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Relationship between hypolimnetic phosphorus and iron release from eleven lakes in Maine, USA

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Abstract. We studied five eutrophic (high phosphorus) and six mesotrophic/oligotrophic (low phosphorus) lakes in Maine, USA, all of which are dimictic and develop anoxic hypolimnia during stratification. The lakes were sampled during the stratified period from May to September 1999. Late summer hypolimnetic total phosphorus (P) concentrations in the high-P lakes ranged from 185 to 460 ppb; epilimnetic total P increased up to 30 ppb from the spring to the fall overturn. During the same period, the low-P lakes had hypolimnetic total P concentrations in the range of 6–19 ppb.Individual high-P lakes demonstrated strong temporal correlations between aqueous hypolimnetic dissolved Fe and total P concentrations ($R^2 \geq 0.88$) with an average molar Fe:P ratio of 11.9 4.2. For the combined data, the high-P lakes exhibited strong correlation between hypolimnetic Fe and P concentrations ($R^2 = 0.82$). The low-P lakes, however, did not show a good correlation between the hypolimnetic Fe and P concentrations. Among the low-P lakes two lakes had hypolimnetic Fe fluxes comparable to the Fe fluxes of the high-P lakes. These two lakes had considerably higher hypolimnetic Fe:P ratios than all other lakes studied here. There were no significant differences in surface sediment Fe(III) or P fractions that correlated with the differences in the relationship between aqueous concentrations of Fe and P in these two outlier low-P lakes. A model for the generation of hypolimnetic acid neutralization capacity (ANC) was developed based on microbially-catalyzed reduction of Fe(III) hydroxide, Mn(IV) oxide and sulfate. Reduction of Fe(III) hydroxide was the most important contributor to the increase in the hypolimnetic ANC in all high-P and the two outlier lakes. Assuming that all hypolimnetic P was due to the reduction of Fe(III) hydroxide by bacteria and sulfide, average summer hypolimnetic P flux for each lake was predicted using the sediment reducible Fe(III):P ratio. The observed and predicted average P fluxes in the high-P lakes corresponded reasonably, suggesting that in these lakes internal P release is closely related to the reduction of Fe(III) hydroxide. Other release or sequestration mechanisms may operate for the release and availability of P in the low-P lakes.

Introduction

Excess phosphorus (P) in Maine lakes poses a significant water quality problem, since one third of the natural water systems on Maine's threatened waters list are lakes, and 77% of those lakes scheduled for total maximum daily load development are listed due to non-point pollution (such as excess P export from nearshore roads and human disturbance of vegetation and soils in the watershed).

Sediment is the dominant source of the internally loaded P for many lakes (Boström and Petterson 1982; Stauffer 1985; Nürnberg et al. 1986;

Sondergaard 1989; Campbell 1994). Sediment-derived internally recycled P is a significant input to the P budget of a lake (Nürnberg 1985). Several mechanisms for the release of P from lake sediment during anoxia have been proposed. These mechanisms all include the direct or indirect involvement of anaerobic bacteria in sediment. Einsele (1936) and Mortimer (1941) pioneered work on the mechanisms of internal P recycling in lakes. They hypothesized that P is largely associated with Fe(III) hydroxide minerals. Reducing conditions in the hypolimnia cause Fe(III) reduction and release of P from the sediment. When the lake mixes in the early fall and the hypolimnion is again oxygenated, some of the P is sequestered by the precipitating Fe(III) hydroxide floc.

The Fe(III) reduction hypothesis is most frequently used to explain P release from sediment. However, this mechanism does not explain patterns of P release from all sediments (Boström et al. 1988; Gächter et al. 1988; Prairie et al. 2001). Several studies have shown that the presence of an anoxic hypolimnion does not necessarily result in significant P release from sediments (Schindler et al. 1973; Levine et al. 1986; Gächter and Meyer 1993; Prairie et al. 2001). These studies have shown the lack of correspondence between hypolimnetic Fe and P release rates. It has been suggested that hypolimnetic P release after the onset of anoxia may be partly controlled by changes in bacterial physiology, and production and decomposition of biomass (Boström et al. 1988; Gächter et al. 1988). de Montigny and Prairie (1993) proposed that bacterial biomass may be the source of hypolimnetic P release as shown in lab experiments: upon death due to the changing redox environment, bacteria lyse and their contents are released. Gächter and Meyer (1993) proposed that the relatively low P content of the sediment bacteria in oligotrophic lakes may lead to their successful competition with Fe(III) hydroxide surfaces for the adsorbed P. This would result in a low hypolimnetic P release rate after the reductive dissolution of Fe(III) hydroxide, or sequestration of the released P by the bacteria. Alternatively, it has been proposed that in lakes that are subject to acidic deposition, sequestration mechanisms such as precipitation with Al hydroxide may result in low dissolved P concentrations (Kopáček et al. 2000, 2001; Ulrich and Pöthig 2000).

Sulfur species may play an important role in cycling of P. Acidic precipitation typically increases H^+ and SO_4 input to the watershed and surface waters. SO_4 is reduced to sulfide ($S(-II)$) as organic matter is decomposed by bacteria. $S(-II)$ also reduces Fe(III) to Fe(II). Subsequently, Fe(II) and any P adsorbed to the surface of Fe(III) hydroxide are liberated. Kinetics of P release due to direct $S(-II)$ attack is a subject of debate (Goltermann 1995). Caráco et al. (1989, 1993) found that surface water SO_4 concentrations correlate positively with hypolimentic P release rates, and negatively with hypolimnetic Fe:P ratios in 51 lakes. They suggested that increased SO_4 concentrations could increase P mobility by enhancing decomposition of organic matter by SO_4-reducing bacteria, and decreasing post-decompositional binding of P in sediments. High levels of SO_4 lead to production of high levels of $S(-II)$ during summer anoxia that can reduce Fe(III) hydroxide and release P, and precipitate the microbially-reduced Fe(II) as FeS (Cook 1984). Acid neutralizing capacity (ANC) has also been positively correlated to P flux (Ostrofsky et al. 1989), and Fe(III) and SO_4 reduction are both ANC-generating reactions. Gächter and Müller (2003) have recently proposed a model where depending on the concentration of the diagenetically produced S(−II) in relation to P and Fe concentrations in the sediment pore water, P could be released due to the dissolution of vivianite ($Fe_3(PO_4)_2$) as FeS precipitates.

In this work, we have carried out an investigation of internal P cycling in 11 lakes in Maine, which exhibit differences among their hypolimnetic P concentrations under similar low dissolved oxygen (DO) conditions. We focused on determining the hypolimnetic P and Fe fluxes from the sediment, and the processes that lead to the reductive dissolution of Fe(III) hydroxide. A model is proposed that considers the effect of microbially-catalyzed reduction of Fe(III) hydroxide, Mn(IV) oxide and SO_4, and the role of S(−II) on the release of sediment-bound P and generation of ANC in the hypolimnion.

Materials and methods

Site description

Lakes were selected based on their historical records of seasonal anoxia and P loading (Figure 1). In particular, these lakes (1) had flushing rates between 0.5 and 1.7/year, (2) had at least 3 recent years with late season (August to mid September) profiles that were all consistent in nature, (3) always showed a large percentage of the hypolimnion volume and bottom sediments overlain with DO <2 ppm, and (4) had total P concentrations in the low DO hypolimnetic water that were consistently <20 ppb or more than 40 ppb.

Among the lakes selected, China Lake, Salmon Lake, Sebasticook Lake, Togus Pond and Webber Pond were eutrophic (high-P). The remaining six lakes, Bryant Pond, Cobbosseecontee Lake, Highland Lake, Island Pond, Keoka Lake and Pennesseewassee Lake were oligotrophic to mesotrophic (low-P). Hypolimnetic DO concentrations close to the sediment–water interface and other relevant lake and watershed physical characteristics are listed in Table 1. The high-P and low-P lakes were also similar in morphological characteristics, as they possessed similar maximum and average depths, and drainage area/surface area ratios (Table 1). More details on physical characteristics are reported elsewhere (Pearce 2000).

The lake basins in Maine were created during the most recent glaciation. After deglaciation (ca. 13,000 years b.p.), ocean water briefly flooded Maine to a present elevation of about 85 m before isostatic rebound caused the marine regression. The marine flooding left behind the Presumpscot Formation, deposits of marine silt and clay (Davis et al. 1978). The soils developed on Presumpscot Formation promote wetland formation and are easily eroded. Erosion increases the concentration of nutrient-rich particulates in runoff destined for lakes. Wetland area, non-forested area (agriculture), and human disturbance within a watershed are all positively correlated to mean P concentration in Maine lakes (Nieratko 1992). All five high-P

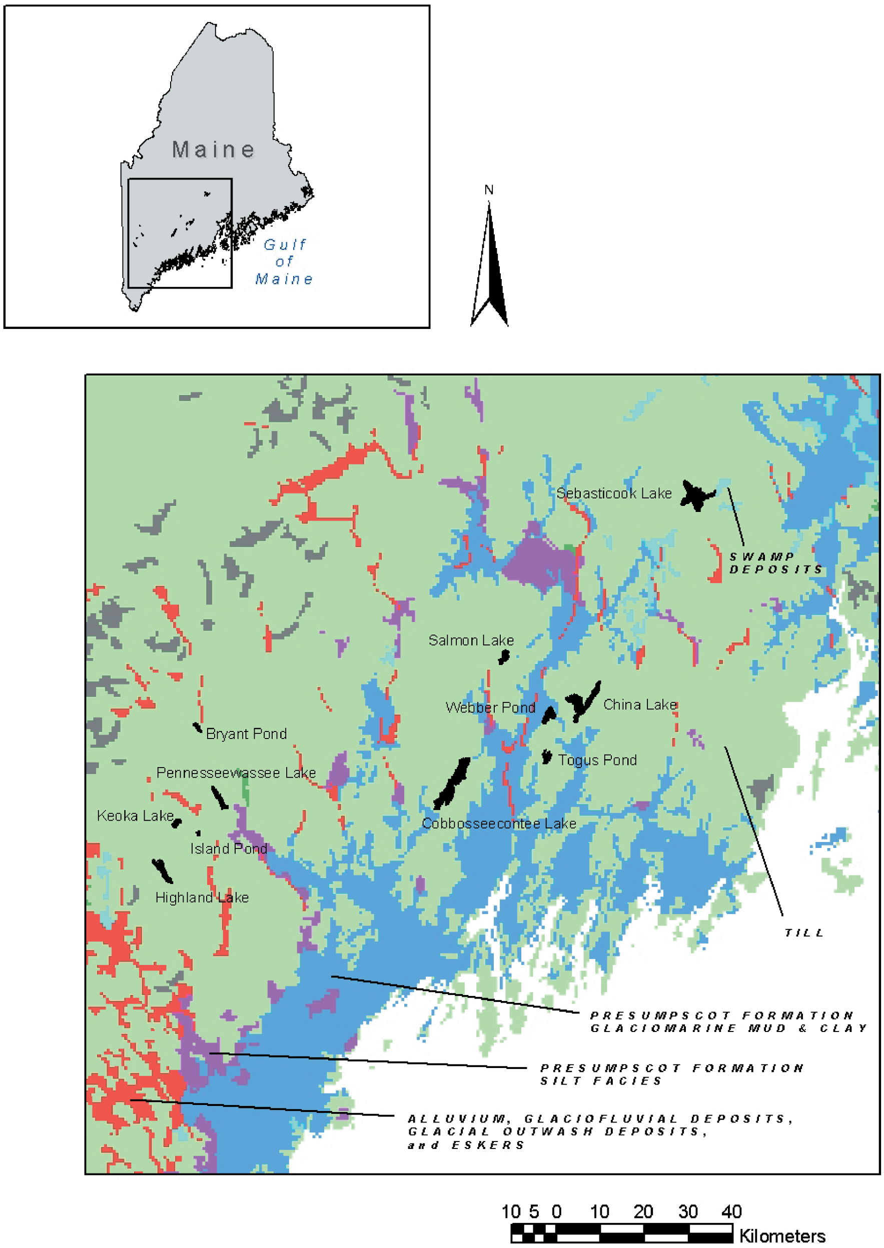

Figure 1. Map of Maine and the lakes in this study.

lakes and Cobbosseecontee Lake have marine clay as a major component of surface material. In the watersheds of the low-P lakes, marine clay is absent and glacial till is the dominant surface material.

Table 1. Lake and watershed physical characteristics.

Lake	Max depth (m)	Mean depth (m)	Surface area (ha)	Drainage area/ surface area	Sediment–water DO (ppm)[1]
Salmon Lake	17.4	7.0	270	7.8	<0.1
Webber Pond	12.5	5.5	85	11.2	<0.1
Sebasticook Lake	15.3	6.1	735	17.3	<0.1
China Lake	25.9	8.5	908	19.3	<0.1
Togus Pond	14.9	6.1	60	8.8	<0.1
Highland Lake	15.3	5.5	24	10.2	<0.1
Pennesseewassee Lake	14.6	5.5	84	31.3	<0.1
Island Pond	14.6	4.9	42	28.6	0.3–0.6
Cobbosseecontee Lake	30.5	11.3	2120	10.2	<0.1
Keoka Lake	12.8	7.6	80	21.2	0.8
Bryant Pond	19.2	9.8	12	20.5	0.1–0.2

[1] Data taken at ≤ 1 m above the sediment–water interface from early July to late August 1999.

The drainage patterns in the watersheds differ between the high- and low-P lakes in this study. Both sets of lakes have approximately the same number of year-round inlets (Pearce 2000). However, the high-P lakes (mostly on the Presumpscot Formation) have many more intermittent inlets than the low-P lakes. This implies that watersheds underlain with clayey deposits are more likely to receive higher flow and more suspended matter from spring melt and storm runoff through these intermittent streams.

Monthly sampling took place at the deepest point in the main basin. The details of the aqueous and solid sampling procedure and analysis techniques are in Pearce (2000).

Aqueous phase

We sampled for total P, anions (SO_4, Cl, NO_3 and $S(-II)$), cations (Na, K, Mg, Ca, Fe, Mn and Al), ANC, and dissolved organic carbon (DOC) using a Van Dorn sampler at a minimum of four depths in the hypolimnion (top of hypolimnion, 1 m from the sediment–water interface, and two equally spaced in between), and two depths in the epilimnion at the deepest point of each lake. Samples for cation analysis were immediately filtered and acidified at the collection site. Samples for $S(-II)$ analysis were collected in a zinc acetate solution. Total P and $S(-II)$ concentrations were measured using colorimetric techniques, and ion chromatography (Dionex Model 2010I) was used to measure other anions. Cations were measured using ICP-OES (Perkin Elmer Optima 3300XL), ANC was measured by Gran titration, and DOC was measured using a TOC analyzer (OI Corporation 700). Temperature and DO were measured at meter intervals (Yellow Springs Instruments).

Equilibrium speciation calculations were performed with MINEQL+ (Schecher and McAvoy 1998). The equilibrium constants were corrected for temperature with

Van't Hoff's equation and for ionic strength with Davies' equation (Stumm and Morgan 1996). Carbonate concentration was calculated from the measured ANC and pH. The saturation index (SI) was calculated for relevant minerals that contain Fe(II), Mn(II), Ca, S(−II), and CO_3 species as

$$\mathrm{SI} = \log \frac{\text{ion activity product}}{\text{solubility constant}} \tag{1}$$

SI values greater than zero indicate that the solution is supersaturated with respect to the mineral, and SI values smaller than zero indicate that the solution is undersaturated with respect to the mineral. In these calculations, an oxidation state of II has been assumed for all dissolved Fe and Mn.

Solid phase

Solid phase samples were collected in triplicate at the deepest point and its vicinity using a gravity corer (2.5 cm dia.) in May 1999 before the onset of summer stratification and anoxia. The cores were sampled from approximately the sediment–water interface to 2.5 cm and from 2.5 to 5 cm. The top interval (0–2.5 cm) was removed from the corer using a large plastic bulb syringe. The next fraction of sediment (2.5–5 cm) was removed using a plastic spatula. All sediment samples were kept on ice until transferred to the lab to be frozen until analysis. The sediments and the associated interstitial water were analyzed for P and Fe. Composite samples from the three cores were centrifuged at 10,000 RPM for 15 min to separate interstitial water from the sediment. The supernatant liquid was then filtered (0.45 µm polycarbonate) into an acid washed 125 ml amber glass bottle and kept in the dark at 4 °C until analysis.

Total solid phase P was extracted using HNO_3 following the EPA method 3051 (Pearce 2000). Sediment Fe(III) was extracted using the Ti(III)-EDTA extraction technique (Heron et al. 1994). This is a reductive dissolution technique that selectively extracts amorphous and crystalline Fe(III) (hydr)oxides. Laboratory and field experiments have shown that this extraction technique is a very good indicator of the solid phase Fe(III) available for reduction by dissolved S(−II) and by the bacteria. The extracted Fe(III) and P were measured using the ICP-OES. Sediment-bound P and Fe (III) fractions were used for predicting the hypolimnetic P flux.

Results

Temperature and DO

All lakes stratified thermally during the summer of 1999. However, the depth and strength of stratification varied from one lake to another. The majority of the lakes had a distinct epilimnion and hypolimnion, with maximum epilimnetic temperatures between approximately 22 and 25 °C and hypolimnetic temperatures between approximately 10 and 15 °C. In Sebasticook Lake, however, after summer stratification had set in, the bottom of the thermocline descended to within 3 m above the deepest part of the lake for a brief period in mid June. This stratification setup seems to be normal, considering the historical data. A strong hypolimnion was observed throughout the summer in Sebasticook Lake. In general, the temperature profiles between high- and low-P lakes were similar. The stratification patterns observed in 1999 were similar to historical patterns.

Hypolimnetic oxygen depletion occurred during summer stratification in all lakes (Table 1). Surface DO concentrations typically varied between 8 and 9 mg/l. The only variation in epilimnetic DO was during algal blooms, when oxygen concentrations sometimes increased to above 12 mg/l. In the high-P lakes, DO was below the detection limit (0.1 mg/l) at or just above the thermocline to the sediment surface during the summer anoxia. Hypolimnetic oxygen loss in the low-P lakes was not as dramatic as in the high-P lakes. In all low-P lakes, however, the DO concentrations below the thermocline dropped to below 2 mg/l between the end of July until the onset of fall overturn (Table 1). The DO concentrations in middle of June in high-P lakes were consistently lower than those in the low-P lakes, including the two outlier lakes.

Phosphorus

Phosphorus concentrations during the summer of 1999 followed the historical pattern. Each of the high-P lakes had an increase in hypolimnetic P concentration in July, August and September. Hypolimnetic P concentrations in the low-P lakes remained low for the duration of the sampling season. Late summer hypolimnetic P concentrations varied from 6 to 15 μM (185–460 ppb as P) in the high-P lakes and from 0.2 to 0.6 μM (6–19 ppb) in the low-P lakes. Epilimnetic total P concentrations ranged from 0.5 to 1.75 μM (15–54 ppb) in the high-P lakes and from 0.2 to 0.3 μM (6–9 ppb) in the low-P lakes. The high-P lakes had epilimnetic total P concentrations increasing by as much as 1 μM from spring to the end of summer. The low-P lakes did not have such increases in epilimnetic total P concentration.

Assuming that lake sediment is the only source of P to the water column, the average P fluxes from the deepest point were calculated on a volume weighted average basis in a 1 m^2 column of water between May and August (Table 2). The results in Table 2 show the contrast in P flux to the water column during summer anoxia between high- and low-P lakes.

Iron

There is a significant variability in the increase of dissolved Fe concentrations during the summer among all the lakes. Maximum hypolimnetic dissolved Fe concentrations (measured at ∼1 m above the sediment–water interface) increased from nearly 0.5 μM in May up to 100 μM in late summer in the high-P lakes. The

Table 2. Hypolimnetic phosphorus and iron fluxes in mg/m^2/day[1].

Lake	Phosphorus flux	Fe flux
Salmon Lake	13.6	212
Webber Pond	12.1	190
Sebasticook Lake	9.3	132
China Lake	7.9	147
Togus Pond	6.3	158
Highland Lake	0.9	188
Pennesseewassee Lake	0.9	130
Island Pond	0.5	45
Cobbosseecontee Lake	0.5	2
Keoka Lake	0.1	11
Bryant Pond	0.1	9

[1] Average flux from mid May to late August 1999.

low-P lakes, Bryant, Cobbosseecontee, Island and Keoka developed summer hypolimnetic Fe concentrations between 5 and 15 μM. The remaining two low-P lakes, Highland and Pennesseewassee, however, had hypolimnetic summer Fe concentrations between 60 and 100 μM, similar to the concentrations of Fe in the high-P lakes. Epilimnetic dissolved Fe concentrations remained below 0.5 μM in all lakes for the summer.

All of the high-P lakes had relatively high Fe fluxes (Table 2). Four of the low-P lakes had low Fe fluxes. However, Highland and Pennesseewassee lakes had low P fluxes but high Fe fluxes.

Individual high-P lakes exhibited a strong correlation between dissolved hypolimnetic P and Fe concentrations ($R^2 \geq 0.88$) with an average molar Fe:P ratio of 11.9 4.2 (Pearce 2000). Figures 2(a) and (b) show the combined hypolimnetic concentrations of P versus Fe for the high- and low-P lakes, respectively. Dissolved P and Fe concentrations are strongly correlated in the high-P lakes (Figure 2(a)). A strong correlation, however, is not observed for the low-P lakes (Figure 2(b)). Both Highland and Pennesseewassee lakes had hypolimnetic Fe concentrations similar to those of the high-P lakes, but did not have the similar corresponding P concentrations (Figure 2(b)). The dissolved Fe:P ratios were consistently higher in Highland Lake (Fe:P ratio of 147; $R^2 = 0.67$) and Pennesseewassee Lake (Fe:P ratio of 75; $R^2 = 0.97$) than in the rest of the lakes. These two lakes also had average hypolimnetic Fe fluxes similar to those of the eutrophic lakes, but P fluxes similar to those of oligotrophic lakes (Table 2).

Sulfur species

After the spring turnover, but before summer stratification developed, SO_4 concentrations were typically between 35 and 50 μM in each lake, regardless of their summer trophic status. The only exception was Sebasticook Lake with a SO_4 concentration of 67 μM throughout the water column after the spring turnover. Sulfate

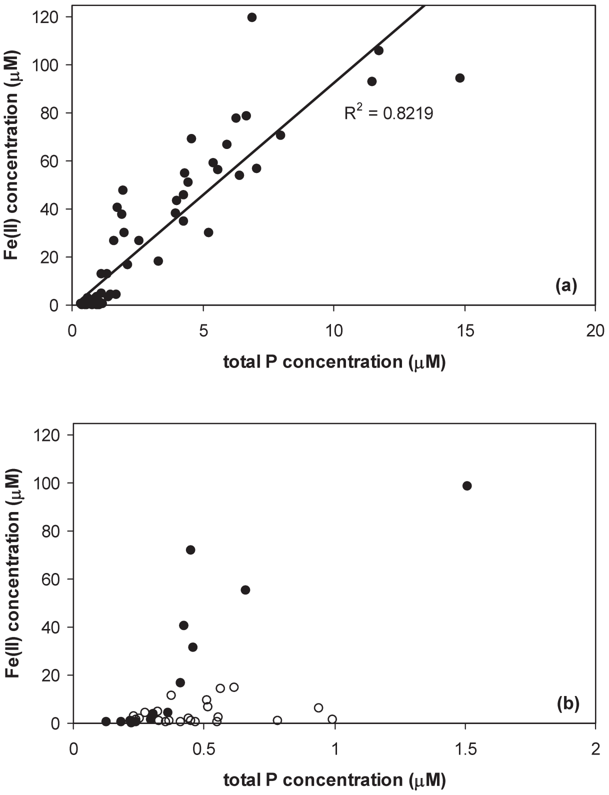

Figure 2. (a) Dissolved hypolimnetic P versus Fe(II) concentrations for the high-P lakes; (b) Dissolved hypolimnetic P versus Fe(II) concentrations for the low-P lakes. Filled circles in panel b are for Highland and Pennesseewassee lakes. For the low-P lakes, $R^2 = 0.33$.

concentrations in the hypolimnion decreased during summer stratification in all of the lakes. Hypolimnetic SO_4 concentrations in the high-P lakes decreased approximately 50–100% from spring turnover to late summer. Among the low-P lakes, Cobbosseecontee, Bryant, Island and Keoka lost no more than 20% of their hypolimnetic SO_4 during this period. From May to August, SO_4 concentrations decreased from 30 to 10 μM in Highland Lake and from 40 to 10 μM in Pennesseewassee Lake.

Dissolved S(−II) concentrations were between 5 and 15 μM in all of the lakes that generated detectable amounts of this species, regardless of the concentration of reduced SO_4 in any particular lake. There was no detectable S(−II) in Bryant, Keoka and Cobbosseecontee lakes.

ANC and DOC

Hypolimnetic ANC in the high-P lakes increased between 150 and 325 μeq/l from spring to summer. The change in hypolimnetic ANC from spring to late summer in

Table 3. Microbially-catalyzed reactions that contribute to the change in ANC.

Reaction		ΔANC per mole of inorganic substrate
Fe(III) reduction	$\langle CH_2O\rangle + 4FeOOH + 8H^+ = CO_2 + 4Fe^{2+} + 6H_2O$	+2
Mn(IV) reduction	$\langle CH_2O\rangle + 2MnO_2 + 4H^+ = CO_2 + 2Mn^{2+} + 2H_2O$	+2
SO_4 reduction	$2\langle CH_2O\rangle + SO_4^{2-} + 2H^+ = 2CO_2 + H_2S + 2H_2O$	+2

the low-P lakes was about 50 μeq/l except for Highland and Pennesseewassee, where the change in hypolimnetic ANC was approximately 150 μeq/l.

Understanding and quantifying the factors that control the ANC generation, namely Fe(III) reduction, are important, as the model to predict hypolimnetic P flux is based on the hypolimnetic Fe(II) flux. The dominant microbially-catalyzed processes that contribute to the change in the hypolimnetic ANC are listed in Table 3. Figure 3 shows the observed and predicted changes in ANC for Webber, Salmon, Highland and Pennesseewassee lakes at the deepest sampling points. The predicted change in ANC was calculated based on the reactions in Table 3 using the measured concentrations of dissolved Fe(II), Mn(II), SO_4, and S(−II). Precipitation of FeS contributed minimally to the change in ANC in lakes in this study. The contribution to ANC change from Fe(III) reduction was corrected by accounting for the decrease in SO_4 and increase in S(−II) concentrations. The agreement between the observed and predicted changes in ANC is reasonable (Figure 3), indicating the validity of our assumptions regarding the factors that control hypolimnetic ANC. Reduction of Fe(III) hydroxide was the dominant mechanism controlling the ANC generation during the summer in all high-P lakes as well as in the low-P Highland and Pennesseewassee lakes (Figure 3). The same approach has been taken previously to model ANC generation in lake water column (Cook et al. 1986; Anderson and Schiff 1987, Brezonik et al. 1987), and lake sediment (Sherman et al. 1994; Furrer and Wehrli 1996), where microbially-catalyzed Fe(III) and SO_4 reduction, and methanogenesis contribute significantly to the ANC generation.

DOC concentrations varied between 3 and 5 ppm regardless of the trophic status of the lakes. There were no clear trends in DOC concentrations with time or depth.

Mineral solubility

Table 4 presents the SI values with respect to several minerals. Solubility calculations indicate saturation or near-saturation conditions with respect to amorphous FeS in the hypolimnia of all high-P lakes ($-0.6 < SI < 0.7$). In August, Highland and Pennesseewassee Lakes possessed hypolimnetic SI values of −1.58 and −0.54, respectively, indicating undersaturation condition in Highland Lake and near-saturation condition in Pennesseewassee Lake with respect to FeS. The hypolimnia of all lakes in this study were undersaturated with respect to siderite, $MnCO_3$ (rhodocrosite), and $CaCO_3$ (calcite) (Table 4).

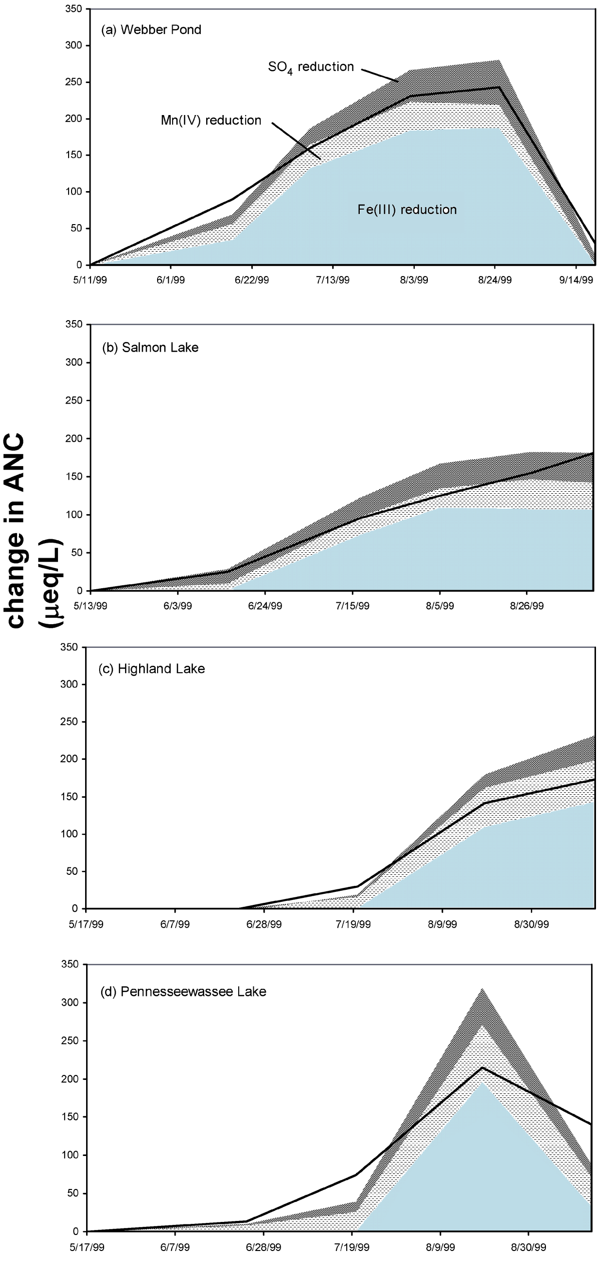

Figure 3. Cumulative ANC contribution from microbially-catalyzed reactions for (a) Webber Pond, (b) Salmon Lake, (c) Highland Lake, and (d) Pennesseewassee Lake. In each plot, the top, middle and bottom splices represent SO_4 reduction, Mn(IV) reduction and Fe(III) reduction processes, respectively, as predicted using the reactions in Table 3. The solid line represents the change in the measured ANC relative to the measured ANC in May 1999.

Table 4. SI of several minerals[1,2].

Lake	FeS	MnS	$FeCO_3$	$MnCO_3$	$CaCO_3$
Salmon Lake	0.24	0.55	−0.89	−1.12	−2.41
Webber Pond	−0.27	−0.59	−0.76	−1.45	−2.34
Sebasticook Lake	0.72	0.52	−0.17	−0.13	−1.21
China Lake	−0.63	−0.26	−1.06	−1.26	−2.35
Togus Pond	0.40	0.59	−0.87	−1.11	−2.39
Highland Lake	−1.58	−0.82	−1.99	−2.26	−3.77
Pennesseewassee Lake	−0.54	−0.23	−1.07	−1.41	−2.66
Island Pond	−2.23	−1.84	−2.90	−3.50	−3.98
Cobbosseecontee Lake	ND [3]	ND [3]	−3.08	−3.39	−2.49
Keoka Lake	ND [3]	ND [3]	−3.72	−3.47	−4.75
Bryant Pond	ND [3]	ND [3]	−1.03	−0.67	−1.51

[1] Calculations are for hypolimnetic samples at the deepest point in each lake in August.

[2] Log solubility constants; FeS: −2.95 (Davison 1991); MnS: −10.5 (Stumm and Morgan 1996); $FeCO_3$: −10.45 (Nordstrom et al. 1990); $MnCO_3$: −10.39 (Nordstrom et al. 1990); $CaCO_3$: −8.48 (Nordstrom et al. 1990). Solubility constants are corrected for temperature and ionic strength.

[3] Not determined due to very low S(-II) concentrations.

Even though solubility calculations (Table 4) suggest that saturation with respect to $MnS_{(S)}$ may be reached in the hypolimnia of all high-P lakes ($-0.6 < SI < 0.6$), MnS precipitation may not be an important removal mechanism for S(−II) and Mn(II). Morse and coworkers (Kornicker and Morse 1991; Arakaki and Morse 1993; Morse and Luther 1999) have argued that despite the higher rate of water exchange for Mn^{2+} than for Fe^{2+}, Mn^{2+} does not readily form a MnS phase. Instead, they have proposed incorporation of Mn(II) into FeS and eventually into pyrite.

Even though dissolved PO_4 concentrations were not measured in this study, solubility with respect to vivianite (log solubility product = −36; Stumm and Morgan, 1996) was calculated assuming total measured P as dissolved PO_4 species. Despite this assumption, all low-P lakes exhibited $SI < -1$ indicating that P concentrations in these lakes were not controlled by vivianite.

Solid phase

No significant correlations exist between the concentrations of Fe and P species in the sediment and the trophic status of the lakes. The hypolimnetic molar Fe:P ratios were not correlated to the extractable molar Fe:P ratios in the sediment, which ranged from 8.0 to 23.4 (Pearce 2000). Interstitial P concentrations ranged from 0.2 μM in Highland Lake to 11.6 μM in Bryant Pond, both of which are low-P lakes. There was no consistent difference between the extractable P concentrations in the top 2.5 cm and the bottom 2.5 cm within and among lakes.

Discussion

In this study, the individual and combined hypolimnetic P and Fe concentrations for all high-P lakes exhibited strong correlations. Even though hypolimnetic P and Fe concentrations in Highland and Pennesseewassee lakes exhibited good correlations individually, the Fe:P ratios in these two lakes were considerably higher than those in the high-P lakes. The 51 North American lakes studied by Caráco et al. (1993) exhibited highly variable hypolimnetic Fe:P ratios ranging from approximately 0.02 to 100. These ratios correlated inversely to SO_4 concentrations that ranged from approximately 10 and 1000 μM. They inferred that epilimnetic SO_4 concentration represents the potential for SO_4 reduction in the hypolimnion, and thus S(−II) generation, Fe(III) hydroxide reductive dissolution and consequent P release. In our study, SO_4 concentrations before the onset of anoxia ranged from 35 to a maximum of 67 μM regardless of the trophic status of the lake. For this relatively narrow range of SO_4 concentrations, even though Fe:P ratios in our lakes do not show an inverse correlation with SO_4 concentrations, the Fe:P ratios in high-P lakes are similar to the Fe:P ratio based on the model proposed by Caráco et al. (1993). As shown in Figure 3, for the range of SO_4 concentrations in this study, Fe(III) reduction, and not SO_4 reduction, is the dominant mechanism in producing ANC in the high-P and Highland and Pennesseewassee lakes, due to the relatively low SO_4 concentrations.

Prairie et al. (2001) did not observe good correlations between hypolimnetic P and Fe concentrations in eight lakes in Québec with relatively low hypolimnetic Fe fluxes. The Fe fluxes in their study ranged from 16 to 210 mg/m^2/day, which is similar to the range observed in our study (Table 2). Their P fluxes, however, ranged from 0 to 4 mg/m^2/day, in range with P fluxes in our low-P lakes (Table 2). Their observations prompted them to conclude that only in lakes where the Fe(III) reducing bacteria contribute substantially to the oxidation of organic matter should the release of P and Fe be coupled. Prairie et al. (2001) also observed a strong relationship between the rate of DO consumption and the net hypolimnetic P flux, concluding that decomposition processes exert a strong control on hypolimnetic P release.

Reduction of Fe(III) hydroxide and P release

Average rates of Fe(III) reduction throughout the summer were calculated from dissolved Fe(II) concentrations in May and August as follows:

$$\text{Average rate of Fe reduction} = \frac{[\mathrm{Fe(II)}]_{\mathrm{August}} + ([\mathrm{SO}_4^{2-}]_{\mathrm{May}} - [\mathrm{SO}_4^{2-}]_{\mathrm{August}}) - ([\mathrm{S}(-\mathrm{II})]_{\mathrm{August}} - [\mathrm{S}(-\mathrm{II})]_{\mathrm{May}})}{\mathrm{Days}} \tag{2}$$

Equation (2) estimates the concentration of Fe(III) hydroxide reduced from the measured dissolved Fe(II), the loss of hypolimnetic SO_4 and the increase in

S(−II) concentrations. This accounts for the contributions of dissimilatory Fe(III) reduction (Table 3) and reduction of Fe(III) hydroxide by S(−II) as described below.

The diagenetic sulfur cycle has been described in detail elsewhere (Davison 1991; Luther et al. 1992). Reactions of S(−II) with Fe(III) and Fe(II) species generally follow two major pathways. The first pathway involves the direct attack on the solid Fe(III) hydroxide by aqueous S(−II) to readily form FeS at the surface as shown in Equation (3).

$$2\mathrm{FeOOH} + 3\mathrm{HS}^- \rightarrow 2\mathrm{FeS} + \text{‘}\mathrm{S}(0)\text{’} + 3\mathrm{OH}^- + \mathrm{H_2O} \qquad (3)$$

This is the main sink for the dissolved S(−II) in most natural systems, where a sufficient pool of available solid Fe(III) hydroxide exists (von Gunten and Zobrist 1993). The FeS formed via this pathway undergoes further reaction to form pyrite (FeS_2) (Berner 1984) as shown in Equation (4).

$$\mathrm{FeS} + \text{‘}\mathrm{S}(0)\text{’} \rightarrow \mathrm{FeS}_{2(\mathrm{S})} \qquad (4)$$

The second pathway is the reaction between dissolved S(−II) and Fe(II) and precipitation as FeS, provided that the solubility limit of the mineral is reached:

$$\mathrm{Fe}^{2+} + \mathrm{HS}^- \rightarrow \mathrm{FeS} + \mathrm{H}^+; \quad \mathrm{K_S} = 2.95 \qquad (5)$$

In Equation (2), August dissolved Fe(II) concentrations were adjusted for loss of S(−II) due to precipitation of FeS. We assumed that the decrease in SO_4 concentrations from May to August was due to microbially-catalyzed reduction to S(−II) as shown in Table 3, and any net loss of S(−II) was due to direct reduction of Fe(III) hydroxide to FeS in the sediment, or due to precipitation of FeS in the hypolimnion.The flux of Fe(III) reduction for each lake calculated based on Equation (2) is shown in the abscissa of Figure 4(a). The microbially-catalyzed reduction of Fe(III) was shown to be the most important factor leading to the generation of hypolimnetic ANC in the high-P as well as the outlier lakes (Figure (3)). Based on the calculated flux of Fe(III) reduction, and using the Ti(III)-EDTA extractable Fe(III):P ratio from the sediment, we predicted an average hypolimnetic P flux. This predicted average P flux is based on the assumption that all released P is associated with Fe(III) hydroxide in the sediment, and is released only when Fe(III) hydroxide is reduced via dissimilatory (Table 3) or S(−II) (Eq. (3)) pathways. All of the high-P lakes plus Highland and Pennesseewassee lakes had high fluxes of Fe into the water column as the iron reducers contribute substantially to the oxidation of organic matter in these lakes. The latter two lakes had Fe(III) reduction rates that are 5–7 times higher than those of the other oligotrophic lakes.

Figure 4(b) is the comparison between the observed and predicted P fluxes. The observed and predicted P fluxes from May to August in the high-P lakes follow approximately a 1:1 relationship (Figure 4(b)). Contrary to prediction, however, Highland and Penneseewassee lakes have higher ratios of predicted versus observed P flux (approximately 12:1). The lack of any correlations between the dissolved Fe

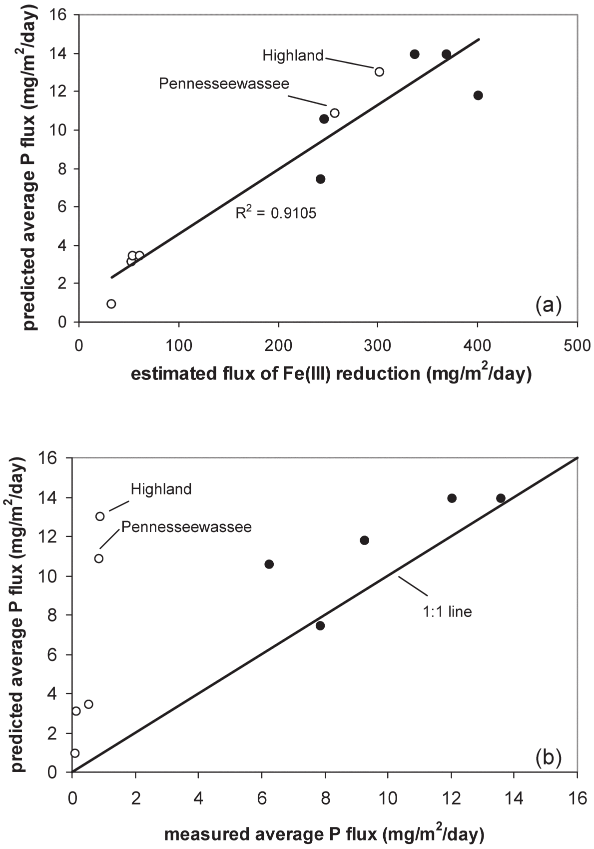

Figure 4. (a) Estimated flux of Fe(III) hydroxide reduction based on Equation (2) versus the predicted average P flux based on the extractable sediment Fe:P ratio; (b) Measured versus predicted average P fluxes for all lakes.

and P in the other four low-P lakes suggests release or sequestration mechanisms other than that in the high-P lakes.

In summary, in the high-P lakes, reduction of Fe(III) hydroxide in the lake sediment during summer controls the hypolimnetic release of P directly. The agreement between the observed P flux and the predicted P flux for these lakes implies that Fe and P are released into the water column in a similar ratio as present in labile form in the sediment (Figure 4(b)). The behavior of the low-P lakes, especially Highland and Pennesseewassee, may be attributed to other release or sequestration mechanisms such as (1) the competition between bacteria and metal hydroxides at the sediment-water interface for P complexation, and scavenging of the released P by the sediment-bound organisms (Gächter and Meyer 1993), or (2) P sequestration following its release due to Fe(III) reduction by precipitating or sediment $Al(OH)_3$ (Kopáček et al. 2000, 2001; Ulrich and Pöthig 2000).

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