Phosphorus sorption and buffering mechanisms in suspended sediments from the Yangtze Estuary and Hangzhou Bay, China

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Abstract. The adsorption isotherm and the mechanism of the buffering effect are important controls on phosphorus (P) behaviors in estuaries and are important for estimating phosphate concentrations in aquatic environments. In this paper, we derive phosphate adsorption isotherms in order to investigate sediment adsorption and buffering capacity for phosphorus discharged from sewage outfalls in the Yangtze Estuary and Hangzhou Bay near Shanghai, China. Experiments were also carried out at different temperatures in order to explore the buffering effects for phosphate. The results show that P sorption in sediments with low fine particle fractions was best described using exponential equations. Some P interactions between water and sediment may be caused by the precipitation of CaHPO₄ from Ca²⁺ and HPO₄²⁻ when the phosphate concentration in the liquid phase is high. Results from the buffering experiments suggest that the Zero Equilibrium Phosphate Concentrations (EPC₀) vary from 0.014 mg L⁻¹ to 0.061 mg L⁻¹, which are consistent with measured phosphate concentrations in water samples collected at the same time as sediment sampling. Values of EPC₀ and linear sorption coefficients (K) in sediments with high fine particle and organic matter contents are relatively high, which implies that they have high buffering capacity. Both EPC₀ and K increase with increasing temperature, indicating a higher P buffering capacity at high temperatures.

1 Introduction

Phosphorus (P) is a major limiting nutrient in many surface waters and is often responsible for triggering eutrophication and toxic algal blooms (Kawasaki et al., 2010; Pratt and Shilton, 2009). In estuarine and coastal waters, P exchange at seawater–sediment interfaces can exert significant influence on P availability and it is, therefore, important to understand and describe this process well. Three equations (Langmuir, Freundlich and Temkin) are commonly used to describe sorption equilibria in water-sediment systems.

P can rapidly react with particle surfaces in natural systems (Froelich, 1988; Borggaard et al., 2004). The physicochemical reactions of P between overlying water and sediment in natural systems include adsorption/desorption and precipitation/dissolution reactions, which together, regulate soluble P concentrations in natural rivers, streams and estuaries (Wauchope and McDowell, 1984; Price et al., 2010). This phenomenon is known as the "phosphate buffer mechanism" (Richardson, 1985), which assumes that sediment, whether benthic or suspended, maintain dissolved reactive phosphate concentrations at some near-constant value regardless of biological removal and exogenic inputs (Froelich, 1988). P is sorbed onto particles in rivers, and then carried into estuaries. In estuaries, where freshwater and seawater mix, phosphorus is desorbed from particles to augment dissolved phosphate, especially in anoxic, saline sediment (Conley et al., 1995). This buffering effect is partly attributed to the adsorption of P onto metal oxide surfaces. Particulate phosphorus associated with iron and aluminium oxides often decreases with increasing salinity, suggesting that dissolved...
phosphate concentrations might be partly buffered by desorption from aluminium and iron oxide phases (Conley et al., 1995; Schippers et al., 2006).

The Yangtze Estuary in eastern China frequently experiences eutrophication problems which are often manifested as red tides and fish kills (Xiang, 2011). Phosphate, primarily from treated wastewater outfalls is believed to be the principal driver for these phenomena (Li et al., 2004). High sediment loads are transported to the estuary by the Yangtze River every year (Liu et al., 2008). This causes the aggregation of sediment particles in the Yangtze Estuary and Hangzhou Bay, which in turn maintains the availability of dissolved-phase P via adsorption and/or desorption reactions.

In this paper, P sorption behavior in sediments collected close to wastewater outfalls in the Yangtze Estuary and Hangzhou Bay was investigated. The suitability of three commonly used sorption isotherm models was evaluated, along with the potential for predicting the dissolved reactive phosphate concentration by buffering experiments.

2 Materials and methods

2.1 Sampling

Surface sediment samples (0–2 cm) were collected from effluent outfall areas in the Yangtze Estuary and Hangzhou Bay using a CN-11 sediment sampler (Beijing Zhuochuan Electronic Technology Co., Ltd.) (Li et al., 2004). The locations of the three outfalls and the five sediment sampling sites are shown in Fig. 1. Two sampling sites (Z4 and W4) are located around the Zuyuan and Bailonggang outfall areas in the Yangtze Estuary. The distances between sampling sites and the outfalls are all approximately 0.5 km. These two outfalls discharge effluent from municipal wastewater treatment plants with chemical enhanced primary treatment processes. The other three sampling sites (A, B and F) are located in the area around the Xinghuo outfall, which discharges effluent from an industrial park wastewater treatment plant, in Hangzhou Bay. The distance between sampling site B and the outfall is also 0.5 km. The distance between sampling site B and A is 1 km and that between B and F is 3 km. Three sediments were obtained at each sampling site and stored together in one air-sealed plastic bag at 4 °C before being transported back to the laboratory (within 12 h). All sediments were subsequently air dried, homogenized and passed through a 0.15 mm sieve and then stored in wide-mouthed amber glass jars in a dry, ventilated place.

A description and characterization of all samples is shown in Table 1. The organic matter (OM) content in the sediment was determined by the potassium bichromate-dilution heat colorimetric method (Bao and Jiang, 1999). The particle size distributions of the sediment samples on a weight basis were determined by the pipette method (Beuselinck et al., 1998). Water samples were also collected around each sediment sampling site at the same time, which were analysed for dissolved inorganic phosphate (DIP) concentration (Table 1). Triplicate samples were used for all determinations and results are presented as means of three replicate analyses. Standard errors (not shown) were always less than ±5 % of the mean value.

2.2 Isothermal adsorption experiments

Phosphate sorption isotherms were determined experimentally. Aliquots of dry, sieved and ground sediment (0.5 g ± 0.0001 g) were placed in 250 mL glass conical flasks. Then, artificial sea water (100 mL, salinity 5), prepared according to the method proposed by Liu et al. (1982), with P were added to each flask. This solution was spiked with KH₂PO₄ to give one of seven nominal phosphorus concentrations (0.5, 2, 4, 8, 12, 16 and 20 mg P L⁻¹). Blank flasks containing no sediment were also prepared. Initial P concentrations in each incubation solution were determined by molybdate colorimetry (Kara et al., 1997). pH, including the blank experiments, was adjusted to a value of 8 using diluted KOH or HNO₃ in order to minimize pH variations due to the different amounts of KH₂PO₄ added. The conical flasks were sealed and shaken continuously at 200 rpm and 25 ±1 °C for 24 h and then centrifuged at 3000 rpm (maximum relative centrifugal force: 1207 g) for 10 min. Phosphate concentrations in the supernatant after centrifugation

<table>
<thead>
<tr>
<th>Site</th>
<th>DIP*(mg L⁻¹)</th>
<th>OM**(%)</th>
<th>Particle size composition (% total volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range Mean</td>
<td></td>
<td>0.25– 0.074– 0.005 mm 0.074 mm 0.005 mm</td>
</tr>
<tr>
<td>Xinghuo</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.040–0.077</td>
<td>0.048</td>
<td>0 73 27</td>
</tr>
<tr>
<td>B</td>
<td>0.02</td>
<td>0.82</td>
<td>0 95 5</td>
</tr>
<tr>
<td>F</td>
<td>0.25</td>
<td>0.77</td>
<td>58 36</td>
</tr>
<tr>
<td>Zhuyuan</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z4</td>
<td>0.004–0.076</td>
<td>0.042</td>
<td>0 72 28</td>
</tr>
<tr>
<td>Bailonggang</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W4</td>
<td>0.028–0.116</td>
<td>0.049</td>
<td>0 80 20</td>
</tr>
</tbody>
</table>

* DIP: Dissolved inorganic phosphate of the water samples; ** OM: Organic matter content of the sediment samples.
were determined and assumed to be the final P concentration. 
The difference between initial and final P concentrations was 
used to calculate phosphate adsorption capacity. Triplicate 
experiments were conducted for all samples and results were 
presented as means of three parallel determinations. Standard 
errors are not shown here since they were always less than ±5% of the mean value.

### 2.3 Phosphate buffer experiments

Phosphate buffering experiments, similar to the adsorption 
experiments described above, were carried out, except using 
very low initial P concentrations of 0, 0.04, 0.08, 0.12, 0.2, 
0.3, 0.4 and 0.5 mg P L\(^{-1}\), which represent the range of 
concentrations commonly encountered under natural conditions. The experiments were conducted at three constant temperatures of 12 °C, 22 °C and 32 °C, respectively, to investigate the influence of temperature on buffering capacity.

\([P_D]_{\text{initial}}\) represents the initial liquid-phase phosphate concentration before shaking, while \([P_D]_{\text{final}}\) represents the equilibrium liquid-phase phosphate concentration. The difference between \([P_D]_{\text{initial}}\) and \([P_D]_{\text{final}}\) is expressed as \(\Delta P_D\). P is absorbed by sediments when \(\Delta P_D\) is positive and desorbed from sediments when \(\Delta P_D\) is negative. \(\Delta P_D\) represents the P adsorbed or desorbed per unit mass of sediment.

### 3 Results and discussion

#### 3.1 Adsorption isotherm models

The adsorption isotherms of five sediment samples are shown in Fig. 2a. Langmuir, Freundlich and Temkin adsorption isotherm equations were well known and used in many previous studies (Borggaard et al., 2005). These three isotherm equations were obtained by least squares fitting to experimental sorption data. The isotherm equations, derived constants \((\Gamma_\infty, b, K \text{ and } n)\), correlation coefficients \((r)\) and standard deviation \((S)\) are shown in Table 2. The theoretical Langmuir and exponential isotherms are also plotted in Fig. 2a. Samples A, Z4 and W4 were all well described using the Langmuir adsorption isotherm with similar parameters. These curves are clearly distinct from the best-fit sorption isotherms obtained for samples B and F which were best described using exponential isotherms.

It is clear from Table 2 that the P-adsorption data for samples A, Z4 and W4 can be well described using all three isotherm models \((r \geq 0.968)\). The best suitable isotherm model for these three sediments was selected on the basis of the highest mean correlation coefficients \((r)\) and lowest mean standard deviation \((S)\) values for the three samples. Overall, the Langmuir equation was considered to give the best fit for these samples.
Sorption data from samples B and F were not well described by any of the isotherm equations ($0.463 < r < 0.801$). Visual inspection of the sorption data for these samples (Fig. 2a) suggests that an exponential model may be more appropriate for describing sorption in these samples. Least squares fitting of exponential equations to data from samples B and F yielded the following results:

B: $\Gamma = 16.464 \exp(0.1125c) \quad r = 0.930$

F: $\Gamma = 30.65 \exp(0.0588c) \quad r = 0.844$.

Equilibrium P-adsorption capacity versus initial liquid-phase phosphate concentrations for samples B and F are shown in Fig. 2b. When the initial P concentrations of the solution are lower than 12mg L$^{-1}$, the P-adsorption capacities of both samples are relatively low and remain approximately constant with increased phosphate concentration. When the initial phosphate concentrations are higher than 12 mg L$^{-1}$, on the other hand, the adsorption capacities increase rapidly. This suggests that precipitation reactions may occur during the adsorption process at high initial phosphate concentrations (Li and Stanforth, 2000). Phosphate exists as HPO$_4^{2-}$ during the adsorption process because the pH of this experimental system is 8. The Ca$^{2+}$ concentration of artificial seawater with salinity 5 used in the experiment is 0.00143M and the solubility product constant $K_{sp}$ of CaHPO$_4$ is $1 \times 10^{-7}$ at a temperature of 25 °C. Therefore, when the initial phosphate concentration of the solution is 12 mg L$^{-1}$, the ion product of HPO$_4^{2-}$ and Ca$^{2+}$ can be calculated as follows:

$$K = [\text{Ca}^{2+}] [\text{HPO}_4^{2-}] = 0.00143 \times 12 \times \frac{0.001}{31} = 5.5 \times 10^{-7} > K_{sp} = 1 \times 10^{-7}.$$  

The result shows that the condition for precipitation of CaHPO$_4$ is satisfied, which means that CaHPO$_4$ can precipitate on the surfaces of sediments B and F and results in
an increase in apparent P-adsorption capacity in these samples. This may also explain why the P-adsorption data of these samples are well described by the exponential equations. Note that the adsorption isotherms of samples A, Z4 and W4 do not show the same distinctive increase of P-adsorption capacity when the initial liquid-phase phosphate concentration is higher than 12 mg L$^{-1}$ (Fig. 2a). The following factors help to explain these different behaviors. First, as shown in Table 1, the percentage of the particles smaller than 0.005 mm in samples B and F is only 5–6%, which is much lower than that in samples A, Z4 and W4 (20–28%). This means that particles in samples A, Z4 and W4 are likely to have higher specific surface areas than those in samples B and F. Second, from Table 2, the P binding energy constants ($b$) calculated using the Langmuir equation for samples A, Z4 and W4 (0.346–0.428) are much higher than those for samples B and F (0.064–0.181). The constant $b$ represents the binding capacity of the sediment surface for phosphate. This means that when the ion product of HPO$_4^{2-}$ and Ca$^{2+}$ in the experimental system is saturated, the adsorption reaction continues to dominate in samples A, Z4 and W4 because of the high specific surface areas and strong P-binding capacities of these sediments (Özacar, 2003).

### 3.2 Buffering effects

The results of buffering adsorption experiments are shown in Fig. 3. At low initial P concentrations, the adsorption curve crosses the $x$-axis, where $\Delta P_s = 0$. This indicates the point at which there is no net P exchange between sediment and the incubation solution. The concentration of P in the equilibrium solution at $\Delta P_s = 0$ is termed the “zero equilibrium phosphate concentration (EPC$_0$)” and represents the concentration at which the sediments typically display their maximum buffering capacities to changes in solution P (Bridgham et al., 2001). The EPC$_0$ value is traditionally considered as the soluble P concentration for natural systems in long-term equilibrium.

The slope of the adsorption curve at $\Delta P_s = 0$ is the linear adsorption coefficient ($K$), which indicates the sediment’s buffering intensity at EPC$_0$ (and also the maximum buffering intensity for certain sediments). The P adsorbed to sediment at EPC$_0$ is called the equilibrium-adsorbed phosphate (Ps$_{EPC_0}$) and is a measure of the mass of reactive phosphate carried on per gram of sediment that is available for release to a solution devoid of phosphate. Ps$_{EPC_0}$ can be calculated by

$$\text{Ps}_{EPC_0} = K \cdot \text{EPC}_0 (\mu g \text{ P g}^{-1}).$$

The values of EPC$_0$, $K$ and Ps$_{EPC_0}$ (Table 3) for four sediment samples used in this study were obtained from the buffering adsorption data. The EPC$_0$ values ranged from 0.014 to 0.061 mg L$^{-1}$. The maximum EPC$_0$ was found in sample A (0.061 mg L$^{-1}$), although the EPC$_0$ value for sample Z4 was similar (0.057 mg L$^{-1}$). The EPC$_0$ values for samples B and F were relatively low (0.014 and 0.029 mg L$^{-1}$, respectively). Similar patterns were observed for $K$ values, which ranged between 0.177 and 0.562 L g$^{-1}$. The highest $K$ value (0.562 L g$^{-1}$) was observed in sample Z4, which also had the highest Ps$_{EPC_0}$ value (32.164 µg P g$^{-1}$). Sediment A also had a relatively high Ps$_{EPC_0}$ value (19.185 µg P g$^{-1}$). One possible explanation for the higher $K$ and Ps$_{EPC_0}$ values derived for samples A and Z4 compared to those of sediments B and F is the higher content of fine particles (< 0.005 mm) and organic matter in these sediments.

**Table 3.** Comparison of the buffering capacity of different sediments to phosphate.

<table>
<thead>
<tr>
<th>Sediment samples</th>
<th>EPC$_0$ (mg L$^{-1}$)</th>
<th>$K$ (L g$^{-1}$)</th>
<th>Ps$_{EPC_0}$ (µg P g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.061</td>
<td>0.314</td>
<td>19.185</td>
</tr>
<tr>
<td>B</td>
<td>0.014</td>
<td>0.177</td>
<td>2.490</td>
</tr>
<tr>
<td>F</td>
<td>0.029</td>
<td>0.220</td>
<td>6.304</td>
</tr>
<tr>
<td>Z4</td>
<td>0.057</td>
<td>0.562</td>
<td>32.164</td>
</tr>
</tbody>
</table>

EPC$_0$: Zero equilibrium phosphate concentration; $K$: Linear adsorption coefficient; Ps$_{EPC_0}$: Equilibrium-adsorbed phosphate.
Fig. 3. Relationship between equilibrium solution P concentration (mg L\(^{-1}\)) and the amounts of adsorbed or desorbed P (µg P g\(^{-1}\)) with very low initial P concentrations in the incubation solutions (up to 0.5 mg L\(^{-1}\)) for sediment samples A, B, F and Z4.

Water quality monitoring conducted at the same time as sediment sampling showed that the concentrations of soluble reactive phosphate in seawater close to the Zhuyuan outfall areas ranged between 0.004 and 0.076 mg L\(^{-1}\) (Table 1), coinciding with the value of EPC\(_0\) (0.057 mg L\(^{-1}\)) determined by the buffering experiment using sample Z4 (collected from the same area). There was similar agreement between experimental and water quality data for the Bailonggang and Xinghuo outfalls, suggesting that the concentration of phosphate in seawater is related to phosphate sorption to sediment.

3.3 Influence of temperature on sediment buffer capacity to phosphorus

The results of buffering experiments at different temperatures are shown in Fig. 4a for sample Z4. Values of EPC\(_0\) and K for this sediment at different temperatures are shown in Fig. 4b and c, respectively.

As the temperature (T) increases, values of EPC\(_0\) and K also increase (due to a shift in the sorption isotherm). However, the slope of the regression line for EPC\(_0\) is not significant. Increasing the temperature from 12 °C to 32 °C resulted in an increase in EPC\(_0\) for sediment Z4 from 0.04 to 0.06 mg L\(^{-1}\), which was similar to the observed
concentration of soluble reactive phosphate in seawater near the Zhuyuan outfall. The value of $K$ also increases with temperature, suggesting that buffering capacity of sediment for phosphate is enhanced as the temperature increases. The rate of both adsorption and desorption will increase with temperature. Thus, as well as shifting the equilibrium ratio between sorbed and dissolved phase P concentrations, the response time to changes in P availability will reduce at higher temperatures.

Most red tide algae tend to grow quickly at high temperatures (Dae-Il et al., 2004). For example, Yamaguchi et al. (2010) reported that *Chattonella ovata* could grow rapidly at temperatures over 20 °C and that maximal growth rates were between 25 and 30 °C. Our finding of increased P buffering capacity at high temperatures might be an explanation for this phenomenon.

4 Conclusions

- P sorption in sediments with a high fraction of fine particles was best described using the Langmuir equation. Sorption of P in sediments with a low fraction of fine particles was best described using an exponential sorption equation.

- The precipitation reaction of CaHPO$_4$ from Ca$^{2+}$ and HPO$_4$$^{2-}$ occurs in parallel with the sorption process in some samples when the dissolved phosphate concentration is higher than 12 mg L$^{-1}$. The increase in apparent P-sorption capacities at high initial P concentrations in these samples may be caused by this precipitation reaction and may explain why the sorption data were best described using an exponential model.

- The EPC$_0$ values derived from the buffer experiments ranged between 0.014 and 0.061 mg L$^{-1}$. These concentrations are consistent with measured phosphate concentrations in water samples collected from the Yangtze Estuary and Hangzhou Bay. They reveal a potential for predicting the dissolved P concentration using a sediment buffer experiment.

- The $K$ values vary from 0.177 to 0.562 L g$^{-1}$ and increase with increasing fine particle and organic matter content. It is suggested that sediments which are rich in fine particles and organic matter have stronger buffering capacities for phosphate.

- Values of sediment EPC$_0$ and $K$ all increase with increasing temperature. This may provide one explanation for why “red tides” tend to occur in warm weather, due to higher P buffering capacity at high temperatures.

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