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Spatial Variation in Sediment-Water Exchange of Phosphorus in Florida Bay: AMP As a Model Organic Compound

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Dissolved organic phosphorus (DOP) has been recognized as dominant components in total dissolved phosphorus (TDP) pools in many coastal waters, and its exchange between sediment and water is an important process in biogeochemical cycle of phosphorus. Adenosine monophosphate (AMP) was employed as a model DOP compound to simulate phosphorus exchange across sediment-water interface in Florida Bay. The sorption data from 40 stations were fitted to a modified Freundlich equation and provided a detailed spatial distribution both of the sediment's zero equilibrium phosphorus concentration (EPC_{0-T}) and of the distribution coefficient (K_{d-T}) with respect to TDP. The K_{d-T} was found to be a function of the index of phosphorus saturation (IPS), a molar ratio of the surface reactive phosphorus to the surface reactive iron oxide content in the sediment, across the entire bay. However, the EPC_{0-T} was found to correlate to the contents of phosphorus in the eastern bay only. Sediment in the western bay might act as a source of the phosphorus in the exchange process due to their high EPC_{0-T} and low K_{d-T} , whereas sediments in the eastern bay might act as a sink because of their low EPC_{0-T} and high K_{d-T} . These results strongly support the hypothesis that both phosphorus and iron species in calcareous marine sediments play a critical role in governing the sediment-water exchange of both phosphate and DOP in the coastal and estuarine ecosystems.

Introduction

Sediments, including suspended solids in the water column, have been identified as the dominant phosphorus reservoir, providing a phosphorus-buffering system in many freshwater, estuarine, and coastal ecosystems (1). The particulate phosphorus can be transformed to biologically available dissolved phosphate through various processes, such as dissolution, desorption, and hydrolysis, and these processes are often influenced by ambient salinity and redox conditions (2, 3). Understanding the processes of phosphorus exchange

across the sediment-water interface is essential in modeling phosphorus cycle in estuarine and coastal waters (4, 5). These processes are particularly important in coastal ecosystems such as Florida Bay, where dissolved phosphate in the water column is present at nanomolar levels (6, 7), and phosphorus has been identified as a limiting nutrient to seagrass, phytoplankton, and bacteria production (8, 9). Recently, we have made systematic studies on the sediment phosphorus speciation and sediment-water exchange of the phosphate in Florida Bay and revealed the importance of the sedimentary phosphorus and iron content in sediment-water exchange of phosphate in Florida Bay (10). However, our long-term water quality monitoring data demonstrated that the DOP in bay waters is consistently higher than that of the dissolved phosphate (6, 7), and approximately 60% of exchangeable phosphorus in sediment is organic (11). Moreover, high concentrations of TDP ($\sim 20 \mu\text{M}$, 60% being DOP) were found to associate with red tide blooms in southwest coastal waters of Florida (12, 13). Despite the relatively high concentration of DOP in natural waters, little is known about the role DOP plays in phosphorus exchange processes across the sediment-seawater interface. This is in part because the chemical composition of DOP pool is unknown (14, 15), and the transformation between different phosphorus species is likely to occur in sediment-water system. Addition of DOP to a sediment-water system can induce many processes other than sorption. For example, change in DOP composition and increase in phosphate concentrations have been reported in soil experiments (16, 17). This has been hypothesized as a result of replacement of native phosphate and organic phosphorus adsorbed on soil surface by the DOP added in the solution (18, 19). But the increase in phosphate in solution can also result from the hydrolysis of added DOP, a process known to be catalyzed by natural enzyme and promoted by some mineral surfaces (20). Therefore, the net change of TDP is used to characterize the overall sediment-water exchange of phosphorus in the presence of DOP in this study.

Because the composition of bulk dissolved organic phosphorus pools in natural waters is unknown (14, 15), a simple organic phosphorus compound is usually used as a model (16, 17). Adenosine monophosphate (AMP) is an ester of phosphoric acid and the nucleoside adenosine, which consists of a phosphate group, the sugar ribose, and the nucleobase adenine, can be produced during ATP synthesis or by the hydrolysis of adenosine diphosphate (ADP). When RNA is broken down by living systems, nucleoside monophosphates, including AMP, are also formed. Since AMP has a relatively simple structure, widely occurs in seawater, and has been demonstrated to adsorb on marine sediments (14, 15, 21, 22), we employed it as a model compound to explore its sorption behavior on Florida Bay sediments. The objective of this study is to identify the linkage between AMP exchange and sediment characteristics, such as sediment P, Fe, and organic matter content that have been documented in previous studies (10, 11). To our knowledge, only very limited works on the sorption of model organic phosphorus compounds in soils have been reported (16, 17, 23–26). This study represents the first systematic study on the exchange of phosphorus induced by addition of model DOP between the marine sediment and seawater. We believe that it is essential to elaborate phosphorus-buffering system in estuarine and coastal ecosystems.

Experimental Procedures

Study Region. Florida Bay is one of the world's largest (2200 km²) coastal lagoons located at the southern end of Florida

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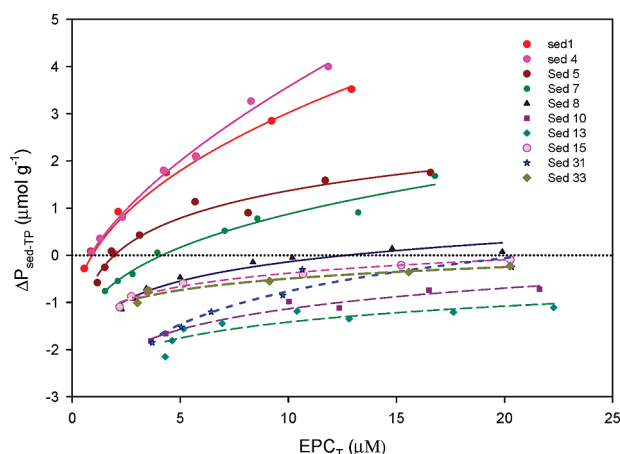


FIGURE 1. Typical phosphorus sorption isotherms obtained from addition of AMP to Florida Bay sediments. The solid lines represent the results of sediments from the eastern bay (stations 1, 4, 5, 7, and 8, respectively), and the dotted lines represent those from the western bay (stations 10, 13, 15, 31, and 33, respectively).

peninsula, USA and its sediment is dominated by biogenic carbonate which strongly adsorbs phosphate (27). The fine-grained carbonate muds are readily resuspended to the surface by wind and tidal mixing in the shallow waters of Florida Bay (average water depth ~ 1 m) (5).

Surface sediment samples were collected at 40 locations across Florida Bay (Figure S2). Detailed sampling information was given elsewhere (11). Different forms of phosphorus in the sediment samples used in this study had been quantified by sequential extraction in previous study (11). Based on the content of sedimentary phosphorus, Florida Bay can be divided into western and eastern bay. The western bay included the stations 9 to 16 and 31 to 35 with total sedimentary phosphorus (TSP) greater than $7 \mu\text{mol g}^{-1}$ (11). The eastern bay included the stations 1 to 8 and 17 to 40 with their TSP lower than $7 \mu\text{mol g}^{-1}$ (11). The western bay is directly influenced by Gulf of the Mexico seawater. In contrast, the major fresh water inputs from Taylor Slough and the C-111 canal are located in eastern bay. It was found that more than 60% of organic matter in the eastern bay sediments is derived from terrestrial (mangrove), whereas seagrass is the main sources of organic matter in the western bay (28).

Sorption Isotherm Experiments. Because of unidentified background DOP present in seawater, salinity 36 artificial seawater was employed for these experiments (29). For each station, a 100 mg of sediment was mixed with 49 mL of artificial seawater in a 60-mL high-density polypropylene bottle. One milliliter of chloroform was added to the mixture to inhibit microbial activity, and sediments were conditioned with the artificial seawater for 4 days to ensure complete hydration. During conditioning, the mixture was agitated by a temperature-controlled orbital shaking incubator at 200 rotations per minute at $25 \pm 0.1^\circ\text{C}$. At the end of conditioning, an aliquot of AMP stock solution was added to samples so that the initial concentration, $[P_{T}]_i$, ranged from 0 to $20 \mu\text{M}$. The samples were then placed back to the shaking incubator and shaken for another 24 h. After 24 h, the slurry was filtered through a $0.45 \mu\text{m}$ pore size filter. The filtrates were analyzed for phosphate and TDP. TDP samples were digested by the persulfate autoclave, with the calibration standards made by the AMP (30, 31). The TDP and phosphate were determined by a modified phosphomolybdenum blue method with a Hewlett-Packard 8453 spectrophotometer (32).

Our preliminary experiments confirmed previous observation from soils that a considerable amount of phosphate can be released in the sorption experiments with the addition

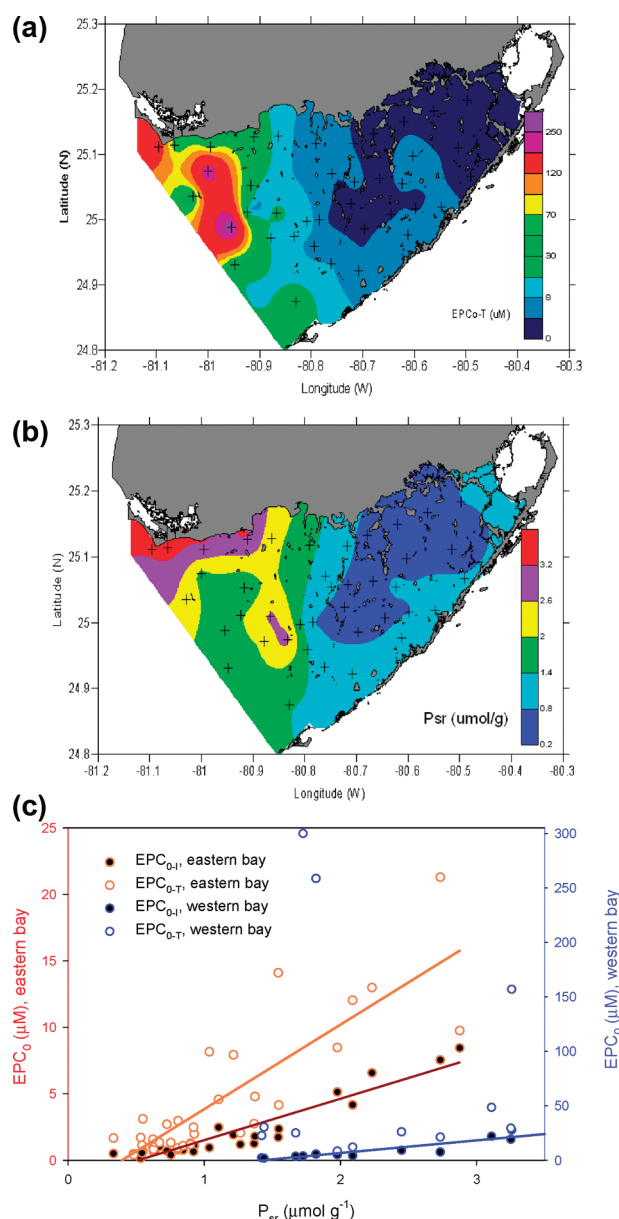


FIGURE 2. Spatial distribution of (a) EPC_{0-T} , (b) P_{sr} in Florida Bay, and (c) their relationships (see Table 1 for respective correlation coefficients). It is noted that there was no significant correlation of the EPC_{0-T} with P_{sr} in the western bay.

of phosphate esters (Figure S1) (16, 17, 23, 24). The results suggest that some of the added phosphate esters were hydrolyzed during the exchange process (16, 17, 20). However, some of phosphate could also result from the replacement of native adsorbed phosphate by the organic phosphorus added as suggested by previous studies (18, 19). Furthermore, it is also possible that the native adsorbed organic phosphorus on sediment is being replaced by the AMP added, resulting in unknown DOP compounds released to seawater. Because the exchange processes result in a change in phosphorus composition in the final solution, the net change in phosphorus (TDP) instead of the added DOP is used to characterize the overall sediment-water exchange processes in this study.

A final concentration of TDP in the suspension, $[P_T]_f$, was operationally defined as an equilibrium TDP concentration, EPC_T . The difference between $[P_T]_i$ and $[P_T]_f$ in seawater was used to calculate the amount of phosphorus adsorbed (if positive) to or desorbed (if negative) from sediment, $\Delta[P_{sed-T}]$.

TABLE 1. Relationships between the Sorption Parameters and the Content of Different Phosphorus Forms in Sediment^a

region	total dissolved phosphorus sorption		inorganic phosphate sorption	
	equation	r^2	equation	r^2
eastern bay (28 stations)	$EPC_{0-T} = 47.94(IP_{exch}) - 1.30$	0.65	$EPC_{0-I} = 22.525(IP_{exch}) - 0.89$	0.75
	$EPC_{0-T} = 17.37(TP_{exch}) - 1.35$	0.67	$EPC_{0-I} = 8.814(TP_{exch}) - 1.14$	0.90
	$EPC_{0-T} = 6.36(P_{sr}) - 2.51$	0.71	$EPC_{0-I} = 3.12(P_{sr}) - 1.61$	0.89
	$EPC_{0-T} = 1.31(TSP) - 0.86$	0.63	$EPC_{0-I} = 0.65(TSP) - 0.85$	0.82
western bay (12 stations)			$EPC_{0-I} = 31.64(TP_{exch}) - 14.93$	0.86
			$EPC_{0-I} = 3.38(TSP) - 26.39$	0.57
			$EPC_{0-I} = 11.49(P_{sr}) - 16.34$	0.85
Florida Bay (40 stations)	$K_{d-T} = 0.0074(IP_{exch})^{-1.325}$	0.38	$K_{d-I} = 0.0366(IP_{exch})^{-0.912}$	0.85
	$K_{d-T} = 0.0229(TP_{exch})^{-1.514}$	0.40	$K_{d-I} = 0.0806(TP_{exch})^{-1.024}$	0.86
	$K_{d-T} = 0.1425(P_{sr})^{-1.699}$	0.38	$K_{d-I} = 0.0279(P_{sr})^{-1.168}$	0.84
	$K_{d-T} = 0.278(TSP)^{-1.619}$	0.48	$K_{d-I} = 1.033(TSP)^{-0.989}$	0.84
	$K_{d-T} = 0.21 \ln(IPS) + 0.11$	0.55	$K_{d-I} = 0.21 \ln(IPS) + 0.17$	0.75

^a All correlations are statistically significant ($p < 0.01$).

$$\Delta[P_{sed-T}] = [P_T]_i - [P_T]_f \quad (1)$$

The results can be described by a modified Freundlich equation as follows

$$\Delta[P_{sed-T}] + NAP_T = K_{f-T}([P_T]_f)^n \quad (2)$$

where NAP_T is the native adsorbed TDP, K_f is the Freundlich coefficient, and n is the exponential factor. A plot of $\Delta[P_{sed-T}]$ versus $[P_T]_f$ is called the adsorption isotherm of TDP. The value of $[P_T]_f$ at $\Delta[P_{sed-T}] = 0$ is EPC_{0-T} , representing a crossover concentration at which sediment is in equilibrium with seawater with respect to exchange of phosphorus. Sediment at EPC_{0-T} displays a maximum capacity for buffering phosphorus in seawater. The slope of the isotherm curve at $\Delta[P_{sed-T}] = 0$ is the distribution coefficient K_{d-T} , which is calculated by taking the derivative of the modified Freundlich equation with respect to $[P_T]_f$ at the EPC_{0-T}

$$K_{d-T} = d[K_{f-T}([P_T]_f)^n] / d([P_T]_f)_{EPC_{0-T}} = nK_{f-T}([P_T]_f)^{n-1} \quad (3)$$

Results and Discussion

The typical sorption isotherms of TDP with addition of AMP shown in Figure 1 demonstrated that sediments from different locations in the bay have different sorption behaviors. Results of fitting data to the Freundlich equation are listed in Table S1. In eastern bay, sediments have the strong tendency to absorb AMP even at a low concentration of AMP, the mean correlation coefficient in fitting data to the modified Freundlich equation is 0.96 ± 0.04 ($p < 0.01$). In western bay, however, $\Delta[P_{sed-T}]$ for most sediments were negative, even at the highest AMP concentration ($20 \mu M$) used. In other words, there were no net adsorptions observed in these sediments under the experimental conditions, though the general patterns can still be described by the modified Freundlich equation (the dotted lines in Figure 1). The mean correlation coefficients of the fitting data to the modified Freundlich equation is 0.88 ± 0.13 , and the poorest correlation coefficients are 0.77 ($p < 0.05$) and 0.64 ($p < 0.10$) for stations 16, and 9, respectively.

The native adsorbed TDP (NAP_T) ranged from $0.72 \mu mol g^{-1}$ at station 18 to $49.5 \mu mol g^{-1}$ at station 8, with an average value of $9.1 \pm 10.5 \mu mol g^{-1}$, whereas the mean value of native adsorbed phosphate (NAP) of these sediments ($1.09 \pm 0.50 \mu mol g^{-1}$) (10) was only 12% of the NAP_T . The K_{f-T} in this study ranged from $0.001 L g^{-1}$ at station 12 to $48.5 L g^{-1}$

at station 8, with an average value of $8.2 \pm 10.4 L g^{-1}$, whereas the mean value of K_{f-I} of phosphate sorption ($0.76 \pm 0.35 L g^{-1}$) (10) was only 9.3% of the K_{f-T} . The n in this study ranged from 0.01 at station 16 to 3.05 at station 12, with an average value of 0.29 ± 0.49 , whereas the mean value of n in phosphate sorption was 0.47 ± 0.16 (10), which is 1.62 times greater than that in this study.

The EPC_{0-T} and K_{d-T} were used to characterize behavior of sediments in response to addition of AMP. The EPC_{0-T} ranged from 0.4 to $300 \mu M$ with an average value of $20.5 \pm 47.5 \mu M$ (Table S1), whereas the corresponding EPC_{0-I} for phosphate sorption was 0.4 to $27.8 \mu M$ with an average value of $4.47 \pm 6.92 \mu M$ (10), an approximately 22% of the EPC_{0-T} . However, the buffer intensity of sediment with respect to phosphate and to added AMP was quite similar. The K_{d-T} ranged from 0.001 to $0.77 L g^{-1}$ with a bay-wide average of $0.23 \pm 0.22 L g^{-1}$, whereas the corresponding K_{d-I} for phosphate sorption was 0.033 to 0.72 with an average value of $0.29 \pm 0.18 L g^{-1}$ (10).

The 40 sampling sites across the bay make it possible generate a relatively high-resolution spatial distribution of EPC_{0-T} and K_{d-T} in Florida Bay. The spatial distribution of EPC_{0-T} (Figure 2) showed a sharp west-east gradient, with more than $100 \mu M$ at stations 11, 13, and 34 in the western bay and less than $1 \mu M$ at stations 1, 2, and 4 in the eastern bay. The average values of EPC_{0-T} and K_{d-T} in the eastern bay was $3.67 \pm 3.71 \mu M$ and $0.32 \pm 0.21 L g^{-1}$, respectively, whereas the corresponding values in the western bay was $76.3 \pm 98.0 \mu M$ and $0.04 \pm 0.04 L g^{-1}$, respectively. The strong west-east spatial gradient is in good agreement with the spatial distribution of various phosphorus forms in sediments measured previously (11), including the exchangeable phosphate (IP_{exch}), exchangeable total phosphorus (TP_{exch}), the sum of the exchangeable total phosphorus and the iron-bound phosphate (defined here as the surface reactive phosphorus, P_{sr}) and the TSP. In the eastern bay, linear correlations between EPC_{0-T} and various sedimentary phosphorus forms were found (Table 1). These correlations suggest that the phosphorus content in the sediments govern the behavior of AMP sorption on these sediments. As shown in Table 1, the slopes in the EPC_{0-I} equations in eastern bay were much smaller than those in the EPC_{0-T} equations. In contrast, in the western bay there are no obvious correlations between EPC_{0-T} and any forms of sedimentary phosphorus. This behavior is quite different from the previous study on phosphate sorption (10) in which a significant linear correlation of EPC_{0-I} to the contents of different forms of sediment

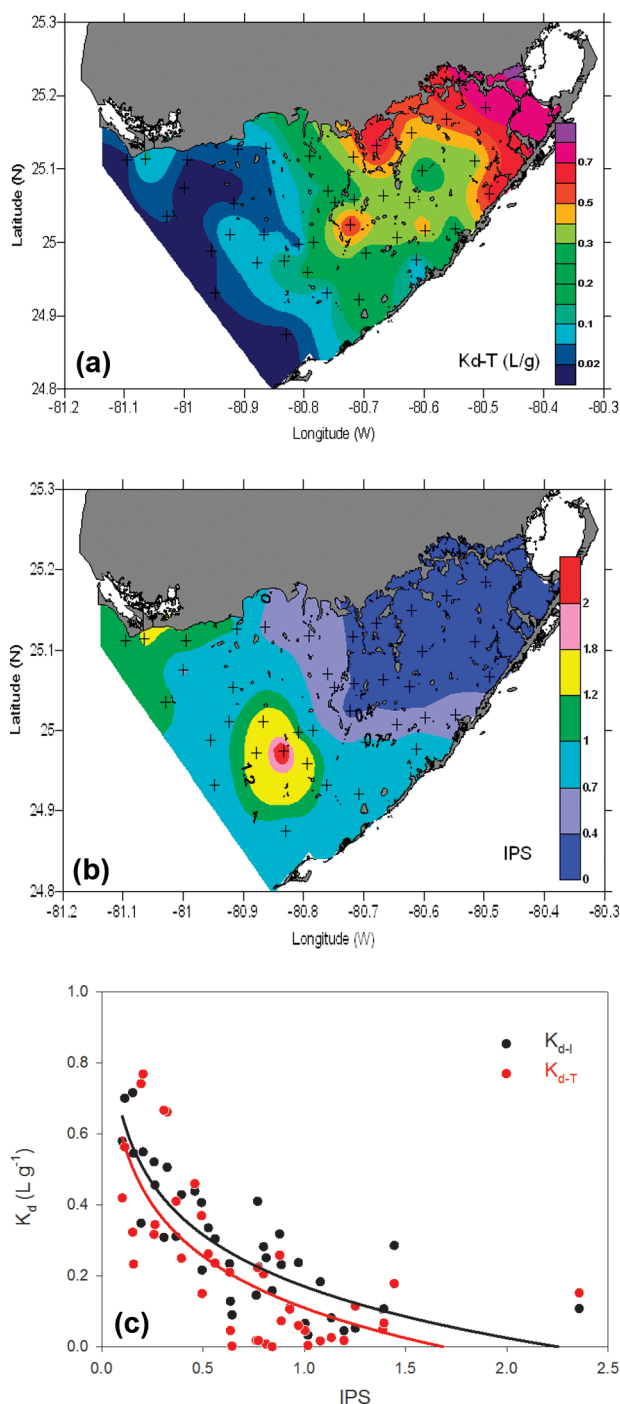


FIGURE 3. Spatial distribution of (a) K_{d-T} , (b) IPS in Florida Bay, and (c) their relationships (see Table 1 for respective correlation coefficients).

phosphorus were observed in the entire bay, though the slope of the linear equation in the western bay were usually much higher than that in the eastern bay (Table 1).

In contrast to the EPC_{0-T} , the spatial variation of the distribution coefficient K_{d-T} (Figure 3) showed a strong east–west gradient, with the highest values of about $0.75\ L\ g^{-1}$ at stations 4 and 1 in the eastern bay and the values less than $0.01\ L\ g^{-1}$ at stations 34, 16, and 11 in the western bay. Similar to phosphate sorption (10), a simple power-law equation of the K_{d-T} as a function of content of different forms of phosphorus was found over the entire bay (Table 1), and the corresponding exponent is always negative. Therefore, the buffer capacity of sediment with respect to AMP decrease with phosphorus contents in the sediments,

which implies competition between surface sites for the phosphorus in the seawater and the native phosphorus on the surface of sediment. However, the absolute value of exponent for TDP sorption was always higher than that for phosphate sorption, indicating that the sorption of phosphorus due to the addition of AMP might involve some mechanisms other than phosphate.

It is commonly believed that the concentrations and forms of iron and aluminum oxides in the soil play a significant role in the sorption of phosphate and dissolved organic matter, though their roles at high pH conditions diminish (19, 33–36). However, EPC_0 has no direct correlation with sediment Fe oxides content for both phosphate and AMP sorption in Florida Bay sediments. On the other hand, we also observed that both K_{d-T} and K_{d-I} in the eastern bay are linearly correlated with the surface reactive iron oxide content as follows

$$K_{d-I} = 0.0978(FeOOH) + 0.0978 \quad (r^2 = 0.31, p < 0.01)$$

$$K_{d-T} = 0.1102(FeOOH) + 0.0487 \quad (r^2 = 0.26, p < 0.01)$$

Previous study has quantified the surface reactive iron oxides (FeOOH) in the sediments were in a range of 0.8 to $4.2\ \mu\text{mol}\ g^{-1}$ (11). The calculated molar ratio of the surface reactive phosphorus to the surface reactive iron oxide content in the sediment (IPS, an index of degree of phosphorus saturation) was in a range of 0.10 to 2.36. We also found, for the first time in the coastal sediment, a significant correlation ($p < 0.001$) between the distribution coefficient K_d and the IPS for the entire bay (Figure 3c). The correlations have been significantly improved ($p < 0.001$) from using either phosphorus content or iron oxide content alone ($p < 0.01$).

This further implies that the iron oxide coating on the carbonate sediments plays a significant role in controlling the buffer capacity of sediments with respect to the sediment–seawater exchange of phosphorus. It is known that the reduction of iron oxides in the sediment occurs in the hypoxia or anoxia events (37, 38) and the phosphorus can drastically release from the sediment under such conditions. By adjusting the reactive iron oxide content in the sediments through addition of iron salts to surface water might significantly increase sediment's retention capacity for dissolved phosphorus in ambient water. This would effectively reduce the availability of phosphorus and thereby diminish the risk of algal blooms in some phosphorus-rich estuarine ecosystems. In fact, adjusting the iron or alum status of sediments has been demonstrated to be one of the effective measures to reduce eutrophication in many shallow lakes (39–41). Our results further support this concept and its applicability to coastal ecosystems.

It is interesting to compare the sorption of phosphate and phosphorus by addition of AMP on Florida Bay sediments in terms of the sorption parameters, EPC_0 and K_d . As expected, there is a linear relationship between K_{d-I} and K_{d-T} in the entire Florida Bay (Figure 4a)

$$K_{d-T} = 0.8563K_{d-I} \quad (r^2 = 0.5344, p < 0.001)$$

For the zero equilibrium phosphorus concentration, a linear relationship in the eastern bay was observed (Figure 4b)

$$EPC_{0-T} = 2.09EPC_{0-I} \quad (r^2 = 0.602, p < 0.001)$$

In the western bay, however, there is no similar correlation between EPC_{0-T} and EPC_{0-I} . This might relate to variation in composition of organic matter in sediment and dissolved organic matter (DOM) in water in the bay (28, 42). The western bay is open to the Gulf of Mexico with frequent seawater exchange. However, tidal advection from the Gulf of Mexico is quickly attenuated by the western mud banks, leaving most

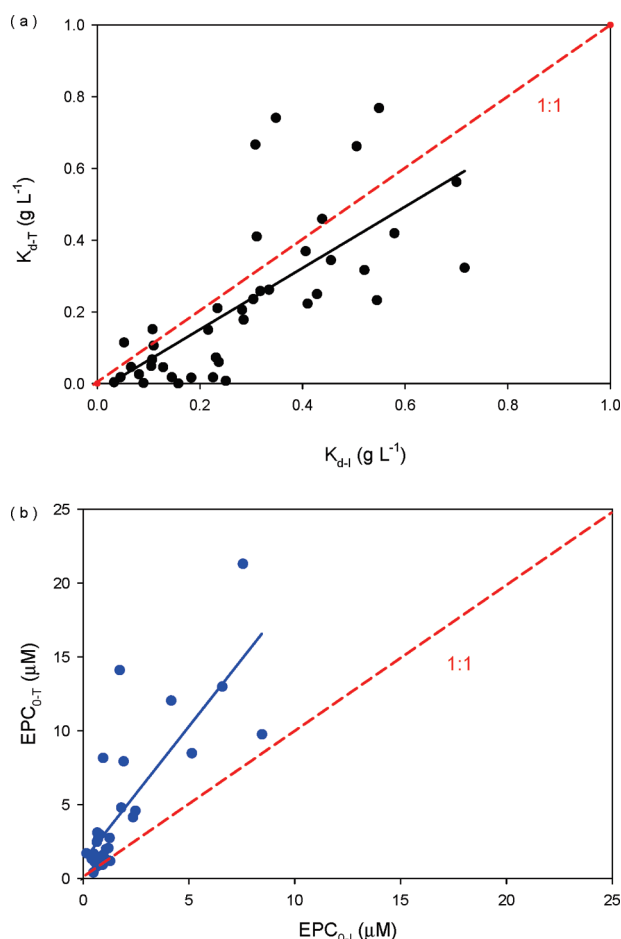


FIGURE 4. The correlations between (a) K_{d-T} and K_{d-I} in the entire Florida Bay with a fitted equation of $K_{d-T} = 0.8563 K_{d-I}$ ($r^2 = 0.5344$, $p < 0.001$, black line) and (b) EPC_{0-T} and EPC_{0-I} in the eastern bay with a fitted equation of $EPC_{0-T} = 2.09 EPC_{0-I}$ ($r^2 = 0.602$, $p < 0.001$, blue line).

of the eastern Florida Bay unaffected by the Gulf of Mexico water (43). On the other hand, through Taylor Slough and C-111 canal, the majority of fresh water carrying terrestrial organic matter flow into the eastern bay. Numerous studies in soil have reported that the low-molecular-weight organic compounds can significantly influence the phosphorus sorption. The strong competitors for phosphate include DOC, citrate, oxalate, and malate (18, 19, 26, 44, 45). The marine and terrestrial organic matter might behave differently in competing AMP on the sorption site of sediment surface.

Because of the highest K_d and lowest EPC_0 for both phosphate and TDP in the eastern bay, sediments in this region have a strong potential to maintain a low water column phosphorus concentration and display a large buffer capacity with respect to external loading of dissolved phosphorus. By comparing the phosphate and DOP concentrations in the ambient water (6, 7) with the zero equilibrium phosphorus concentrations of the sediment, we can predict the role of the sediments with respect to phosphorus cycling in a resuspension event. In most cases, TDP concentrations in the western bay water are much lower than those of the EPC_{0-T} of sediments, which indicate the sediment can become a source of phosphorus to the overlying water. On the other hand, in the eastern bay, once the TDP concentrations are higher than that of the EPC_{0-T} of sediments, sediments can serve as a sink to the dissolved phosphorus in the water column. Therefore, sediments play different roles in different parts of the bay.

This significantly affects the ecosystem function in different regions of the bay (5, 8, 9). While previous study demonstrated the importance of unoccupied surface sites provided by iron oxides and calcium carbonate on sediment surface in governing the sorption of phosphate, the relationship between IPS and K_{d-T} in this study reveals the same mechanisms controls the sorption of dissolved organic phosphorus. This is not surprising since the unoccupied sites on the sediment surface are available for adsorption of phosphate as well as organic phosphorus. The availability of unoccupied sites depends upon sediment's index of phosphorus saturation. This hypothesis should be further validated with other organic phosphorus model compounds and different coastal and estuarine environments. Further studies on the phosphorus sorption on sediments should also focus on the phosphorus and iron forms in the sediment as well as the influence of redox conditions, because of the ratio of phosphorus to iron thus the amount of surface reactive sites unoccupied by phosphorus is essential in predicting the behavior of sediment in phosphorus exchange across the sediment-water interfaces.

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Supporting Information Available

Table S1 and Figures S1, S2, S3, and S4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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