The Role of Iron Oxides in Marine Phosphorus Cycling

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Abstract: Dissolved and particulate phase iron (Fe) and phosphorus (P) concentrations were characterized in Effingham Inlet, a fjord located on the west coast of Vancouver Island. The effect of redox conditions on Fe and P cycling was investigated through comparison of sediment and water samples taken above and below a water column redox boundary in the fjord. The data show that sharp increases in the concentration of dissolved P across the redox boundary cannot be explained solely by release of absorbed phosphorus associated with dissolution of iron oxide phases. These findings support new theories of P cycling in oceans, which suggest that redox sensitive cycling of polyphosphates by microorganisms may be a significant source of dissolved phosphorus in marine environments.

1. Introduction

Phosphorus (P) is an essential nutrient that drives global primary productivity in oceans on present and geologic timescales (Benitez-Nelson, 2000; Diaz et al., 2008; VanCappellen and Ingall, 1996). Understanding P cycling between oceans and sediments is important in understanding present and historic trends of nutrient supply (Algeo and Ingall, 2007). Since P is often the limiting nutrient for primary production in the oceans, characterizing the mechanisms that transport P between the sediments and water column is crucial for predicting productivity trends on local and global scales, which is directly linked to the global climate system (Algeo and Ingall, 2007; Benitez-Nelson, 2000). A better understanding of the mechanisms responsible for cycling P is necessary for accurate estimations of P driven productivity in oceans. Redox chemistry in particular is a very important factor in the transport of P.

It is well known that the relationship of P and Fe-oxyhydroxides is a key factor in P cycling that is primarily controlled by redox conditions (Algeo and Ingall, 2007; Krom and Berner, 1981; Lehtoranta and Heiskanen, 2003). In ocean waters oxygen is depleted at depth as respiration begins to dominate photosynthesis, and a redox boundary can be defined at the depth where O_2 is completely depleted. Similarly, respiration processes in sediments lead to the development of a very clear redox boundary typically a few centimeters below the sediment-water interface. Under oxidizing conditions Fe-oxyhydroxide phases are stable; when these phases encounter reducing conditions at the redox boundary, they dissolve and release P (Krom and Berner, 1980a; Krom and Berner, 1980b; Krom and Berner, 1981). This mechanism has been found to contribute significantly to the flux of dissolved P from marine sediments to overlying waters, but in many environments the iron contribution is insufficient to fully account for the observed flux (Bostrom et al., 1988; Froelich et al., 1979; Ingall et al., 2005; McManus et

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al., 1997; Sundby et al., 1992). The phenomenon of an increased concentration of dissolved P at the redox boundary has historically been explained by the Fe-oxyhydroxide mechanism, however, a recent study suggests that polyphosphates formed in microorganisms may be a critical component of the marine P cycle (Diaz et al., 2008). Moreover, it is well known from waste water treatment plants that bacteria cycle polyphosphate in response to redox changes. The purpose of this paper is to evaluate the relative contribution of P released by dissolution of Fe-oxyhydroxides at the redox boundary in a coastal marine environment.

2. Methods

2.1. Study Site and Sample Collection

Effingham Inlet, a fjord on the southwestern tip of Vancouver Island, was sampled during cruises in April and July of 2007. The fjord is approximately 17 km long and 1 km wide, located at approximately 49°01 N latitude and 125°09 W longitude. The fjord is ideal for this study because it contains a clear redox transition in the water column and the underwater topography of the fjord is such that water column and sediments above and below the redox transition can be easily sampled. Hydrographic sampling casts measuring the Conductivity, Temperature vs. Depth (CTD) properties of the water column, as well as sediment cores, and sediment traps were collected at various sites along the fjord, with sampling depths ranging from 10 m to 150 m. During the April cruise two sediment core samples were taken at one site far below the water column redox boundary and the other near the boundary. During July four sediment core samples were taken at sites along a transect including sites above and below the water column redox boundary. Water column samples were collected in vertical profiles using a sampling system on the CTD instrument. Dissolved oxygen concentrations were measured for these vertical profiles using a sensor mounted on the CTD instrument. Total dissolved P and Fe concentrations in the

water column samples were measured in selected profiles shortly after collection in land based laboratories.

Data from the cruises in April and July of 2007 exhibited a clear peak of Fe and P in the water column at the redox boundary (Fig. 1 and 2). Fe-oxyhydroxide particles collected as particles sinking in the water column in sediment traps and from surface sediments were analyzed. These analyses yield insights into the potential for P release during dissolution of Fe as these particles pass through the redox boundary. To evaluate the contribution of dissolving Fe-oxyhydroxide particles to the peak in P, we examined the Fe:P ratios of the samples taken above and below the redox boundary. Both the surface layers of the sediment cores and the sediment traps provided Fe:P ratios indicative of the composition of sinking Fe-oxyhydroxide particles. The resulting Fe:P ratios found from the sediment data are compared to the apparent Fe:P ratio of dissolved Fe and P in the water column.

2.2. Determination of Fe:P ratios in Particulate Samples

To determine the relative contribution of Fe-oxyhydroxides to the peak of P at the redox boundary, Fe:P ratios were determined by sequential extraction techniques. Fe oxyhydroxides were extracted with a citrate, ascorbate, and bicarbonate (CAB) solution. This solution reduces solid Fe in iron oxides to Fe^{2+}, a dissolved and soluble form of iron. Additionally, P associated with solid iron oxides dissolved in the CAB solution is released and measured as soluble reactive P (SRP) (Hyacinthe and Van Cappellen, 2004). The molar amounts of P and Fe released were determined by colorimetric and Atomic Absorption (Flame AA) methods, respectively. Fe:P ratios were calculated using the CAB extracted P after removing loosely bound P.

2.2.1. MgCl₂ Extraction of Loosely Bound P

In order to determine baseline P concentrations (P that is not associated with Fe) in sediment samples, an $MgCl_2$ extraction was performed prior to the CAB extraction. A 1 M solution of $MgCl_2$ was prepared according to SEDEX sequential extraction technique (Ruttenberg, 1992). A 25 mL volume of solution was added to approximately 150 mg of sediment, and was allowed to shake for two hours before filtration and analysis. After two hours the sediment solutions were centrifuged and filtered with a 0.45 µm Whatman filter. Using a standard molybdenum blue SRP colorimetric method, the P in solution was measured at a wavelength of 880 nm (Klaus Grasshoff, 1999).

2.2.2. CAB Extraction of Fe Bound P

After decanting the $MgCl_2$ extract, the remaining sediment was processed further by adding 25 mL of CAB solution and allowed to shake for 24 hours. The CAB solution was made by adding 10 g of Sodium Bicarbonate, 10 g of Sodium Citrate, and 4 g of Ascorbic Acid to 200 mL deionized water to achieve a pH of approximately 8.0 (Ruttenberg, 1992). After 24 hours the sediments were again centrifuged and filtered. Of the extracted solution 5 mL were taken, diluted twofold, acidified with 0.5 mL of 12 N HCl, and analyzed for Fe with a Flame AA at a wavelength of 372 nm. 15 mL of the remaining filtered extract was taken for SRP analysis. Direct colorimetric analysis for SRP in the filtered extract was not possible due to interferences with citrate and ascorbate. In order remove these interferences, the extract solution was dried at 80 °C overnight and then combusted in a muffle furnace at 550 °C for two hours to burn off the organic citrate and ascorbate. The leftover ash was assumed to retain all the P from the combusted extract solution, as P is non-volatile. The P in the ash was then dissolved with 5 mL of 1 N HCl which resulted in a solution with a pH between 8 and 10, which could be filtered, diluted, and finally measured colorimetrically for P concentration.

3. Results and Discussion

3.1. Water column profiles

In April the redox boundary was located at approximately 66 m (Fig. 1). The disappearance of oxygen at this depth coincides with a sharp increase in total dissolved P (TDP) and a corresponding increase in dissolved Fe. An additional peak in dissolved Fe occurs deeper but without a concurrent increase in TDP. The smaller peak of Fe corresponds, by depth, to the peak in P; however, there is no corresponding P increase with the larger Fe peak at 70 m. Therefore, from these peaks, and assuming that all dissolved Fe is originating from Fe mineral dissolution, it suggests that the majority of Fe oxides dissolving must not contain P. If we conclude that P bound to Fe dissolves at a shallower depth, it also suggests that the Fe particles that do release P dissolve more readily than those that do not have associated P. It is important to note that if the Fe oxyhydroxides do in fact explain this P increase, a ratio of Fe to P (Fe:P) in particles sinking within the oxic zone equivalent to the ratio observed in the water column would be expected. Thus, if the Fe oxyhydroxides do explain the P peak, there should be a Fe:P ratio of approximately one in the sinking particles above the redox boundary.

3.2. Fe and P in particulates

Loosely bound P was found in higher concentrations for samples collected deeper in the water column for both sediment cores and traps. Higher concentrations of loosely bound P in deeper particulates are consistent with the higher dissolved P concentrations at depth in the water column (Table 1, Fig. 2). The CAB extractable P concentrations in the sediment cores vary significantly between the two seasons but exhibit almost no change relative to depth of collection

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in the water column (Fig. 3). Extractable Fe, however, remains approximately constant between the two seasons and decreases with depth (Table 1, Fig. 3). The decrease of particulate Fe with depth is expected from dissolution, yet a correspondingly strong decrease in extractible P from dissolution with depth is only observed in the April samples. These observations are further supported by the sediment trap data. The particles collected in the sediment traps contained very little P per mass compared to the sediments, but had equal or more Fe relative to mass extracted, revealing that only a minute amount of Fe associated P is released by sinking particles (Fig. 4). The decrease in Fe at depth is once again observed in the sediment traps, but there is virtually no difference in P. By examining these data in terms of the ratios between particulate and dissolved Fe and P, discussion of the processes involved can be made based upon the direct relationship between Fe and P observed in the system.

3.3.   Fe:P Ratios

A full record of extracted Fe and P is presented in Table 1, where all analyzed samples are delineated by depth and O_2 concentration. The mechanism of Fe oxyhydroxide particles dissolving to release P at the redox boundary requires a corresponding variation of Fe:P in the dissolving particles in relation to the Fe:P dissolved in the water column. We see that the Fe:P in the water column remains below 1.0 (Fig. 2). There are several possibilities that could explain the very low Fe:P ratio in the water column. First, there could be a very large quantity of P released as Fe is dissolved. If P release via the dissolution of Fe oxyhydroxides can explain the redox peak in dissolved P and Fe, then there must be an equal Fe:P ratio present in particulates sinking through the oxic zone. However, based on the examination of Fe:P in particulates, this is not the case. Fe:P ratios for the April sediment samples are at least two moles Fe per mole P (Fig. 5). Additionally, comparing the Fe:P ratios between July sediments and the July sediment

traps, we see that the actual particles in the water column, captured by the traps, have far less P than the sediment core samples (Fig. 4 and 5). These observations lead us to the conclusion that there is not enough P released by dissolving Fe to explain the dissolved concentrations in the water column. Further supporting this reasoning, there is an extraordinary discrepancy, of an order of magnitude or two different, between the Fe:P ratios found in the July sediment traps and the Fe:P in the water column. Although Fe has not been measured for the CTD cast in July, a cruise at the very same sampling site in June of 1997 found no more than 1.5 μM Fe in the water column, and the sediment core data show there is not a significant variation of Fe between April and July (Ingall et al., 2005). Dissolved P in the water column also did not exhibit a significant change between the seasons (Fig. 1 and 2). The traditional explanation of Fe oxyhydroxide particles dissolving to release P is contradicted by our data, therefore current theory of P cycling at redox transitions should be re-examined. Additional mechanisms must be playing a role in this system to explain these observations.

Although Fe-oxyhydroxide dissolution is known to play a role in releasing P at the redox boundary, it is clearly not the only mechanism of P release. The minute amounts of P in sinking particles suggest that release of P associated with Fe oxide particles may comprise only a minor source of P in the Effingham system (Fig. 4). Regarding the unexpectedly low dissolved Fe:P ratios found in the water column, a secondary explanation could be that Fe is rapidly remineralized into sulfides in the anoxic waters, directly lowering the Fe:P ratio by decreasing the amount of dissolved Fe in the column. This explanation potentially accounts for the lower Fe concentrations. However, if dissolving Fe is not releasing sufficient amounts of P to produce the sustained peak of P in the water column, then there must be another mode of transportation of P to the dissolved phase to explain the high P that contributes to the low Fe:P ratios. Recent studies

have shown the likelihood of microorganisms playing a significant role in this transport, in a similar way that the Fe particulates do (Ingall and Jahnke, 1997). In particular, P may be sequestered by key microorganisms, such as diatoms, as polyphosphates; when these organisms die and sink below the redox boundary, they dissolve just as the Fe particulates do and release P into the water column (Diaz et al., 2008). Further investigations of these organisms and the efficiency of their uptake and transport of P as polyphosphates are needed to ascertain the relative contribution of these mechanisms. If polyphosphates are indeed a major source of dissolved P in the water column, current global productivity models and estimations could be grossly underestimating P transport and availability.

4. Conclusions

This study provides evidence that the Fe oxyhydroxide mechanism is not the only important source of P release at the redox boundary in marine environments. In particular, particulates sinking through the oxic zone in July have been found to release no P as they pass into anoxic waters. April samples reveal a seasonal variation in sediment P concentrations, and they do exhibit a decline in Fe related P under anoxic conditions. However, if sinking particles are not in fact releasing P associated with Fe, then perhaps a seasonally driven P transport mechanism exists. It is possible that the spring productivity bloom provides an increased amount of P to the bottom waters via biological activity. Recent studies have proposed that microorganisms sequester P as polyphosphates in the oxic zone and subsequently release P as they dissolve at the redox boundary. Ultimately, the overall mechanism for P transport and release at the redox boundary remains unclear. Further investigations of the relative contributions of these mechanisms could be invaluable for the understanding and prediction of P driven productivity in oceans on current and geologic timeframes.

5. References

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6. Tables and Figures

Table 1: Sediment extraction data

Site	Month	Sed. Depth (cm)	O_2 (mg/L)	Depth (m)	Loosely-Bound P (µmol/g sed)	Fe-bound P (µmol/g sed)	CAB extracted Fe (µmol/g sed)	Fe:P (Fe-bound P)
E1-5	April	0-1	0	150	8.47	5.14	10.20	1.98
E1-5	April	1-2	0	150	4.35	4.66	9.43	2.03
E1-6	April	0-1	0.01	76	1.81	9.50	16.68	1.76
E1-6	April	1-2	0.01	76	1.01	4.66	15.73	3.38
E2-26	July	0-1	0.01	90	1.33	2.00	6.24	3.12
E2-26	July	1-2	0.01	90	1.01	0.70	9.54	13.53
E2-80	July	0-1	0.05	77	N/A	1.97	12.91	6.56
E2-80	July	1-2	0.05	77	0.01	1.24	12.45	10.08
E2-81	July	0-1	0.43	66	N/A	1.82	17.45	9.57
E2-81	July	1-2	0.43	66	0.24	1.18	21.57	18.34
E2-82	July	0-1	0.61	58	N/A	1.69	15.39	9.12
E2-82	July	1-2	0.61	58	0.30	1.03	20.18	19.54
E2-7	July		.84	45	3.75	0.29	36.27	123.29
E2-8	July		.02	87	11.44	0.29	14.70	51.09

* Loosely bound P was not extracted for the other July 0-1 samples, so when comparing these data in Figure 3 the $MgCl_2$ extracted P was combined with the CAB for a total of 2.00 µmol/g sed.
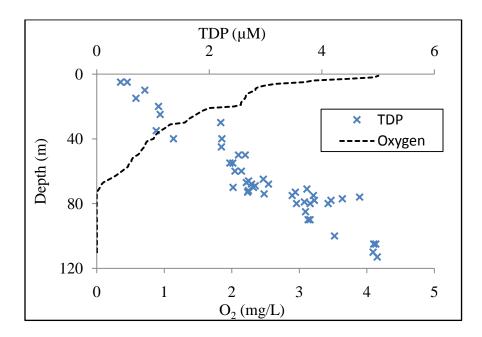
Figure 1. Total dissolved phosphorus (TDP) and Oxygen (O₂) with depth in a July CTD cast. The redox boundary is defined by the O₂ depletion at about 75 m. A sharp increase in P is also observed at this depth.
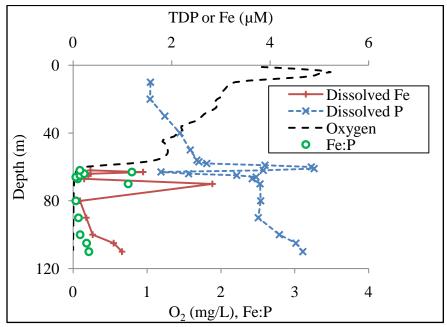

Figure 2. Total Dissolved P (TDP), Fe, Oxygen (O₂), and Fe:P ratios with depth in April CTD cast. The redox boundary is defined by the O₂ depletion at about 60 m. A sharp increase in P is also observed at this depth, followed by a similar increase in Fe several meters later.
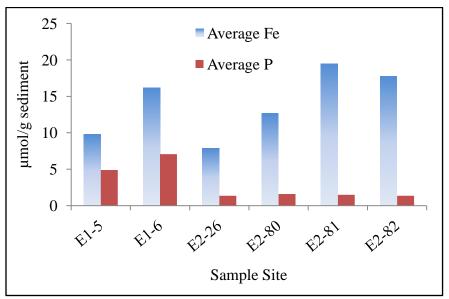

Figure 3. Average Fe and P found in the first two centimeters of sediment. E1 samples correspond to the April cruise and E2 to July.
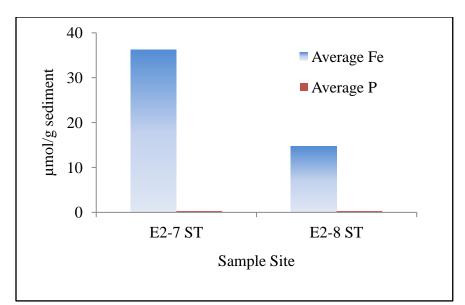
Figure 4. Fe and P concentrations (µmol/g sediment) in sediment traps. E2-7 is the oxic sample, and E2-8 is anoxic.
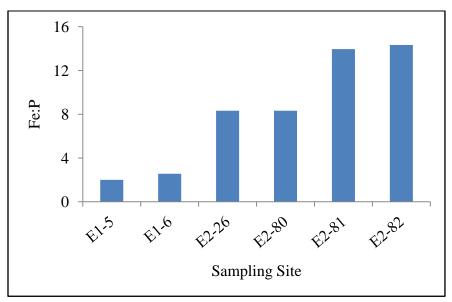

Figure 5. Average Fe to P ratios found in the first two centimeters of sediment. E1 samples correspond to the April cruise and E2 to July.