

## Phosphorus sorption characteristics of intertidal marsh sediments along an estuarine salinity gradient

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### *Abstract*

The phosphate sorption capacity of intertidal vegetated marsh sediments was measured along a salinity gradient in the Cooper River estuary, South Carolina. The phosphate sorption capacity of the surface sediments (0–10 cm) of a freshwater marsh was higher than the sorption capacity of sediments from brackish and saline marshes, and surface sediments had greater sorption capacity than subsurface (10–20 cm) sediments. These trends were opposite that of available phosphorus, which increased downstream and with depth. Freshwater marsh sediments trap phosphorus in a less-bioavailable form as evidenced by the low zero equilibrium phosphorus concentration (ZEPC) of the ambient sediment and low exchangeable phosphorus found there. Soil ZEPC values were similar to the in situ mean pore-water phosphate concentrations, which shows that sorption has a major effect on the spatial distribution of pore-water phosphorus along the estuarine salinity gradient. The magnitude of phosphorus sorption by the freshwater marsh sediments greatly reduced the pore-water phosphate concentration, while the phosphorus sorption properties of brackish and salt marsh sediments maintained in situ equilibrium pore-water phosphorus concentrations at surplus levels (with respect to its availability to plants). These differences in P sorption properties of the sediments can be explained on the basis of their physical and chemical characteristics. For instance, approaching the sea, the surface area of sediments declined, with freshwater marsh sediments (0–10 cm) supporting 8.5× higher surface area than the salt marsh sediments. However, the sorption capacity of freshwater sediments was 33× greater than that of salt marsh sediments, which indicates that other properties such as sediment mineral composition are important. The concentrations of important elements such as Al and Fe in sediments also declined downstream. The results suggest that the differences in phosphorus exchange properties among these marshes are a function of sediment type and sedimentary concentrations of Fe and Al. These in turn are related to the changes in ionic strength and associated parameters (e.g., pH) and physical sorting mechanisms.

Phosphorus bioavailability (operationally defined here as the molybdate-reactive phosphorus) in wetlands is controlled by complex in situ biotic and abiotic processes. The latter include removal of dissolved phosphate from pore-water through sorption onto sediment particles and organic aggregates. Sorption–desorption processes within a sediment chemical environment are influenced by the mineral composition of the sediment. For example, P sorption is positively correlated with the amount of free iron oxide in acid sulfate soils (Jugsujinda et al. 1995). Furthermore, organic molecules can form complexes with metal ions such as iron (Fe) and aluminum (Al), which in turn can sorb phosphorus and reduce its bioavailability (Jones et al. 1993). This is consistent with the high phosphorus sorption capacity of mineral-rich, freshwater wetland sediments (Richardson 1985). Calcium carbonate also has a high affinity for phosphate adsorption (de Kanel and Morse 1978). These inorganic complexes are susceptible to changes in pH and redox conditions.

In river-dominated tidal estuaries, mixing processes form salinity and pH gradients that dominate the chemistry and

biology of marsh sediments (Eyre 1993). For instance, suspended particles and organic aggregates, which can account for a significant fraction of riverborne P, desorb a fraction of their bound phosphorus as electrolyte concentrations increase toward the mouth of the estuary (Fox et al. 1986; Froelich 1988). Furthermore, metal oxides carry a net positive charge at typical freshwater pH and a net negative charge at sea water pH (Barrow et al. 1980). Hence, changes in salinity and pH can modify the composition of particles that bind phosphorus, and alter the P sorption capacity of intertidal sediments. Though the influence of the sorptive capacity of sediments on the availability of nutrients is realized (e.g., McGlathery et al. 1994), the role of this process has received little attention in estuaries. We hypothesize that changes in the sorption capacity of the sediments governed by their physical and chemical characteristics and ultimately mediated by salinity are important factors in the control of phosphate dynamics in estuarine systems.

The objective of this study was to examine the P sorption characteristics of intertidal vegetated marsh sediments along a salinity gradient on the Cooper River (South Carolina) and to relate the observed changes in sorption capacity to the respective sediment composition. We have investigated the pore-water chemistry of four permanent stations along the salinity gradient since 1991 and have found significant inter- and intrasite differences in nutrient dynamics (e.g., Paludan and Morris 1999). The results presented here on P sorption characteristics explain the observed trends in the pore-water concentrations of dissolved reactive phosphorus (DRP) and further our understanding of phosphorus dynamics in estuaries.

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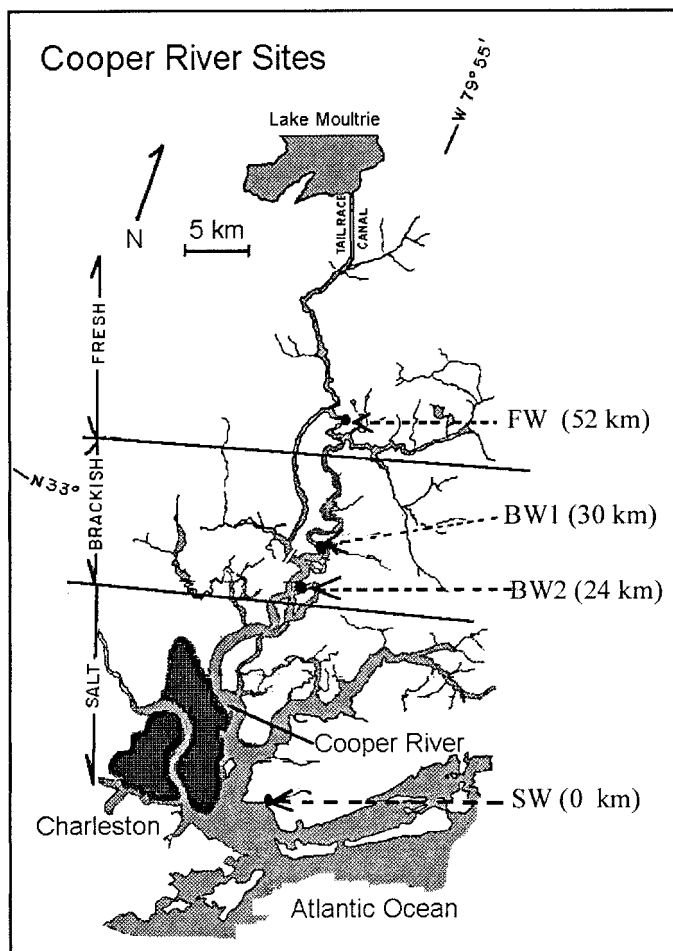


Fig. 1. Map showing the location of the Cooper River Study sites. FW = freshwater site, BW1 = oligohaline site, BW2 = mesohaline site, and SW = saltwater site.

## Materials and methods

**Study area**—Sediment samples were collected from four stations along the salinity gradient on the Cooper River, South Carolina (Fig. 1). The freshwater site (FW) is 52 km upstream from a saltwater site (SW) at the mouth of the estuary in Charleston Harbor. The two brackish water sites (BW1 and BW2) are 30 and 24 km from SW. BW1 is an oligohaline site with a mean surface water salinity of 0.44‰ (upper 95% confidence limit: 0.65‰), whereas BW2 is a mesohaline site with a mean salinity of 4.3‰ (5.8‰). There is a turbidity maximum in the Cooper River in the vicinity of BW2 (Althausen and Kjerfve 1992). The mean surface water salinity at the SW site is 16.5‰ (26‰) and it is 0.06‰ (0.08‰) at the FW site.

The Cooper River drains into Charleston Harbor and has been subjected to two major water diversion projects that altered the freshwater discharge (Kjerfve and Magill 1990). The Cooper River Diversion project in 1941 increased freshwater discharge. The present salinity distribution along the river was established after a Cooper River redirection project in 1985 that caused a reduction in average flow from

418  $\text{m}^3 \text{s}^{-1}$  to 122  $\text{m}^3 \text{s}^{-1}$  (Kjerfve and Magill 1990). As a result, salinity in Charleston Harbor increased and the average tidal intrusion moved upstream (Bradley et al. 1990).

**Sediment sampling and analysis**—Phosphorus sorption: In the autumn of 1996, triplicate sediment cores from each site were collected 15 m inland from the river bank. The cores were collected with minimal compaction using 7-cm-diameter piston core. The extruded cores were sectioned into 0–10-cm- (surface sediment) and 10–20-cm-depth intervals and sections were homogenized and passed through a 2-mm nylon sieve. Sorption experiments were carried out using a wet soil : solution ratio of 2 g : 25 ml of 0.03 M KCl. Microbial activity was inhibited by the addition of toluene to each tube (Richardson and Vaithyanathan 1995). The initial dissolved phosphate concentrations used were 0, 0.01, 0.03, 0.1, 0.2, 1, 10, 50, and 100  $\text{mg liter}^{-1}$  as P. The soil suspensions were equilibrated aerobically under identical conditions for 24 h on a shaker table. We have observed that when sediments from FW and SW sites are incubated under aerobic and anaerobic conditions, there is no treatment effect on the phosphorus uptake efficiency of either sediment type as measured by the phosphorus remaining in solution after 13 d of incubation (see Fig. 2). After the incubation period, the tubes were centrifuged at  $2,135 \times g$  for 20 min, and phosphate in the supernatant was analyzed spectrophotometrically by the ammonium molybdate–ascorbic acid method (Strickland and Parsons 1968).

**Sediment mineral element analysis**: Sediment subsamples from each core (total of three replicates per site, per depth) were analyzed for total Si, Fe, Al, P, Ca, Mg, K, and Na by X-ray fluorescence on a Phillips PW-1400 X-ray fluorescence spectrometer. The major elements were analyzed on fused glass disks using a method similar to Taggart et al. (1987). Sediment subsamples were ignited at 550°C overnight to determine loss on ignition, to oxidize all the Fe to  $\text{Fe}_2\text{O}_3$ , and to oxidize any sulfides that could react with the platinum crucibles. The ignited samples were powdered, weighed (approximately 1 g), and mixed with lithium tetraborate in a 5:1 ratio of flux : sample. The fluxed mixture was placed in a 95% platinum and 5% gold crucible and melted in a muffle furnace at 1,200°C for 5–10 min. The melt was shaken periodically to promote thorough mixing. The homogenized melt was poured into a platinum-gold disk mold preheated to an incandescent yellow-red color over a forced-air Meeker burner and quenched with the air blast to form the glass disk. Calibration curves were established using a series of selected U.S. Geological Survey and international standards prepared identically to the samples. The values for total Ca, Mg, K, and Na for all samples were corrected for their pore-water concentrations using their respective porosities.

**CHN analysis**: Subsamples of the dried sediments were analyzed for total carbon and total nitrogen on a Perkin-Elmer (PE 2400) elemental analyzer.

**Exchangeable ammonium and phosphate**: Exchangeable P measurements were carried out on a separate set of sediment

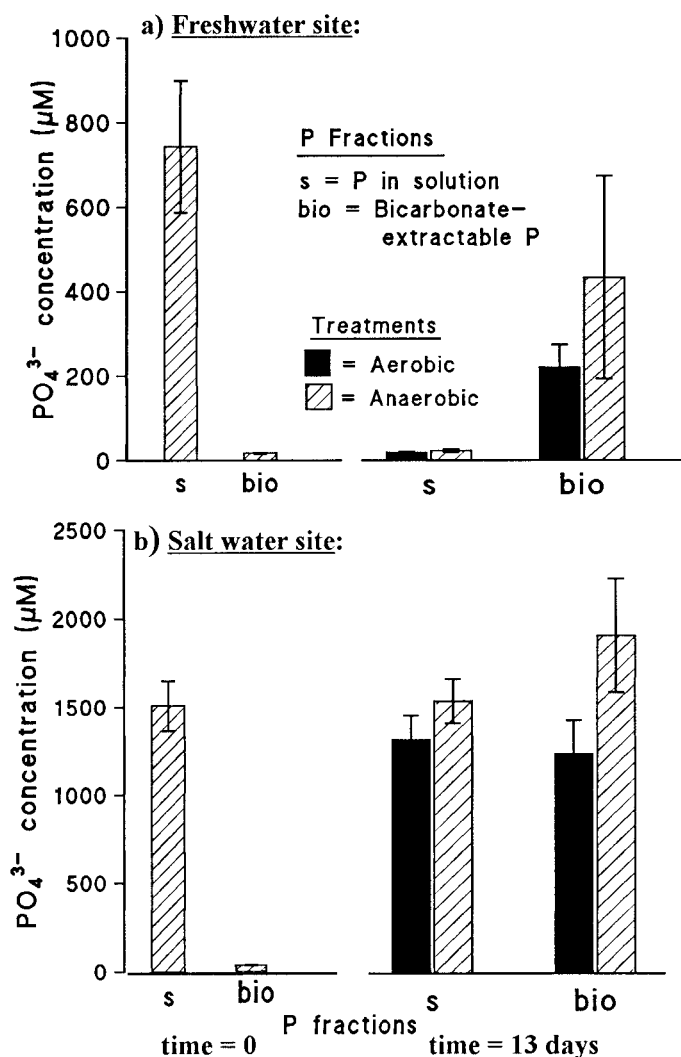


Fig. 2. Concentrations of different P fractions from (a) FW and (b) SW surface sediments at time zero and after a 13-d incubation period. There was no significant treatment effect on P sorption at either of the sites.

cores. Duplicate sediment cores (up to a depth of 110 cm for FW and SW sites and 85 cm for sites BW1 and BW2) were collected using a 10-cm-diameter aluminum corer equipped with a piston. The cores were extruded in the field and sectioned into 0–10-, 15–25-, 45–55-, 70–80-, and 95–105-cm-depth fractions. The sections were placed in a plastic bag and transported to the laboratory on ice. The sediment samples were processed within 24 h of sample collection. Three subsamples from each section ( $n = 6$  per depth per site) were collected anaerobically in a glove bag purged with helium. Each intact section was subsampled approximately every 2 cm from top to bottom using a 1-cm-diameter cork borer. The sediment samples (~3–4 g wet weight per subsample) were incubated with 25 ml of degassed 2 M KCl solution for 24 h and subsequently centrifuged at  $2,135 \times g$  for 20 min. The DRP in the supernatant was measured spectrophotometrically (Strickland and Parsons 1968). These values were corrected for DRP in the pore water using the

respective porosities and expressed as exchangeable PO<sub>4</sub>-P mg kg<sup>-1</sup> sediment dry weight. This provided a measure of bound, but potentially exchangeable, DRP in the sediments.

**Sediment redox potential:** Sediment redox potentials at the study sites were measured at 5- and 15-cm depths. The measurements were made using platinum and calomel electrodes standardized against a solution of known potential (Zobell 1946). The values reported in Table 2 are means of five replicates at each site and depth.

**Cation-exchange capacity (CEC):** The CEC of surface sediments from our study site was measured as described in Hendershot and Duquette (1986). Briefly, 2–5 g of air-dried sediment from duplicate cores (0–10 cm depth) was washed four times with a 0.1 M BaCl<sub>2</sub> solution (first wash) and a 0.025 M BaCl<sub>2</sub> solution (three subsequent washes). The sediment samples were incubated on a shaker table for 2 h during each step. Subsequently, the samples were centrifuged and the adsorbed Ba in the sediment pellet was extracted with four washes of 0.5 M MgCl<sub>2</sub> solution. The supernatant from each step was pooled and analyzed for Ba concentration by ion chromatography on a Dionex DX100. The CEC was calculated after correcting for entrained Ba.

**Sediment surface area:** Surface area of surface sediments (0–10 cm depth) from FW, BW1, BW2, and SW sites was measured on a Coulter SA 3100 surface area analyzer. Triplicate surface sediment samples from each site were homogenized and wet sieved through a 2-mm nylon sieve. The samples were ignited at 300°C overnight to remove organic matter, and approximately 1 g was used for surface area analysis.

**Pore-water sampling and analysis—**Pore water from the four locations in the intertidal marshes along the Cooper River estuary was sampled using a diffusion sampler on a monthly or bimonthly basis from August 1991 to October 1996. Triplicate samples were collected at each marsh site (FW, BW1, BW2, and SW) 15 m from the river bank at two depths (10 and 25 cm) within the rooting zone. The pore-water sampling device consisted of a PVC pipe that held glass sample vials (30 ml volume) at the specified depths. The sampling vials were filled with deionized water and screened with a 45-µm mesh Nitex membrane held in place by a serum cap. These samplers were inserted into the sediment and allowed to equilibrate with the pore water for 1 month. Retrieved samples were analyzed spectrophotometrically for DRP and NH<sub>4</sub><sup>+</sup> (Strickland and Parsons 1968), sulfides (Otte and Morris 1994), and Cl<sup>-</sup> by coulometric titration. Major cations such as Ca, Mg, K, and Na were measured by ion chromatography on a Dionex DX100. Cations were measured using CS12 guard and analytical columns with auto suppression and 20 mM methane sulfonic acid as eluent, while anions were measured using AS11 guard and analytical columns and 21 mM NaOH as the eluent.

**Calculation and statistical analysis**—We fitted the DRP sorption data to a modified Freundlich adsorption model (Barrow 1978):

$$Y = kC^b - Q, \quad (1)$$

where  $Y$  is the amount of phosphate-P sorbed ( $\text{mg kg}^{-1}$ ) after a 24-h equilibration of the sediment slurry,  $k$  is the Freundlich adsorption coefficient ( $\text{liter kg}^{-1}$ ),  $C$  is the solution phosphate-P concentration ( $\text{mg liter}^{-1}$ ) measured after equilibration and is also termed the equilibrium phosphate-P concentration (EPC),  $b$  is a constant related to bonding energy, and  $Q$  is the amount of phosphate-P sorbed onto the sediment ( $\text{mg kg}^{-1}$ ) prior to any treatment. After fitting the model, solving for  $C$  when  $Y = 0$  yields an estimate of the equilibrium concentration of pore-water DRP at time zero. This estimate is termed the zero-equilibrium-phosphate concentration (ZEPC) and should serve as a proxy for the ambient pore-water phosphorus concentration in the absence of plant uptake or losses due to advection and diffusion.

The Langmuir sorption model, an alternative model, assumes a finite number of available surface sorption sites, whereas the Freundlich model assumes that chemisorption processes supplement surface adsorption. For our DRP sorption data, the Freundlich adsorption model provided a better fit than the Langmuir model, which suggests that the mechanisms involved in sorption of DRP on to sediments at our study sites are more complex and not limited to simple surface adsorption processes.

Model parameters (Eq. 1) were estimated by regression analysis.  $Q$  was estimated by linear regression ( $Y = mC + Q$ , where  $m$  is the slope) of the linear portion of the data set (Olila and Reddy 1993), while  $k$  and  $b$  were estimated by nonlinear regression (PROC MODEL in SAS) after substituting the fitted value of  $Q$  into model Eq. 1.

Geometric means of pore-water DRP concentrations were calculated from log-normalized data. Here we report the grand geometric mean of temporally distributed data from each site and depth. Significant differences among sites and depths in log-normalized pore-water DRP concentrations, sediment mineral composition, and their molar ratios were evaluated using Tukey's studentized range test. Significant differences in  $k$  estimates (Eq. 1) across sites and depths were tested by constructing a 95% Sidak simultaneous confidence interval (Hochberg and Tamhane 1987) using the S-Plus statistical software system (distributed by MATH-SOFT).

## Results

**P sorption parameters**—Estimates of P sorption parameters (Eq. 1) varied in a consistent manner along the salinity gradient. The amount of P sorbed by the sediments decreased toward the saltwater end of the gradient (Fig. 3a). Surface sediments (0–10 cm) from FW had the highest P sorption coefficient ( $k$ ) and the greatest amount of time zero sorbed P ( $Q$ ), while subsurface sediments (10–20 cm) from the SW site had the lowest  $k$  and  $Q$  values. Sediments from the two brackish sites, BW1 and BW2, supported intermediate values. There were also significant differences in  $k$  values between depths at the FW and BW2 sites (Table 1). The P-

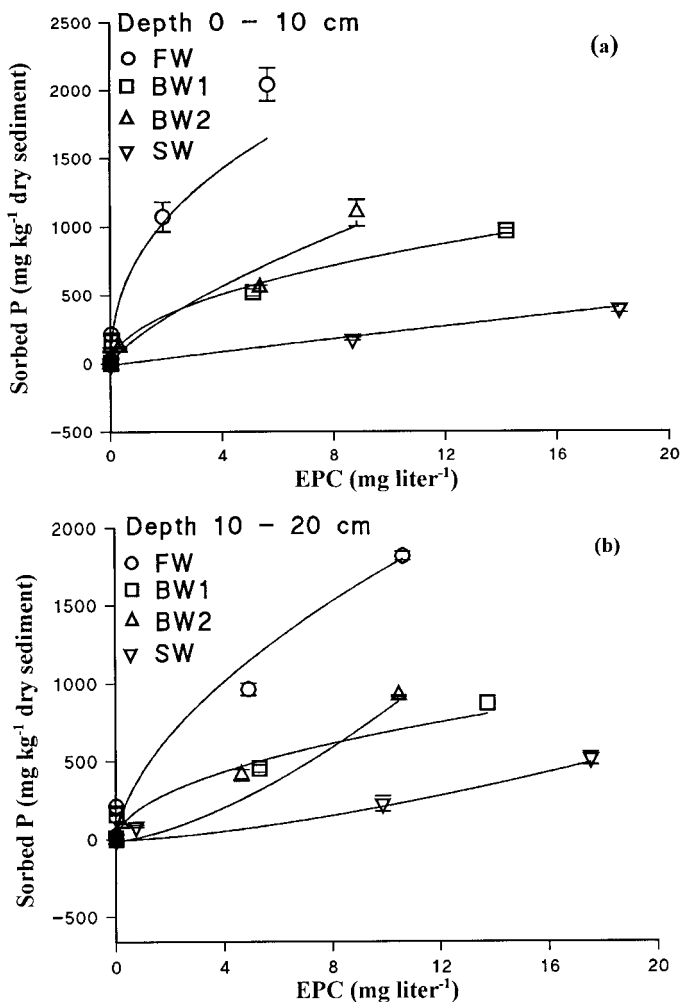


Fig. 3. P-sorption isopleths of (a) surface sediments (0–10 cm depth) and (b) subsurface sediments (10–20 cm) from four sites located along a salinity gradient on the Cooper River estuary. The equilibrium phosphorus concentrations (EPC) ( $\text{mg liter}^{-1}$ ), achieved after a 24-h equilibration period, are plotted against the amount of P sorbed at that EPC ( $n = 27$  per site).

sorption coefficient ( $k$ ) for surface sediment at BW2 was approximately 10 times higher than the  $k$  value for the 10–20-cm-depth fraction at that site. Overall, both  $k$  and  $Q$  values for the subsurface sediments were lower than the corresponding surface values at all sites (Table 1), but subsurface sediments exhibited the same trend in P-sorption along the salinity gradient as surface sediments (Fig. 3b).

The trend in ZEPC values was opposite that of  $k$  and  $Q$ . ZEPC values were positively correlated with salinity ( $r^2 = 0.75$ ,  $P < 0.006$ ,  $n = 8$ ) with highest ZEPC for subsurface sediments at the SW site and lowest for surface sediments at FW. Generally, surface sediments supported a lower soil ZEPC than deeper fractions at all locations along the salinity gradient (Table 1). The dramatic difference in  $k$  values across depths for sediments at BW2 yielded strikingly dissimilar ZEPC values for these fractions such that the ZEPC value for subsurface sediments at this site was about 10 times higher than the value for the surface sediments.

Table 1. Phosphorus sorption characteristics of surface (0–10-cm depth) and subsurface (10–20-cm depth) sediments from a freshwater (FW), two brackish water (BW1 and BW2), and a salt marsh (SW) site in the Cooper River estuary. The parameters  $k$  (Freundlich adsorption coefficient),  $Q$  (the amount of phosphate-P already adsorbed onto the soil), ZEP (zero equilibrium phosphorus concentration), and  $b$  (bonding energy constant) were estimated by fitting the Freundlich model (*see text*). Superscript letters indicate significant differences among and within site based on a 95% Sidak simultaneous confidence interval.

Site	Salinity (g liter <sup>-1</sup> )	0–10-cm depth				10–20-cm depth			
		$k$ (liter kg <sup>-1</sup> )	$b$	$Q$ (mg kg <sup>-1</sup> )	ZEP (mg liter <sup>-1</sup> )	$k$ (liter kg <sup>-1</sup> )	$b$	$Q$ (mg kg <sup>-1</sup> )	ZEP (mg liter <sup>-1</sup> )
FW	0.07	858.92 <sup>a</sup>	0.40	84.66	0.003	477.22 <sup>b</sup>	0.57	43.83	0.015
BW1	0.9	281.85 <sup>b,c</sup>	0.47	35.80	0.013	240.57 <sup>b,c</sup>	0.47	30.78	0.013
BW2	4.7	215.91 <sup>c</sup>	0.71	17.34	0.029	26.27 <sup>d</sup>	1.50	8.46	0.470
SW	20.5	25.83 <sup>d</sup>	0.96	12.44	0.469	7.21 <sup>d</sup>	1.48	5.79	0.863

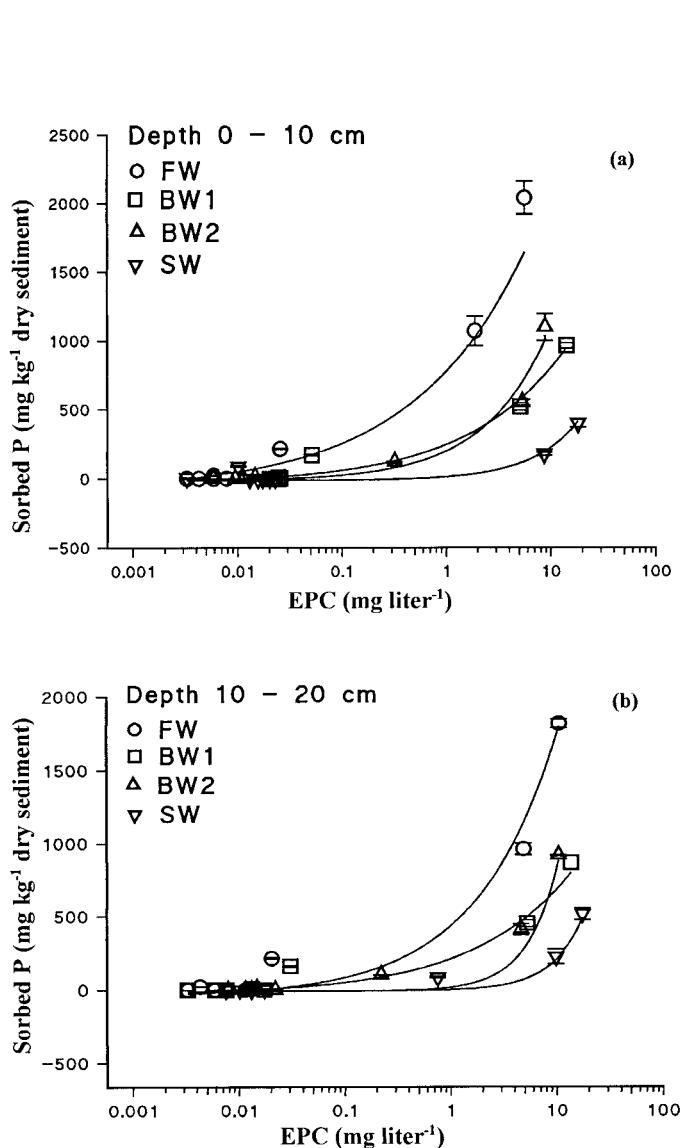


Fig. 4. A semilog plot of the P-sorption isopleths for (a) surface sediments (0–10 cm) and (b) subsurface sediments (10–20 cm) from sites along the Cooper River. This plot illustrates the relative differences in sediment P-sorption efficiency along the salinity gradient. Note the decline in P sorption efficiency of subsurface sediments from FW and BW2 sites.

Semilog plots of the P-sorption isopleths (Fig. 4a,b) clearly show that surface sediments at FW began to sorb appreciable quantities of phosphorus at loading rates that correspond to EPC values lower than 0.1 mg liter<sup>-1</sup>, while the oligohaline (BW1) and mesohaline (BW2) sites showed significant uptake only at loading rates that raised the EPC above 1 mg liter<sup>-1</sup>. SW sediments were least efficient at adsorbing phosphorus and showed appreciable uptake only at loading rates that raised the EPC above 10 mg liter<sup>-1</sup> (Fig. 4a). Subsurface sediments at all sites exhibited a similar trend (Fig. 4b); however, there was a significant decrease in the uptake efficiency of FW and BW2 sediments.

*Sediment C, N, and P*—The molar ratios of total C:total P and total N:total P generally increased with salinity and were significantly higher for SW sediments, while the C:N ratio appeared to be greatest in the midestuarine sites (Table 2). The SW sediments had a significantly greater C:N ratio than the surface sediments at the FW site (Table 2). FW sediments had the highest concentration of total phosphorus (TP) that generally declined along the salinity gradient. Neither total C nor total N concentrations showed any obvious trends along the salinity gradient.

*Pore-water nutrients*—Pore-water concentrations of ammonium and DRP increased with depth at all sites and increased downstream along the salinity gradient. The molar ratio of pore-water ammonium to DRP (N:P) was highest for FW and generally lower for the brackish and salt marsh sites (Table 2).

*Sediment mineral composition*—Surface sediments from all locations along the Cooper River differed in their mineral composition (Table 3). FW was relatively rich in mineral content per unit dry weight, especially in total Al and total Fe. The Al concentration at FW was significantly higher than all other sites. Likewise, total Fe concentration declined with salinity and differed significantly among all sites. The FW surface sediments had a significantly higher P:(Fe + Al) ratio, while the brackish and salt marsh sites supported similar, lower values. Total Ca concentration generally declined along the salinity gradient to a minimum at the mesohaline site (BW2). Ca concentration in surface sediment from the SW site was significantly higher than BW2 but lower than FW and BW1. However, Mg concentrations were highest in

Table 2. Total C, N, and P and their molar ratios for surface and subsurface sediments from FW, BW1, BW2, and SW sites on the Cooper River. FWD, BW1D, BW2D, and SWD refer to the 10–20-cm depth fraction at each respective site. Significant differences ( $\alpha = 0.05$ ) are indicated by different superscript letters (Tukey's studentized range test). Also shown are arithmetic means ( $n = 5$ ) of sediment redox potentials (Eh) at 5- and 15-cm depth.

Site	C (%)	N (%)	Total P (mg kg <sup>-1</sup> )	C:N	C:P	N:P	N:P in pore water	Eh (mV)
FW	38.0 <sup>ab</sup>	3.1 <sup>a</sup>	1752 <sup>a</sup>	14.4 <sup>a</sup>	560 <sup>a</sup>	39.0 <sup>a</sup>	22.3	+202
FWD	45.8 <sup>b</sup>	2.9 <sup>ab</sup>	982 <sup>b</sup>	18.7 <sup>b,c</sup>	1204 <sup>b</sup>	64.4 <sup>b,d</sup>	17.8	+48
BW1	46.1 <sup>b</sup>	2.5 <sup>ab,c</sup>	921 <sup>b,f</sup>	21.9 <sup>b,d</sup>	1297 <sup>b,c</sup>	59.2 <sup>a,b</sup>	2.7	-129
BW1D	46.0 <sup>b</sup>	2.3 <sup>b,c</sup>	697 <sup>c,e</sup>	24.0 <sup>d</sup>	1708 <sup>c</sup>	71.6 <sup>b,c</sup>	2.9	-139
BW2	40.6 <sup>ab</sup>	2.4 <sup>b,c</sup>	914 <sup>b,f</sup>	20.1 <sup>b,c</sup>	1146 <sup>b</sup>	56.9 <sup>a,b</sup>	5.6	-92
BW2D	37.6 <sup>ab</sup>	2.4 <sup>b,c</sup>	798 <sup>c,d,f</sup>	18.6 <sup>b,c</sup>	1218 <sup>b</sup>	65.5 <sup>b,d</sup>	2.9	-145
SW	33.7 <sup>a</sup>	2.2 <sup>b,c</sup>	572 <sup>e</sup>	17.9 <sup>c</sup>	1526 <sup>b,c</sup>	85.3 <sup>c,d</sup>	6.2	-178
SWD	32.8 <sup>a</sup>	2.1 <sup>c</sup>	703 <sup>c,d,e</sup>	18.3 <sup>c</sup>	1207 <sup>b</sup>	66.1 <sup>b,d</sup>	4.6	-166

the midestuarine region, while concentrations of K and Na in sediments were lowest toward the upper reaches of the estuary. As mentioned earlier, the sedimentary TP values were negatively correlated with salinity, while the pore-water DRP concentrations generally exhibited a positive correlation. In contrast, sedimentary Si concentrations were positively correlated with salinity ( $r^2 = 0.75$ ,  $P < 0.0001$ ,  $n = 24$ ). The mean Si concentrations (mean  $\pm$  SE,  $n$ ) over the rooting zone (0–20 cm depth) at FW, BW1, BW2, and SW sites were 29.45% of dry weight  $\pm$  0.43,  $n = 6$ ; 28.87% of dry weight  $\pm$  0.12,  $n = 6$ ; 29.95% of dry weight  $\pm$  0.23,  $n = 6$ ; and 33.23% of dry weight  $\pm$  0.67,  $n = 6$ , respectively.

**Sediment redox potentials**—The sediment redox potentials decreased along the salinity gradient (Table 2). The freshwater marsh sediments exhibited a positive redox potential while the brackish and salt marsh sediments showed increasingly negative redox potential. Generally, redox potential at 15 cm depth was lower than the redox potential at 5 cm depth at all sites except SW.

**Sediment CEC**—The CEC of surface sediments decreased along the salinity gradient ( $r^2 = 0.75$ ,  $P = 0.0052$ ,  $n = 8$ ). The (mean  $\pm$  SE) CEC value of duplicate measurements for FW was 40.84 cmoles(+) kg<sup>-1</sup> dry sediment  $\pm$  0.5; for BW1

and BW2 the CEC values were 27.3 cmoles(+) kg<sup>-1</sup> dry sediment  $\pm$  0.7, and 31.38 cmoles(+) kg<sup>-1</sup> dry sediment  $\pm$  1.54, respectively; and for SW it was 14.92 cmoles(+) kg<sup>-1</sup> dry sediment  $\pm$  0.86. The CEC values of sediments from the freshwater, the brackish water, and the salt marsh sites differed significantly from each other at the  $\alpha = 0.05$  level. However, the mean CEC values of sediments from the two brackish water sites BW1 and BW2 were not significantly different.

**Sediment surface area**—Sediment surface area also declined with increasing salinity along the Cooper River and differed significantly among the freshwater, the brackish water, and the salt marsh sites ( $\alpha = 0.05$ ). Freshwater sediments had the highest surface area (54.9 m<sup>2</sup> g<sup>-1</sup>  $\pm$  0.51), and salt marsh sediments had the lowest (6.4 m<sup>2</sup> g<sup>-1</sup>  $\pm$  0.8). Surface sediments from brackish water sites (BW1 and BW2) had intermediate surface areas of 31.9 m<sup>2</sup> g<sup>-1</sup>  $\pm$  1.3, and 30.1 m<sup>2</sup> g<sup>-1</sup>  $\pm$  1.1, respectively.

## Discussion

There is a trend of decreasing P-sorption potential of intertidal marsh sediments with increasing salinity along the Cooper River, that appears to be controlled by abiotic mechanisms such as salinity, sediment surface area, CEC, and the

Table 3. Mineral composition of the surface and subsurface sediments from the four study sites. FWD, BW1D, BW2D, and SWD refer to the 10–20-cm depth fraction at each respective site. Data on Si concentrations are provided in the text (see Results). Significant differences ( $\alpha = 0.05$ ) are shown as superscript letters (Tukey's studentized range test).

Site	Al (%)	Fe (%)	Ca (%)	Mg (%)	K (%)	Na (%)	Total P (mg kg <sup>-1</sup> )	Sedimental P:(Al + Fe) ( $\mu$ mol mmol <sup>-1</sup> )
FW	11.5 <sup>a</sup>	9.2 <sup>a</sup>	0.65 <sup>a,b,c</sup>	0.65 <sup>a</sup>	0.75 <sup>a</sup>	0.17 <sup>a</sup>	1752 <sup>a</sup>	9.6 <sup>a</sup>
FWD	10.9 <sup>b</sup>	7.2 <sup>b</sup>	0.70 <sup>b</sup>	0.83 <sup>b</sup>	0.90 <sup>b</sup>	0.16 <sup>a</sup>	982 <sup>b</sup>	5.9 <sup>b</sup>
BW1	9.5 <sup>c</sup>	7.4 <sup>b</sup>	0.61 <sup>c</sup>	0.96 <sup>c,d</sup>	1.14 <sup>c</sup>	0.53 <sup>b</sup>	921 <sup>b,f</sup>	6.1 <sup>b</sup>
BW1D	9.1 <sup>d</sup>	8.7 <sup>c</sup>	0.61 <sup>c</sup>	0.97 <sup>d</sup>	1.00 <sup>d</sup>	0.55 <sup>b</sup>	697 <sup>c,e</sup>	4.6 <sup>c</sup>
BW2	10.2 <sup>e</sup>	4.6 <sup>d</sup>	0.48 <sup>d</sup>	0.93 <sup>c,d</sup>	1.18 <sup>e</sup>	0.65 <sup>b,c</sup>	914 <sup>b,f</sup>	6.4 <sup>b</sup>
BW2D	10.0 <sup>e</sup>	6.0 <sup>e</sup>	0.42 <sup>e</sup>	0.90 <sup>b,c</sup>	1.03 <sup>d</sup>	0.69 <sup>b,d</sup>	798 <sup>c,d,f</sup>	4.8 <sup>b,c</sup>
SW	6.3 <sup>f</sup>	3.4 <sup>f</sup>	0.55 <sup>f</sup>	0.53 <sup>e</sup>	1.17 <sup>c,e</sup>	0.84 <sup>c,d,e</sup>	572 <sup>e</sup>	6.3 <sup>b</sup>
SWD	8.2 <sup>g</sup>	4.5 <sup>d</sup>	0.64 <sup>a,c</sup>	0.70 <sup>a</sup>	1.15 <sup>c,e</sup>	1.07 <sup>e</sup>	703 <sup>c,d,e</sup>	5.9 <sup>b</sup>

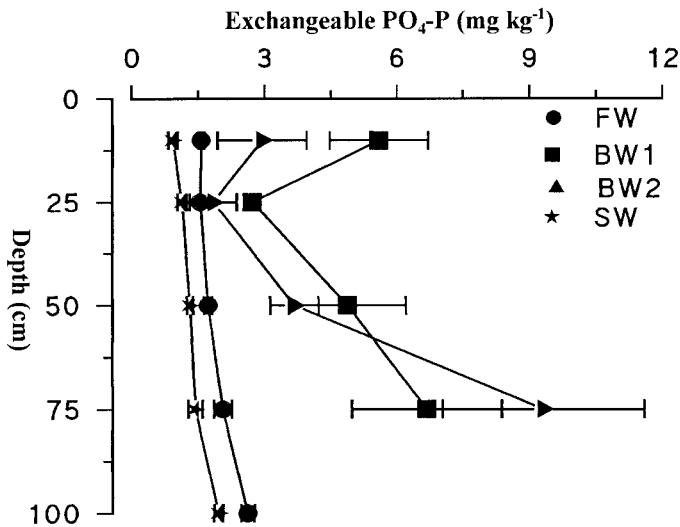


Fig. 5. Depth profile of bound but potentially exchangeable phosphorus at the four study sites on the Cooper River estuary.  $n = 6$  per site per depth.

mineral composition of the sediments. These impose varying degrees of control on the observed trend in P-sorption capacity of marsh sediments. For instance, the influence of salinity on the P-exchange properties of the sediments is evident from the observed trend in exchangeable phosphorus along the Cooper River. The brackish and salt marsh sediments are flushed frequently by high ionic strength surface waters and experience in situ extraction. This accounts for the decreasing concentration of exchangeable P from site BW1 to SW observed in the laboratory experiments (Fig. 5). In addition, sediment surface area and CEC declined in sediments with increasing salinity.

Though the sediment surface area is a major determinant of sorption and CEC, surface area alone cannot explain these trends. For example, while the mean P-sorption coefficient ( $k$ ) of FW surface sediments is 3, 3.9, and 33 times higher than that of the surface sediments from BW1, BW2, and SW sites, respectively, the mean surface area of FW sediments is only, 1.7, 1.8, and 8.5 times higher than the respective surface areas. Furthermore, FW sediments yield low exchangeable P (Fig. 5), even though these sediments have the greatest total P concentration and are not subject to salt water intrusions. A previous study has shown that, at the FW site, P is preferentially bound to humic acids and trapped in the Fe(III) and Al pools (Paludan and Morris 1999). This suggests that other factors such as the mineral composition of these sediments also contribute to the observed differences in their P-exchange properties.

The inverse relationship between total sedimentary P and salinity may be attributed to decreases, with salinity, in iron hydroxide content of sediments (Upchurch et al. 1974; Strom and Biggs 1982) or in total sedimentary Fe and Al concentrations. For example, Paludan and Morris (1999) found that the Fe(III) concentration was highest in the Cooper River surface sediments at FW (approximately  $150 \mu\text{mol g}^{-1}$  dry sediment), then declined to approximately  $50 \mu\text{mol g}^{-1}$  dry sediment at site BW2, and was below detection in SW sed-

iments. Though Al concentrations also declined with increasing salinity, Al was predominantly bound to humic acids. This humic acid Al was 5–10 times more concentrated than the pool of amorphous Al. Correspondingly, they also reported a decline in reactive P associated with Fe and Al fractions along the salinity gradient. Interestingly, in their study, the humic-bound P also declined with increasing salinity, while the humic acid—metal: humic acid P ratio increased with salinity.

Previous studies using estimates of free sorption sites have demonstrated the importance of total Al, Fe, and Ca concentrations on total sedimentary P (Lopez et al. 1996). A comparison of the relative degree of free sorption sites on metal particles, as estimated by the sedimentary P:(Fe + Al) ratio (Table 3), indicates that surface sediments at the FW site support significantly more sorption sites than the other locations. This is also supported by the positive correlation between the total phosphorus and total Al + Fe concentration along the salinity gradient (Fig. 6). The total sediment Fe and Al concentrations decreased from the freshwater site to the saltwater site (Table 3) as a function of changes in CEC of respective sediments, possibly related to grain size. For instance, sedimentary silica (Si) concentrations increased along the salinity gradient (29% of dry weight at the FW site to 33% at the SW site), which is consistent with a change from clay-dominated to sand-dominated sediments. This suggests that the trends in sedimentary concentrations of Al, Fe, and Ca are related to CEC, which is a function of surface area. There is also a trend with depth in the P-sorption potential of these sediments that is clearly related to the distribution of Fe species. For instance, at BW2, iron predominantly occurs in the Fe(III) state in surface sediments and in the Fe(II) state in subsurface sediments (Paludan and Morris 1999). Because Fe(III) is more efficient at binding P, the iron-bound P pool rapidly declines with depth, which is consistent with the higher sorption coefficient for the surface sediments observed in this study.

Factors such as sulfide production and pH also control the P dynamics in wetland sediments. Caraco et al. (1989) proposed sulfide production as being important in controlling P availability by competing for iron and decreasing this important sink for P. Furthermore, the P-sorption capacity of sediments containing Fe-hydroxides and nonredox-sensitive species such as Al-hydroxides is expected to decrease along the salinity gradient due to corresponding changes in pH. The pore-water pH (20 cm depth) in our study sites generally ranged from 4.5 at the FW site, to 7.0 at the BW2 site, and 8.0 at the SW site (Paludan and Morris 1999). Under freshwater conditions, such as those at the FW site, the hydroxides of metals such as Fe and Al carry a net positive charge that would facilitate P sorption, while under saltwater conditions they carry a net negative charge (e.g., Barrow et al. 1980; Stumm and Morgan 1981; Smith et al. 1998). While the pH corresponding to the point of zero charge (condition where the surface charge caused by binding of  $\text{H}^+$  or  $\text{OH}^-$  is zero) of various oxides of Fe and Al ranges from 5.6 to 9.1, the presence of anions such as  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  serves to reduce the isoelectric point (pH where a particle is electrokinetically neutral) of these metal hydroxides (e.g., Stumm

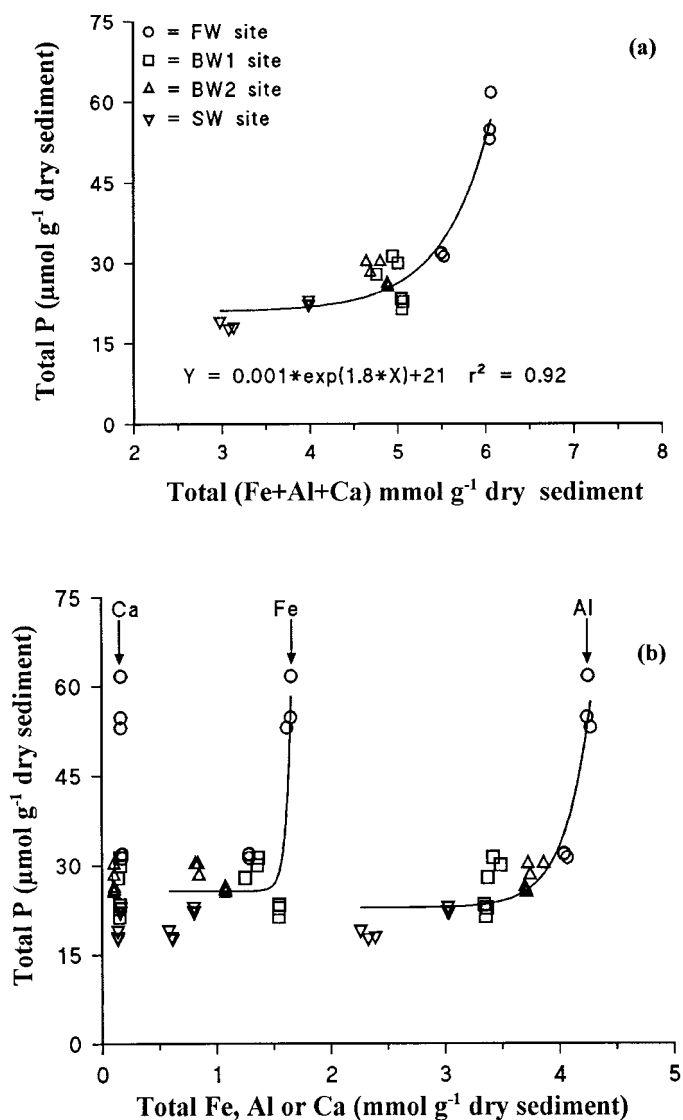


Fig. 6. (a) A plot of sediment mineral composition versus total sedimentary P for surface and subsurface sediments from the Cooper River study sites ( $n = 3$  per site per depth). (b) The relative importance of Ca, Fe, and Al in controlling the total sedimentary P concentration at the four study sites. No relationship exists for Ca and TP. For Fe ( $\text{mmol g}^{-1}$ ) the relationship is:  $\text{TP} (\mu\text{mol g}^{-1}) = 4.4 \times 10^{-15} e^{22.1X} + 25.7$ ,  $r^2 = 0.77$ ; while Al ( $\text{mmol g}^{-1}$ ) appears to be most important ( $\text{TP} [\mu\text{mol g}^{-1}] = 2.1 \times 10^{-7} e^{4.4X} + 22.8$ ,  $r^2 = 0.89$ ).

and Morgan 1981). These anions also compete with  $\text{PO}_4^{3-}$  for the available sorption sites. Thus, changing redox potential, pH, and ionic strength along the salinity gradient will alter the P-sorption capacity of these hydroxide sinks. For instance, surface sediments at BW1, BW2, and SW sites share similar estimates of free sorption sites on metal particles (Table 3) but support increased pore-water DRP concentrations at higher salinities.

Freshwater sediments are more efficient in sequestering P than brackish and salt marsh sediments, as evidenced by the decline in the sorption coefficient ( $k$  value) with increasing

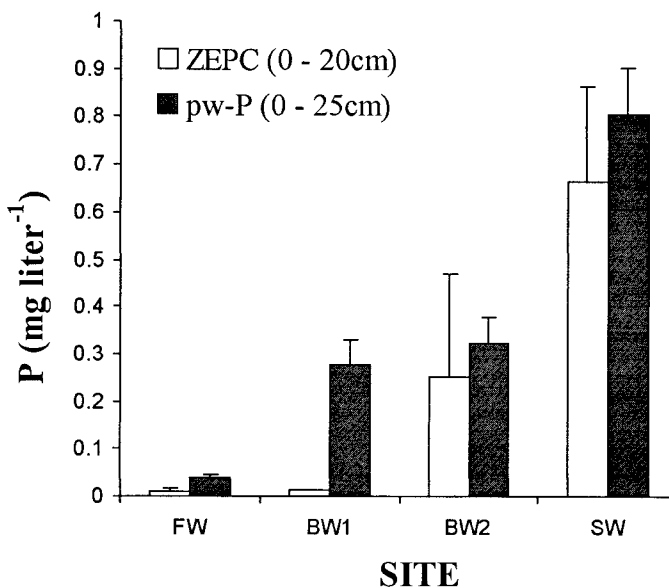


Fig. 7. A comparison of the zero equilibrium phosphorus concentration (ZEPc) estimated from Eq. 1 and the grand geometric mean of pore-water concentration of dissolved reactive phosphorus (DRP). Presented here are the depth-averaged values of each to provide an estimate over the rooting zone (0–25 cm depth). The error bars represent the standard error of the mean for ZEPc and the upper 95% confidence limit for the grand mean of pore-water phosphate-P concentration at the respective sites.

salinity. The range of  $k$  values for the Cooper River wetland sediments is comparable to those observed in other systems (Krom and Berner 1980; Mayer and Gloss 1980; Wauchop and McDowell 1984). Total P and the estimated  $Q$  value were also highest at the freshwater end, while DRP was highest in the salt marsh. The inverse relationship between total sediment phosphorus concentration and salinity along the Cooper River estuary is in agreement with similar observations in other estuaries (Upchurch et al. 1974; Strom and Biggs 1982). Likewise, the soil ZEPc (estimated from Eq. 1) increased with salinity along the Cooper River and predicted the in situ pore-water DRP concentrations reasonably well ( $r^2 = 0.83$ ,  $P = 0.0016$ ,  $n = 8$ ). Other studies have also shown such a positive correlation between salinity and equilibrium phosphorus concentration (Clavero et al. 1990). There are many biotic factors such as absorption and mineralization of P by plants (Stephen et al. 1997) and microbes (Roden and Edmonds 1997) that regulate the phosphorus dynamics of a site, but the close agreement between depth-averaged estimates of the soil ZEPc and the corresponding pore-water DRP concentrations (Fig. 7) suggests that the abiotic P-sorption characteristics of sediments dominate. Our data clearly indicate that differences in sediment chemical and physical characteristics along the Cooper River, perhaps ultimately a consequence of changes in ionic strength of flood water and associated parameters, contribute to the observed differences in availability of pore-water DRP.

The availability of phosphorus, as measured by the depth-averaged ZEPc, in relation to the half-saturation constant ( $k_m$ ) for phosphate uptake by plants is consistent with the

generally accepted paradigm of a switch from P limitation in freshwater ecosystems to N limitation in salt marshes. For instance,  $k_m$ s for phosphate uptake for various plant species range from 2.4  $\mu\text{M}$  to 21.6  $\mu\text{M}$  and are commonly about 5  $\mu\text{M}$  (Cogliatti and Clarkson 1983; Sentenac and Grignon 1985; Perez and Niell 1995). In contrast, the soil ZEP is considerably lower than this  $k_m$  value (5  $\mu\text{M}$ ) at the FW site and higher at the SW site. This indicates that DRP concentrations are likely to be limiting to primary production at the freshwater end of the Cooper River estuary but not at the saltwater end. Hence, the relative difference in P availability is ultimately a function of the abiotic controls on P-sorption characteristics of the sediments.

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