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Effect of Temperature and Salinity on Phosphate Sorption on Marine Sediments

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S *Supporting Information*

ABSTRACT: Our previous studies on the phosphate sorption on sediments in Florida Bay at 25 °C in salinity 36 seawater revealed that the sorption capacity varies considerably within the bay but can be attributed to the content of sedimentary P and Fe. It is known that both temperature and salinity influence the sorption process and their natural variations are the greatest in estuaries. To provide useful sorption parameters for modeling phosphate cycle in Florida Bay, a systematic study was carried out to quantify the effects of salinity and temperature on phosphate sorption on sediments. For a given sample, the zero equilibrium phosphate concentration and the distribution coefficient were measured over a range of salinity (2−72) and temperature (15−35 °C) conditions. Such a suite of experiments with combinations of different temperature and salinity were performed for 14 selected stations that cover a range of sediment characteristics and geographic locations of the bay. Phosphate sorption was found to increase with increasing temperature or decreasing salinity and their effects depended upon sediment's exchangeable P content. This study provided the first estimate of the phosphate sorption parameters as a function of salinity and temperature in marine sediments. Incorporation of these parameters in water quality models will enable them to predict the effect of increasing freshwater input, as proposed by the Comprehensive Everglades Restoration Plan, on the seasonal cycle of phosphate in Florida Bay.

INTRODUCTION

Because of low solubility of P-bearing minerals in the earth's crust and a strong affinity of dissolved phosphate to adsorb on the solid surfaces, it is not surprising that sediment, including suspended particles, has been identified as the dominant P reservoir in both freshwater and coastal marine environments.[1−5] It has also been proposed that sediment can act as a phosphate buffer system that regulates dissolved phosphate concentrations in the overlying waters through phosphate exchange across the sediment−water interface, particularly during sediment resuspension.[6,7] The direction of such exchange is controlled by the chemical potential of phosphate across the sediment-water interface, which is in turn related directly to the relative abundance of phosphate in solid and aqueous phases. The rate of exchange and the final equilibrium state approached are also influenced by chemical composition and physical property of both sediment and ambient water. Among a variety of laboratory-synthesized minerals, amorphous iron oxides have shown the greatest adsorption capacity for phosphate.[8−12] Field studies have demonstrated that abundance of iron oxides in soils and sediments has a significant effect on their sorption capacity for phosphate. In addition to sediment composition, temperature and salinity are the most common environmental variables that influence the sediment−water exchange of phosphate. Salinity typically varies from 0 to 36 in most estuaries with hyper-salinity occurring in many semienclosed bays. Water temperature typically oscillates in diurnal and seasonal cycles in response to air temperature. Despite their considerable variation in estuarine and coastal waters, few phosphate sorption studies were carried out over a range of temperature and salinity that are comparable to natural variability.

The sediment−water exchange of phosphate becomes more important in supplying bioavailable P in shallow water of Florida Bay where dissolved phosphate in the water column is depleted to nanomolar levels[13,14] and P has been identified as a limiting nutrient to the biological production.[15−17] Florida Bay sediments consist mainly of biogenic carbonate (81−96% by weight) with variable content of iron oxides,[18] and are a strong adsorbent for P.[19−22] The fine-grained carbonate mud in the bay is readily suspended to the surface by wind and tidal mixing, enhancing the sediment−water exchange of phosphate.[23,24] Our previous study on the phosphate sorption in Florida Bay documented the spatial distributions both of the sediment's zero equilibrium phosphate

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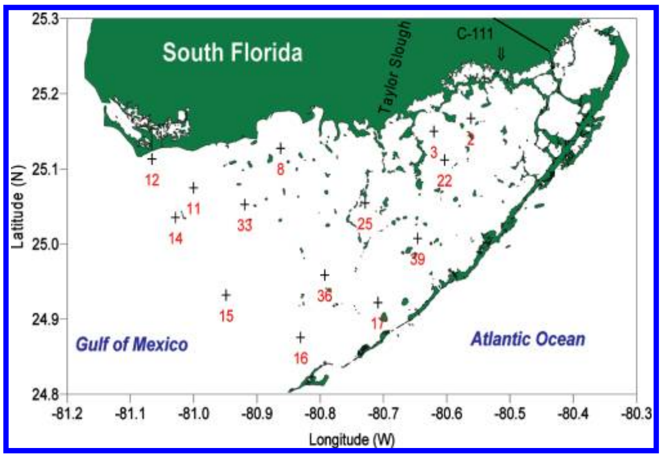

Figure 1. Map of Florida Bay and the location of the 14 sediment sampling sites in the bay.

concentration (EPC_0) and of the distribution coefficient (K_d), and provided the first quantitative relationships between sorption characteristics (EPC_0 and K_d) and the exchangeable phosphate content of marine sediments.[18,19] Similar spatial distributions have also been observed on the organic phosphorus (AMP) sorption in Florida Bay.[20] While previous studies provide a spatial pattern of sediment characteristics with respect to phosphate exchange processes it must be emphasized that these parameters were measured at a single salinity (36) and temperature (25 °C) condition. As in any estuarine and coastal waters, both salinity and temperature in Florida Bay vary over a wide range in both time and space.[25,26]

Water temperatures vary both seasonally and daily in response to air temperature changes, ranging from 8 °C in winter to 37 °C in summer.[27] A considerable spatial variation in water temperature has been observed, which is often correlated with water depth. The extreme temperature was found in the shallowest waters on top of mud banks where diurnal temperature variation reaches 5 °C whereas corresponding variation in deeper water of basins is less than 2 °C.[27,28]

Salinity varies greatly both in space and time, with a range of less than 5 near the freshwater canals at northern boundary to greater than 50 in semi-isolated basins. The temporal variation of salinity in the bay is mainly regulated by precipitation and about 70% of annual rainfall ($\sim$110 cm y^{-1}) occurs from June to October.[29] The annual minimum salinity usually occurs during wet season as a result of heavy rainfall in the bay and increased runoff from the land. Low salinity water persistently occurs in the eastern and north central regions as a result of freshwater runoff through C-111 canal system and Taylor Slough (see Figure 1), whereas high salinity water usually occurs in central bay during early summer at the end of dry season due to excessive evaporation in confined shallow waters.[26] For example, Little Madeira Bay in the north central region exhibited the largest range in salinity, varying from 3 in wet season to 68 during dry season.[30]

Hypersalinity is thought of as a major factor that caused a dramatic die-off of seagrass around 1987, although other factors, such as hypoxia and sulfide toxicity, abnormally warm summer, and pathogens have also been proposed to have contributed to the die-off.[25] The hypersalinity is widely considered a result of reduced freshwater flow from Everglades by regional water management practice. Since the 1950s, freshwater flow in northern Everglades has been diverted to the Atlantic and Gulf of Mexico coasts by canals to provide flood control and drainage of wetland for agriculture and urban development. Historical sheet flow across the marl prairies of southern Everglades through the Buttonwood embankment into the north central bay and from numerous creeks fed by Taylor Slough has diminished and the discharge from C-111 canal into wetlands bordering on the northeastern bay has become the major freshwater input into the bay.

Comprehensive Everglades Restoration Plan proposes to increase freshwater flow to historical level to restore Everglades and Florida Bay habitats. Some scientists argue that the benefits of restoring historical runoff are uncertain because the sensitivity of Florida Bay ecosystem to variation of freshwater runoff is unknown.[29] Despite the lack of data and models for prediction, plans for water management and ecosystem restoration in south Florida are progressing. Because P is a limiting nutrient for seagrass over the entire bay and for phytoplankton in much of the bay, it is critical to understand how changes in freshwater runoff, hence salinity distribution, affect the internal cycling of P between sediment and water column.

The objective of this study is to quantify the influence of temperature and salinity on the sediment−water exchange of phosphate in Florida Bay. The results from this study will provide essential parameters needed in water quality models that can simulate biogeochemical cycle of P in Florida Bay and predict the response of P cycle to seasonal temperature fluctuation and increasing fresh water input in Florida Bay.

EXPERIMENTAL SECTION

Study Region. Florida Bay is one of the world's largest (2200 km^2) coastal lagoons located at the southern end of the Florida peninsula (Figure 1). Its triangular-shaped area is bordered to the north by the Everglades wetlands. A chain of islands known as the Florida Keys separates the shallow bay from the Atlantic Ocean, forming its eastern and southern boundaries. Its westerly margin is open to the Gulf of Mexico, although water exchange is highly restricted by extensive shallow western margin mudbanks. Dotted mangrove islands and a complex network of carbonate mudbanks divide the interior bay into numerous isolated sub-basins with maximal water depths of 2−3 m. Water exchange between subbasins is limited through narrow cuts and overbank wash.

Sediment Samples. To cover sediment characteristics and geographic region of the bay, a total of 14 sampling stations were selected for this study (Figure 1). Details of sampling and sample processing were given elsewhere.[18] To simulate resuspension events, easily resuspended fine-grained sediments (<124 μm) at each station were used in sorption experiments. The chemical forms of P in these sediments had been previously determined using an improved sequential extraction technique.[18] The exchangeable phosphate of sediment, P_{exch}, was operationally defined as inorganic P extracted by $MgCl_2$ solution and surface reactive iron oxides content of sediments, Fe(III)O, was extracted by reductive dissolution using a bicarbonate-dithionate solution.[18]

Adsorption−Desorption Isotherm Experiments. Different salinity seawaters were prepared by diluting with a 2 mM $NaHCO_3$ solution or adding NaCl to the filtered low-nutrient seawater collected from the surface of the Gulf Stream in the Florida Straits. Such prepared seawaters maintain the carbonate system constant, minimizing the potential dissolution or precipitation of $CaCO_3$ at extreme salinities. For each experiment, 100 mg of sediment were mixed with 49 mL seawater of an appropriate salinity in 60 mL high-density polypropylene bottles. One ml of chloroform was added to the slurry to inhibit microbial activity. The slurry was conditioned by agitating it in a temperature-controlled orbital shaking incubator at a given temperature. A period of 4-day conditioning was used to ensure sediments reached equilibrium with seawater at the ambient condition. At the end of the conditioning, an appropriate phosphate standard solution was added to each bottle. Eight initial phosphate concentrations, $[P]_i$, were used for each sediment and maximum concentrations ranged from 10 to 60 μM, depending on sediment native P contents. After another 24 h shaking, the suspension was filtered through a 0.45 μm pore-size filter. Phosphate in the filtrate was determined by a modified phosphomolybdenum blue method with a Hewlett-Packard 8453 spectrophotometer.[31] The precision of replicate experiments was 1−2%.

The final phosphate concentration in seawater, $[P]_f$, was operationally defined as an equilibrium phosphate concentration, EPC. The difference between $[P]_i$, and $[P]_f$ was used to calculate the amount of phosphate adsorbed to or desorbed from the sediment,

$$\Delta[P_{sed}] = [P]_i - [P]_f \qquad (1)$$

A plot of $\Delta[P_{sed}]$ versus $[P]_f$ from each experiment was used to represent a sediment's adsorption isotherm at a given temperature and salinity condition (e.g., Figure 2a). A modified Freundlich equation was used to parameterize the adsorption isotherm data,

$$\Delta[P_{sed}] + \mathrm{NAP} = K_f([P]_f)^n \qquad (2)$$

where NAP is the native adsorbed phosphate, K_f is the Freundlich coefficient, and n is the exponential factor. NAP was introduced in eq 2 to account for desorption of native adsorbed phosphate from sediments at low EPC. The value of EPC at $\Delta[P_{sed}] = 0$ is the zero equilibrium phosphate concentration, EPC_0, and represents the concentration at which sediment is in equilibrium with seawater with respect to the exchange of phosphate across their interface. The distribution coefficient K_d was calculated from the slope of the isotherm curve at $\Delta[P_{sed}] = 0$ by taking the derivative of eq 2 with respect to $[P]_f$ at the EPC_0.

$$K_d = d\{K_f([P]_f)^n\}/d([P]_f)_{EPC0} = nK_f([P]_f)^{n-1} \qquad (3)$$

For a given sediment sample, its EPC_0 and K_d were measured over a range of seawater salinity (2−72) and ambient temperature (15−35 °C) conditions. Such a suite of experiments with combinations of different temperature and salinity were repeated with 14 sediment samples collected from locations that represent different sediment characteristics and geographic region of the bay. To achieve this goal, a total of more than 220 sorption experiments were conducted.

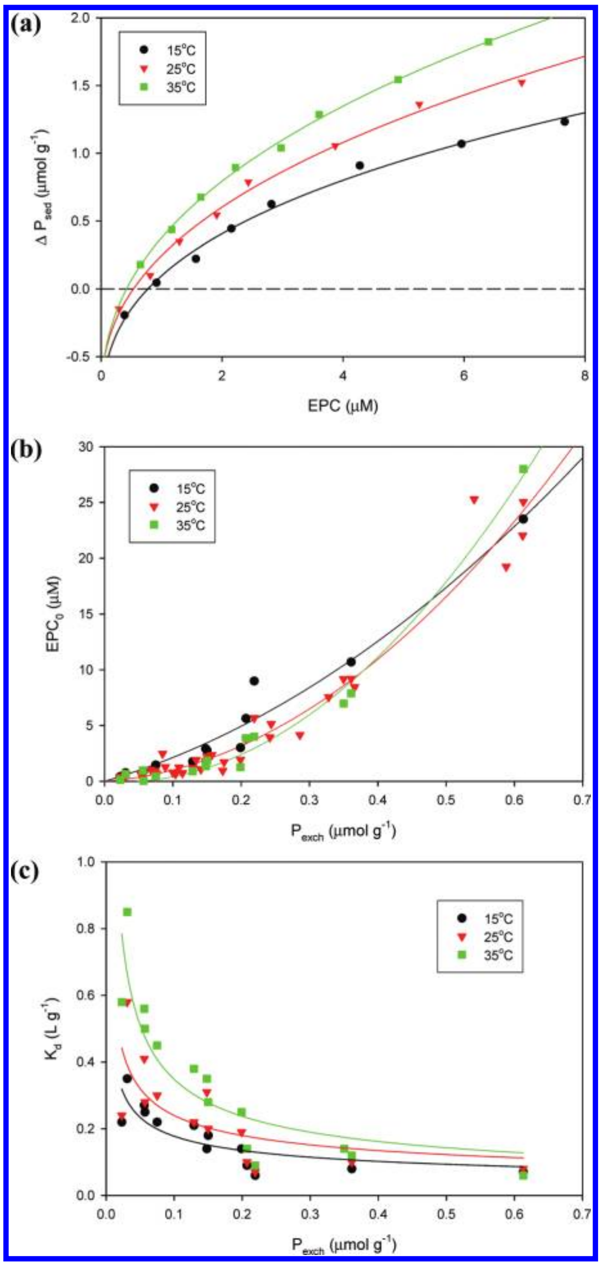

Figure 2. Effect of temperature on phosphate sorption (a) isotherms from a sediment sample (station 2) in salinity 36 seawater; (b) EPC_0 in salinity 36 seawater at different temperatures as a function of P_{exch}; (c) K_d in salinity 46 seawater at different temperatures as a function of P_{exch}.

RESULTS AND DISCUSSION

Effect of Temperature on Phosphate Sorption. For a given sediment sample, increasing ambient temperature increased the phosphate adsorption on sediment. A typical effect of temperature on phosphate sorption in seawater is shown in Figure 2. In Figure 2a, sediment was collected from station 2 in the eastern bay with relatively low P and high Fe content.[18] As a result, there was little release of native adsorbed phosphate to seawater. On the other hand, strong adsorption of phosphate was observed even at the lowest temperature used in this experiment (15 °C). As shown in Figure 2a, the slopes of isotherm curves increase with increasing temperature, resulting in an increased K_d and a decreased EPC_0 when temperature increases. The adsorbed phosphate on sediment increased approximately 1.3 times for every 10 °C increase in temperature at a given EPC in seawater. This pattern was observed on all sediments used in this study, including the sediments with high P content.

As demonstrated in our previous study, EPC_0 (determined at 25 °C and 36 salinity) increases with increasing P_{exch} and can be expressed as a polynomial function of P_{exch}.[19] This pattern was also observed at other temperatures. The EPC_0 determined over a temperature range of 15 to 35 °C (in salinity 36 seawater) as a polynomial function of P_{exch} in Florida Bay is shown in Figure 2b.

Our previous study also demonstrated that K_d can be expressed as a power function of P_{exch} in Florida Bay.[19] Comparison of K_d as a function of P_{exch} measured at different temperatures (15−35 °C) is shown in Figure 2c, which indicates that the effect of temperature on K_d is the greatest in sediments with low P_{exch}, diminishing with increasing P_{exch}.

The effect of temperature on K_d can be used to estimate the changes in enthalpy (ΔH) and entropy (ΔS) for the adsorption by following van't Hoff equation,

$$\ln K_d = -\Delta H/RT + \Delta S/R \tag{4}$$

where T is temperature in K and R is the gas constant. Calculated ΔH varied from 9 ± 5 (station 14) to 31 ± 3 (station 2) kJ mol^{-1}, whereas calculated ΔS ranged from 11 ± 17 (station 14) to 100 ± 11 (station 2) J mol^{-1}. Both ΔH and ΔS (both in J mol^{-1}) were found to be inversely proportional to P_{exch} as follows:

$$\Delta H = 30824 - 53145\, P_{exch}\ (r^2 = 0.57) \tag{5}$$

$$\Delta S = 99.2 - 227.6\, P_{exch}\ (r^2 = 0.68) \tag{6}$$

The decrease in ΔS with increasing P_{exch} reflects the less available sites (therefore less degree of freedom) on sediment surface as a consequence of more reactive surface sites being occupied by the increased native adsorbed phosphate.

The effect of temperature we observed in marine sediments is consistent with those observed in phosphate sorption on laboratory synthesized calcium carbonate minerals. A 1.2 times increase in phosphate sorption on aragonite for every 10 °C increase in temperature has been observed in seawater.[22] There are a few studies on the influence of temperature on phosphate sorption on natural sediments. For example, an increase in adsorption of phosphate with temperature increasing from 10 to 35 °C has been reported in sediments of Taihu lake in the lower Yangtze delta region of China.[32]

Effect of Salinity on Phosphate Sorption. For a given sediment sample, decreasing salinity increased the phosphate adsorption on sediment. A typical effect of salinity on phosphate sorption is shown in Figure 3a. In Figure 3a, sediment was collected from station 15 in the western bay with relatively high P and low Fe content. As a result, there was a significant release of native adsorbed phosphate to seawater, particularly in high salinity waters. Adsorption of phosphate on sediment was observed only at relatively high EPC in seawater. As shown in Figure 3a, the slopes of isotherm curves increase with decreasing salinity, resulting in an increased K_d when salinity decreases. The isotherm curves also shift to the right with increasing salinity, resulting in an increased EPC_0 as salinity increases. At a given EPC the adsorbed phosphate increased approximately 1.5 times for a reduction of salinity by a half. Increasing phosphate adsorption with decreasing salinity was observed on all the sediments tested. This trend is in agreement with the laboratory and field observations that particle-bound P was released to seawater when riverine particles were transported into estuarine mixing zones.[33,34]

As an example, EPC_0 of all sediment samples determined at 15 °C in seawater salinity from 9 to 72 as a function of P_{exch} in Florida Bay is shown in Figure 3b. For a given salinity and temperature condition, EPC_0 in Florida Bay sediments can be expressed as a polynomial function of $P_{exch.}$ in the sediments (Table S1). The effect of salinity on EPC_0 becomes greater in sediments with high P_{exch}.

Comparison of K_d determined at 15 °C in different salinity seawater (9−72) as a function of P_{exch} in sediments is shown in Figure 3c. The effect of salinity on K_d is similar to that of temperature. Influence of salinity on K_d is the greatest in sediments containing low P_{exch} and diminishes in sediments with high P_{exch}. For a given salinity and temperature condition, K_d in Florida Bay sediments can be expressed as a power function of $P_{exch.}$ (Table S2).

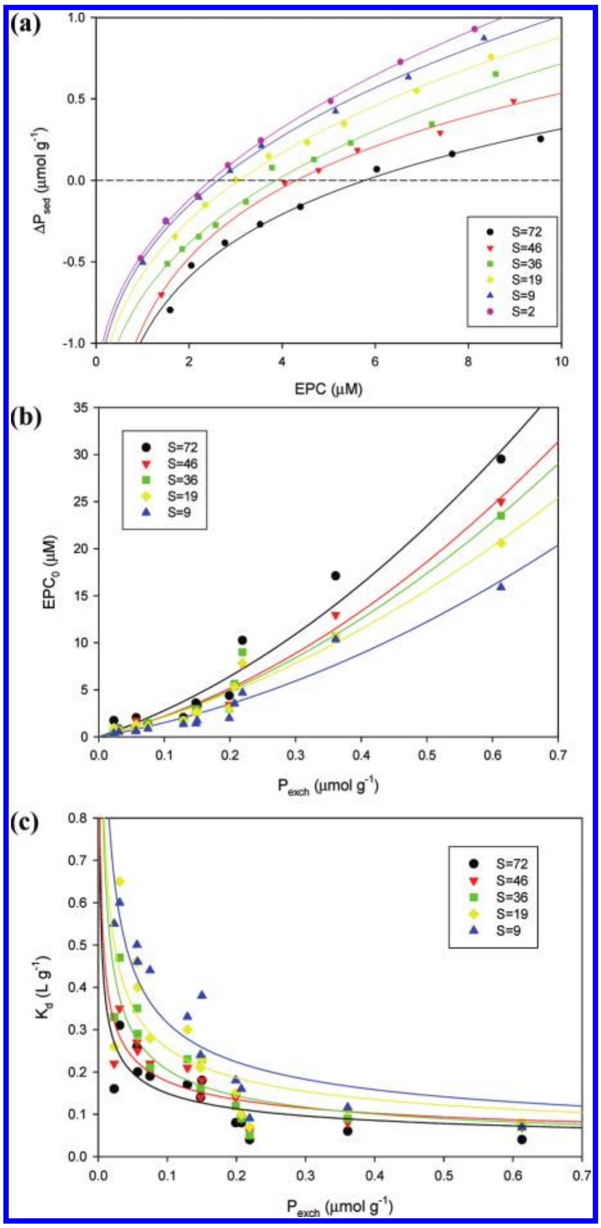

Figure 3. Effect of salinity on phosphate sorption (a) isotherms from a sediment sample (station 15) at temperature 35 °C; (b) EPC_0 at temperature 15 °C in different salinities as a function of P_{exch}; (c) K_d at temperature 15 °C in different salinity seawaters as a function of P_{exch}.

The effect of salinity on phosphate sorption we observed in marine sediments is in agreement with laboratory synthesized calcium carbonate mineral (aragonite).[22] There is no systematic study on the influence of salinity of seawater on sorption by natural sediments. A few studies on the influence of ionic strength of electrolyte solutions on phosphate sorption on natural sediments showed similar effects. An increase in EPC_0 from 1 to 10 μM with increasing NaCl concentration from 10 to 70 g L^{-1} has been

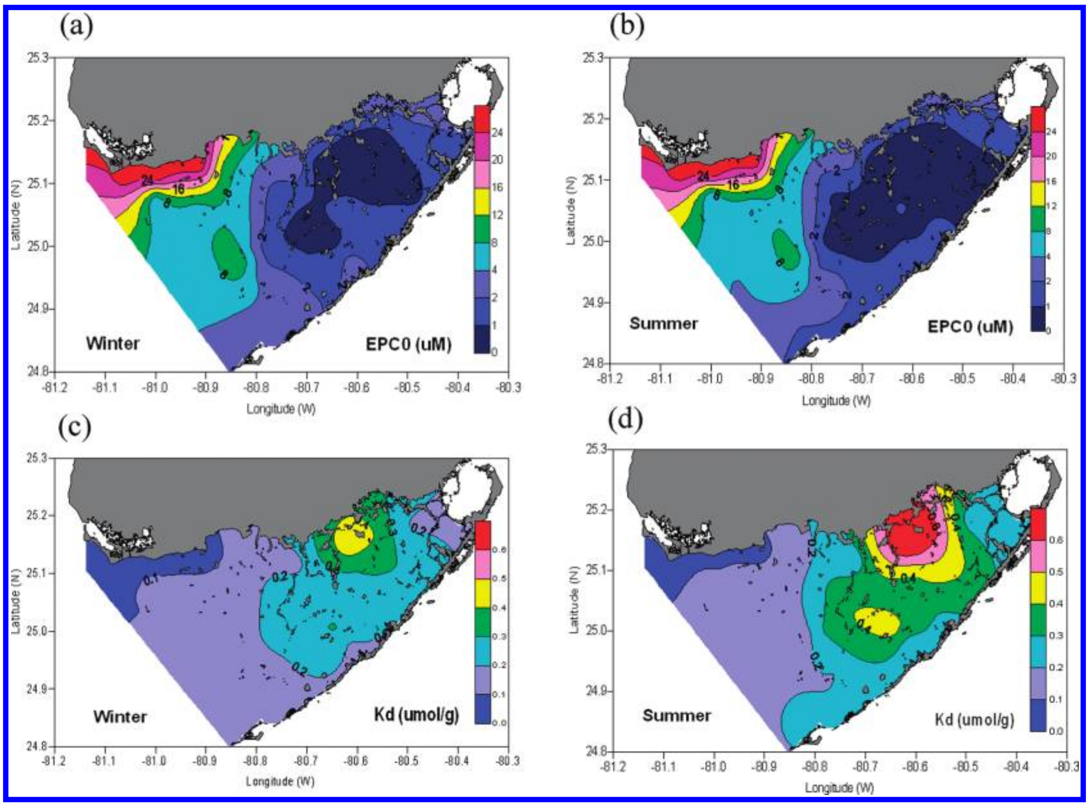

Figure 4. Comparison of spatial distribution of EPC_0 (a) in winter, (b) in summer and K_d (c) in winter, and (d) in summer in Florida Bay sediments.

observed in a short-term equilibrium experiment (1−3 h) with coastal lagoon sediments in Spain.[35] A decrease of phosphate sorption on lake sediments was found when the ionic strength of KCl solution increased from 1 to 10 mM.[36] However, none of the previous studies have provided a systematic investigation into the effect of temperature and salinity. Moreover, this study revealed for the first time that both EPC_0 and K_d of marine sediments vary considerably with the salinity and temperature conditions, and these variations can be quantified as a function of the exchangeable phosphate content in the sediments.

Combined Effect of Salinity and Temperature on Phosphate Sorption on Marine Sediments. As demonstrated above, a change in seawater salinity or temperature will have a separate effect on phosphate sorption on sediment. However, in any estuarine waters, changes in seawater salinity and temperature are likely to occur simultaneously. To predict the combined effect of salinity and temperature on phosphate exchange process, sorption parameters should be expressed as a function of salinity and temperature in addition to other essential variables. Sorption experiments conducted for a combination of different salinity and temperature condition enable us to perform multiparameter regression on the isotherm data. As demonstrated before, EPC_0 and K_d for Florida Bay sediments can be expressed as a function of P_{exch} at any given salinity and temperature condition as follows:

$$EPC_0 = AP_{exch} + B(P_{exch})^2 \tag{7}$$

$$K_d = C(P_{exch})^D \tag{8}$$

Since EPC_0 and K_d have been determined over a range of salinity and temperature (Table S1 and S2), it is feasible to formulate their coefficients (A, B, C, D) as a function of salinity and temperature through multiparameter regression analysis. Such analysis derived the coefficients for eqs 7 and 8 as a function of salinity and temperature as follows:

$$A = -140.5 + 1098.2(t^{-1}) + 30.67\ln(t) + 0.0907S \tag{9}$$

$$B = 1225.96 - 6880.49(t^{-1}) - 278.77\ln(t) + 0.4561S \tag{10}$$

$$C = 0.2911 - 1.3588(t^{-1}) - 0.0597\ln(t) + 0.00027S \tag{11}$$

$$D = 3.1571 - 15.5472(t^{-1}) - 0.976\ln(t) - 0.002416S \tag{12}$$

where t is temperature in °C and S salinity. The coefficients of determination (r^2) for the regression are 0.855, 0.656, 0.410, and 0.700 for A, B, C, and D, respectively. Combination of eqs 7, 9, and 10 can be used to predict EPC_0 for any salinity and temperature condition in Florida Bay with known P_{exch} content in the sediments. Likewise, combination of eqs 8, 11, and 12 can be used to predict K_d for any salinity and temperature condition in Florida Bay with known P_{exch} content in the sediments.

Since the spatial distribution of exchangeable phosphate in fine-grained sediment has been measured in Florida Bay,[18] these equations can be used to predict the sorption behavior of sediment in response to seasonal variation of salinity and temperature in Florida Bay. Using average winter (November−January) and summer (May−July) salinity distribution of the bay[26] and average winter and summer temperature of 20 and 28 °C, respectively, we derived the spatial distribution of the calculated EPC_0 and K_d in winter and summer as shown in Figure 4. From winter to summer, the bay-wide averaged EPC_0 decreased 0.5 ± 0.2 μM and the bay-wide averaged K_d increased

0.08 ± 0.07 L g^{-1}. The observed changes in EPC_0 and K_d are a combined effect of seasonal changes in salinity and temperature. While seasonal temperature changes were assumed to be uniform throughout the bay (8 °C) in this calculation, seasonal salinity changes were based on observational data that show a distinct spatial pattern with a maximum increase of >10 in the central bay due to intensive evaporation in summer.[26] EPC_0 in the eastern bay decreased from 0.3 in winter to 0.2 μM in summer, representing a reduction of 30−45% from respective winter values. These resulted in an expansion of the areal extent of the minimal contour ($EPC_0 < 1$ μM) in the eastern bay from winter to summer (Figure 4a and b). In fact, decreases in EPC_0 were more pronounced in the western and central bay (0.7−0.9 μM) where the exchangeable phosphate in sediment is the highest. This is evident in a reduction of the areal extent of a contour (EPC_0 = 8−12 μM) in central bay from winter to summer. Because the high absolute EPC_0 and its steep gradient in the western bay, the change in the areal extent of a contour (EPC_0 = 8−24 μM) in the western bay from winter to summer is not discernible in Figure 4. In contrast, the relative change in seasonal K_d was greater than that of EPC_0. An increase in maximum K_d of 0.32 L g^{-1} from winter to summer occurred in the eastern bay (Figure 4c and d). This represents a 168% increase from respective winter value. Seasonal increase in temperature (8 °C), overcoming the salinity increase (8 in this area), enhanced the phosphate sorption capacity of the carbonate sediments that are rich in Fe but poor in P, which are typical in the eastern bay.[18] In the western bay, on the other hand, the average summer K_d was only 0.01 higher than that of its winter value, representing 7−20% increase.

This study provides essential parameters for predicting the effect of increase freshwater discharge, as well as seasonal and diurnal temperature variation, on phosphorus cycle in Florida Bay. The results indicate the low salinity water will enhance phosphate adsorption on sediment surface, resulting in lower EPC_0 in the ambient water. The Comprehensive Everglades Restoration Plan proposed a dramatic increase in flow down Shark River Slough relative to the current condition. Increased freshwater flow to the north-central and the western bay regions may reduce dissolved phosphate concentration by enhancing sorption capacity of sediments in the region where relatively high dissolved phosphate concentration persists.[14,37] On the other hand, frequent hypersalinity in central bay during dry season may enhance the release of sedimentary phosphorus to ambient water during resuspension events. Based on the effect of temperature and salinity, it is also expected that there is a seasonal difference in the magnitude of phosphate fluxes during sediment resuspension events; namely, more phosphate will be released from suspended particles to ambient water in winter than in summer. However, quantitative prediction of P cycle requires a water quality model to integrate the physical, biological and geochemical processes contributing to P fluxes in the bay. Incorporation of sorption parameters derived from this study to water quality models will enable them to predict the change in freshwater input as well as seasonal variation in temperature on phosphate cycle in Florida Bay.

Although this study was conducted exclusively on sediments from Florida Bay, the general trend with respect to the influence of salinity and temperature on phosphate sorption on sediment surface is applicable to both freshwater and marine environments. To apply this finding to freshwater and other coastal and estuarine sediments, however, the coefficients for sorption parameters (EPC_0 and K_d) may require slight modification to accommodate any differences in chemical composition and physical property of sediment that might affect its sorption behavior.[38]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Coefficients A and B for eq 7 (Table S1) and C and D for eq 8 (Table S2) determined at given salinity and temperature conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Meybeck, M. Carbon, nitrogen, and phosphorus transport by world rivers. *Am. J. Sci.* **1982**, *282*, 401–450.

(2) Lebo, M. E. Particle-bound phosphorus along an urbanized coastal-plain estuary. *Mar. Chem.* **1991**, *34*, 225–246.

(3) Conley, D. J.; Smith, W. M.; Cornwell, J. C.; Fisher, T. R. Transformation of particle-bound phosphorus at the land sea Interface. *Estuar. Coast. Shelf Sci.* **1995**, *40*, 161–176.

(4) Paludan, C.; Morris, J. T. Distribution and speciation of phosphorus along a salinity gradient in intertidal marsh sediments. *Biogeochemistry* **1999**, *45*, 197–221.

(5) Zwolsman, J. J. G. Seasonal variability and biogeochemistry of phosphorus in the Scheldt Estuary, South-west Netherlands. *Estuar. Coast. Shelf Sci.* **1994**, *39*, 227–248.

(6) Froelich, P. N.; Bender, M. L.; Luedtke, N. A.; Heath, G. R.; DeVries, T. The marine phosphorus cycle. *Am. J. Sci.* **1982**, *282*, 474–511.

(7) Froelich, P. N. Kinetic control of dissolved phosphate in natural rivers and estuaries: a primer on the phosphate buffer mechanism. *Limnol. Oceanogr.* **1988**, *33*, 649–668.

(8) Hingston, F. J.; Posner, A. M.; Quirk, J. P. Anion adsorption by goethite and gibbsite. 2. Desorption of anions from hydrous oxide surfaces. *J. Soil Sci.* **1974**, *25*, 16–26.

(9) Sigg, L.; Stumm, W. The interaction of anions and weak acids with hydrous goethite (α-FeOOH) surface. *Colloids Surf.* **1980**, *2*, 101–117.

(10) Hawke, D.; Carpenter, P. D.; Hunter, K. A. Competitive adsorption of phosphate on goethite in marine electrolytes. *Environ. Sci. Technol.* **1989**, *23*, 187–191.

(11) Krom, M. D.; Berner, R. A. Adsorption of phosphate in anoxic marine sediments. *Limnol. Oceanogr.* **1980**, *25*, 797–806.

(12) Slomp, C. P.; Malschaert, J. F. P.; Van Raaphorst, W. The role of adsorption in sediment-water exchange of phosphate in North Sea continental margin sediments. *Limnol. Oceanogr.* **1998**, *43*, 832–846.

(13) Boyer, J. N.; Fourqurean, J. W.; Jones, R. D. Seasonal and long-term trends in the water quality of Florida Bay (1989—1997). *Estuaries* **1999**, *22*, 417–430.

(14) Zhang, J.-Z.; Chi, J. Automated analysis of nanomolar concentrations of phosphate in natural waters with liquid waveguide. *Environ. Sci. Technol.* **2002**, *36*, 1048–1053.

(15) Fourqurean, J. W.; Zieman, J. C.; Powell, G. V. N. Phosphorus limitation of primary production in Florida Bay - evidence from C-N-P ratios of the dominant seagrass Thalassia-Testudinum. *Limnol. Oceanogr.* **1992**, *37*, 162–171.

(16) Fourqurean, J. W.; Jones, R. D.; Zieman, J. C. Process influencing water column nutrient characteristics and phosphorus limitation of phytoplankton biomass in Florida Bay, FL, USA: Inferences from spatial distributions. *Estuar. Coast. Shelf Sci.* **1993**, *36*, 295–314.

(17) Cotner, J. B.; Sada, R. H.; Bootsma, H.; Johengen, T.; Cavaletto, J. F.; Gardner, W. S. Nutrient limitation of heterotrophic bacteria in Florida Bay. *Estuaries* **2000**, *23*, 611–620.

(18) Zhang, J.-Z.; Fischer, C. J.; Ortner, P. B. Potential availability of sedimentary phosphorus to sediment resuspension in Florida Bay. *Global Biogeochem. Cy.* **2004**, *18*, GB4008, DOI: 10.1029/2004GB002255.

(19) Zhang, J.-Z.; Huang, X.-L. Relative importance of solid-phase phosphorus and iron in sorption behavior of sediments. *Environ. Sci. Technol.* **2007**, *41*, 2789—2795, DOI: 10.1021/es061836q.

(20) Huang, X.-L.; Zhang, J.-Z. Spatial variation in sediment-water exchange of phosphorus in Florida Bay: AMP as a model organic compound. *Environ. Sci. Technol.* **2010**, *44*, 7790—7795, DOI: 10.1021/es100057r

(21) Kanel, d. J.; Morse, J. W. The chemistry of orthophosphate uptake from seawater on to calcite and aragonite. *Geochim. Cosmochim. Acta* **1978**, *42*, 1335–1340.

(22) Millero, F.; Huang, F.; Zhu, X. R.; Liu, X. W.; Zhang, J.-Z. Adsorption and desorption of phosphate on calcite and aragonite in seawater. *Aquat. Geochem.* **2001**, *7*, 33–56.

(23) Lawrence, D.; Dagg, M. J.; Liu, H.; Cummings, S. R.; Ortner, P. B.; Kelble, C. Wind events and benthic-pelagic coupling in a shallow subtropical bay in Florida. *Mar. Ecol.: Prog. Ser.* **2004**, *266*, 1–13.

(24) Wang, J. D.; van de Kreeke, J.; Krishnan, N.; Smith, D. Wind and tide response in Florida Bay. *B. Mar. Sci.* **1994**, *54*, 579–601.

(25) Fourqurean, J. W., Robblee, M. B. Florida Bay: A history of recent ecological changes. *Estuaries* **1999**, *22*, 345-357.

(26) Kelble, C. R.; Johns, E. M.; Nuttle, W. K.; Lee, T. N.; Smith, R. H.; Ortner, P. B. Salinity patterns of Florida Bay. *Estuar. Coast. Shelf Sci.* **2007**, *71*, 318–334.

(27) Holmquist, J. G.; Powell, G. V. N.; Sogard, S. M. Sediment, water level and water temperature characteristics of Florida Bay's grass-covered mud banks. *Bull. Mar. Sci.* **1989**, *44*, 348–364.

(28) Ginsburg, R. N. Environmental relationships of grain size and constituent particles in some south Florida carbonate sediments. *Bull. Am. Assoc. Pet. Geol.* **1956**, *40*, 2384–2427.

(29) Nuttle, W. K.; Fourqurean, J. W.; Cosby, B. J.; Zieman, J. C.; Robblee, M. B. Influence of net freshwater supply on salinity in Florida Bay. *Water Resour. Res.* **2000**, *36*, 1805–1822.

(30) Swart, P. K.; Price, R. Origin of salinity variations in Florida Bay. *Limnol. Oceanogr.* **2002**, *47*, 1234–1241.

(31) Zhang, J.-Z.; Fischer, C. J.; Ortner, P. B. Optimization of performance and minimization of silicate interference in continuous flow phosphate analysis. *Talanta* **1999**, *49*, 293–304.

(32) Jin, X.; Wang, S.; Pang, Y.; Zhao, H.; Zhou, X. The adsorption of phosphate on different trophic lake sediments. *Colloids Surf., A* **2005**, *254*, 241–248.

(33) Gardolinski, P. C. F. C.; Worsfold, P. J.; McKelvie, I. D. Seawater induced release and transformation of organic and inorganic phosphorus from river sediments. *Water Res.* **2004**, *38*, 688–692.

(34) Fox, L. E.; Sagre, S. L.; Wosfy, S. C. The chemical control of soluble phosphorus in the Amazon estuary. *Geochim. Cosmochim. Acta* **1986**, *50*, 783–794.

(35) Clavero, V.; Fernandez, J. A.; Niell, F. X. Influence of salinity on the concentration and rate of interchange of dissolved phosphate between water and sediment in Fuente piedra lagoon (S. Spain). *Hydrobiologia* **1990**, *197*, 91–97.

(36) Wang, S.; Jin, X.; Bu, Q.; Zhou, X.; Wu, F. Effects of particle size, organic matter and ionic strength on the phosphate sorption in different trophic lake sediments. *J. Hazard. Mater.* **2006**, *128*, 95–105.

(37) Huang, X.-L.; Zhang, J.-Z. Neutral persulfate digestion at sub-boiling temperature for total dissolved phosphorus determination in natural waters. *Talanta* **2009**, *78*, 1129–1135.

(38) Lin, C.; Wang, Z; He, M.; Li, Y.; Liu, R.; Yang, Z. Phosphorus sorption and fraction characteristics in the upper, middle and low reach sediments of the Daliao river systems, China. *J. Hazard. Mater.* **2009**, *170*, 278–285.