

Effects on Phosphorous Cycling in Fresh and Marine Sediments with Iron and Sulfate Additions

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Introduction

As human population growth continues to increase, estuaries, coastal seas and fresh bodies of water are bearing the brunt of multiple forms of pollution. Increased nutrient inputs from wastewater effluent and septic tank seepage are changing oligotrophic systems eutrophic and acid rain is changing freshwater lake pH. Caraco et al. (1991) showed evidence that sulfur inputs, in the form of sulfate from atmospheric deposition, to fresh water systems increases phosphorus (P) release from the sediments in both anoxic and oxic conditions. P is an important nutrient to rate of primary production in aquatic systems yet research has shown that the surface photic waters are continuously losing P by the sinking of particles to the sediments (Caraco et al. 1991) causing P to be ultimately limiting.

A study done by Giblin et al. (1990) found the correlation between SO_4^{2-} and Fe in fresh water sediments to be closely tied: most SO_4^{2-} generated via dissimilatory SO_4^{2-} reduction is stored as inorganic reduced sulfur, primarily in the form of FeS_2 .

I am interested in examining the rate of P burial and release from sediments in reaction to changes in sulfate and Fe (III) in the overlying water of fresh and marine sediments. Fe (III) traps P in oxic sediments as oxygen and iron react to form Fe_2O_3 , which then occludes P and sinks to the sediments. At increased levels sulfate releases more P from the sediments by chemically reducing the Fe_2O_3 and releasing P. These two processes define P levels in aquatic systems. In marine systems there is a naturally high concentration of SO_4^{2-} whereas freshwater system concentrations are very low.

Methods

My experiment will entail a manipulation of .00866 m² ($\sqrt{\pi}$ square root) sediment cores taken from 2 fresh water systems and 1 marine (Table 1). Cores will be taken by SCUBA divers in week 10 with help from Anne Giblin and partner (Fig. 1). The two fresh water sites have different characteristics that could be affecting their rates of P recycling. Most importantly John's Pond is a much deeper system (20m max) that becomes anoxic after approximately 8 meters during the summer months. Mares Pond (17m max) stays oxic throughout the year. At each site 1 core will be taken for an immediate solid phase P fractionation analysis of total, inorganic, Fe_2O_3 occluded P and carbon which will be done with the CHN analyzer. 2 control cores will be taken from each site along with 2 that will be incubated with SO_4^{2-} addition and another 2 cores that will be made anoxic. The controls and the added SO_4^{2-} cores will be bubbled to keep them oxic. From the marine system I will also take a core for solid phase analysis, 2 for controls and 2 which will have decreased amounts of SO_4^{2-} . I will be making artificial seawater without SO_4^{2-} for these cores. The incubation will last approximately 3 weeks. In the final week I will add Fe to one core from each site. The choice of core will be determined at that time. Every 7 days I will take measurements of water column SO_4^{2-} , PO_4 , dissolved oxygen and possibly Fe.

PO₄ will be analyzed with the method we used in our week 5-6 aquatic element cycles lab (a modified single solution method for the determination of P in natural water adapted from Murphy J. And Reily J.P. (1962). It uses ascorbic acid instead of stannous chloride *Analytical Chemistry, Acta* 27, 31-36).

SO₄²⁻ will also be analyzed with the method used in our week 5-6 aquatic element cycles lab (an adapted method from: N. Gilboa-Garber (1971). Direct spectrophotometric determination of inorganic sulfide in biological materials and in other complex mixtures. *Analytical Biochemistry* 43:129-133)

Fe analysis procedure is yet to be determined.

Before incubation I will assess the redox state of the sediments to better understand rates of P release. We will begin incubation on the 10th of November and sample every 7 days (Fig. 1). During incubation I plan to take a total of 64 sub samples for PO₄ analysis. If Fe analysis is feasible, there could be an added 64 sub samples. I will be checking the DO concentration daily to ensure that our oxic cores stay oxic.

Solid phase cores will be sectioned into 5 sections equaling 15 total solid phase analyses. I will be performing P fractionation on these 15 sections with methods to be determined at a later date.

Expected Results

I hypothesize that adding SO₄²⁻ will cause PO₄ to be released from the sediments resulting in an increase in P in the overlying waters in relation to the controls. I conclude this from multiple papers stating the same (Caraco et al. 1991 and Rozan et al. 2002). With the addition of Fe, I should see a decrease in P concentration in the overlying waters in relation to the controls (Fig. 2). In the marine system there should be a higher P concentration in the controls than in the fresh water system with decreased sulfate in the overlying waters of the experimental cores.

Collaborators

I will be collaborating with Beth Bernhardt and Melanie Hayn. Beth will be working primarily with the sulfate and iron manipulations with me. We will be sharing the analysis load along with Melanie. Beth will be looking primarily at alkalinity of our lakes and sulfur storage in their sediments as a response to increased sulfate concentrations in the overlying waters. Her rain gage information will fill in my explanation of sulfur inputs to each of these systems. Melanie's data is almost entirely separate from Beth and my data. We will simply be sharing cores to decrease the number of total cores to take care of.

Materials, Analyses, and Supplies Needed

- I will be using a total of 64 scintillation vials for PO₄
- Possibly another 64 scintillation vials for Fe
- I will need a DO meter
- 16 incubation cores plus 3 for solid phase analysis
- Artificial seawater
- Spectrophotometer for PO₄ analysis
- Ascorbic acid
- Sulphuric acid
- Potassium Antimonyl-Tartrate
- Ammonium molybdate
- Materials for CHN analysis
- Bubbler
- Materials and reagents for P fractionation

- Aluminum plates
- Mortar and pestle
- Write-in-the-rain notebook
- Gas money = 5\$

Sources Sited

Caraco, Nina, Cole, Jonathan J., Likend, Gene E. 1991. A Cross-System Study of Phosphorous Release from Lake Sediments. Pages 241-257 in Cole, Jonathan, Lovett, Gary, Findlay, Stuart, editors. Comparative Analyses of Ecosystems, Patterns, Mechanisms, and Theories. Springer-Verlag New York, Inc. USA.

Rozañ, Tim F., Martial Taillefert, Robert E. Trouwborst, Brian T. Glazer, Shufen Ma, Lexia M. Valdes, Kent S. Price, George W. Luther III. Iron–sulfur–phosphorus cycling in the sediments of a shallow coastal bay: Implications for sediment nutrient release and benthic macroalgal blooms 2002. American Society of Limnology and Oceanography, Inc. 47(5), 1346–1354 2002.

Table 1. Sites and core manipulations for each site
After 2 weeks Fe will be added to one freshwater core, which will be determined at that time.

	freshwater		marine
Treatment	John's	Mares	Mass Bay
control	2	2	2
add sulfate	2	2	---
minus sulfate	---	---	2
anoxic	2	2	---

Figure 1. Timeline of experiment

Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
2	3	4	5	6	7	8
Collect cores from John's Pond and Mares Pond						
Possible solid phase analysis						

9	10	11	12	13	14	15
	Begin incubation		Solid phase analysis			
16	17	18	19	20	21	22
	Sample H ₂ O					
23	24	25	26	27	28	29
	Sample H ₂ O Add Fe					
30	1	2	3	4	5	6
	Sample H ₂ O Final sample		Final solid phase analysis			

Figure 3. Hypothesized mechanism for sulfur control of P release from sediments. P immobilization in sediments is proportional to amount of iron oxide in the sediments. Sulfide affects this iron oxide pool in 2 ways: first, sulfide binds Fe (as iron sulfides) and inhibits reformation of iron oxides at the oxic-anoxic border; second, sulfide may enhance dissolution of iron oxides, as chemical reduction of iron oxides by sulfide may occur more rapidly (or more completely) than dissolution by microbial reduction. Both processes, in systems with high amounts of A may remove FeOOH layer to outpace regeneration leading to P release. This interaction of S and Fe could be driving the correlation between sulfate concentration of waters and P release. (Source: Cacaco et al. 1991)

