

A comparison of phosphorus immobilization in sediments of freshwater and coastal marine systems

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Abstract. The extent to which sediments of aquatic systems immobilize or release phosphorus can affect dramatically the P content of overlying waters. Data from 48 different aquatic systems suggests that there may be a major difference between fresh- and salt-water systems in this immobilization. Under oxic conditions (water overlying sediments had dissolved oxygen > 0.5 mg/L) P is strongly immobilized in sediments of most fresh-water systems. In sediments of most salt-water systems P is released from sediments and behaves, essentially, as a conservative tracer of benthic decomposition. This difference in P cycling is large enough to have an influence on the often cited difference in phytoplankton nutrient limitation between fresh- and salt-water systems.

Introduction

Eutrophication, due to increased nutrient loading, is a major problem in both freshwater and coastal marine systems (D'Elia 1987; Larsson 1984; Likens 1972; Vollenweider 1968). Concern about eutrophication has led to a large amount of research on nutrient limitation of primary production in aquatic systems. This body of research suggests that there may be a major difference between nutrient limitation in freshwater lakes and coastal marine systems (Howarth & Cole 1985; Howarth 1988). In freshwater lakes a multitude of data indicates that P is most frequently the primary limiting nutrient (Hecky & Kilham 1988; Schindler 1977; here we define 'limitation' as limiting to the potential rate of net primary production sensu Howarth 1988). In contrast, although fewer data exist, coastal marine systems are generally believed to be P sufficient and it is believed that N is often the primary limiting nutrient (Frithsen et al. 1988; Caraco et al. 1987; Graneli 1987; D'Elia et al. 1986; Vince & Valiela 1973; Ryther & Dunstan 1971).

Whereas the difference in nutrient limitation between freshwater and marine systems is of obvious practical concern, it has also sparked interest in the possibility that nitrogen cycling may differ in fresh and saltwater systems (Howarth et al. 1988; Paerl et al. 1987; Cole et al. 1986; Howarth

& Cole 1985; Seitzinger & Nixon 1985; Nixon et al. 1980). Although, a difference in P cycling between fresh and salt-water systems could also augment this difference in nutrient limitation, there have been few studies on how P cycling, specifically P immobilization in sediments, might differ between fresh and saltwater systems (Seitzinger 1988; but see Fox et al. 1986). In this paper we try to determine if such a difference in P immobilization, in fact, occurs. In order to have enough comparable data we restrict our analysis in this study to the P release from sediments when overlying waters are oxidic.

Approach and methods

The extent of P immobilization in sediments can be calculated by comparing measured P release to that expected if decomposition alone controlled P release. The amount of P release expected from decomposition is:

$$\text{Organic } (x\text{P}:y\text{C}) \rightarrow y\text{DIC} + x\text{P}_i \quad (1)$$

where: x and y are the respective mole-fractions of phosphorus (P) and carbon (C) in decomposing organic matter, DIC is dissolved inorganic carbon and P_i is liberated dissolved P.

When P release from sediments is less than that expected from decomposition models (Redfield et al. 1963; Richards 1965), it is concluded that sediment immobilization is occurring (Burns & Ross 1971; Sen Gupta 1973).

There are numerous studies in coastal marine and estuarine systems in which the release of P from sediments is measured along with other decomposition by-products; these studies include both the examination of the accumulation of materials in chambers and measurements of the accumulation of materials in bottom waters of stratified systems (Table 1). Comparable data are less available for freshwater systems. In addition to literature values we, therefore, collected our own data for 15 freshwater lakes.

On two to four occasions during summer stratification periods we measured total dissolved P in the bottom waters of freshwater lakes which varied in trophic state, water-column chemistry, and sediment chemistry. Water was collected at 2–6 depths below the thermocline of lakes using a peristaltic pump. Water for dissolved P analysis was filtered, in line, through a Whatman GF/F filter and later analyzed according to Menzel & Corwin (1965). Additionally samples for the analysis of dissolved inorganic carbon (DIC) were pumped into air-tight BOD bottles; samples were kept on ice for less than 24 h until DIC was measured by gas chromatography (Stainton 1973). Dissolved oxygen was measured using a Digital Yellow Springs

Instrument oxygen meter in situ and/or by Winkler titrations after collection in air-tight BOD bottles (Wetzel & Likens 1979).

In addition to the bottom water samples, for all 15 lakes studied we measured P:C ratios of seston in epilimnetic waters. Because sestonic P:C ratios are similar to P:C ratios of material sinking from the epilimnetic waters (Uehlinger & Bloesch 1987) they may be representative of the supply ratio for decomposition in hypolimnetic waters and underlying sediments. Particulate P and C were measured on samples collected on GF/F filters (above). Samples for particulate P analysis were ashed and hydrolyzed in acid (Solorzano and Sharp 1980). Particulate C was measured on a Carlo Erba CNS analyzer.

In one lake, Mirror Lake, N.H., in addition to the in situ approach used in all 15 lakes, we also deployed benthic chambers to assess P loading from sediments. Benthic chambers were deployed on epilimnetic sediments in the lake at 6 locations in quadruplicate during summer 1987 (see Mattson 1989). Samples for dissolved P and DIC were removed through a syringe fitting and analyzed as described above. Samples were taken at dusk and again at dawn.

Phosphorus accumulation in both chambers and bottom waters was compared with that expected from the accumulation of dissolved inorganic carbon (DIC) or oxygen utilization. For the chamber studies this was done by subtracting the initial P concentration in the chamber from the concentration at the end of a 12-hour incubation (P accumulation) and dividing by the DIC accumulation over the same period. In the case of the in situ studies, linear regressions of DIC in bottom waters (or oxygen equivalents) vs P in bottom waters were done. The slope of this regression is the average P release relative to metabolism (Sen Gupta 1973) and we refer to this value as relative P release (RPR). When calculating DIC production from oxygen utilization, we used a respiratory quotient of 1 mole O₂/mole DIC (Hargrave 1973). This respiratory quotient corresponds well to the O₂ depletion/DIC accumulation in the bottom waters of the 15 lakes we studied. If, however, a respiratory quotient of 106 DIC to 138 O₂ were used it would not significantly alter our results. When bottom waters had oxygen concentrations that were less than 0.5 mg/L, samples were excluded from linear regression analysis (above) as we are only considering P release into oxic waters.

Results and discussion

In shallow marine systems and lakes, up to 50% of the primary production in surface waters is remineralized in bottom waters and on sediments (Nixon 1981; Hargrave 1980). Thus, the extent to which P is retained on particles

or recycled to a dissolved, available, form is critical in controlling productivity. Phosphorus is chemically very reactive; post-decompositional uptake of P by mineral formation or sorption may play a major role in controlling the extent to which P is, in fact, recycled. Additionally, biological uptake of P is thought to reduce significantly P release from decomposing organic compounds in bottom waters and sediments (Carlton & Wetzel 1988; Gachter et al. 1988; Tezuka 1986). Whether due to chemical or biological processes, P immobilization by particles in bottom waters or sediments can reduce P supply to surface waters.

In marine and brackish systems the P content of organic material is generally reported to be about 9.5 mmol P/mol C (Redfield et al. 1963). This value is not significantly different from the P release from sediments of marine systems, suggesting that, on average, there is little uptake of P after decomposition in the sediments of marine systems. For the 24 brackish and coastal marine systems for which we had data, the average RPR was 10.5 ± 4.5 mmole P/mole C (mean \pm 95% confidence interval; Table 1, Fig. 1).

In most freshwater systems P release from decomposing material is far lower than the average value in marine systems. In the 24 freshwater lakes examined, RPR was on average 1.2 ± 0.8 mmole P/mole C (Fig. 1, Table 2), a value significantly lower than the 9.5 value predicted by Redfield (*t*-test, $p < 0.001$). Indeed in 17 of the 24 systems for which we had data the RPR values were less than 10% of the value predicted by Redfield.

The lower RPR values in freshwater than marine systems suggests three possibilities:

1. The finding is an artifact due to a difference in sampling or analysis between these fresh- and salt-water systems.
2. Decomposing organic matter in fresh-water systems are extremely depleted in P relative to that in salt-water systems and the low P release is simply a reflection of this depletion.
3. P immobilization in freshwater sediments is far greater than in marine sediments.

We address each of these possibilities below:

1. Sampling-analytical artifacts

Whereas most of the RPR measurements from the freshwater systems are from measurements of in situ accumulation in bottom waters, most of the marine-brackish data are from chamber incubations. There are theoretical reasons why chamber data could either over or underestimate P release from sediments (Sundby et al. 1986; Fisher et al. 1982). Nevertheless, if chamber data were consistently overestimating P release values, it could potentially

Table 1. Relative phosphorus release (RPR) from sediments of marine and brackish systems.

System	Location	RPR (mmole P/mole DIC)	Reference
<i>Chamber studies</i>			
South River	North Carolina	3.5	Fisher et al. 1982 ^{1,*}
Neurse River	North Carolina	9.3	Ibid.
La Jolla Bight	California	7.0	Ibid.
Narragansett Bay	Rhode Island	8.2	Ibid.
Buzzards Bay	Massachusetts	-1.3	Ibid.
Cap Blanc	Africa	60.0	Ibid.
Georgia Bight	Georgia	9.8	Hopkinson & Wetzel 1982
Tomales Bay	California	3.3	Smith et al. 1987
(Inner)			
Tomales Bay	California	13.2	Ibid.
(Outer)			
San Francisco Bay	California	10.0 ²	Hammond et al. 1985
(site 1)			
San Francisco Bay	California	4.3 ²	Ibid.
(site 2)			
Narragansett Bay	Rhode Island	17.0	Nixon 1980 ^{3,*}
Vostoc Bay	USSR	14.3	Ibid.
Patuxent River	Maryland	12.2	Ibid.
Eel Pond	Massachusetts	11.4	Ibid.
Kaneohe Bay	Hawaii	5.0	Ibid.
New York Bight	New York	1.8	Ibid.
Potomac River	Virginia	4.5	Callender & Hammond 1982
<i>In situ studies</i>			
Baltic Sea	N. Europe	5.6	Sen Gupta 1973
Siders Pond	Massachusetts	4.0	Caraco 1986
Amazon R.	Brazil	10.0	Edmond et al. 1981
Saanich Inlet	British Columbia	9.5	Richards 1965
L. Nittinat	British Columbia	9.5	Richards et al. 1965
York River	Virginia	2.3, ⁴ 27 ⁵	D'Elia et al. 1980

¹Calculated from Table 3²Seasonal average from Table 4³Calculated from values presented in Table 1⁴For oxygen values above ca. 60 μ M⁵For oxygen values below 60 μ M

* Both of these papers present a review of other studies, where the same study was reviewed by both of these papers it was cited only once in this table.

The last 6 studies are based on the accumulation of P in bottom waters of stratified systems the remaining studies are from chamber incubations. In the studies on Tomales Bay and Siders Pond phosphorus accumulation was measured as total dissolved P (TDP). In the remaining studies only soluble reactive P was measured.

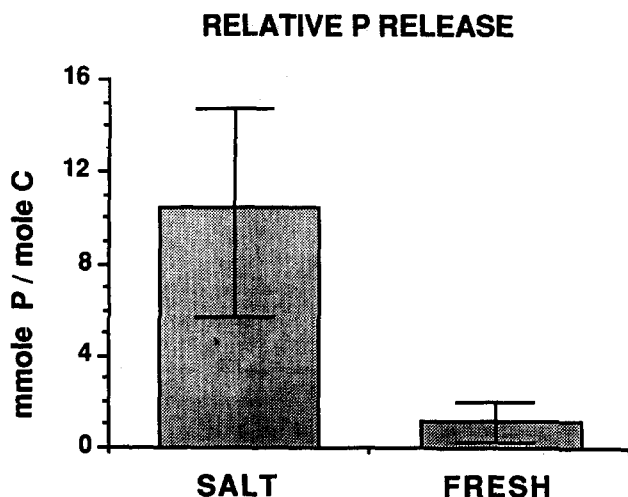


Fig. 1. Average (with 95% confidence limit) of relative phosphorus release (RPR) for brackish and coastal marine, 'MARINE', and freshwater, 'FRESH', systems (see Tables 1 and 2). The extremely low RPR in freshwater systems suggests that in these systems sediments immobilize a large fraction of the P released from organics by decomposition. In most marine and brackish systems, essentially all of the remineralized P is returned to solution.

account for our findings. We found, however, that there was no significant difference (*t*-test, $p = 0.63$) between chamber and in situ measurements within the marine-brackish data set (Table 1). Both the chamber and in situ sub-sets for marine-brackish data (Table 1) were, however, significantly different from the freshwater release data presented in Table 2 (*t*-test, $p < 0.001$). These results taken together suggest that the difference in P release between fresh and coastal marine systems is not due to artifacts from sampling differences.

Another possible explanation concerns analytical differences. Most of the RPR values for the marine data set are based on the accumulation of dissolved reactive P only (Table 1); most of the freshwater data set is based on measurements of TDP which includes both dissolved organic and dissolved reactive P. This analytical difference could bias the data, but it would tend to detract from the difference in RPR between fresh and coastal marine systems. That is had TDP accumulation been measured in the marine systems RPR values for these systems would likely be even greater (Smith et al. 1987).

2. Differences in P:C of decomposing organics

A possible explanation for the low P:C release ratios from sediments of freshwater systems is that P:C ratios of decomposing material in freshwater

Table 2. Relative phosphorus release (RPR) from sediments of freshwater lakes.

System	Location	RPR (mmole P/mole DIC)	Reference
<i>Chamber study</i>			
Mirror Lake	New Hampshire	0.4	This study
<i>In situ studies</i>			
Lake 227	Ontario	0.1	Schindler unpubl.
Lake 226-E.	Ontario	0.2	ibid.
Lake 226-W.	Ontario	0.1	ibid.
Lake 223	Ontario	0.3	ibid.
Lake 261	Ontario	0.6	ibid.
Mirror Lake	New Hampshire	0.3	This study
Jabe Pond	New York	0.1	ibid.
Stinson Lake	New Hampshire	0.1	ibid.
Russell Pond	New Hampshire	0.1	ibid.
Ellsworth Pond	New Hampshire	0.2	ibid.
Bashan Lake	Connecticut	0.2	ibid.
Iron Mine Pond	New York	0.2	ibid.
Black Pond	New Hampshire	0.3	ibid.
Lake Lacawac	Pennsylvania	0.5	ibid.
Lake Mohonk	New York	0.5	ibid.
Squam Lake	New Hampshire	0.8	ibid.
Partridge Pond	New Hampshire	1.0	ibid.
Mount Tom Pond	Connecticut	2.8	ibid.
Taughanick Lake	New York	3.4	ibid.
Copake Lake	New York	3.6	ibid.
Esthwaite Waters	Great Britain	1.4	Heaney et al. 1986
Lake Erie	Ohio	2.0	Burns & Ross 1971
Lake Ogelthorpe	Georgia	0.3	Porter unpubl.
Green Lake	Wisconsin	10.0	Stauffer 1985 ¹

¹ Average below 40 m for 15 May 15–15 August

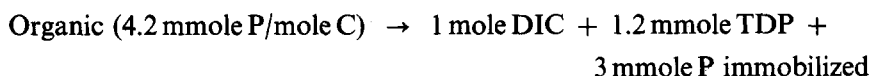
In the study in Green Lake phosphorus accumulation was estimated from measurements of total P (particulate P + TDP) in all studies TDP accumulation was measured.

systems are extremely depleted in P. Compared to phytoplankton, terrestrial plant litter has low concentrations of mineral nutrients such as P. For example, leaf litter has a P:C ratio of roughly 1.5 mmole P/mole C (Delwiche & Likens 1977; Mackenthum 1973). Thus, if decomposition on sediments and bottom waters in freshwater lakes were fueled primarily by allochthonous inputs of terrestrial plant litter, it could, in large part, explain the low RPR observed (Fig. 1). Although decomposition in some lakes may be fueled primarily by allochthonous inputs with low P:C ratios (e.g., Findley Lake; Odum & Prentki 1978), in many lakes decomposition of autochthonous material dominates (Odum & Prentki 1978). For example, an annual organic carbon budget for Mirror Lake, N.H., a lake with extremely

low RPR (Table 2), demonstrates that phytoplankton production represents the major (ca. 80% of annual total C inputs) organic C input to this lake (Jordan and Likens 1975). Further, in agreement with this C budget, P:C ratios of seston in surface waters and particles reaching sediments (collected in sediment traps) are both about 4.5 mmole P:mole C (Likens 1985; Moeller & Likens 1978). This value is less than the Redfield Ratio, but considerably greater than the P:C values of terrestrial litter, and roughly 10-fold greater than release ratios from sediments of this lake (Table 2). Additionally, Lake 227 of the Experimental Lakes Area, Ontario, has been fertilized with N and P for 15 years (Schindler et al. 1987) and has high primary production dominated by phytoplankton. Despite the increase in P rich particles to the sediments and bottom waters, P release from sediments of Lake 227 remains extremely low (Schindler et al. 1987). Finally, the average P:C ratio of seston in surface waters of the lakes shown in Table 2 (excepting Green Lake and Lake Ogelthorpe for which no data were available) is 4.2 ± 0.6 mmole P:mole C. This sestonic P:C ratio is more than 3 times larger than the observed average RPR in the lakes (1.2 ± 0.8 mmole P:mole C). It is likely that P:C ratios of seston are similar to P:C ratios of settling particles, which fuel decomposition on sediments (Uehlinger and Bloesch 1987; Likens 1985). Thus, although P:C ratios of decomposing material in freshwater lakes are, on average, lower than the Redfield Ratio for marine plankton of 9.5 mmole P/mole C, this lower P:C ratio is not sufficient to explain the extremely low RPR from sediments of freshwater lakes.

3. Difference in P immobilization in sediments of fresh and coastal marine systems

In marine systems the P:C ratio of organic matter reaching sediments (ca. 9.5 mmol P/mol C) appears to be very similar to the P:C release ratio from sediments (10.5 mmol P/mol C). This is in contrast to the case in freshwater systems where the P:C release ratio from sediments (1.2 mmol P/mol C) is lower than our estimate of the P:C of organics reaching sediments (ca. 4.2 mmol P/mol C). Thus, our data indicate that decomposition models have to be modified in freshwater systems to accommodate P immobilization. We propose the following revised model for 'average' freshwaters:



This revised model reflects our finding that on average immobilization of P in sediments of fresh water systems significantly reduces P supply to the water column. This finding of significant P immobilization by sediments is,

perhaps, not surprising. Indeed many workers have studied factors which could immobilize P in sediments including: P sorption, mineral formation and biotic uptake (Baccini 1985; Holdren & Armstrong 1980; Jackson & Schindler 1975; Tessenow 1972; Hutchinson & Bowen 1950; Mortimer 1941, 1942; Einsele 1936). It is generally believed that when waters overlying sediments are oxic, sediments act as an efficient phosphorus trap (Bostrom et al. 1982; Fenchel & Blackburn 1979). What is surprising, therefore, is that in many marine systems net sediment immobilization of P is not large even under oxic conditions. There are many possible chemical and biological explanations for low retention of P by sediments or suspended particles in coastal marine systems (Hawke et al. 1989; Tezuka 1989; Caraco et al. 1989). We believe an important factor is the high sulfate reduction which occurs in the sediments of coastal marine systems (Capone & Kiene 1988). This high sulfate reduction could lead to a decrease in the abundance of iron oxides in sediments (Carignan & Tessier 1988) and decreased P sorption (Schindler 1985; Caraco et al. 1989). Further, geochemical studies on sediments and porewaters are needed to determine the extent to which this or other processes contribute to the low P retention in coastal marine systems as compared to freshwater systems.

Conclusions and implications

A comparison of P release in fresh-water and coastal marine systems reveals that there may be a major difference in the extent to which P is recycled from sediments in these two types of aquatic systems. In marine and brackish systems most of the P liberated from decomposition in the sediments is released into solution. In fresh-water lakes, on the other hand, much of the P is bound by particles in bottom waters and sediments with little recycling to the water-column (Fig. 1). Such a major difference in P immobilization by sediments could have a significant control on the difference in nutrient limitation between fresh and coastal marine systems. For example, Nixon et al. (1980) showed that the average molar ionic N:P release ratio (as $\text{NH}_4^+ + \text{NO}_3^-$ / reactive P) from sediments in coastal marine systems is 8, about 1/2 of the ratio generally required by phytoplankton. This low release ratio from sediments is due to the fact that roughly 50% of the N mineralized in sediments is lost via denitrification in sediments (Howarth 1988; Seitzinger 1988; Nixon et al. 1980) while, as we have discussed, essentially all of the P is returned to solution (Fig. 1). Thus, in marine systems, even if they received a relatively high N:P loading ratio from the watershed, the system could be driven towards N limitation (Howarth 1988;

Caraco 1988; Nixon et al. 1980). This scenario is highly dependent on the extent to which P is immobilized in sediments. Suppose that sediment P immobilization in marine systems was as high as it appears to be in freshwater systems (70% of P immobilized). Given a 70% immobilization, the RPR in marine systems would be 2.85 mmole P/mole C (assuming material reaching sediments had a 'Redfield' P:C ratio of 9.5 mmole P:mole C). Thus, with denitrification again equal to 50% of N release from sediments, the ionic N:P release ratio from marine sediments would be roughly 30, about 2 times the Redfield ratio and 4 times the actual release ratio for many marine systems. Given this hypothetical high N:P loading ratio from the sediments of coastal marine systems, these systems would not tend toward N limitation. Indeed a high N:P loading ratio from sediments could cause a tendency toward P limitation even when watershed inputs of N:P occur at ratios less than the Redfield ratio of 16 (Schindler 1976). We suggest, therefore, that the difference in P immobilization by sediments of marine and freshwater systems may help explain why primary production in many marine systems is P sufficient whereas primary production in freshwater lakes is usually P limited.

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