Phosphorus Sorption Characteristics of Estuarine Sediments under Different Redox Conditions

H.K. Pant and K.R. Reddy*

ABSTRACT

Phosphorus (P) plays a major role in eutrophication of aquatic systems. Estuarine sediments could function as sources or sinks for P to the overlying water column depending upon their physico-chemical characteristics. Understanding of P sorption phenomena in estuarine sediments is important in regulating the P availability in estuaries. Phosphorus sorption characteristics of sediments from the Indian River Lagoon, Florida, USA, were determined to examine the role of selected physico-chemical properties of the sediments on soluble reactive P status in estuary water. Mean equilibrium P concentrations (EPC) of 0.75 mg L⁻¹ and mean P sorption maxima (Sₘₐₓ) of 32.2 mg kg⁻¹ were obtained under anaerobic conditions, compared with EPC of 0.95 mg L⁻¹ and Sₘₐₓ of 132.7 mg kg⁻¹ under aerobic conditions. The higher EPC values under anaerobic conditions and the greater Sₘₐₓ values under aerobic conditions were associated with amorphous and poorly crystalline iron. These results suggest that sediments enriched with amorphous and poorly crystalline forms of iron act as an excellent reservoir for P by adsorbing excessive P in aerobic sediment zones and releasing it upon burial under anaerobic conditions. This study also indicates that P compounds in sediments independently maintain equilibrium with P in solutions. Thus, heterogeneous systems like soil and sediment simply behave as a mixture of homogeneous surfaces as far as their P sorption characteristics are concerned, and hence can be successfully described by the Langmuir and Freundlich models.

Phosphorus occupies an important position in biological systems due to its key role in biochemical reactions. Phosphorus is a component of nucleic acids and nucleoside triphosphates, the basis of enzyme synthesis and energy transfer systems at the cellular level. Thus, P is one of the limiting nutrients and its adequate supply to biota is very important in regulating primary productivity. However, P is also a major contributor of eutrophication of surface water systems. Though there is a reduction of P reaching aquatic systems from point sources, nonpoint sources such as agricultural runoff are still bringing a substantial amount of P into aquatic systems. Moreover, knowledge is still limited on the role of sedimentary P in surface water P enrichment.

Understanding P sedimentation in the ocean is particularly important for quantifying outputs in the P cycle. There is much interest in the capability of sediments to sequester P because of its effect on oceanic P budget (Ruttenberg and Berner, 1993; Howarth et al., 1995) and productivity of estuaries (Caraco et al., 1990). Only a small portion of P is buried in sediments (Blazer, 1986; Sundby et al., 1992; Anschutz et al., 1998). Sedimentary P can function as an internal load to the overlying water column for a long period (Lijklema, 1993; Reddy et al., 1996).

The exchange of nutrients across the sediment–water interface in shallow coastal and estuarine systems has been the focus of number of studies (Hargrave, 1973; Collender and Hammond, 1982; Koop et al., 1990). Depending on limnological conditions, sediments can function either as sources or sinks for P (Fisher et al., 1982; Koop et al., 1990; Oliia and Reddy, 1995). The adsorption and desorption of P by sediments mainly depend on their physical, chemical, and biological properties. In general, sediments retain inorganic P at considerably greater concentrations than those observed in sediment porewater, whereas at low water column P concentrations, sediments function as a source of P (Froelich, 1988; Affif et al., 1993; Ravan and Hossner, 1993). In shallow lakes and lagoons, wind-driven sediment resuspension is a common phenomenon (Reddy et al., 1996; Kleeberg and Duda, 1997). During the process, surface layers of anaerobic bottom sediments can be resuspended into the aerobic water column and result in oxidation of ferrous ion, followed by retention of P as ferric phosphate (Moore and Reddy, 1994; Chambers et al., 1995). Phosphorus sorption phenomena have received extensive research because of their functional role in maintaining a bioavailable P pool for algal growth in aquatic systems and for higher plants in wetlands and terrestrial ecosystems. This study was conducted to (i) investigate the effects of selected physico-chemical characteristics of sediments on P sorption phenomena in estuaries and (ii) determine the capacity of estuarine sediments to function as sinks or sources for P to the overlying water column.

MATERIALS AND METHODS

Site Description

The Indian River Lagoon system is an integral component of water quality management and restoration of seagrass programs of the St. Johns River Water Management District, Florida. The lagoon system comprises Mosquito Lagoon, Banana River Lagoon, Indian River Lagoon, and all the tributaries and drainage canals, which deliver freshwater to these lagoons. This lagoon system covers a distance of 251 km along the east-central coast of Florida, extending southward from New Smyrna Beach (Volusia County) to Hobe Sound (Martin County) (Fig. 1). The major sources of freshwater for this lagoon system are natural streams, runoff, and a number of wastewater treatment plants. Mosquito Lagoon has one direct connection to the Atlantic Ocean and a connection to the

Abbreviations: EPCₑ, equilibrium phosphorus concentration; SRP, soluble reactive phosphorus; TOC, total organic carbon; TP, total phosphorus.

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Indian River Lagoon through Haulover Canal, an intracoastal waterway. The Banana River Lagoon also has some water exchange with the Atlantic Ocean via a system of locks at Port Canaveral, a home for commercial shipping and fishing. U.S. naval submarines, support vessels for the Kennedy Space Center, and Canaveral Air Force Station. The lagoon also has a connection with the Indian River Lagoon at the southern tip of Merritt Island. The Indian River Lagoon, however, has four connections to the Atlantic Ocean: Sebastian Inlet, Fort Pierce Inlet, St. Lucie Inlet, and Jupiter Inlet via Hobe Sound. This lagoon system has a surface area of 928 km² and an average depth of 1 m. Hydrodynamic energy is low in the northern part of the lagoon system (Mosquito Lagoon, the Banana River Lagoon, and the northern part of Indian River Lagoon); consequently, the waters are prone to stagnation and long pollutant residence times, although occasional flushing by large storms does occur (Ryther, 1985). This lagoon system is a biogeographic transition zone with the highest biological species diversity of any estuary in North America, about 2200 species, 35 of which are listed as endangered (St. Johns River Water Management District and South Florida Water Management District, 1994). There is a growing concern in the decline of biological integrity and slow transformation of the lagoon from a macrophyte-based ecosystem to a phytoplankton-based ecosystem due to poor sediment and water qualities caused by nutrient overenrichment.

**Sediment Sampling**

Triplicate sediment cores of 0 to 10 cm depth were obtained from nine representative locations of the Indian River Lagoon system (Fig. 1). The sediment samples were then immediately homogenized and sieved through a 5-mm sieve, and stored at 4°C until they were used for sorption experiments. Subsamples of the sediments were dried at 70°C and finely ground for total phosphorus (TP) analysis.

**Physico-Chemical Analysis**

The particle size distributions of the sediments were determined by the pipette method as described by Gee and Bauder (1986). Amorphous and poorly crystalline Fe and Al (hydr)oxides were determined by the oxalate method as described by Loepert and Inskeep (1996). Sediment (1 g) was extracted with 0.175 M ammonium oxalate + 0.1 M oxalic acid at a sediment to solution ratio of 1:60 by shaking on a end-over-end mechanical shaker for 4 h. The suspensions were then centrifuged at 5000 × g for 15 min and filtered through a 0.45-μm membrane filter. The filtrates were analyzed for Fe and Al by inductively coupled argon plasma spectrometry (Model 61E; Thermo Jarrell Ash, Franklin, MA). Oxalate-extractable P was determined in the filtrates using an automated ascorbic acid method as described for soluble reactive phosphorus (SRP) determination (Method 365.1; USEPA, 1983).

Total organic carbon (TOC) in sediments was determined as the difference between total carbon (TC) and total inorganic carbon (TIC). Total C was determined in sediments with a CNS analyzer (Carlo Erba [Milan, Italy] Model NA-1500) and TIC was determined in ash obtained after burning off the sediment samples at 550°C in a muffle furnace for 5 h.

Calcium (Ca) and magnesium (Mg) were extracted from sediments using 1 M HCl and analyzed by inductively coupled argon plasma spectrometry. The extracts were analyzed for SRP using the automated ascorbic acid method as described previously.

For total phosphorus (TP) determination, 0.5 to 1.0 g finely ground dry sediments were combusted at 550°C in a muffle furnace for 4 h and the ash was dissolved in 6 M HCl (Anderson, 1976). The digestate was analyzed for P using an automated ascorbic acid method (Method 365.4; USEPA, 1983).

**Phosphorus Sorption Experiments**

Batch incubation experiments were performed to determine P sorption characteristics of sediments under aerobic and anaerobic conditions. For incubation under aerobic conditions, 5 g (wet) sediments were placed in 50-mL centrifuge tubes and treated with 10 mL of solution containing 0, 0.1, 0.2, 0.5, 1, 2, 5, 10, 25, and 50 mg P L⁻¹ prepared in lagoon water (filtered through a 0.45-μm membrane filter). Thereafter, the tubes were shaken for a 24-h equilibration using an end-over-end mechanical shaker at 25 ± 2°C. The equilibrated samples were centrifuged at 5000 × g for 15 min and filtered through a 0.45-μm membrane filter. The filtrates were acidified with a drop of concentrated H₂SO₄ and stored at 4°C. Soluble reactive P was measured in the filtrates using the automated ascorbic acid method. Phosphorus not recovered in solutions was considered as the amount adsorbed by the sediments. The sediment residues were saved to perform the P desorption experiment.

Another set of similar experiments was conducted to study P adsorption by sediments under anaerobic conditions. Each sediment sample (5 g) was weighed in 50-mL centrifuge tubes and 9.0 mL of filtered lagoon water was added. Thereafter, the centrifuge tubes were fitted with rubber septa and purged with N₂ gas to create anaerobic conditions, and incubated in a water bath for 4 wk at 25 ± 2°C. To maintain anaerobic con-
conditions, the tubes were purged once a week during the preincubation period. At the end of the preincubation, 1.0 mL of 0, 1, 2, 5, 10, 20, 50, and 100 mg P L⁻¹ (to obtain the final concentrations 0.1, 0.2, 0.5, 1, 2.5, and 10 mg P L⁻¹) prepared in filtered lagoon water was added to each centrifuge tube. The tubes were purged again with N₂ gas and shaken on an end-over-end mechanical shaker for a 24-h equilibration. Following the equilibration, the samples were centrifuged at 5000 × g for 15 min and filtered through a 0.45-μm membrane filter under an N₂ atmosphere. The filtrates were then acidified with a drop of concentrated H₂SO₄ and analyzed for SRP as described above. The sediment residues were saved for the desorption experiment. The P desorption experiment was performed on sediment residues immediately after adsorption experiments. Sediment residues from aerobic adsorption experiments were equilibrated with 10 mL filtered lagoon water (filtered through a 0.45-μm membrane filter) using an end-over-end mechanical shaker for 24 h at 25 ± 2°C. Thereafter, desorbed P was measured in filtrates as described in adsorption experiments after centrifuging the sample at 5000 × g for 15 min and filtering through a 0.45-μm membrane filter. The filtrates were acidified with concentrated H₂SO₄ and analyzed for SRP as described previously. The difference in the amounts of P adsorbed and P recovered in solutions after equilibration was considered as the amount retained by the sediments (Pₐ) in a relatively stable form. The retention of adsorbed P was calculated from the slope of P adsorbed (Pₐ) vs. P solution (forced through origin). A similar desorption experiment was also performed on the sediment residues obtained from anaerobic P adsorption experiments by maintaining anaerobic conditions throughout the procedure using N₂ gas, as described previously.

**Data Analysis**

Unless otherwise stated, all experiments were conducted in triplicates and mean values are reported. Statistical analysis was performed using Statgraphics Plus Version 3.1 (Statistical Graphics Corp., 1997).

**Sorption Parameter Calculations**

The total amount of P adsorbed on sediments can be calculated as follows:

\[ S = S' + S₀ \]  \[ \text{[1]} \]

where \( S \) = total adsorbed P in sediment (mg kg⁻¹), \( S' \) = amount of added P retained by sediment (mg kg⁻¹), and \( S₀ \) = initial or native sorbed P in sediment (mg kg⁻¹).

Since at low equilibrium concentrations the relationship between \( S' \) and \( C \) (equilibrium concentrations) is typically linear (Rao and Davidson, 1979), the \( S₀ \) can be estimated by a least square fit using the following equation (Reddy et al., 1998):

\[ S' = K_d \times C \]  \[ \text{[2]} \]

where \( C \) = solution P concentration measured after a 24-h equilibration (mg L⁻¹).

By plotting the linear form of Eq. [2] (i.e., \( S' \) vs. \( C \)), the intercept is equal to \( S₀ \) and slope is equal to \( K_d \), a linear adsorption coefficient (L kg⁻¹) estimated without taking into account initially sorbed P (\( S₀ \)).

A frequently used term in P sorption phenomena, EPC₀, an equilibrium P concentration (mg L⁻¹), can be defined as the concentration of P in solution where no net adsorption or desorption of P occurs (i.e., \( S' = 0 \)).

Thus, by substituting the values of \( S' \) and \( C \) in Eq. [2], EPC₀ can be calculated as follows:

\[ EPC₀ = S'/K_d \]  \[ \text{[3]} \]

The P sorption parameters, sorption maxima (\( S_{max} \)) and bonding energy constant (\( k \)), were estimated using Langmuir equation:

\[ C_l/S = 1/k \times S_{max} + C/S_{max} \]  \[ \text{[4]} \]

where \( S_{max} \) = P sorption maximum (mg kg⁻¹) and \( k \) = a constant related to P bonding energy (L mg⁻¹). By plotting \( C_l/S \) vs. \( C_l \), the slope is equal to \( 1/S_{max} \) and the intercept is equal to \( 1/k \times S_{max} \).

Similarly, another P sorption parameter, energy of adsorption (\( K_l \)), was calculated using the Freundlich equation:

\[ S = K_l C_\text{l}^{1/n} \]  \[ \text{[5]} \]

where \( K_l \) = P adsorption energy (L mg⁻¹) and \( n \) = a correction factor.

By plotting the linear form of Eq. [5] (i.e., log S vs. log \( C_l \)), the slope is equal to \( 1/n \) and the intercept is equal to log \( K_l \).

Phosphorus retention (\( P_r \)) is defined as the amount of P adsorbed irreversibly onto the adsorbing surfaces. The \( P_r \) or hysteretic amount of P can be determined by equilibrating sediment, which is used for the P adsorption experiment, with water of no added P. The difference in the amounts of P adsorbed (\( P_a \)) and P recovered in solution after a 24-h equilibration is \( P_e \):

\[ P_e = P_a \times f \]  \[ \text{[6]} \]

where \( P_a \) is the P adsorbed and \( f \) is the ratio of \( P_e \) to \( P_a \). By plotting \( P_e \) vs. \( P_a \) and forcing the intercept through the origin, the slope is equal to the mean fraction of P retained. Thus, mean \( P_e = f \times 100\% \).

**RESULTS**

Sediments from Site 11 (Fig. 1; muddy sediments from the vicinity of Melbourne, FL), had the highest oxalate-extractable Fe and Al content compared with other sites examined in this study (Table 1). Despite the different ranges, a linear relationship \( (r^2 = 0.98) \) was observed between oxalate-extractable Fe and Al contents with Fe to Al mass ratios ranging from 2.4 to 4.5. The HCl-extractable Ca and Mg in Site 11 sediments were also highest compared with sediments from other sites. Though pH could vary under aerobic and anaerobic conditions and ultimately affect the P sorption phenomena in sediments, no significant changes in pH were observed between these conditions. The HCl-extractable P represented 24 to 90% of TP, whereas oxalate-extractable P represented only 4 to 16% of TP in sediments.

Higher equilibrium P concentrations (EPC₀) were observed under anaerobic conditions compared with aerobic conditions (Table 2). Though higher EPC₀ values under anaerobic conditions were associated with higher oxalate-extractable Fe content in the sediments (Table 3), some sediment had higher EPC₀ in spite of a lower oxalate-extractable Fe content (Table 1). A multiple linear regression analysis showed that total organic carbon (TOC) played a reverse role compared with oxalate-extractable Fe in determining EPC₀ under anaerobic conditions (Table 4). Under aerobic conditions,
Table 1. Selected physico-chemical characteristics of sediments from the Indian River Lagoon (n = 3).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxalate-extractable</th>
<th>HCl-extractable</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>Fe</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>mg kg$^{-1}$</td>
<td>%</td>
<td>mg kg$^{-1}$</td>
</tr>
<tr>
<td>I-1</td>
<td>308</td>
<td>1399</td>
<td>145</td>
</tr>
<tr>
<td>I-2</td>
<td>186</td>
<td>775</td>
<td>64</td>
</tr>
<tr>
<td>I-3</td>
<td>45</td>
<td>191</td>
<td>15</td>
</tr>
<tr>
<td>I-5</td>
<td>134</td>
<td>495</td>
<td>42</td>
</tr>
<tr>
<td>I-8</td>
<td>58</td>
<td>196</td>
<td>13</td>
</tr>
<tr>
<td>I-11</td>
<td>1172</td>
<td>3 863</td>
<td>260</td>
</tr>
<tr>
<td>I-13</td>
<td>133</td>
<td>320</td>
<td>11</td>
</tr>
<tr>
<td>I-15</td>
<td>79</td>
<td>264</td>
<td>21</td>
</tr>
<tr>
<td>I-21</td>
<td>84</td>
<td>231</td>
<td>24</td>
</tr>
</tbody>
</table>

† Total organic carbon.  
‡ Total phosphorus.

However, EPC$_0$ was affected by oxalate-extractable Al, and HCl-extractable Ca and Mg contents.

All P sorption isotherms were L-shaped (Langmuir isotherms) regardless of the redox (anaerobic or aerobic) conditions. In general, both under anaerobic and aerobic conditions, the P sorption isotherms were better fitted to the Langmuir model than to the Freundlich model, except for sediments with high oxalate-extractable Fe and Al. An increase in distinctness of multiple slopes in Freundlich isotherms under aerobic conditions was observed corresponding to increasing oxalate-extractable Fe and Al, and HCl-extractable Mg (Fig. 2).

A lower P sorption maxima ($S_{\text{max}}$) and energy of adsorption ($K_t$) were observed under anaerobic conditions compared with aerobic conditions (Table 2). A multiple linear regression analysis indicated a dominant role of HCl-extractable Mg and oxalate-extractable Fe in determining $K_t$ under anaerobic conditions, whereas oxalate-extractable Fe was the component that dominated under aerobic conditions (Table 4). Though both Ca and Mg could play a significant role in determining $K_t$ under anaerobic conditions, Mg showed a major role. Total organic C could explain 81% of the variability in $S_{\text{max}}$ under anaerobic conditions, whereas oxalate-extractable Fe could explain 94% of variability in $S_{\text{max}}$ under aerobic conditions.

Under anaerobic conditions, desorption of P was higher in sediments with high oxalate-extractable Fe compared with sediments with low oxalate-extractable Fe (Table 2). In other words, a negative correlation existed between oxalate-extractable Fe and P retained ($P_r$) under anaerobic conditions (Table 3). On the contrary, under aerobic conditions, sediments with high oxalate-extractable Fe desorbed virtually no P; that is, there was a positive correlation between oxalate-extractable Fe and $P_r$. A multiple linear regression analysis also indicated that oxalate-extractable Fe was positively correlated with $P_r$ under aerobic conditions and negatively correlated under anaerobic conditions (Table 4). Under aerobic conditions, $P_r$ was positively correlated to HCl-extractable Ca, however, it was negatively correlated to oxalate-extractable Al. Under anaerobic

Table 2. Phosphorus sorption characteristics of the Indian River Lagoon sediments under different redox conditions.

<table>
<thead>
<tr>
<th>Redox condition</th>
<th>Sampling site</th>
<th>$K_t$</th>
<th>$S_{\text{max}}$</th>
<th>EPC$_0$</th>
<th>$S_{\text{max}}$</th>
<th>$k$</th>
<th>$P_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L kg$^{-1}$</td>
<td>mg kg$^{-1}$</td>
<td>mg L$^{-1}$</td>
<td>mg kg$^{-1}$</td>
<td>L mg$^{-1}$</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Aerobic</td>
<td>I-1</td>
<td>190.8</td>
<td>16.5</td>
<td>0.01</td>
<td>222.2</td>
<td>6.43</td>
<td>616</td>
</tr>
<tr>
<td></td>
<td>I-2</td>
<td>82.6</td>
<td>0.6</td>
<td>0.01</td>
<td>67.1</td>
<td>0.59</td>
<td>29.3</td>
</tr>
<tr>
<td></td>
<td>I-3</td>
<td>15.9</td>
<td>2.9</td>
<td>0.19</td>
<td>85.8</td>
<td>0.16</td>
<td>9.8</td>
</tr>
<tr>
<td></td>
<td>I-5</td>
<td>26.1</td>
<td>0.4</td>
<td>0.01</td>
<td>64.1</td>
<td>0.36</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td>I-8</td>
<td>15.2</td>
<td>1.2</td>
<td>0.01</td>
<td>188.7</td>
<td>0.15</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>I-11</td>
<td>346.6</td>
<td>4.3</td>
<td>0.01</td>
<td>500.0</td>
<td>4.00</td>
<td>1467</td>
</tr>
<tr>
<td></td>
<td>I-13</td>
<td>21.1</td>
<td>-1.3</td>
<td>0.06</td>
<td>31.2</td>
<td>0.32</td>
<td>5.8</td>
</tr>
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<td></td>
<td>I-15</td>
<td>38.6</td>
<td>-1.6</td>
<td>0.08</td>
<td>67.6</td>
<td>0.23</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td>I-21</td>
<td>42.6</td>
<td>-0.9</td>
<td>0.02</td>
<td>47.8</td>
<td>0.62</td>
<td>10.7</td>
</tr>
<tr>
<td>Anaerobic</td>
<td>I-1</td>
<td>2.3</td>
<td>-8.6</td>
<td>3.74</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td></td>
<td>I-2</td>
<td>14.7</td>
<td>-2.0</td>
<td>0.14</td>
<td>38.8</td>
<td>0.61</td>
<td>10.2</td>
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<td></td>
<td>I-4</td>
<td>5.5</td>
<td>-1.5</td>
<td>0.28</td>
<td>42.2</td>
<td>0.16</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>I-5</td>
<td>14.8</td>
<td>-5.4</td>
<td>0.36</td>
<td>24.6</td>
<td>0.71</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>I-8</td>
<td>17.6</td>
<td>-3.1</td>
<td>0.18</td>
<td>27.5</td>
<td>0.72</td>
<td>10.1</td>
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<td>14.4</td>
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<td>0.23</td>
<td>1.7</td>
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<td></td>
<td>I-15</td>
<td>9.9</td>
<td>-1.3</td>
<td>0.15</td>
<td>24.1</td>
<td>0.44</td>
<td>6.4</td>
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<tr>
<td></td>
<td>I-21</td>
<td>7.8</td>
<td>-1.3</td>
<td>0.17</td>
<td>20.0</td>
<td>0.52</td>
<td>5.3</td>
</tr>
</tbody>
</table>

† Linear adsorption coefficient.  
‡ Initial adsorbed P at C = 0 (— sica represents the desorbable P).  
§ Equilibrium P concentration.  
¶ Sorption maxima.  
# Bonding energy.  
†† Phosphorus retained.  
§§ Percent phosphorus adsorbed.  
¶¶ Not determined.
conditions, TOC was positively correlated to $P_r$, and together with oxalate-extractable Fe, TOC could explain 71% of variability in the $P_r$. Sediments containing a low amount of oxalate-extractable Al and Fe, and HCl-extractable Ca and Mg did not show a major difference in P retained under aerobic and anaerobic conditions.

**DISCUSSION**

A linear relationship was observed between clay content, and oxalate-extractable Fe and Al because of the occurrence of Fe and Al oxides predominantly in clay (Bertsch and Bloom, 1996; Loeppert and Inskeep, 1996). The oxalate-extractable Fe and Al represent amorphous and poorly crystalline forms (Loeppert and Inskeep, 1996), which are important in regulating P sorption (Nair et al., 1998; Reddy et al., 1998). Though Ca and Mg could also adsorb P, however, the formation of recalcitrant P compounds including apatite permanently sequesters P (Ruttenberg and Berner, 1993), which could be dominant in oceanic systems and estuaries.

The EPC, is defined as the P concentration in the sediment porewater at which neither adsorption nor desorption occurs. Higher EPC, values under anaerobic conditions were expected because of the reduction of Fe(III) to Fe(II) under anaerobic conditions and consequent release of Fe-bound P. A reverse role of TOC compared with Fe in determining EPC, under anaerobic conditions may imply that the P released by Fe could be picked up by sediment organic matter and ultimately reduce the EPC, Under aerobic conditions, a positive correlation of EPC, with oxalate-extractable Al and HCl-extractable Ca, and a negative correlation with HCl-extractable Mg, may indicate that Mg adsorbs P from solutions and contributes in lowering EPC,. These results indicate that every P compound in sediments maintains equilibrium independently with P in solutions. This may help to explain why Langmuir and Freundlich models, which are basically derived to describe sorption phenomena in homogeneous surfaces, could also successfully describe the phenomena in heterogeneous systems like soil and sediment. The maintenance of independent equilibrium by P compounds may suggest that the heterogeneous systems like soil and sediment simply behave as a mixture of homogeneous surfaces as far as their sorption characteristics are concerned. This implies that P advection or sequestration in estuarine sediments involves complex mechanisms mainly regulated by redox conditions. Redox-dependent P retention–release phenomena have been reported in laboratory incubation of coastal sediments (Blazer, 1984), and several continental margin environments (Aller, 1980; Ingall and Jahnke, 1994). Perhaps, in relatively deeper estuarine and oceanic systems, sediments may release P because of the absence of an oxidized sediment layer. However, in shallow estuaries and coastal areas, sediments could either supply needed P for the primary

<table>
<thead>
<tr>
<th>Parameter†</th>
<th>Aerobic</th>
<th>Anaerobic</th>
<th>Aerobic</th>
<th>Anaerobic††</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ox-Fe</td>
<td>0.971*</td>
<td>0.893*</td>
<td>-0.422</td>
<td>0.975*</td>
</tr>
<tr>
<td>Ox-Al</td>
<td>0.960*</td>
<td>0.880*</td>
<td>-0.395</td>
<td>0.979*</td>
</tr>
<tr>
<td>HCl-Ca</td>
<td>0.752*</td>
<td>0.791*</td>
<td>0.039</td>
<td>0.647*</td>
</tr>
<tr>
<td>HCl-Mg</td>
<td>0.962*</td>
<td>0.894*</td>
<td>-0.446</td>
<td>0.971*</td>
</tr>
<tr>
<td>TOC</td>
<td>0.943*</td>
<td>0.901*</td>
<td>-0.347</td>
<td>0.975*</td>
</tr>
</tbody>
</table>

* Significant at the 0.05 probability level.
† Ox, oxalate-extractable (mg kg$^{-1}$); HCl, HCl-extractable (mg kg$^{-1}$); TOC, total organic carbon (mg kg$^{-1}$).
‡ Sorption maxima.
§ Equilibrium P concentration.
¶ Adsorption energy.
†† Data from sample 1-1 not included.

### Table 4. Multiple linear regression analysis of P sorption parameters and selected independent variables under different redox conditions ($n = 9$; $P \leq 0.1$)

<table>
<thead>
<tr>
<th>Redox condition</th>
<th>Fitted model equation†</th>
<th>$R^2$</th>
<th>SE§</th>
<th>DW¶</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aerobic</strong></td>
<td>$EPC, = 0.021 + 0.0004$ (ox-Al) $+ 0.0000002$ (HCl-Ca) $- 0.00001$ (HCl-Mg)</td>
<td>93.5</td>
<td>0.011</td>
<td>1.9</td>
</tr>
<tr>
<td>$K_r = -114.6 + 0.413$ (ox-Fe)</td>
<td>96.7</td>
<td>97.2</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>$S_{max} = 28.6 + 0.121$ (ox-Fe)</td>
<td>94.3</td>
<td>38.1</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>$P_r = 84.2 - 0.071$ (ox-Al) $+ 0.021$ (ox-Fe) $+ 0.0003$ (HCl-Ca)</td>
<td>81.5</td>
<td>3.36</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td><strong>Anaerobic</strong></td>
<td>$EPC, = -0.231 + 0.004$ (ox-Fe) $- 0.0003$ (TOC)</td>
<td>87.4</td>
<td>0.496</td>
<td>2.8</td>
</tr>
<tr>
<td>$K_r = 6.7 - 0.016$ (ox-Fe) $+ 0.017$ (HCl-Mg)</td>
<td>64.6</td>
<td>2.85</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>$S_{max} = 22.8 + 0.001$ (TOC)</td>
<td>81.2</td>
<td>8.89</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>$P_r = 90.0 - 0.04$ (ox-Fe) $+ 0.0027$ (TOC)</td>
<td>71.3</td>
<td>8.47</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

† EPC, equilibrium P concentration; ox-Al, oxalate-extractable Al (mg kg$^{-1}$); HCl-Ca, 1 M HCl-extractable Ca (mg kg$^{-1}$); HCl-Mg, 1 M HCl-extractable Mg (mg kg$^{-1}$); $K_r$, adsorption energy; ox-Fe, oxalate-extractable Fe (mg kg$^{-1}$); $S_{max}$, sorption maxima; $P_r$, phosphorus retained; TOC, total organic carbon (mg kg$^{-1}$).
‡ Equivalent to variability explain.
§ Standard error of estimation.
¶ Durbin–Watson statistic (value > 1.4 indicates no autocorrelation in the residuals).
# Data from 1-1 not included.
production of water columns and result in eutrophication or sequester P depending on the changes in redox status as mainly affected by wind-induced turbulence. The L-shape of all P sorption isotherms (Langmuir isotherms) regardless of the redox conditions (anaerobic or aerobic) indicated that affinities of the sediment components for P increased at low P solution concentrations, and decreased at high P solution concentrations, as the adsorbent in sediments were saturated with P. In general, the better fit of P sorption isotherms to the Langmuir model compared with the Freundlich model under both aerobic and anaerobic conditions may suggest that amorphous and poorly crystalline forms of Fe and Al play major roles in P sorption phenomena in estuarine sediments. This supports a view that nonsilicates, especially freshly precipitated forms of Fe oxides, possess high P sorption capacities (Efimov et al., 1996), although they also release P upon reduction of Fe(III) to Fe(II). Since P release from sediments is an important mechanism in estuaries, a wind-driven sediment resuspension phenomena could substantially increase P in the water column by repetitive washoff of sediments by relatively low P seawater, ultimately increasing its primary productivity.

A lower P sorption maxima (S_{max}) and adsorption coefficient (K_s) under anaerobic conditions compared with aerobic conditions were expected because of the desorption of P from Fe–P compounds due to the reduction of Fe(III) to Fe(II). Though both Ca and Mg could play a significant role in determining K_s under anaerobic conditions, Mg showed a major role. The mass ratio of Ca to Mg was high (>10), that is, the system was relatively dominated with CaCO_3 compared with MgCO_3, which left Mg available for adsorption of P. Thus, a dominating role of Mg over Ca could be expected in determining K_s in these sediments under anaerobic conditions. Amorphous and poorly crystalline Fe and Al are known to control P sorption in sediments; it appears that calcareous materials including Ca and/or Mg carbonates could also play a greater role than previously thought in P sequestration or advection processes in sediments. In shallow marine or lakes, up to 50% of the primary production of surface waters is remineralized in sediments (Hargrave, 1980; Nixon et al., 1980). Though biological uptake of P during decomposition of organic materials is significant (Tezuka, 1986; Carlton and Wetzel, 1988) due to the very reactive nature of P, its specific sorption after remineralization by various minerals dictates its availability for primary production of aquatic ecosystems. Despite a clearly established linkage of solid P minerals to solution P chemistry, it is widely realized that in solution, P quickly sorbs onto or releases from a wide variety of surfaces through sorption reactions (Froelich, 1988). The combined effect of rapid adsorption and desorption of P may create a sharp gradient in soluble P to be sustained in the sediment–water interface of aquatic systems, which could result in a significant flux of P to the water column.

Phosphorus, once sorbed, is not easily desorbed (Barrow, 1983). Under aerobic conditions, P_s was positively correlated to HCl-extractable Ca, but negatively correlated to oxalate-extractable Al. This may indicate that P adsorbed on amorphous and crystalline forms of Al is not as stable as P adsorbed on crystalline and amorphous forms of Fe or HCl-extractable Ca. A positive correlation between TOC and P_s under anaerobic conditions may explain the reason for higher P_s in some sediment despite the higher amorphous and poorly crystalline forms of Fe.

CONCLUSIONS

This study indicates that P sorption phenomena in lagoon sediments are highly influenced by amorphous and poorly crystalline forms of Fe, as shown by highly significant correlation (r > 0.95) between oxalate-extractable Fe and EPC_a under anaerobic conditions, and P adsorption energy (K_s) under aerobic conditions. However, the difference in the P sorption nature of poorly crystalline and amorphous Fe and Al, and Ca and/or Mg carbonates under different redox conditions may suggest that their collective role in sediments primarily controls the productivity of estuarine or coastal waters. The salinity gradients of estuaries generally show characteristic behaviors along the profiles (Froelich, 1988), for example, offshore upwelling of P-rich seawater (van Bennekom et al., 1978), regeneration of detritus (Edmond et al., 1981), benthic fluxes (Nixon et al., 1980), and input from pollution sources. Though marine systems are mainly N-limited (Ryther and Dunstan, 1971; Frithsen et al., 1988), several freshwater and estuarine systems are P-limited (Caraco et al., 1990), including the Indian River Lagoon. With the average depth of 1 m, in general, the Indian River Lagoon is a shallow estuarine system and prone to wind-induced turbulence. This may create a sharp gradient of soluble P in the sediment–water interface due to rapid adsorption–desorp-
tion phenomena, and consequently increase $P$ flux to the water column and degrade water quality by algal growth.

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