Interaction between dissolved phosphorus and suspended sediments in a tropical estuary

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Abstract

Nutrients from the Fitzroy River (Queensland, Australia) may impact on the Great Barrier Reef, a marine area of world significance. In this study, experiments were carried out to determine the equilibrium distribution of phosphorus between Fitzroy River sediments and estuarine water under a range of conditions. The kinetics of sorption processes were also studied. Sorption reactions reached a steady state after about 2 days. The sorption of P was weaker at higher pH values, but did not decrease with an increase in ionic strength. The amount of P bound by sediment particles was limited by the surface site density of the solid phase (about 140 μmol/g). The Fe content of suspended particles increased moving down the estuary, due to the precipitation of amorphous Fe-oxides. Adsorption of P on freshly precipitated Fe-oxides may therefore be a significant mechanism of P removal from the aqueous phase. At higher pH values and salinities, solid $CaCO_3$ appears to play an increasing role in limiting the amount of dissolved P, either by surface adsorption or co-precipitation. The interaction of P with Fe-oxide surfaces was modelled using a surface complexation sorption model with the geochemical code MINTEQA2.

1 Introduction

Excessive input of nutrients to the Great Barrier Reef (located in the coastal waters of Queensland, Australia) may result in eutrophication and can have more specific impacts. In the case of phosphorus (P), increased levels may impair growth of the coral skeleton (Hunter & Rayment [11]). Understanding the processes which affect P cycling in the estuaries of the region is therefore important for the environmental management of the reef.

A number of mechanisms have been proposed as being of significance in the estuarine cycling of P (Froelich [8]). These include adsorption / desorption in response to pH or salinity gradients (Eyre & Twigg [6]), and precipitation or co-precipitation of P with Fe-oxides (Fox [7]). The aim of the present study is to develop a chemical model of the behaviour of P in the estuary of the Fitzroy River, which is the largest river on the central Queensland coast.

2 Experimental

2.1 Water and particle samples

The Fitzroy River has a pattern of summer flooding and winter drought. A barrage has been constructed across the river at Rockhampton to retain fresh water and prevent sea water intrusion into the resulting impoundment. Samples of filtered water and suspended particles were collected during the dry season at the locations shown in Figure 1. The first sample (S1) was fresh water obtained upstream of the barrage. Samples S2, S3 and S4 were obtained progressively down the estuary. Sample S5 was from near the limit of the estuary, and was similar to sea water. The major elemental composition of the water samples was determined by standard techniques, with phosphate analysed using the ascorbic acid / molybdenum blue method (APHA [2]).

A sample of bottom sediments was obtained from location S1. A slurry of fine particles (<20 μm) for laboratory sorption experiments was obtained from this sample by sedimentation in the S1 water. The mass loading in this slurry was measured by carefully drying samples of known volume. The extractable P content of the fine particles was determined after a persulfate extraction of an aliquot (APHA [2]). The surface area of the particles was measured using the BET method, which is commonly used for characterising particles in sorption studies (Davis & Kent [4]). An XRD spectrum of the particles was also obtained. The total elemental contents of sediment and suspended particles were measured after digestion with a mixture of HF and HNO_3.

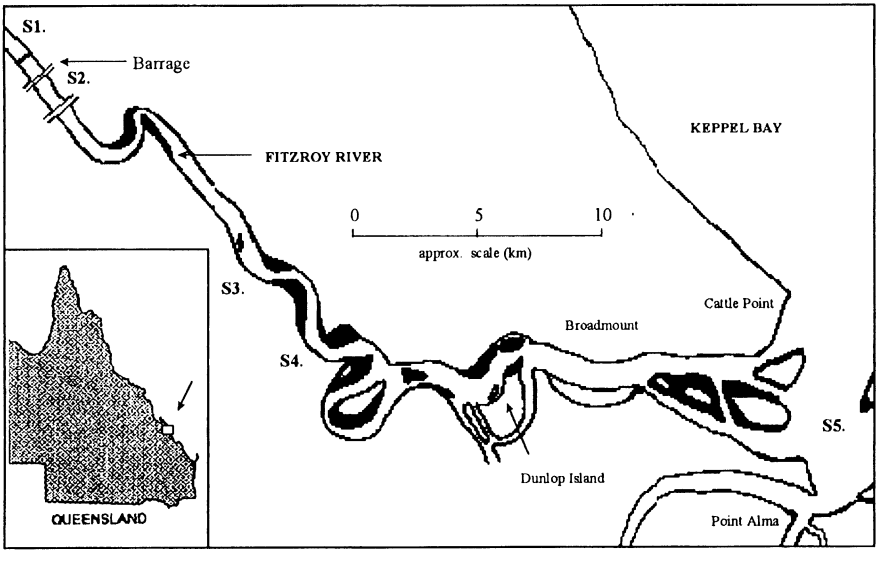

Figure 1. Sketch map of the lower section of the Fitzroy River, showing sample locations.

2.2 Sorption experiments

Sub-samples for sorption experiments were obtained from the fine particle slurry by thorough agitation followed by removal of a known volume by pipette. Sorption experiments were carried out with a mass loading of 1 g/L or 100 mg/L. The aqueous phases consisted of S1 or S5 water, containing added P of 10 or 100 μmol/L. Experiments were maintained at 25°C.

Kinetic experiments were carried out in agitated 500 mL vessels which were ventilated to ensure equilibrium with atmospheric CO_2 and to maintain aerobic conditions. The P content of the aqueous phases as a function of time was determined after filtration of sub-samples through a 0.45 μm membrane.

Batch sorption experiments were carried in ventilated 30 mL centrifuge tubes. The pH was adjusted using dilute HCl or NaOH, with $NaHCO_3$ added at pH values above 8.0 to ensure equilibrium with atmospheric CO_2. The solid and liquid phases were separated after 2 days equilibration by centrifugation (10000 rpm). The amount of dissolved P was determined by analysing the supernate. Additional experiments were undertaken with freshly precipitated amorphous Fe-oxide (ferrihydrite),

prepared using the method of Waite *et al.* [15], with an aqueous phase of 0.5 mol/L NaCl.

A P sorption isotherm (at pH 8.2) was obtained using S1 water. In these experiments, high P concentrations were used to enable measurements close to surface saturation. Under these conditions, initial and final dissolved P concentrations in the experiments were similar, which meant that large errors were associated with estimating sorbed P by difference. To avoid this problem, the P sorbed on the particles was measured directly by collecting the particles on an ultrafiltration membrane and measuring their P content after extraction by the persulfate method (APHA [2]).

3 Results and Discussion

3.1 Characterisation of waters and particles

The water conductivity in the estuary showed a distinct boundary between fresh and saline water below site S1, due to the barrage (Table 1). The major ion chemistry of S1 comprised Na (0.49 mmol/L), Mg (0.38 mmol/L), Ca (0.29 mmol/L), and Cl (1.79 mmol/L). Downstream of the barrage there was an increase in dissolved P, with the P concentration in estuarine water being between about 2 and 6 μmol/L. At the time of sampling, the pH of the river water (S1) was similar to that of sea water. However, the pH of coastal rivers is affected by flow conditions, and can reach significantly lower values. For example, Eyre & Twigg [6] measured pH values of 6.5 in the Richmond River in northern NSW.

Table 1. Summary of chemical data for water and suspended particles

Sample site	pH	conduct-ivity (mS/cm)	dissolved P (μmol/L)	Suspended sediment (mg/L)	Fe in suspended particles (mmol/g)
S1	7.92	0.189	1.2	18.9	0.45
S2	8.08	26.4	6.1	38.8	0.51
S3	7.98	43.2	2.2	29.9	0.32
S4	8.19	35.1	5.1	38.3	0.91
S5	8.19	51.3	2.6	67.5	1.77

The XRD results indicated that the S1 bottom sediments consisted predominantly of quartz and kaolinite. The Fe content of the S1 particles was 0.40 mmol/g, which was similar to the suspended particles at this location. The amount of P in the persulfate extraction of the particles was

21.8 μmol/g. This P should be considered when interpreting the results of sorption experiments with this material. The suspended solid load and the Fe content of suspended particles showed a marked increase at location S5.

The data indicate that the parameters previously suggested as being significant (pH, salinity, suspended sediment load, and Fe-oxide precipitation) could play a significant role in the cycling of P in the Fitzroy River estuary. These parameters were therefore subjected to detailed study in the sorption experiments.

3.2 Kinetic adsorption experiments

The kinetic experiments followed P sorption for time periods of up to 400 hours. In the experiments with 10 μmol/L added P, there was little difference between the sea water (S5) and river water (S1) at pH 8.0 (Figure 2a). The data suggest that about 2 days was required to reach sorption equilibrium. Adjustment of the pH to 6.0 significantly reduced the amount of dissolved P. Surprisingly, the amount of dissolved P was lower in the sea water than the river water. This indicates that, in the absence of a pH change, the salinity increase from river water to sea water should not release P from suspended particles. However, a pH increase between fresh and sea water may release adsorbed P.

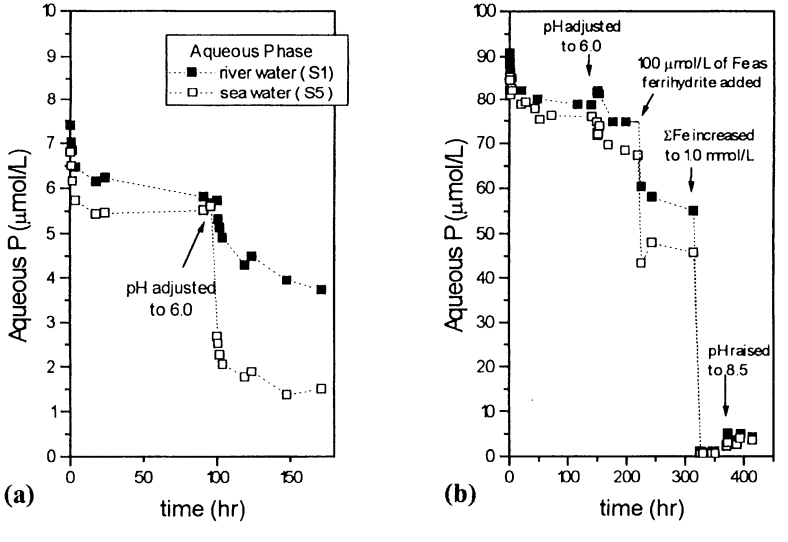

Figure 2. P in the aqueous phase in kinetic experiments with 1 g/L of S1 sediment suspended in S1 or S5 water (initial pH 8.0). Changes to the conditions are shown. Added P of a) 10 μmol/L and b) 100 μmol/L.

In the experiments with higher added P (Figure 2b), adjusting the pH to 6.0 caused a smaller relative decrease in dissolved P concentration. The data suggest that with these high levels of P, sorption sites on the particle surfaces are approaching saturation with P. During the course of the experiments, freshly precipitated ferrihydrite was added in order to study the response of the system to increases in particulate Fe-oxides. The addition of 100 μmol/L of Fe as ferrihydrite removed approximately 20 μmol/L of P from solution with both S1 and S5 waters. These data are consistent with the conclusion of Dzombak & Morel [5] that the sorption behaviour of ferrihydrite can be modelled with approximately 0.2 mol of surface sites per mole of Fe. With a total of 1.0 mmol/L of Fe as ferrihydrite, excess sorption sites were available and the P was quantitatively removed from solution (Figure 2b). The subsequent increase of the pH to 8.5 released some of the adsorbed P.

3.3 Batch adsorption experiments

The results of batch sorption experiments with S1 sediments again showed a strong pH dependence (Figure 3a). The levels of P in solution at high pH in the experiments with 1 g/L solid loading exceed the total added P (10 μmol/l) in the experiment. This was attributed to desorption of some of the existing P content of the particles.

The much higher amounts of P in solution up to pH 8.0 in the experiment with the lower mass loading (Figure 3b) show that sorption is the dominant process at low to neutral pH values, as precipitation would not be sensitive to the solid mass loading. However, the removal of P from the solution phase in experiments at high pH values with the S5 water occurred with both mass loadings, and was associated with the formation of a visible precipitate. The removal of P did not occur in the S1 river water, and appears to be related to the precipitation of $CaCO_3$ (discussed below).

3.4 Geochemical modelling

In the past 20 years, the modelling of aqueous systems has advanced rapidly due to the application of computer models for chemical speciation. The standard approach has been to define a set of components from which the stoichiometry of the system can be uniquely formulated (e.g. H^+, CO_3^{2-}, Cl^-). Each system is described by a number of linear mass balance equations and non-linear mass action equations involving these components (see Morel & Hering [13]). This type of approach permits complex chemical equilibrium problems to be solved iteratively using a computer.

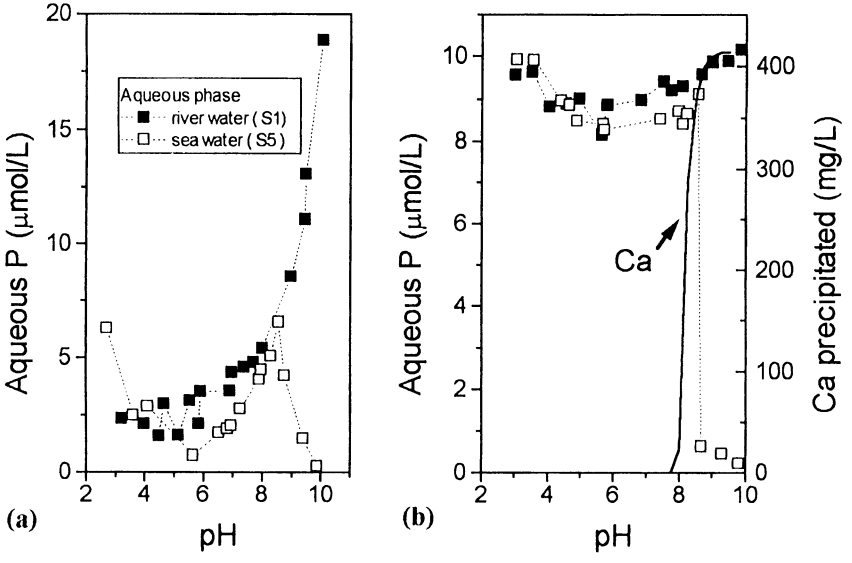

Figure 3. Dissolved P in experiments with added P of 10 μmol/L, and mass loadings of a) 1 g/L and b) 100 mg/L. The removal of P from the aqueous phase at high pH values occurred only in S5 water. This is attributed to sorption or co-precipitation with $CaCO_3$ (solid curve).

Numerous computer codes for calculating the equilibrium distribution of species in geochemical systems have been developed. The geochemical code MINTEQA2 (Allison *et al.* [1]) was used to examine the reason for the decrease in dissolved P in the batch experiments at high pH values in S5 water. In order to explain the data (Figure 3), a solid phase which becomes supersaturated in S5 water but not S1 water at about pH 8.5 is required. The most likely possibility is $CaCO_3$, which is predicted to precipitate from sea water (S5) but in negligible amounts from the S1 river water (which contains only low levels of Ca). A possible alternative mechanism would involve direct precipitation of a Ca-phosphate mineral such as hydroxyapatite. Although some Ca-phosphate phases were supersaturated under the experimental conditions, none was predicted to become supersaturated in the S5 water within the pH range of interest. Therefore, precipitation would not be limited to the experiments at high pH values in the S5 water. An association of P with precipitating $CaCO_3$ minerals therefore appears to be a reasonable explanation of the data.

The adsorption and co-precipitation of P on calcite has been studied by House & Donaldson [10]. These authors found that the amount of co-precipitated P increased with the precipitation rate of calcite, and did not find evidence for the control of solution compositions by a distinct calcium phosphate phase. This is consistent with the present results. The extent to which this P removal mechanism may operate in nature is uncertain, but it may be expected to become significant when the pH increases above about 8, which can result from photosynthetic activity (Richardson *et al.* [14]). A recent study (House & Denison [9]) has indicated that changes in sediment composition in an English river were consistent with deposition of calcite and co-precipitation of inorganic phosphate, possibly in association with algal biofilms.

3.5 Sorption modelling

To extend geochemical models to include sorption, simple isotherms (such as the Freundlich or Langmuir isotherms) have been used. However, the more mechanistic surface complexation model (SCM) treats interactions between dissolved species and surface functional groups in a similar way to complex formation with ligands in solution. Each surface reaction is expressed as a reaction involving components, with an associated equilibrium constant (log K). A significant component of the model is the inclusion of electrostatic terms to allow for changes in surface charge due to adsorption reactions. The SCM has been applied to modelling the adsorption of a wide range of inorganic cations and anions on the surface of amorphous Fe-oxide (Dzombak & Morel [5]).

In order to model the data for the pH dependence of P sorption on ferrihydrite (shown in Figure 4), it is necessary to incorporate a suite of surface reactions into the geochemical model. Dzombak & Morel [5] reviewed the available literature for P sorption on ferrihydrite, and proposed the suite of surface reactions in Table 2. These are consistent with a surface area for ferrihydrite of 600 m^2/g and a site density of 0.2 mol/mol Fe (approximately 3.8 $\mu mol/m^2$). When implemented using MINTEQA2, this model provided an acceptable fit to the sorption data in the ferrihydrite / P system (Figure 4). Although there is a slight discrepancy between the model and the experimental data, this may be due to uncertainty in the equilibrium constants. Dzombak & Morel [5] suggested that the 90% confidence interval for the log K for reaction 3 (Table 2) ranged from 17.34 to 18.09. Adjustment of this parameter within this range significantly affects the model curve (Figure 4).

Table 2. Surface complexation reactions used in modelling the ferrihydrite / phosphate system

	Surface reaction	Log K^{int}
1.	$>FeOH^{\circ} + PO_4^{3-} + 3H^+ \Leftrightarrow >FeH_2PO_4^0 + H_2O$	31.29
2.	$>FeOH^{\circ} + PO_4^{3-} + 2H^+ \Leftrightarrow >FeHPO_4^- + H_2O$	25.39
3.	$>FeOH^{\circ} + PO_4^{3-} + H^+ \Leftrightarrow >FeH_2PO_4^{2-} + H_2O$	17.72
4.	$>FeOH_2^+ \Leftrightarrow >FeOH^0 + H^+$	-7.29
5.	$>FeOH^{\circ} \Leftrightarrow >FeO^- + H^+$	-8.93

>Fe represents a binding site on the Fe-oxide surface

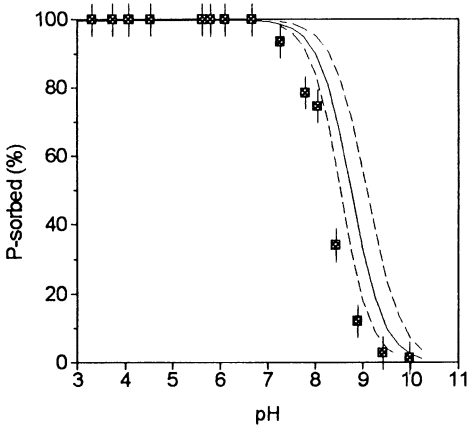

Figure 4. Adsorption of P on ferrihydrite in 0.5 M NaCl. The solid curve was calculated with the data in Table 2. The dashed lines show calculated curves with log K (for reaction 3 in table 2) of 17.34 and 18.09.

The sorption isotherm for the natural substrate in S1 water at pH 8.0 (Figure 5) levelled off at high P concentrations, indicating that site saturation was being approached. The extension of the SCM model to natural materials is a difficult problem due to the complexity of the phenomena and the multiplicity of potential sorbing sites (Davis & Kent [4]). The data for the natural substrate were modelled assuming the surface sites had the same properties as the ferrihydrite sites (using the reactions in Table 2), and using the BET surface area (81.3 m^2/g). The site density was adjusted for the best fit, which was achieved with a site density of 140 μmol/g. This corresponded to a site density of about 1.7 $\mu mol/m^2$, which is

at the lower end of the range (1.7 - 11.6 μmol/m^2) for geologic substrates proposed by Davis & Kent [4].

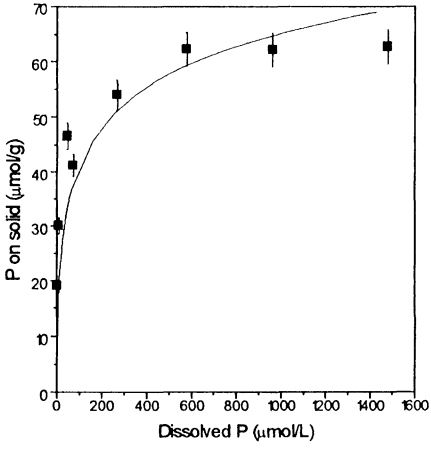

Figure 5. Isotherm for P sorption on Fitzroy River S1 sediments. The curve was calculated with the reactions in Table 2 (site density of 140 μmol/g).

The model fits the sorption isotherm on the natural substrate reasonably well, and is able to qualitatively explain the response of experimental systems to pH changes and the input of ferrihydrite (Figures 2 and 3). However, further work is required to fully understand the natural substrate. In particular, the inclusion of other site types such as those on clay minerals should improve the simulation of the experimental data.

It appears from the experimental and modelling results that that the number of sites on the S1 particle surfaces is in the range 100 - 150 μmol/g. This considerably exceeds the measured P load of the particles (21.8 μmol/g), although it is comparable to the maximum concentrations of adsorbed P reported by Lebo [12] for industrialised estuaries in the northern hemisphere (140-250 μmol/g). This would be consistent with the higher degree of pollution in the estuaries studied by Lebo [12].

Given the excess of sites relative to the P content, it would be expected that the particles may act as a sink rather than a source of P. This is shown by the net adsorption (rather than release) of P in most of the batch experiments (Figure 3a and 3b). Increases in aqueous P only occurred at high pH values, outside the natural range. Similarly, the kinetic experiments (Figure 2) showed an overall decrease in aqueous P.

While the particles tend to adsorb rather than release P there is only a modest decrease in dissolved P by adsorption with 10 μmol/L of added P and a mass loading of 100 mg/L (Figure 3b). As this exceeds the suspended particle load in the estuary (Table 1), a significant decrease in P levels by sorption on suspended particles may not occur without the precipitation of additional Fe-oxides.

In the Fitzroy River estuary, there are inputs of nutrients from sources such as sewage treatment plants and abattoirs, as well as zones of oxygen depletion (Connell *et al.* [3]). Lebo [12] suggested that phosphate may be released from sedimented Fe solids under reducing conditions. Given the high levels of dissolved phosphate at locations S2 and S4 (Table 1), and the measured suspended solid loads, it appears that suspended particles are insufficient to adsorb dissolved P in this part of the estuary.

4 Conclusions

In this study, we have shown the potential of controlled laboratory experiments and geochemical computer modelling to help understand P cycling in the Fitzroy River. The following conclusions may be drawn:

a. In the lower part of the estuary, oxygenation, a pH increase, and mixing increase the amount of suspended Fe-oxides, and $CaCO_3$ may also precipitate. In this region, sorption and co-precipitation on Fe-oxides and $CaCO_3$ are possible mechanisms of P removal from the aqueous phase.
b. The surface complexation model with parameters from Dzombak & Morel [5] adequately simulates P sorption on the Fe-oxide phase.
c. Particles flowing over the barrage from upstream probably provide a net sink rather than a source of P in the estuary. However, sorption on suspended particles appears insufficient to entirely remove dissolved P derived from local inputs within the estuary.

Acknowledgements

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