.6
NO_3^- addition (day 2–5)	17.6	17.7	-7.8 to 48.6	1.7	1.7	-0.4 to 3.8
NO_3^- control (day 0–2)	207.9	205.1	86.1 to 302.8	1.1	1.3	-2.7 to 3.8
NO_3^- control (day 2–5)	86.3	88.0	7.2 to 178.9	1.9	1.9	0.7 to 3.0
River site	-15.2	-15.1	-12.1 to 75.1	-1.1	-1.1	-1.6 to -0.7
18 September						
River site						
NO_3^- addition (day 0–2)	-5.8	-5.7	-10.7 to -1.1	-1.8	-1.8	-3.3 to -0.4
NO_3^- addition (day 2–5)	11.3	11.5	0.1 to 26.4	-1.7	-1.8	-3.3 to -0.1
NO_3^- control (day 0–2)	-11.4	-11.4	-17.1 to -5.4	-2.3	-2.3	-2.7 to -1.9
NO_3^- control (day 2–5)	16.4	16.5	-6.3 to 34.3	-0.2	-0.2	-0.4 to -0.01
25 September						
River site						
NO_3^- addition (day 0–2)	0.5	0.8	-13.3 to 16.3	-1.1	-1.0	-2.2 to -0.3
NO_3^- addition (day 2–5)	38.2	38.1	25.4 to 51.2	-1.7	-1.7	-1.8 to -1.5
NO_3^- control (day 0–2)	21.3	21.2	-12.2 to 53.2	0.5	-2.3	-1.5 to 3.3
NO_3^- control (day 2–5)	19.3	19.3	-8.8 to 46.9	-1.9	-1.9	-3.5 to -1.0
Dam site	356.4	356.4	314.3 to 392.3	0.2	0.2	-0.7 to 1.2
27 October						
Dam site	-2.0	-1.7	-23.0 to 23.1	0.7	0.7	-1.6 to 2.6
River site	-40.0	-39.7	-101.4 to 37.7	0.2	0.1	-1.4 to 1.8

ally on 27 October, after fall turnover (Fig. 5a). River and dam site sediment core SRP release rate were similar on this date and the bootstrap 95% confidence intervals overlapped (Table 3).

The mean sediment core NH_4^+ release rates from the river and dam sites during the summer strati-

fication period did not differ greatly from one another (0.95 and 1.39 $\text{mmol NH}_4^+\text{-N m}^{-2}\text{ day}^{-1}$, respectively; Fig. 5b). Bootstrap 95% confidence intervals for NH_4^+ release rates from river and dam site sediment cores overlapped on all four dates of concurrent incubations (using both standard

incubation and NaCl 'control' cores), suggesting no significant difference in NH_4^+ release rates between sites (Table 3). NH_4^+ release rates at both sites did not appear to temporally vary in a predictable fashion over the course of stratification period (Fig. 5b). On two dates at the river site (11 and 18 September), NH_4^+ release rates were negative, possibly indicating a net flux of NH_4^+ to sediments. Unlike sediment SRP release rates at the dam site, fall turnover did not dramatically affect sediment NH_4^+ release rates.

Addition of NO_3^- did not significantly affect the SRP release rate from sediment cores from the river site (Fig. 6a; Table 3), with both NO_3^- addition and control cores exhibiting relatively low SRP release rates and overlapping bootstrap 95% confidence intervals. NO_3^- additions to sediment cores from the dam site resulted in a substantially decreased SRP release rates when compared with control cores (Fig. 6b). SRP release rates from dam site cores for the first time interval of the incubation (day 0–2) were very low or negative (Fig. 6b; Table 3). On the two dates NO_3^- addition experiments were conducted, there was no overlap in bootstrap 95% confidence intervals between the NO_3^- addition and control cores for the day 0–2 period, indicating NO_3^- addition led to a significant reduction in sediment SRP release rates. The second time interval (day 2–5) only showed a significant between NO_3^- addition and control core SRP release rates on one date (4 September).

The NO_3^- addition had no significant effect on the release of NH_4^+ from sediments from either site. At both the dam site and river site, bootstrap 95% confidence intervals of NH_4^+ release rates for NO_3^- addition and control cores overlapped on all dates experiments were conducted (Table 3).

Nürnberg's (1988) regression equation. Nürnberg's (1988) world-wide regression equation was used to predict TP release rates from the dam site during summer 1996. In general, predicted TP release rates were similar to release rates obtained from sediment core incubations (Fig. 5a). Predicted release rates did not exhibit the same large temporal variation observed in sediment core incubations because TP_5 (used to predict sediment release rate) exhibited little temporal variation between sampling dates. The mean predicted P release rates from

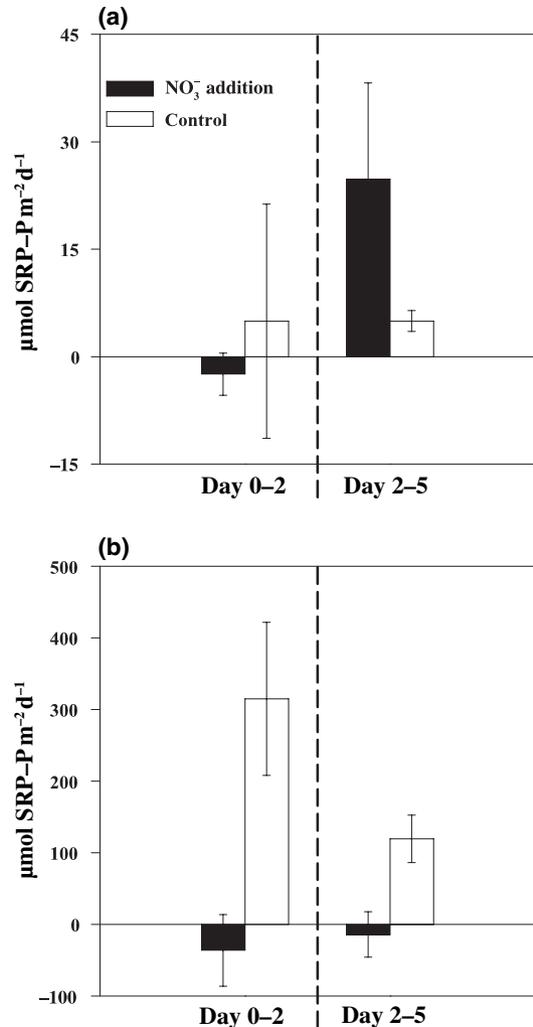


Fig. 6 Sediment SRP release rates from NO_3^- addition experiments for cores receiving NO_3^- and control cores. Data are the mean release rates of the (a) river site and the (b) dam site for the day 0–2 and day 2–5 time intervals. Bars are the mean release rates of all experiments conducted at a site across all dates and error bars are ± 1 SD.

sediments from May to September was $294.4 \mu\text{mol P m}^{-2} \text{day}^{-1}$.

Comparison of nutrient release estimation methods

Sediment TP and SRP release rates at the dam were dependent upon the specific method used to estimate P release rate. The *in situ* hypolimnetic accumulation method yielded mean summer TP and SRP release rates much lower than the release rates measured in sediment core incubations (SRP release rate difference = 61-fold; Table 4) or predicted with the

Table 4 Mean summer release rates of total phosphorous (TP), soluble reactive phosphorous (SRP) and ammonia (NH_4^+) at the dam site in Acton Lake from the three methods of estimating sediment nutrient release rates

Method of estimation	Nutrient release rate		
	TP ($\mu\text{mol P}$ $\text{m}^{-2} \text{ day}^{-1}$)	SRP ($\mu\text{mol P}$ $\text{m}^{-2} \text{ day}^{-1}$)	NH_4^+ (mmol N $\text{m}^{-2} \text{ day}^{-1}$)
<i>In situ</i> hypolimnetic accumulation	27.1	4.9	2.3
Sediment core incubation	na	299.7	1.4
Nürnberg (1988) regression equation	294.4	na	na

na, not applicable.

Nürnberg (1988) regression equation (TP release rate difference = 11-fold; Table 4). The mean summer release rates of P estimated from sediment core incubations and the Nürnberg (1988) regression equation were remarkably similar ($299.7 \mu\text{mol P m}^{-2} \text{ day}^{-1}$ and $294.4 \mu\text{mol P m}^{-2} \text{ day}^{-1}$, respectively), assuming that all of the P released from sediments during sediment core incubations was SRP (see Methods and Nürnberg, 1988). The large difference between release rates estimated from *in situ* hypolimnetic accumulation and the sediment core incubations was not apparent for NH_4^+ (Table 4). Both methods predicted similar mean summer NH_4^+ release rates from anoxic sediments at the dam site in 1996.

Discussion

Measurement of sediment nutrient release with different methods

Previous studies that compared sediment P release rates derived from sediment core incubations and *in situ* hypolimnetic P accumulation have found that rates generated by both methods generally correspond with one another (Nürnberg, 1987; Auer *et al.*, 1993). Nürnberg (1987) found that, while P loading rates determined from sediment core incubation experiments and *in situ* hypolimnetic accumulation methods were similar in a set of 34 lakes, lakes with relatively low internal P loads (*in situ* release rate $<1.5 \text{ mmol P m}^{-2} \text{ summer}^{-1}$) had sediment core incubation P loading rates significantly lower than *in situ* rates. In contrast, Acton Lake (1996 *in situ* loading rate = $2.0 \text{ mmol P m}^{-2} \text{ summer}^{-1}$) P release rates at the dam site determined from sediment core incubations were more than an order of magnitude greater than rates determined from *in situ* loading. Two alternative explanations could account for the

pronounced discrepancy between the two methods of estimating internal P loading. The first is that P release rates from core incubations accurately reflect anoxic sediment P release rates (i.e. P release rates occurring in Acton Lake) and the release rates based on *in situ* hypolimnetic P accumulation underestimate sediment P release rates. The differences in P release rates between the two methods are likely because of the relative time scale of each method: sediment core incubations are short-term (2–5 days) and represent gross P release rates, and *in situ* accumulation of P is integrated over an entire summer and represents a net P release rate from sediments. The differences between these gross and net release rates suggest that, while Acton Lake sediments release relatively high amounts of P during summer anoxia at the dam site, most of the released P is somehow 'lost' from the hypolimnion and does not accumulate in hypolimnetic waters. The alternative explanation for the difference observed in P flux rates between the two methods is that the *in situ* hypolimnetic P accumulation rates accurately reflect sediment release rates and the rates obtained from sediment core incubations are overestimates of internal P loading from anoxic sediments in Acton Lake.

It is possible that P release rates determined from core incubations are overestimates of the rates for Acton Lake anoxic sediments because NO_3^- could have been depleted in the overlying water in cores during the course of incubations. Addition of NO_3^- significantly reduced SRP release from anoxic sediments in sediment core incubations. Therefore, it is possible that in the absence of added NO_3^- , ambient nitrate in overlying waters was quickly depleted during sediment cores incubations, leading to inflated SRP release rates. However, we have several lines of evidence indicating that SRP release rates determined from sediment core incubations were not enhanced by this methodological artefact. First, all sediment core

incubations were conducted when hypolimnetic nitrate concentrations at the dam site were at seasonal lows (approximately $21 \mu\text{mol NO}_3^- \text{-N L}^{-1}$) and further rapid depletion of NO_3^- during the relatively short incubation period would seem unlikely to enhance P release. We further determined NO_3^- concentration in a subset of five sediment cores after the incubation period (excluding those which received NO_3^-) and, assuming that the initial NO_3^- concentration in sediment cores was equal to *in situ* NO_3^- concentrations at 8 m, NO_3^- concentrations declined in the five cores over the incubation period by an average of $1.9 \mu\text{mol NO}_3^- \text{-N L}^{-1} \text{ day}^{-1}$. While this indicates that NO_3^- declined slightly in sediment cores during incubation, this decrease in NO_3^- concentration is minimal compared with the seasonal decline observed in the hypolimnion (from $>600 \mu\text{mol NO}_3^- \text{-N L}^{-1}$ to $<14 \mu\text{mol NO}_3^- \text{-N L}^{-1}$; Fig. 3c). Furthermore, if hypolimnetic NO_3^- concentration and SRP release rates from sediments are related, we would expect to observe a significant relationship between the NO_3^- concentration at the 8 m depth interval and the measured SRP release rates in sediment cores. However, we did not observe this relationship for the five core incubations in which we collected NO_3^- concentration data ($r^2 = 0.33$, $P > 0.10$). Thus, while large additions of NO_3^- clearly inhibited SRP release from anoxic sediments at the dam site, it seems unlikely that the small changes in ambient NO_3^- we observed in cores over the incubation period significantly altered SRP release rates.

It is important to note that the mean summer SRP release rate derived from our core incubations ($300 \mu\text{mol P m}^{-2} \text{ day}^{-1}$) was very similar to mean summer TP release rates predicted by the Nürnberg (1988) regression equation ($294 \mu\text{mol P m}^{-2} \text{ day}^{-1}$; Fig. 5, Table 4). This regression equation was created with the sediment core incubation release rates from 63 lakes, therefore our sediment core release rates are in general agreement with a large number of lakes with similar TP_5 values (see Table 6 in Nürnberg, 1988). Mean summer sediment SRP release rates determined from sediment core incubations in Acton Lake ($300 \mu\text{mol P m}^{-2} \text{ day}^{-1}$) were also within the range observed in more recently published studies of other productive waterbodies. Auer *et al.* (1993) found that the SRP release rate determined from sediment cores in hypereutrophic Onondaga Lake was $419 \mu\text{mol P m}^{-2} \text{ day}^{-1}$. In eutrophic Lake Okeechobee

under anoxic conditions, sediment cores released SRP at rates ranging from 80 to $397 \mu\text{mol P m}^{-2} \text{ day}^{-1}$ (Moore *et al.*, 1998). It is highly unlikely that release rates in all of these studies were artificially elevated by NO_3^- depletion during sediment core incubations.

The improbability of ambient NO_3^- depletion during core incubations affecting SRP release rates and the similarity of our sediment core incubation P release rates with those of numerous studies suggest that P release rates determined from our sediment core incubations are indicative of anoxic sediment release rates in Acton Lake. The large difference observed in gross (sediment cores) and net (*in situ* accumulation) sediment P release rates suggests that P released from sediments is 'lost' from the hypolimnion in processes which require more time than the duration of a sediment core incubation (2–5 days). However, the close agreement between release rates of NH_4^+ determined from sediment core incubations and *in situ* hypolimnetic accumulation (Table 4) is evidence that the observed 'loss' of sediment-derived P from the hypolimnion must be because of processes associated with the biogeochemical cycling of P in Acton Lake.

A possible explanation is that environmental conditions in Acton Lake might favour the precipitation of sediment-derived P with inorganic material. Acton Lake is a hardwater lake supersaturated with calcite (CaCO_3 ; Green *et al.*, 1985). Precipitation of P with calcite and deposition onto sediments can be an important process regulating P concentration in lakes (Kleiner & Stabel, 1989; Driscoll *et al.*, 1993; Danen-Louwerse, Lijklema & Coenraats, 1995). For example, in Lake Constance, it has been estimated that 35% of the seasonal TP loss from the water column is because of P co-precipitation with calcite (Kleiner, 1988). Nürnberg (1998) reported lakes with relatively high Ca^{2+} concentrations ($>11 \text{ mg Ca}^{2+} \text{ L}^{-1}$) exhibited higher than predicted annual retention of P inputs and hypothesised that this was because of the authigenic co-precipitation of P inputs with Ca^{2+} . Acton Lake Ca^{2+} concentration is 53 mg L^{-1} (Green *et al.*, 1985), higher than the mean Ca^{2+} concentration in North American and North Temperate surface waters (North American large rivers = 21 mg L^{-1} : Wetzel, 1983; worldwide north temperate large rivers = 25 mg L^{-1} : Kalff, 2002). Seasonal changes in lake pH can also be responsible for the precipitation or dissolution of P in Ca or Fe containing compounds,

however we did not observe wide fluctuations in lake pH in Acton Lake in 1995–96 and the pH of the hypolimnion was consistently >7.5 during the summer stratification period of 1996.

Uptake of sediment-released SRP by planktonic organisms in the hypolimnion and their subsequent deposition onto sediments represents another possible mechanism which could have led to the large differences in net and gross sediment P release rates. It is possible that bacteria or phytoplankton took up SRP as they sank through the hypolimnion, eventually depositing P onto sediments. Unfortunately, we have no way to directly evaluate this because we did not measure SRP uptake in the hypolimnion or P sedimentation rates. Further, it is unlikely that we would detect such sinking events in our monthly collected sediment cores because of the high P concentrations of sediments. For example, the largest decline in mean hypolimnetic TP concentration observed between sampling intervals in 1996 was $2.4 \mu\text{mol P L}^{-1}$. Assuming all of this P resettled on the sediment surface during this time interval, this would increase TP_S by $29 \mu\text{g P g sediment}^{-1}$, representing approximately 4% of observed TP_S ($>1500 \mu\text{g P g sediment}^{-1}$; Fig. 4). It is questionable that such a small increase in TP_S could be detected and attributed to the deposition of P released from sediments.

In Acton Lake, TP and SRP did not accumulate in the hypolimnion at the same rates in 1996; mean summer *in situ* TP release rate was approximately fivefold greater than the release rate of SRP (Table 4). Similarly, Porter *et al.* (1996) reported a seasonal increase of hypolimnetic TP, but not SRP, in Lake Oglethorpe and attributed this pattern to bacterial uptake of SRP released by sediments during the summer. In Acton Lake, SRP comprised 2–47% of the TP pool in the hypolimnion from late June to mid-September ($\bar{x} = 9\%$) indicating that the majority of the hypolimnetic TP pool was bound in particulates or dissolved organic P. It is known that P released from anaerobic sediments is overwhelmingly in the form of SRP (Nürnberg *et al.*, 1986; Nürnberg, 1988; Moore *et al.*, 1991; Auer *et al.*, 1993) and there is no reason to assume that P from anaerobic sediments in Acton Lake was in a form other than SRP. It is critical to point out that, while hypolimnetic TP accumulation was greater much greater than SRP accumulation, the *in situ* TP release rates ($27 \mu\text{mol P m}^{-2} \text{day}^{-1}$) were still substantially less than P release rates estimated by

sediment core incubations ($300 \mu\text{mol P m}^{-2} \text{day}^{-1}$). Therefore, we hypothesise that SRP released from sediments in Acton Lake during the summer of 1996 was changed to another form (such as particulate P) through abiotic or biotic means (i.e. precipitation with calcite or uptake by plankton) and subsequently deposited onto sediments. Furthermore, because SRP released from sediments in Acton Lake was apparently re-deposited onto sediments at high rates, we suggest that the *net* P retention of anoxic sediments in Acton Lake is actually relatively high.

Another mechanism that could lead to the 'loss' of P from the hypolimnion after its release from sediments is the downward migration of the thermocline and subsequent entrainment of P-rich hypolimnetic waters into the epilimnion. Significant amounts of hypolimnetic P can be entrained into the epilimnion of lakes following periodic thermocline migration events or during thermocline erosion at the end of stratification season (Kortmann *et al.*, 1982; Nürnberg, 1985; Effler *et al.*, 1986; Stauffer, 1987; Soranno, Carpenter & Lathrop, 1997). Our calculation of the *in situ* accumulation of P in 1996 was performed for the time period beginning after the thermocline had stabilised (based upon weekly observations) between 4 and 5 m in late June to immediately prior to the erosion of the thermocline in the fall, thus eliminating fall entrainment events from our estimates. However, Acton Lake has a morphometric factor ($\bar{z}/A^{0.5}$) of 2.5, indicating periodic mixing events can occur during summer stratification (Nürnberg, 1995). Several prominent entrainment events were evident Acton Lake in 1995, but events of similar magnitude were not observed in 1996. We collected temperature and DO profiles every 5–7 days during the stratification period, and it is possible that there may have been unobserved rapid entrainment events that could have transported much of this 'lost' hypolimnetic P to the epilimnion in 1996. If significant amounts of hypolimnetic P were entrained over the course of the summer and there was no discharge of epilimnetic water (and therefore P) from the reservoir during this period, then we would expect epilimnetic TP concentration to increase over the course of the summer (Nürnberg & LaZerte, 2001). Outflow of epilimnetic water over the dam did not occur in the summer of 1996, but the volume-weighted epilimnetic TP concentration was not a significant function of time (day of year) during the stratified period (TP: $r^2 = 0.15$,

$F = 2.6$, $P = 0.14$). In addition, there were no obvious large increases or fluctuations in the epilimnetic TP concentration between sequential sampling dates (Fig. 3a). However, we did not have continuous temperature logging equipment present in Acton Lake throughout the summer stratification period and we cannot omit the possibility that sediment-derived P was entrained into the epilimnion. It is unlikely, but nonetheless possible, that some hypolimnetic P was rapidly entrained into the epilimnion, assimilated by plankton and subsequently redeposited onto sediments during the 5–7 day intervals when we did not measure temperature profiles or collect water samples.

Effect of mixing conditions on nutrient release rates in Acton Lake

Large differences in the SRP release rates from the river and dam sites are presumably because of differences in the physical conditions and DO concentrations of the waters in contact with the sediment–water interface at the two sites. However, there was no significant difference between NH_4^+ release rates at both sites, suggesting that differences in stratification and DO were important in determining only the SRP release rates from sediments in Acton Lake. River site SRP release rates were on average an order of magnitude less than release rates at the dam site, probably because of the increased SRP release rates from anoxic sediments through a potentially large number of well-studied abiotic and biotic pathways (Boström *et al.*, 1988; Gächter & Meyer, 1993; Pettersson, 1998). In addition, NO_3^- concentration above sediments at the river site may have affected the SRP release rates. Unlike the dam site, NO_3^- concentrations above sediments at the river site were $>100 \mu\text{mol NO}_3^- \text{-N L}^{-1}$ throughout the summer. Results from our sediment core NO_3^- addition experiments also showed that the addition of NO_3^- had no significant effect on sediment SRP release rates at the river site, contrary to the results from the dam site. The mean SRP release rate from the oxic sediments at the river site was $20.9 \mu\text{mol P m}^{-2} \text{ day}^{-1}$ during the summer, however, on two dates river sediment cores exhibited a net uptake of SRP (negative SRP release rates). Previous studies have also noted the net uptake of SRP in aerobic environments (Holdren & Armstrong, 1980). The mean summer SRP release rate

from the river site was within the range of SRP release rates observed in other oxic sediments. Holdren & Armstrong (1980) found that release rates from Lake Mendota and Lake Wingra, two hardwater eutrophic lakes in Wisconsin, U.S.A., ranged from -61 to $2686 \mu\text{mol P m}^{-2} \text{ day}^{-1}$ and -18 to $110 \mu\text{mol P m}^{-2} \text{ day}^{-1}$, respectively. SRP release rates from oxygenated sediments in Lake Okeechobee were, on average, $8.4 \mu\text{mol P m}^{-2} \text{ day}^{-1}$ (Moore *et al.*, 1998).

Although SRP release rates from Acton Lake were comparable with other published aerobic sediment release rates, it is important to note that the release rates for Acton Lake are based upon sediment core incubations and may therefore represent the gross SRP release from aerobic sediments. Some of the same abiotic and biotic mechanisms responsible for the 'loss' of hypolimnetic P at the dam site are presumably also present at the river site. However, because of the lack of thermal stratification at the river site, we are not able to estimate the *net* P release from these sediments. Jensen & Andersen (1992) estimated aerobic sediment P release from four shallow eutrophic Danish lakes using both sediment core incubations and lake mass-balances. The authors found that SRP sediment release rate estimates derived from lake mass balances were on average fourfold less than sediment core incubation estimates. Therefore, it is probable that the SRP release rates exhibited by the sediment core incubations at the river site in Acton Lake are overestimates of what is eventually incorporated into the euphotic zone of the water column, and a portion of this SRP is lost back to the sediments through some of the various potential biotic and abiotic mechanisms affecting hypolimnetic P accumulation at the dam site.

Sediment P concentration and sediment P fractions in Acton Lake

Dam site sediments had greater TP_s , as well as higher concentrations of each of the five sediment P fractions than the river site. This site-dependent shift in P concentration in sediments of Acton Lake is related to longitudinal variation in the overall sediment deposition rate and the source of material accumulating on the sediment surface at each site in the reservoir. In the riverine regions of reservoirs, overall sedimentation rates are typically higher and streams discharging into this area are high in terrestrial organic matter, silt

and suspended clays (Thornton, 1990b). In contrast, downstream lacustrine regions are characterised by lower overall sedimentation rates and a higher proportion of deposited material coming from autochthonously produced organic matter (Thornton, 1990b). In Acton Lake, lower sediment P concentrations at the river site could come from higher overall sedimentation rates and a larger proportion of terrestrial-derived material in sediments decreasing the relative amount of P within sediments, when compared with the dam site.

The TP₅ concentration was significantly lower in the deeper sediment depth interval (1–5 cm) at both the river and dam sites in Acton Lake, a pattern often observed in lake sediments (Carignan & Flett, 1981; Moore *et al.*, 1991; Gonsiorczyk, Casper & Koschel, 1998). Decreasing TP₅ concentration with sediment interval depth has been attributed to P mobilisation and migration from deeper sediment intervals toward upper sediments prior to release (Carignan & Flett, 1981). In Acton Lake, the dam site exhibited a larger decrease in TP₅ with sediment depth than the river site, which may be associated with higher P release rates from the anoxic sediments at the dam site. Another explanation for the decrease in TP₅ with increasing depth may be that present day particulate matter is higher in P concentration than sediment that settled in previous years, however, this explanation is unlikely because sediment TP₅ profiles may not always indicate historical changes in P loading because of the mobilisation and diagenesis of P in sediments (Carignan & Flett, 1981; Moore & Reddy, 1994).

The Org-P fraction made up the majority of TP₅ at both sites in Acton Lake, accounting for approximately 50% of sediment P. A relatively high percentage of Org-P in sediments is not unexpected, as other studies have found similar values (Moore *et al.*, 1991; Brunberg, 1995). Fe bound-P (Fe-P) often occupies a larger proportion of TP₅ in sediments under oxidising conditions and this proportion should decrease under reducing conditions as P is released from anaerobic conditions (Moore & Reddy, 1994). Fe-P concentration also decreases with depth, because of its mobilisation in deeper highly reduced sediments (Moore *et al.*, 1991). Therefore, we expected that the proportion of Fe-P would decrease with depth at both sites, and the dam site in Acton Lake would have a lower proportion of Fe-P than the river site. This was clearly not the case. Fe-P did not vary with depth at either site, and

the proportion of Fe-P was higher at the dam site than at the river site. Although this result is unexpected, Messer *et al.* (1984) found that sediment Fe-P was poorly correlated with anaerobic sediment P release rates in Flaming Gorge Reservoir, Wyoming, U.S.A. The authors found that the combined Al- and Fe-P pool in sediments was highly correlated with anaerobic sediment P release rate. There is considerable disagreement about the relationship between Al-P in sediments and sediment P release rates. Studies have found that Al-P is largely refractory, and Al-P concentration is poorly correlated with sediment P release rate (Nürnberg, 1988; Golterman, 1995). However, James *et al.* (1995) reported that the concentrations of both Fe-P and Al-P were significantly correlated with sediment P release rates of in a eutrophic reservoir (Lake Pepin, MN, U.S.A). Therefore, it is probable that both the Fe- and Al-P sedimentary pools in Acton Lake interact with environmental conditions to play a role in the sediment P release in Acton Lake.

Comparison of P fluxes from sediments and other sources to Acton Lake

Here, we compare the relative importance of SRP inputs from sediments and several well-studied sources of P to the epilimnion of Acton Lake. We examine inputs of 'new' P to Acton Lake (from outside the water column or the upper mixed layer) and do not address 'recycled' P sources from within the water column, such as planktonic regeneration (Caraco, Cole & Likens, 1992; Hudson, Taylor & Schindler, 1999). Obviously, stream inputs are an important source of nutrients to lakes and reservoirs and the daily stream SRP discharges into Acton Lake have been monitored since 1994 (Vanni *et al.*, 2001). Gizzard shad (*Dorosoma cepedianum*) are the dominant fish species in Acton Lake (Schaus, Vanni & Wissing, 2002) and nutrient regeneration by this fish has been extensively studied (Mather *et al.*, 1995; Schaus *et al.*, 1997). Adult gizzard shad feed on sediments (Schaus *et al.*, 2002) and the excretion sediment-derived P into the water column by gizzard shad represents a 'new' SRP input to the reservoir. Therefore, we chose to examine the relative magnitude of SRP inputs of anaerobic sediments, aerobic sediments, stream inputs and gizzard shad populations for summer 1996 in Acton Lake.

We compared aerial SRP loading rates ($\mu\text{mol P m}^{-2}$ lake surface area) to the reservoir from sediments, streams inputs and gizzard shad excretion for the period of late June to mid-September, 1996. This time period was selected because the thermocline was stable at approximately 4 m and we were able to calculate fluxes during this interval. SRP inputs from streams discharging into Acton Lake for the late June to mid-September time period were taken from Vanni *et al.* (2001). SRP inputs through gizzard shad excretion were calculated from the summer 1996 gizzard shad biomass in Acton Lake (approximately 35 kg ha^{-1} ; Schaus *et al.*, 2002) and gizzard shad SRP excretion rates ($0.02\text{--}0.06 \mu\text{mol P L}^{-1} \text{ day}^{-1}$; Schaus *et al.*, 1997). Although the thermocline in Acton Lake is assumed to be stable at 4 m in our analysis (thus omitting hypolimnetic entrainment events) SRP can diffuse across the thermocline along the concentration gradient from the hypolimnion to the epilimnion (vertical diffusion; Wodka *et al.*, 1983; Auer *et al.*, 1993). Therefore, we calculated the vertical diffusive flux of SRP from the hypolimnion to the epilimnion. We calculated the diffusion of SRP across the thermocline (J ; $\mu\text{mol SRP-P m}^{-2}$) with the equation

$$J = v_t(P_h - P_e)$$

where v_t is the vertical exchange coefficient (m day^{-1}) and P_h and P_e are the average summer SRP concentrations of the depth intervals immediately above and below to the thermocline. We used a v_t value of $0.01 \text{ cm}^2 \text{ s}^{-1}$ (Wodka *et al.*, 1983; Auer *et al.*, 1993).

To calculate SRP fluxes from aerobic sediments in Acton Lake we used the SRP release rates obtained from sediment core incubations and assumed that all SRP released from aerobic sediments was incorporated into the water column. For anaerobic sediments, we assumed that SRP release rate from sediment core incubations represented the actual SRP release rates occurring in Acton Lake anaerobic sediments. However, we have hypothesised that a majority of this released P is 'lost' from the hypolimnion through biological uptake or chemical precipitation and is presumably re-deposited on sediments. Therefore, we used the *in situ* hypolimnetic accumulation of TP as the measure of *net* release rate of SRP from anaerobic sediments (see *Measurement of sediment nutrient release with different methods* above for justification of use of TP).

The largest SRP flux into the reservoir on a reservoir-wide basis was from anaerobic sediments (Fig. 7). However, a significant portion of this was probably subject to chemical precipitation or biological uptake and then re-deposited through particle sedimentation. Thus, there is a $-136.4 \mu\text{mol P m}^{-2} \text{ day}^{-1}$ 'loss' of released P back to the sediments, making the *net* flux of P to the hypolimnion from anaerobic sediments $13.6 \mu\text{mol P m}^{-2} \text{ day}^{-1}$. Based upon our weekly sampling intervals and the lack of increasing or fluctuating epilimnetic TP concentrations, we assume that there were no major thermocline migration events during this interval in 1996, and it is therefore unlikely much of the P regenerated from anaerobic sediments would end up in the epilimnion until the fall when the thermocline descended toward sediments. The diffusion of SRP from the hypolimnion across the thermocline to the epilimnion was a relatively small flux when compared with other sources of SRP to the epilimnion ($0.4 \mu\text{mol P m}^{-2} \text{ day}^{-1}$; Fig. 7), further indicating that the epilimnion was receiving a limited amount of hypolimnetic sediment-derived P during the summer stratification period. The largest SRP flux to the reservoir was from gizzard shad excretion ($25.2 \mu\text{mol P m}^{-2} \text{ day}^{-1}$), and this flux was slightly greater than stream inputs ($21.6 \mu\text{mol P m}^{-2} \text{ day}^{-1}$), and more than two times the release rate from aerobic sediment surfaces ($10.4 \mu\text{mol P m}^{-2} \text{ day}^{-1}$). These results are in agreement with the notion that P loading from benthivorous feeding fish, when compared with other P inputs, can represent a potentially important nutrient source during summer (Persson, 1997). Brabrand, Faafeng & Nilssen (1990) similarly found that mid-summer P loading from benthivorous fish excretion in Lake Gjersjøen (Norway) was greater than stream inputs.

It is critical to acknowledge that the mid-summer SRP fluxes represented in Fig. 7 are specific to the fluxes occurring in 1996 only. The relative magnitude of the flux from sediments, streams, and gizzard shad excretion can vary substantially between years. For example, we assumed that the thermocline in 1996 was stable at 4 m and did not have any large mid-summer migration events, based upon the seasonal thermocline data in Acton Lake. In 1995, however, the thermocline had two large migration events, which presumably entrained significant amounts of hypolimnetic P into the epilimnion. Further, stream nutrient inputs into lakes and reservoirs vary with

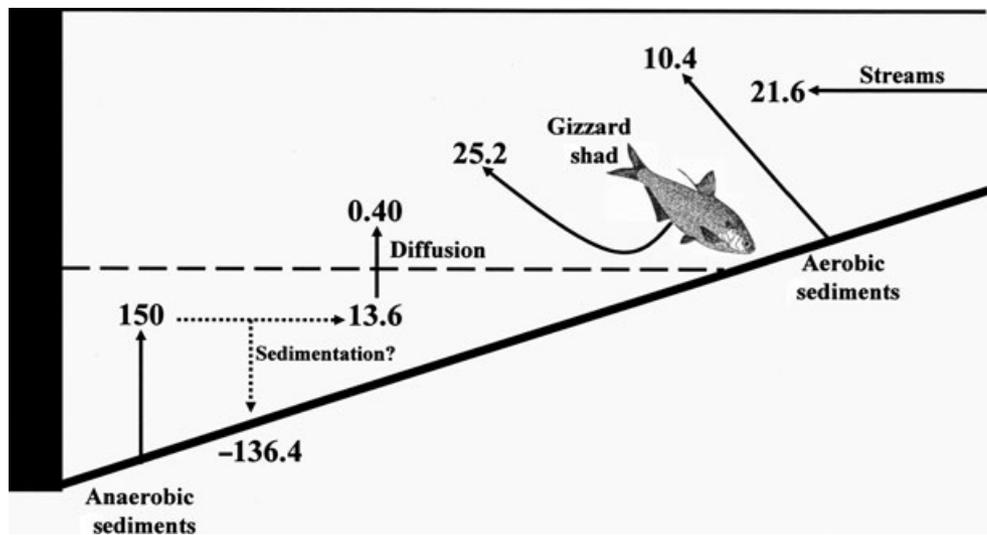


Fig. 7 Diagrammatic representation of the mean summer SRP fluxes into Acton Lake during the stratification period, 1996. Values in the figure represent SRP fluxes in $\mu\text{mol P m}^{-2}$ lake surface area. Inputs of 'new' SRP to the lake from streams, aerobic sediments, gizzard shad excretion, anaerobic sediments and diffusion across the thermocline are represented. The horizontal dashed line represents the thermocline. See text for calculation methods for fluxes.

discharge volumes. Mean annual stream discharge into Acton Lake from 1994 to 1998 varied from $1.4 \text{ m}^3 \text{ s}^{-1}$ to $5.2 \text{ m}^3 \text{ s}^{-1}$ (Vanni *et al.*, 2001). Gizzard shad biomass can also have large interannual variation in Acton Lake. Gizzard shad biomass estimates from 1994 to 1997 varied from <40 to $>400 \text{ kg ha}^{-1}$ (Schaus *et al.*, 2002). Therefore, construction of a similar budget for Acton Lake for other years (or, in reality, any lake or reservoir) must account for year-to-year variation in parameters such as thermocline stability, stream discharge volume, and gizzard shad biomass.

Conclusions

In eutrophic Acton Lake, sediment SRP release rates exhibited spatial variation, presumably because of differences in the physical mixing environment at sites within the reservoir. The anoxic sediment SRP release rates at the deeper stratified dam site were approximately an order of magnitude greater than SRP release rates of aerobic sediments at the shallow unstratified river site. Despite the high SRP release rate from anaerobic sediments, SRP did not accumulate in the hypolimnion at the expected rate. NH_4^+ was released at similar rates at both sites and accumulated in the dam site hypolimnion at close

to expected rates. This suggests that sediment-derived P is 'lost' from the hypolimnion through processes specific to P in Acton Lake. In the summer of 1996, the mean daily SRP input rate from anaerobic sediments to Acton Lake was larger than the input rates from aerobic sediments, streams and gizzard shad excretion. However, it is unlikely that a significant amount of the SRP released from anaerobic sediments made its way to the upper mixed layer of Acton Lake during the summer. An accounting of SRP inputs to Acton Lake should acknowledge that large interannual variation in thermocline stability, stream discharge and gizzard shad biomass will affect the relative magnitude of SRP inputs from these sources.

Acknowledgments

We would like to thank E. Thobaben for his valuable field assistance and J. Auch, J. Headworth, S. Hughes, and M. Schaus for help in the laboratory. We would also like to thank J. Auch, T. Crist, C. Drutis, J. Devine, W. Green, T. Muenz, W. Parisi, M. Schaus, J. Vaughn, and J. Woyke for their input on an earlier draft of this manuscript. This research was funded by NSF grants DEB 9318452 and DEB 0235755 to M.J.V.

References

- American Public Health Association. (1992) *Standard Methods for the Examination of Water and Wastewater*, 18th edn. American Water Works Association, Washington, DC.
- Andersen V.J.M. (1974) Nitrogen and phosphorus budgets and the role of sediments in six shallow Danish lakes. *Archiv für Hydrobiologie*, **74**, 528–550.
- Andersen V.J.M. (1982) Effect of nitrate concentration in lake water on phosphate release from the sediment. *Water Research*, **16**, 1119–1126.
- Andersen F.O. & Jensen H.S. (1992) Regeneration of inorganic phosphorus and nitrogen from decomposition of seston in a freshwater sediment. *Hydrobiologia*, **228**, 71–81.
- Auer M.T., Johnson N.A., Penn M.R. & Effler S.W. (1993) Measurement and verification of rates of sediment phosphorus release for a hypereutrophic urban lake. *Hydrobiologia*, **253**, 301–309.
- Auer M.T., Tomasoski K.A., Babiera M.J. & Needham M.L. (1998) Phosphorus bioavailability and P-cycling in Cannonsville Reservoir. *Journal of Lake and Reservoir Management*, **14**, 278–289.
- Boström B., Andersen J., Fleischer S. & Jansson M. (1988) Exchange of phosphorus across the sediment–water interface. *Hydrobiologia*, **170**, 229–244.
- Boström B., Jansson M. & Forsberg G. (1982) Phosphorus release from lake sediments. *Archiv für Hydrobiologie*, **18**, 5–59.
- Brabrand Å., Faafeng B.A. & Nilssen J.P.M. (1990) Relative importance of phosphorus supply to phytoplankton production: fish excretion versus external loading. *Canadian Journal of Fisheries and Aquatic Sciences*, **47**, 364–372.
- Brunberg A. (1995) Microbial activity and phosphorus dynamics in eutrophic lake sediments enriched with *Microcystis* colonies. *Freshwater Biology*, **33**, 541–555.
- Canfield D., Green W.J., Gardner T.J. & Fredelman T. (1984) Elemental residence times in Acton Lake, Ohio. *Archiv für Hydrobiologie*, **100**, 501–519.
- Caraco N.F., Cole J.J. & Likens G.E. (1992) New and recycled primary production in an oligotrophic lake: insights for summer phosphorus dynamics. *Limnology and Oceanography*, **37**, 590–602.
- Carignan R. & Flett R.J. (1981) Postdepositional mobility of phosphorus in lake sediments. *Limnology and Oceanography*, **26**, 361–366.
- Crumpton W.G., Isenhardt T.M. & Mitchell P.D. (1992) Nitrate and organic N analyses with second-derivative spectroscopy. *Limnology and Oceanography*, **37**, 907–913.
- Danen-Louwerse H.J., Lijklema L. & Coenraats M. (1995) Coprecipitation of phosphate with calcium carbonate in Lake Veluwe. *Water Research*, **29**, 1781–1785.
- Dillon P.J. & Rigler F.R. (1974) The phosphorus-chlorophyll relationship in lakes. *Limnology and Oceanography*, **19**, 767–773.
- Dixon P.M. (1993) The bootstrap and the jackknife: describing the precision of ecological indices. In: *Design and Analysis of Ecological Experiments* (Eds S.M. Scheiner & J. Gurevitch), pp. 290–318. Chapman and Hall, New York.
- Driscoll C.T., Effler S.W., Auer M.T., Doerr S.M. & Penn M.R. (1993) Supply of phosphorus to the water column of a productive hardwater lake: controlling mechanisms and management considerations. *Hydrobiologia*, **253**, 61–72.
- Effler S.W., Wodka M.C., Driscoll C.T., Brooks C., Perkins M. & Owens E.M. (1986) Entrainment-based flux of phosphorus in Onondaga Lake. *Journal of Environmental Engineering*, **112**, 617–622.
- Evarts J.L. (1997) *Spatial and Temporal Variation in Release of Nitrogen and Phosphorus in a Eutrophic Reservoir*. Masters thesis, Miami University, Oxford, Ohio.
- Gächter R. & Meyer J.S. (1993) The role of microorganisms in mobilization and fixation of phosphorus in sediments. *Hydrobiologia*, **253**, 103–121.
- Gardner W.S., Yang L., Cotner J.B., Johengen T.H. & Laventyev P.J. 2001. Nitrogen dynamics in sandy freshwater sediments (Saginaw Bay, Lake Huron). *Journal of Great Lakes Research*, **27**, 84–97.
- Goldman C.R. & Kimmel B.L. (1978) Biological processes associated with suspended sediment and detritus in lakes and reservoirs. In: *Current Perspectives on River-Reservoir Ecosystems. Proceedings – Symposium of the 25th Annual Meeting of the North American Benthological Society, Roanoke, Virginia, 1977* (Eds J. Jr. Cairns, E.F. Benfield, & J.R. Webster), North American Benthological Society, Schaumburg, Illinois.
- Golterman H.L. (1995) The role of the ironhydroxide-phosphate-sulfide system in the phosphate exchange between sediments and overlying water. *Hydrobiologia*, **297**, 43–54.
- Gonsiorczyk T., Casper P. & Koschel R. (1998) Phosphorus-binding forms in the sediment of an oligotrophic and eutrophic hardwater lake of the Baltic Lake District. *Water Science and Technology*, **37**, 51–58.
- Green W.J., Canfield D.E. & Steinly B.A. (1985) Spatial variations in and controls on the calcite saturation index in Acton Lake, Ohio. *Freshwater Biology*, **15**, 525–533.
- Hieltjes A.H.M. & Lijklema L. (1980) Fractionation of inorganic phosphates in calcareous sediments. *Journal of Environmental Quality*, **9**, 405–407.
- Holdren G.C. & Armstrong D.E. (1980) Factors affecting phosphorus release from intact lake sediment cores. *Environmental Science and Technology*, **14**, 79–87.

- Hudson J.J., Taylor W.D. & Schindler D.W. (1999) Planktonic nutrient regeneration and cycling efficiency in temperate lakes. *Nature*, **400**, 659–661.
- James W.F., Barko J.W. & Eakin H.L. (1995) Internal phosphorus loading in Lake Pepin, upper Mississippi River. *Journal of Freshwater Ecology*, **10**, 269–276.
- Jensen H.S. & Andersen F.O. (1992) Importance of temperature, nitrate, and pH for phosphate release from aerobic sediments of four shallow, eutrophic lakes. *Limnology and Oceanography*, **37**, 577–589.
- Kalff J. (2002) *Limnology: Inland Water Ecosystems*. pp. 207. Prentice Hall, New Jersey.
- Kamp-Nielsen L. (1974) Mud-water exchange of phosphate and other ions in undisturbed sediment cores and factors affecting the exchange rates. *Archiv für Hydrobiologie*, **73**, 218–237.
- Kleiner J. (1988) Co-precipitation of phosphate with calcite in lake water: a laboratory experiment modeling phosphorus removal with calcite in Lake Constance. *Water Research*, **22**, 1259–1265.
- Kleiner J. & Stabel H.-H. (1989) Phosphorus transport to the bottom of Lake Constance. *Aquatic Sciences*, **51**, 181–191.
- Kortmann R.W., Henry D.D., Kuether A. & Kaufman S. (1982) Epilimnetic nutrient loading by metalimnetic erosion and resultant algal responses in Lake Warmaug, Connecticut. *Hydrobiologia*, **92**, 501–510.
- Martin W.D. (1984) Origin of the Cincinnati series limestones (upper Ordovician) of southwestern Ohio, southeastern Indiana, and northern Kentucky. In: *Hueston Woods State Park and nature preserve: Proceedings of Symposium, Held at Hueston Woods State Park April 16–18, 1982 Under the Sponsorship of the Departments of Botany, Geology, and Zoology and the Institute of Environmental Sciences* (Ed. G.E. Willeke), Miami University, Oxford, Ohio.
- Mather M.A., Vanni M.J., Wissing T.E., Davis S.A. & Schaus M.H. (1995) Regeneration of nitrogen and phosphorus by bluegill and gizzard shad: effect of feeding history. *Canadian Journal of Fisheries and Aquatic Sciences*, **52**, 2327–2338.
- Medley K.E., Okey B.W., Barrett G.W., Lucas M.F. & Renwick W.H. (1995) Landscape change with agricultural intensification in a rural watershed, southwestern Ohio, U.S.A. *Landscape Ecology*, **10**, 161–176.
- Messer J.J., Ihnat J.M. & Wagner D.L. (1984) Phosphorus release from the sediments of Flaming Gorge Reservoir, Wyoming, U.S.A. *Verhandlungen – Internationale Vereinigung für Theoretische und Angewandte Limnologie*, **22**, 1457–1464.
- Moore P.A. & Reddy K.R. (1994) Role of Eh and pH on phosphorus geochemistry in sediments of Lake Okeechobee, Florida. *Journal of Environmental Quality*, **23**, 955–964.
- Moore P.A., Reddy K.R. & Fisher M.M. (1998) Phosphorus flux between sediment and overlying water in Lake Okeechobee, Florida: spatial and temporal variation. *Journal of Environmental Quality*, **27**, 1428–1439.
- Moore P.A., Reddy K.R. & Graetz D.A. (1991) Phosphorus geochemistry in the sediment–water column of a hypereutrophic lake. *Journal of Environmental Quality*, **20**, 869–875.
- Mortimer C. (1941) The exchange of dissolved substances between mud and water in lakes, 1–2. *Journal of Ecology*, **29**, 280–329.
- Mortimer C. (1942) The exchange of dissolved substances between mud and water in lakes, 3–4. *Journal of Ecology*, **30**, 147–201.
- Nürnberg G.K. (1984a) Iron and hydrogen sulfide interference in the analysis of soluble reactive phosphorus in anoxic waters. *Water Research*, **18**, 369–377.
- Nürnberg G.K. (1984b) The prediction of internal phosphorus load in lakes with anoxic hypolimnia. *Limnology and Oceanography*, **29**, 111–124.
- Nürnberg G.K. (1985) Availability of phosphorus upwelling from iron-rich anoxic hypolimnia. *Archiv für Hydrobiologie*, **104**, 459–476.
- Nürnberg G.K. (1987) A comparison of internal phosphorus loads in lakes with anoxic hypolimnia: laboratory incubation versus in situ hypolimnetic phosphorus accumulation. *Limnology and Oceanography*, **32**, 1160–1164.
- Nürnberg G.K. (1988) Prediction of phosphorus release rates from total and reductant-soluble phosphorus in anoxic lake sediments. *Canadian Journal of Fisheries and Aquatic Sciences*, **45**, 453–461.
- Nürnberg G.K. (1995) Quantifying anoxia in lakes. *Limnology and Oceanography*, **40**, 1100–1111.
- Nürnberg G.K. (1998) Prediction of annual and seasonal phosphorus concentrations in stratified and polymictic lakes. *Limnology and Oceanography*, **43**, 1544–1552.
- Nürnberg G.K. & LaZerte B.D. (2001) Predicting lake water quality. In: *Managing Lakes and Reservoirs* (eds C. Holdren, W. Jones & J. Taggart), pp. 139–163. North American Lake Management Society and the Terrene Institute in cooperation with Office of Water Assessment, Watershed Protection Division, United States Environmental Protection Agency, Madison, Wisconsin.
- Nürnberg G.K. & Peters R.H. (1984) Biological availability of soluble reactive phosphorus in anoxic and oxic freshwaters. *Canadian Journal of Fisheries and Aquatic Sciences*, **41**, 757–765.

- Nürnberg G.K., Shaw M., Dillon P. & McQueen D. (1986) Internal phosphorus load in an oligotrophic Precambrian shield lake with an anoxic hypolimnion. *Canadian Journal of Fisheries and Aquatic Sciences*, **43**, 574–580.
- Persson A. (1997) Phosphorus release by fish in relation to external and internal load in a eutrophic lake. *Limnology and Oceanography*, **42**, 577–583.
- Peters R.H. (1981) Phosphorus availability in Lake Memphremagog and its tributaries. *Limnology and Oceanography*, **26**, 1150–1161.
- Pettersson K. (1998) Mechanisms for internal loading of phosphorus in lakes. *Hydrobiologia*, **373/374**, 21–25.
- Porter K.G., Saunders P.A., Haberyan K.A., Macubbin A.E., Jacobsen T.R. & Hodson R.E. (1996) Annual cycle of autotrophic and heterotrophic productions in a small monomictic Piedmont lake (Lake Oglethorpe): analog for the effects of climatic warming on dimictic lakes. *Limnology and Oceanography*, **41**, 1041–1051.
- Ruban V., López-Sánchez J.F., Pardo P., Rauret G., Muntau H. & Quevauviller Ph. (1999) Selection and evaluation of sequential extraction procedures for the determination of forms in lake sediments. *Journal of Environmental Monitoring*, **1**, 51–56.
- Ruttenberg K.C. (1992) Development of a sequential fractionation technique for different forms of phosphorus in marine sediments. *Limnology and Oceanography*, **37**, 1527–1542.
- Schaus M.H., Vanni M.J. & Wissing T.E. (2002) Biomass-dependent diet shifts in omnivorous gizzard shad: implications for growth, food web, and ecosystem effects. *Transactions of the American Fisheries Society*, **131**, 40–54.
- Schaus M.H., Vanni M.J., Wissing T.E., Bremigan M.T., Garvey J.A. & Stein R.A. (1997) Nitrogen and phosphorus excretion by detritivorous gizzard shad in a reservoir ecosystem. *Limnology and Oceanography*, **42**, 1386–1397.
- Smith V.H. (1979) Nutrient dependence of primary production in lakes. *Limnology and Oceanography*, **24**, 1051–1064.
- Søndergaard M., Jensen J. & Jeppesen E. (1999) Internal loading in shallow Danish lakes. *Hydrobiologia*, **408/409**, 145–152.
- Soranno P.A., Carpenter S.R. & Lathrop R.C. (1997) Internal phosphorus loading in Lake Mendota: response to external loads and weather. *Canadian Journal of Fisheries and Aquatic Sciences*, **54**, 1883–1893.
- Stainton M., Capel M. & Armstrong F. (1977) *The Chemical Analysis of Freshwater*. Miscellaneous Special Publication No. 25. pp. 119. Freshwater Institute, Winnipeg.
- Stauffer R. (1987) Vertical nutrient transport and its effects on epilimnetic phosphorus in four calcareous lakes. *Hydrobiologia*, **154**, 87–102.
- Thornton K.W. (1990a) Perspectives on reservoir limnology. In: *Reservoir Limnology: Ecological Perspectives* (Eds K.W. Thornton, B.L. Kimmel & F.E. Payne), pp. 1–14. John Wiley and Sons, Inc., New York.
- Thornton K.W. (1990b) Sedimentary processes. In: *Reservoir Limnology: Ecological Perspectives* (Eds K.W. Thornton, B.L. Kimmel & F.E. Payne), pp. 43–69. John Wiley and Sons, Inc., New York.
- Vanni M.J., Renwick W.H., Headworth J.L., Auch J.D. & Schaus M.H. (2001) Dissolved and particulate nutrient flux from three adjacent agricultural watersheds: A five-year study. *Biogeochemistry*, **54**, 85–114.
- Vannote R.L., Minshall G.W., Cummins K.W., Sedell J.R. & Cushing C.E. (1980) The river continuum concept. *Canadian Journal of Fisheries Aquatic Sciences*, **37**, 130–137.
- Wetzel R.G. (1983) *Limnology*, 2nd edn. pp. 180. Harcourt Brace Publishers, New York.
- Winner R.W., Strecker R.L. & Ingersoll E.M. (1962) Some physical and chemical characteristics of Acton Lake Ohio. *Ohio Journal of Science*, **62**, 55–61.
- Wodka M.C., Effler S.W., Driscoll C.T., Field S.D., Asce A.M. & Devan S.P. (1983) Diffusivity-based flux of phosphorus in Onondaga Lake. *Journal of Environmental Engineering*, **109**, 1403–1415.

(Manuscript accepted 25 October 2004)