Biogenic calcite–phosphorus precipitation as a negative feedback to lake eutrophication

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Abstract: Lakes in carbonate-rich watersheds commonly precipitate calcium carbonate as calcite, and this is accelerated by photosynthetic uptake of carbon dioxide. Co-precipitation of phosphate with calcite is one reason that algal growth in such lakes tends to be strongly phosphorus (P) limited. The extent to which calcite precipitation can be a sink for added P, and thus act as a potential negative feedback to eutrophication, was demonstrated using large enclosures within a Michigan lake. Nitrogen and P were added over 45 days in the summer to produce mesotrophic and eutrophic conditions. Algal biomass and production increased markedly with the nutrient additions, elevating the pH (9–10) and greatly increasing calcite precipitation, reducing concentrations of calcium and alkalinity by up to 60%. Sediment traps indicated that calcite sedimentation was a major sink for added P. By the end of the experiment, only about half of the added P remained in the water column. Major ion concentrations in a larger set of Michigan lakes showed calcite precipitation to be widespread, reflecting the abundant carbonate minerals in this glacial region.

Résumé : Dans les lacs situés dans des bassins versants riches en carbonates, il se fait ordinairement une précipitation de carbonate de calcium sous forme de calcite, un phénomène accéléré par l'incorporation de dioxyde de carbone par la photosynthèse. La précipitation de phosphate conjointe à celle de la calcite est une raison qui explique pourquoi la croissance des algues dans de tels lacs a tendance à être fortement limitée par le phosphore (P). Nous avons démontré l'importance de la précipitation de calcite comme piège pour le P ajouté, et ainsi comme rétroaction négative potentielle à l'eutrophisation, à l'aide de grands enclos érigés dans un lac du Michigan. Nous avons fait des additions de N et de P sur une période de 45 jours en été pour produire des conditions de mésotrophie et d'eutrophie. La biomasse et la production d'algues ont augmenté de façon marquée après l'addition des nutriments, ce qui a fait monter le pH (9–10) et a accru fortement la précipitation de calcite, réduisant ainsi les concentrations de calcium et l'alcalinité de jusqu'à 60 %. Des trappes à sédiments montrent que la sédimentation de calcite sert d'important piège pour le P ajouté. À la fin de l'expérience, il ne demeurait qu'à peu près la moitié du P ajouté dans la colonne d'eau. Les concentrations d'ions majeurs dans un ensemble plus étendu de lacs du Michigan indiquent que la précipitation de calcite est répandue, ce qui est un reflet de l'abondance des minéraux carbonatés dans cette région glaciaire.

[Traduit par la Rédaction]

Introduction

Groundwater-fed lakes in regions where carbonate minerals occur in the rocks and soils are rich in dissolved Ca^{2+} and HCO_3^- and commonly precipitate calcium carbonate in the mineral form of calcite ($CaCO_3$). Such lakes are particularly common in glaciated regions of North America and Europe. In temperate climates, calcite precipitation increases greatly during the summer as a result of both seasonal warming, which reduces the solubility of calcite, and enhanced photosynthetic uptake of carbon dioxide (CO_2) by algae and vascular plants (Kelts and Hsü 1978). Algal and plant growth in such lakes tends to be strongly limited by phosphorus (P) availability (Wetzel 2001), and above pH ~ 9, the co-precipitation of phosphate with calcite contributes to the limited availability of P. The precipitation of calcite, its binding with P, and its rapid sedimentation out of the water column present a potential negative feedback to aquatic primary production, potentially ameliorating eutrophication caused by nutrient loading (Koschel et al. 1983; Robertson et al. 2007). In addition to P binding, calcite precipitation can act as a negative feedback to aquatic primary production by attenuation of light in the water column and by flocculation and consequent sedimentation of algal cells (Koschel et al. 1983). Calcite precipitation and deposition on underwater surfaces impact the ecology and biogeochem-

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istry of lakes in many other ways, for example, by binding trace metals and dissolved organic matter and by smothering biofilms and underwater plant leaves, and over time, the accumulation of carbonate-rich lake sediments contributes to the infilling of lake basins (Kelts and Hsü 1978; Wetzel 2001).

Limnological studies of calcite precipitation have been mostly observational in nature, although lab experiments have explored the chemistry of calcite and phosphate co-precipitation (House et al. 1986) and the role of algae in inducing the reaction (Hartley et al. 1995; Olsen et al. 2006). Calcium has been experimentally added to lake water in enclosures to abiotically increase calcite supersaturation and strip out P via co-precipitation (e.g., Dittrich et al. 1997). Here we report results from a large-scale enclosure experiment in an oligotrophic lake in Michigan (USA). We sought to determine how nutrient additions affect calcite precipitation and co-precipitation of phosphate via stimulation of algal growth, thereby creating a sink for added P and potentially attenuating the eutrophication response to P loading. We monitored calcite precipitation and concomitant removal of P in large enclosures (~37 000 L) to which we periodically added nitrogen (N) and P over 45 days in the summer to produce mesotrophic and eutrophic conditions. This experiment demonstrates how nutrient loading, via stimulation of phytoplankton growth, draws down dissolved CO_2 and elicits biogenic calcite precipitation, with consequent loss of dissolved Ca^{2+}, carbonate alkalinity, and P from the water column. Comparison of these results with data from lakes across southern Michigan shows that calcite precipitation is widespread and is likely to be important as a negative feedback to eutrophication.

Materials and methods

The enclosure experiments were conducted in Gull Lake (surface area = 8.2 km^2, mean depth = 12 m, maximum depth = 31 m), an alkaline, groundwater-fed lake in southwestern Michigan. Gull Lake is low in P (summer total P in the epilimnion is ~5–12 $\mu g \cdot L^{-1}$) and oligotrophic to mesotrophic in productivity. A water budget for the lake indicated that groundwater supplies 75% of the annual input, either directly via underwater seepage (40% of annual input) or indirectly via spring-fed streams (Tague 1977). Calcite precipitation is readily visible on underwater surfaces during the summer, and the sediments are rich in calcite.

Large tubular enclosures (diameter, 2.5 m; depth, ~8 m; volume, ~37 000 L) constructed of clear polyethylene were suspended from a floating platform at a 15 m deep nearshore site in Gull Lake. Enclosures were open to the atmosphere at the top and sealed from the sediments at the bottom and extended through the ~8 m deep epilimnion but not into the metalimnion (the thermocline in the lake was at a depth of ~10 m). Enclosures were installed and filled with lake water during the first week of July 2005, with nutrient additions performed weekly beginning on 9 July (day 1).

The nine enclosures were randomly assigned to three treatments: control (no nutrients added), medium nutrient availability (target total P = 20 $\mu g \cdot L^{-1}$), and high nutrient availability (target total P = 40 $\mu g \cdot L^{-1}$). P and N were added

as a concentrated solution of reagent-grade inorganic P (as $NaH_2PO_4 \cdot H_2O$) and N (as $NaNO_3$) with a molar N–P ratio of 20. The nutrient solution was added through a tube that was slowly raised through the water column. Each week, the required volume of concentrated nutrient solution was determined for each enclosure based on its target total P concentration and the actual concentration measured 2 days prior to the addition.

Water samples were collected with a vertically integrating tube sampler from the enclosures, as well as from the lake beside the platform on days 0 (8 July, just before adding nutrients), 4, 11, 18, 25, 32, 39, and 45 (22 August), spanning a period of stable summer stratification of the lake water column. Sampling was performed 4–6 days after each weekly nutrient addition. Temperature, dissolved oxygen, and pH at depths of 0.5 and 6 m were measured during midday with a Hydrolab multisonde. Measurements were made in random order over ~90 min, and the data from the two depths were averaged for comparison with integrated water samples. The pH electrode was calibrated with buffers of pH 7.0 and 10.0. Water samples were immediately taken to a lakeside laboratory in completely full carboys. Vacuum filtration was performed within 1–2 h after water sampling, and labile nutrients, major ions, and chlorophyll *a* concentrations were analyzed within 24 h.

Solutes were measured in water filtered using Gelman (now sold as Pall) A/E glass-fiber filters. Concentrations of major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) were measured by flame atomic absorption spectrophotometry, adding 0.5% HNO_3 as a preservative. An acidic solution of lanthanum was added before measurement of Ca^{2+} and Mg^{2+} to suppress interferences. Concentrations of major anions (Cl^-, NO_3^-, and SO_4^{2-}) were measured by Dionex membrane-suppression ion chromatography. Total alkalinity was determined by Gran titration with HCl over a pH range of 4.0 to 3.3 (Cantrell et al. 1990). Soluble reactive P (SRP) and ammonium (NH_4^+) were analyzed using standard colorimetric techniques and long-pathlength spectrophotometry (Wetzel and Likens 2000). Total P was analyzed via persulfate digestion followed by colorimetric analysis of SRP. The calcite saturation index was calculated from major ion concentrations, pH, and temperature (Kempe 1982). The saturation index is the $\log_{10}$-transformed ratio of the ion activity product (IAP) to the calcite solubility product (K_{eq}); values above zero imply theoretical supersaturation.

Particulate matter in the integrated water samples (seston) was collected on glass-fiber filters (Gelman A/E, 1.0 μm effective pore size) and immediately frozen. Chlorophyll *a* was extracted from the filters in cold 90% ethanol and measured via fluorometry (Welschmeyer 1994). Acid-soluble Ca and SRP were measured by HCl titration of the particulate matter to pH 3.9, aided by the use of bromcresol green as a pH indicator, adding more acid as needed to maintain this pH for 30 min. At this pH, calcite dissolves while leaving algal cells intact (Vanderploeg et al. 1987). Tests with samples from nutrient-saturated algal cultures indicated that this method produced no detectable leaching of Ca but did leach some P from algal biomass, with no consistent difference between refrigerated and frozen samples (data not shown).

Sedimented material was collected in traps deployed near

Fig. 1. Total P concentrations in the enclosure treatments, including control (●), medium nutrients (▲), and high nutrients (■), and in the lake epilimnion (◇). Letters indicate significant differences ($P < 0.05$). Error bars on this and subsequent figures are standard errors of the mean.

Fig. 2. (*a*) Chlorophyll *a* concentrations and (*b*) dissolved O_2 saturation in the enclosure treatments, including control (●), medium nutrients (▲), and high nutrients (■), and in the lake epilimnion (◇). Letters indicate significant differences ($P < 0.05$ after $\log_{10}$ transformation).
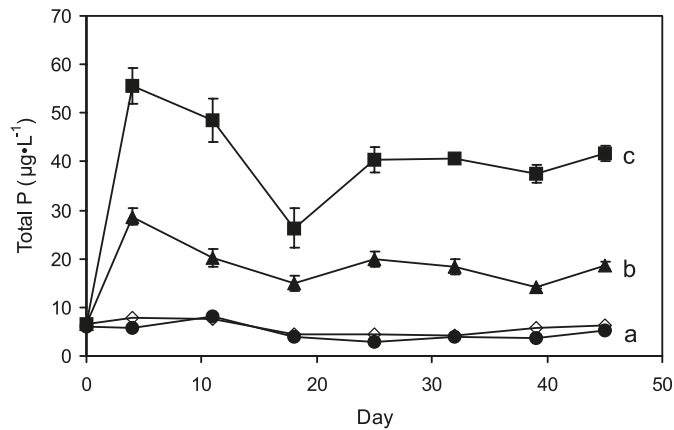
the bottom of each enclosure at day 0, with one set sampled after 12 days and another after 26 days. The traps were plastic cups 6 cm in diameter and 8 cm deep and were deployed to collect sedimented material for chemical analysis rather than to estimate enclosure sedimentation rates. Particulate matter in the traps was suspended in a slurry and collected on filters that were frozen for later measurement of chlorophyll *a* and acid-soluble Ca and P, using the same methods as detailed above for seston samples. Upon removal of the experiment, visual observations indicated that the mass of sedimented organic material and calcite in the bottoms of the enclosures was vastly greater than that of attached algae and calcite on the walls of the enclosures.

Differences among treatments over time were determined using repeated-measures analysis of variance (ANOVA), and treatment differences in the chemical composition of seston and sedimented material were assessed using one-way ANOVA. Error bars in figures are standard errors of the mean.

Lake surveys were conducted in August of 1998, 1999, 2002, and 2003 from across the Lower Peninsula of Michigan (Raikow et al. 2004; Knoll et al. 2008), and survey data are presented here to compare the degree of calcite precipitation in lakes with what we observed in the experiment. The data in this paper are dissolved Ca^{2+} and Mg^{2+} concentrations in the epilimnion from 141 lake samples, of which 51 samples represent replicate samplings of sites in different years. Sampling and analytical methods were identical to those used in the Gull Lake experiment. These lakes lie on glacial terrain in rural or residential areas, with little potential pollution that would affect their Ca^{2+} and Mg^{2+} concentrations, but with variable degrees of anthropogenic N and P loading from non-point sources such as agriculture and lawn fertilization.

Results

Total P concentrations in the enclosures indicate that after an initial overshoot caused by inaccurate enclosure volume estimates, our target concentrations were approximated with clear differences among the three treatments throughout the
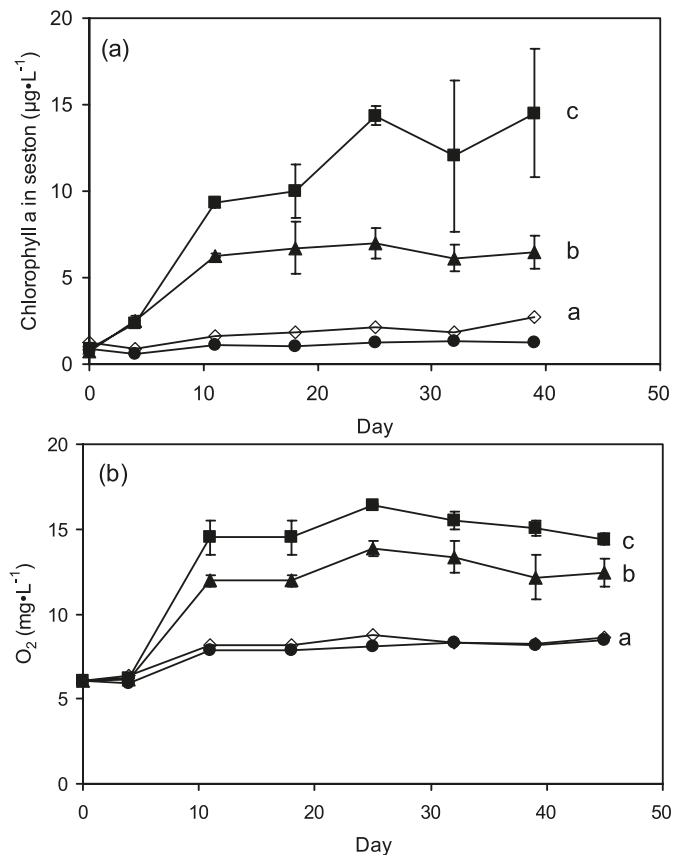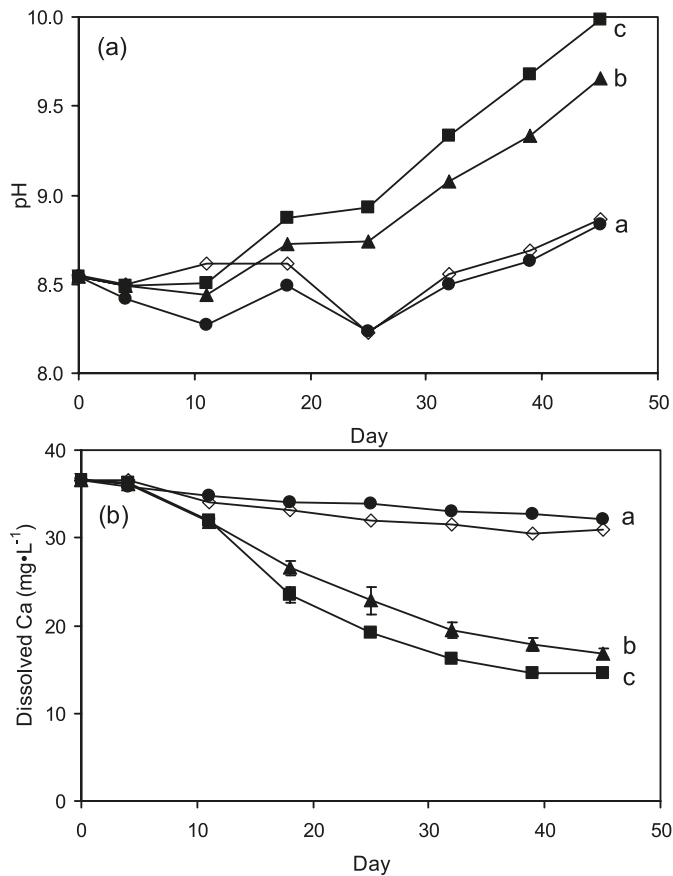
experiment and close correspondence between controls and the lake (Fig. 1). Phytoplankton responded strongly to the P and N additions, increasing in biomass and productivity as reflected by concentrations of chlorophyll *a* (Fig. 2*a*) and dissolved O_2 (Fig. 2*b*). Temperature, dissolved oxygen, and conductance measurements showed that the enclosures remained well mixed throughout the experiment (data not shown).

A marked increase in pH coincided with the increase in phytoplanktonic productivity produced by nutrient additions, reflecting assimilation of dissolved CO_2, and dissolved Ca^{2+} concentrations decreased by up to 60% as pH increased (Fig. 3). Decreases in total alkalinity mirrored those of Ca^{2+}, as expected for precipitation of calcite (Table 1). The other major ions did not change except for a slight increase in Na^+ from the added nutrient salts. Nitrate remained between 0.3 and 0.4 mg $N\cdot L^{-1}$ in the controls but varied more in treatments with added nutrients, and much of the added nitrate was clearly removed (data not shown). Nitrate assimilation by the phytoplankton would have contributed to the elevation of pH, together with CO_2 assimilation (Murphy et al. 1983). Water temperatures ranged from 24.6 to 27.2 °C in the enclosures.

The decrease in dissolved Ca^{2+} was due to calcite precipitation and sedimentation. The calcite saturation index (SI)

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Fig. 3. (*a*) pH and (*b*) dissolved Ca^{2+} concentration in the enclosure treatments, including control (●), medium nutrients (▲), and high nutrients (■), and in the lake epilimnion (◇). Letters indicate significant differences ($P < 0.05$, after log_{10} transformation in the case of Ca^{2+}).

Table 1. Concentrations of Ca^{2+} and total alkalinity in the lake and enclosures (means with standard errors in parentheses) at the end of the experiment (day 45).

Treatment	Ca^{2+} $(mg·L^{-1})$	Alkalinity $(\mu equiv.·L^{-1})$	pH
Lake	30.9	2.971	8.87
Control	32.1 (0.4)	3.101 (0.011)	8.83 (0.02)
Medium	16.8 (0.5)	2.319 (0.057)	9.66 (0.07)
High	14.6 (0.1)	2.191 (0.094)	9.98 (0.01)

Note: Ca^{2+} and alkalinity are strongly correlated ($R = 0.99$), and decreases in the nutrient addition treatments relative to the control are close to the 2:1 molar ratio of Ca^{2+} to HCO_3^- expected for calcite precipitation. Mg^{2+} concentrations were ~22 $mg·L^{-1}$ and showed no evidence of precipitation in any treatment.

come from algal biomass (Sañudo-Wilhelmy et al. 2004), and (*ii*) some very fine calcite and associated P could have passed through the AE filters, resulting in underestimation of total particulate calcite and acid-soluble P (Dittrich et al. 2004). Iron content in the acid-soluble fraction was below detection limits using flame atomic absorption spectrophotometry, indicating that on a molar basis, there was less iron than P in this material and thus iron-bound P was unlikely to be significant. The remainder of the P that was not soluble in acid was likely to be organic P in living and detrital biomass.

Mass balances of P in the enclosures over the first 26 days were computed in two ways: (*i*) from the decrease in dissolved Ca^{2+} concentration (considered the best indicator of total calcite sedimentation) and the ratio of acid-soluble P to Ca in sedimented material; and (*ii*) from the difference between total P at the beginning and end of the period and the P added over that period. Comparison of these two estimates suggests that sedimentation of P co-precipitated with calcite can explain most to all of the net P loss in the enclosures (Fig. 7).

The total P concentrations measured at the end of the experiment on day 45 can be compared with those that would have been expected in the absence of losses of P from the water column (Fig. 8). The measured total P concentrations averaged 47% of expected concentrations across the medium- and high-nutrient treatments, with no significant difference between the treatments. Thus about half of the P loading evidently sedimented out of the water column, with no evidence of saturation of P sinks at higher P loading rates.

Lake surveys performed during the same season as the experiment show that calcite precipitation is common, as indicated by the departure of lake waters from the groundwater Mg–Ca ratio (Fig. 9). Southern Michigan groundwaters tend to be at equilibrium with dolomite $(CaMg(CO_3)_2)$ and calcite in the glacial drift, and thus they have a characteristic Mg–Ca ratio and, in general, are little affected by other sources of these solutes (Hamilton et al. 2007). The median Mg–Ca mass ratio (0.31) is depicted for groundwater in Kalamazoo County, Michigan, where Gull Lake is situated (broken line in Fig. 9, 25 $mg·L^{-1}$ Mg^{2+} and 81 $mg·L^{-1}$ Ca^{2+}; Rheaume 1990). As this groundwater emerges into surface waters such as lakes, streams, and wetlands, calcite precipitation removes Ca^{2+} but the Mg^{2+} is essentially conserved in solution (Stauffer 1985, Szramek and Walter 2004). Rain and snow carry negligible concentrations of Ca^{2+} and Mg^{2+}

indicated consistent supersaturation by approximately an order of magnitude. The lake and control enclosures began with a calcite SI of 0.98 on day 0 (expressed as the ratio of IAP to K_{eq}, log_{10}-transformed), and by day 45, both had increased to 1.17. The calcite saturation index in the medium- and high-nutrient treatments had increased by day 45 to 1.46 and 1.55, respectively. Acid-soluble Ca was found in the seston and in sedimented material (Fig. 4), and microscopic examination confirmed that calcite crystals were abundant in these samples.

Acid solution of the seston and sedimented material also yielded P, with higher concentrations and sedimentation rates of acid-soluble P in the nutrient-amended treatments compared with the control (Fig. 5). The Ca–P ratios were much lower in the seston than in the sedimented material (Table 2), suggesting selective remobilization of the calcite-bound P as the material sedimented and resided in the traps. Preferential dissolution of P relative to Ca has been observed in calcite sedimenting into a lake hypolimnion (Murphy et al. 1983).

Comparison of acid-soluble P with total P in samples of sedimented material shows that about half of the total P sedimentation losses can be explained by P co-precipitation with calcite (Fig. 6), with the caveats that (*i*) an unknown but probably small fraction of the acid-soluble P could have

Fig. 4. (*a*) Acid-soluble Ca concentration in seston throughout the 45-day experiment and (*b*) rates of sedimentation into the traps over the first 26 days of the experiment. Letters indicate significant differences (*P* < 0.05 after $\log_{10}$ transformation).
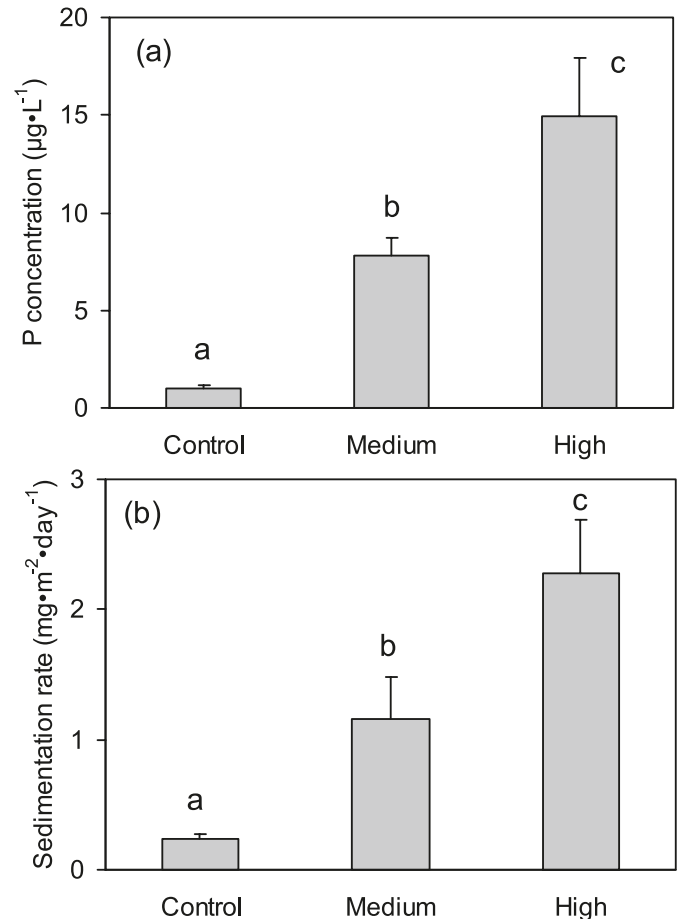

Fig. 5. (*a*) Acid-soluble P concentration in seston throughout the 45-day experiment and (*b*) rates of sedimentation into the traps over the first 26 days of the experiment. Letters indicate significant differences (*P* < 0.05).
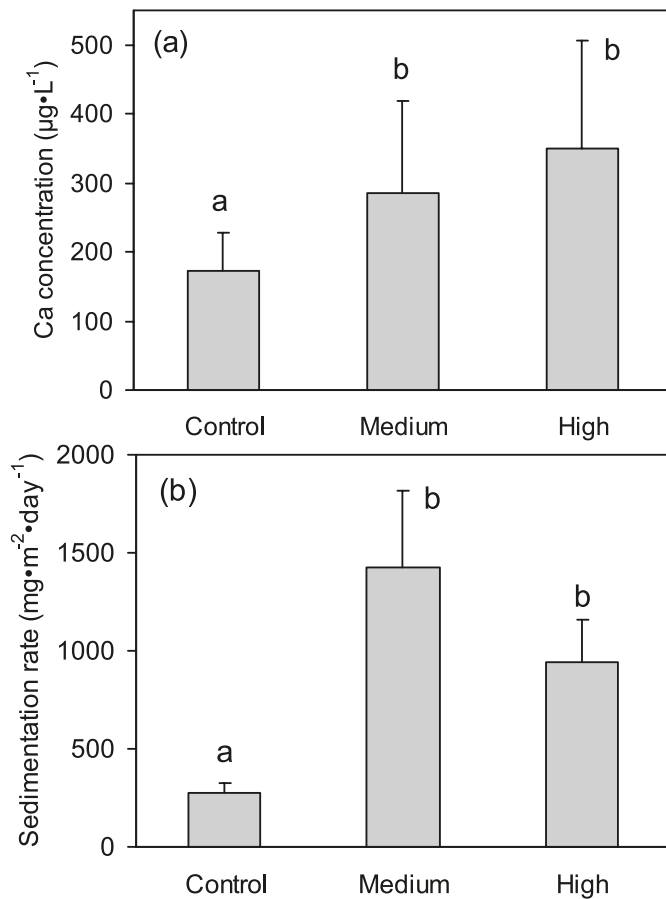
(Rheaume 1990) and hence dilute the groundwater but do not affect Mg:Ca at the concentrations found in these lakes, nor does evaporative concentration (unless it contributes to calcite supersaturation). Thus the points depart to the left of the broken line in proportion to the total Ca^{2+} precipitation that has occurred since the groundwater discharged to the surface (Fig. 9).

Our experimental imposition of high nutrient loading to the normally oligotrophic epiliminion of Gull Lake pushed calcite precipitation further than was observed in most Michigan lakes (Fig. 9). Note that the water at the start of the experiment (and in the controls) already had lost more than half of the Ca^{2+} concentration that would have been present in the groundwater entering the lake, based on the leftward displacement from the broken line in Fig. 9. Much of this precipitation may have occurred in previous years; the water residence time of the lake is ~3–4 years (Tague 1977).

Discussion

Loss of P by sedimentation with biogenically precipitated calcite appeared to be an important sink for P added to the experimental enclosures and would have contributed to the amelioration of the impacts of P addition on algal growth.

Table 2. Mass ratios of acid-soluble Ca to P in seston (all dates combined) and sedimented material (collected on days 12 and 26).
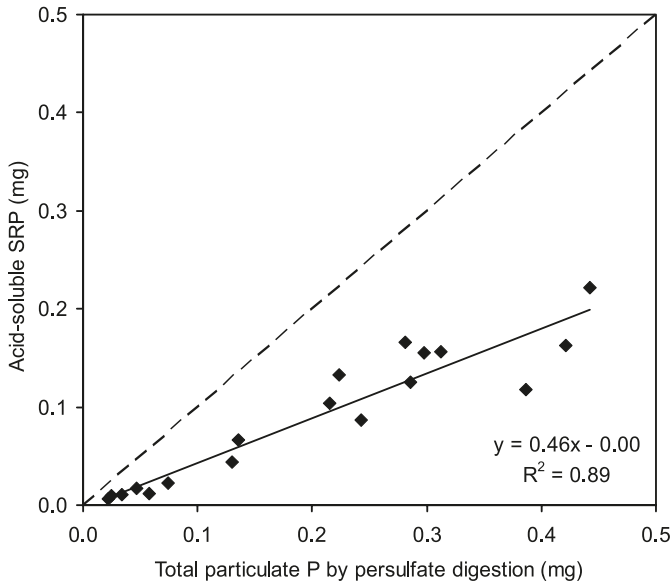
Treatment	Seston Ca:P	Sedimented Ca:P
Lake	257 (131)	—
Control	198 (67)	2036 (586)
Medium	39 (21)	1113 (615)
High	25 (11)	381 (45)

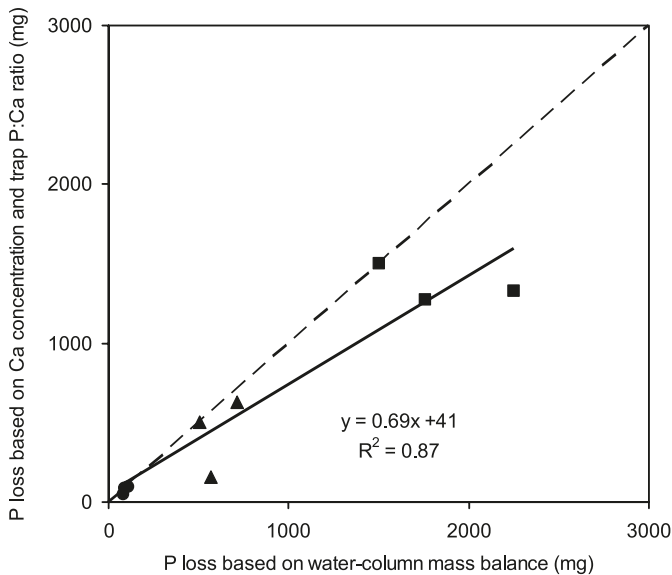**Note:** Data are means with standard errors in parentheses.

This loss mechanism may be particularly important because it removes phosphate, the most bioavailable P form. Both Ca-bound P and organic P are potentially subject to remobilization during sedimentation and in the sediments, and the relative remobilization rates of these P forms in this case are not known. Nevertheless, in a thermally stratified lake, net P loss will occur as sedimenting particles exit the epilimnion, and P that is remobilized below that point does not become available to phytoplankton in the epilimnion until the lake mixes once again (Robertson et al. 2007).

The experimental results reported here are consistent with inferences made in observations of individual lakes in which

Fig. 6. Comparison of acid-soluble P with total P content in sedimented material collected over the first 12 days and the first 26 days (all treatments combined). The broken line is a 1:1 line.
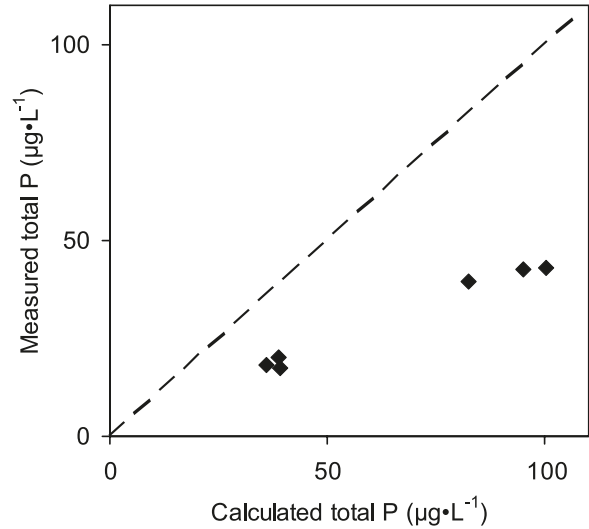

Fig. 8. Enclosure total P concentrations measured at the end of the experiment (day 45) compared with those that would have been produced in the P-addition treatments had no P losses occurred (broken line). The measured total P concentrations averaged 47% of those calculated based on P additions, with no significant difference between medium- and high-nutrient treatments.

Fig. 7. Enclosure P mass balance for the first 26 days based on the observed drawdown in dissolved Ca^{2+} concentration and the P:Ca in sedimented material (ordinate), compared with the water-column mass balance of total P concentration, with the P additions accounted for (abscissa). Control, ●; medium nutrients, ▲; high nutrients, ■. The broken line is a 1:1 line.

Fig. 9. Comparison of dissolved Mg^{2+} and Ca^{2+} concentrations in lakes across southern Michigan (○) and in the experimental enclosures (control, ●; medium nutrients, ▲; high nutrients, ■). The broken line shows the ratio of dissolved Mg to dissolved Ca in groundwaters; departure of points to the left of the broken line reflects Ca^{2+} removal by precipitation of calcite.
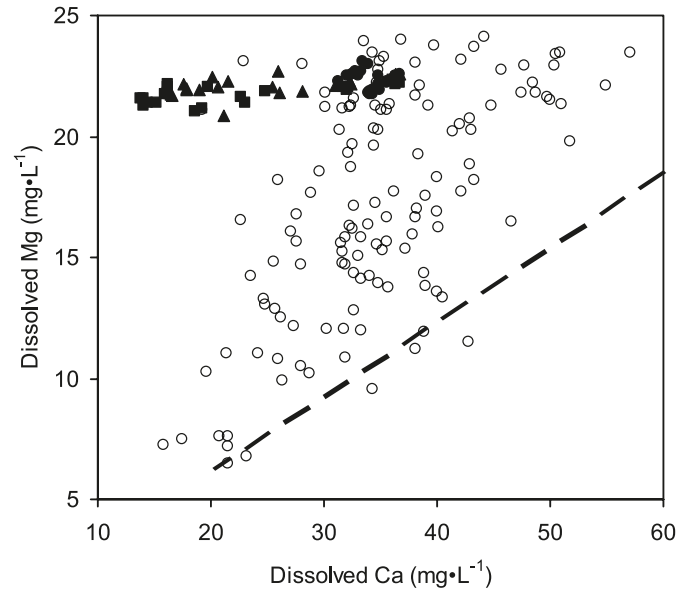

calcite precipitation has been studied. Studies of several lakes have estimated that co-precipitation with calcite could explain 25%–30% of the P removal from the water column, including Lakes Wallersee (Jäger and Röhrs 1990) and Constance (Kleiner 1988) in Germany and the Ca-polluted and eutrophic Onondaga Lake in New York (Effler et al. 1996). In Lawrence Lake, a small, oligotrophic, groundwater-fed lake near Gull Lake, an estimated 61%–76% of P removal was ascribed to calcite co-precipitation (Otsuki and Wetzel 1972). Observed seasonal declines in epilimnetic Ca^{2+} con-

centrations in individual lakes have ranged from 41% to 48% (Otsuki and Wetzel 1974; Murphy et al. 1983; Stable 1986), less than the 60% decline produced by the high-nutrient treatment in our study but still substantial. The sestonic Ca concentrations that we report here are similar to those measured in Fayetteville Green Lake in New York (Brunskill 1969) and Lake Breiter Lucin in Germany (Koschel et al. 1983). The Ca sedimentation rates shown herein overlap with those reported for Lake Constance

(Stable 1986), Fayatteville Green Lake (Brunskill 1969), and Lawrence Lake (Otsuki and Wetzel 1974) but are higher than were observed in Lake Breiter Lucin (Koschel et al. 1983) and lower than in Onondaga Lake (Effler and Driscoll 1985). We have observed daytime pH values in the range of 9 to 10 in several productive Michigan lakes, and thus the high pH observed in the mesocosms with added nutrients is not unrealistic in the open waters of naturally alkaline lakes with abundant nutrients.

This study provides an experimental demonstration of how calcite precipitation and consequent removal of phosphate are directly coupled to the productivity of phytoplankton and how this process can act as a negative feedback to eutrophication by rapidly removing available P from the epilimnion. These experimental results support the eutrophication feedback hypothesis of Koschel et al. (1983) and are consistent with a number of observational studies of individual lakes cited above. Increased loading of nutrients to lakes that are prone to calcite precipitation will enhance the removal of Ca^{2+} and alkalinity, generating calcite deposits on surfaces and leading to accumulation of calcitic sediments. The massive quantities and reactive nature of calcite deposited in lakes produces myriad ecological and biogeochemical implications. In addition, because calcite is less soluble at higher temperatures, warmer and longer periods of summer stratification associated with climate change would be expected to increase the total seasonal precipitation of calcite, even if rates of primary productivity were to remain unchanged. Where lakes and reservoirs are important hydrologic storages in watersheds, this enhanced calcite precipitation could potentially reduce the flux of Ca^{2+} and alkalinity from land to sea, although at the broader watershed scale, other anthropogenic activities such as agricultural liming may have counteracting impacts (Hamilton et al. 2007).

Acknowledgements

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