



Distribution and speciation of phosphorus along a salinity gradient in intertidal marsh sediments

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Abstract. We examined forms of solid phosphorus fractions in intertidal marsh sediments along a salinity (0–22‰) gradient in a river-dominated estuary and in a marine-dominated salt marsh with insignificant freshwater input. Freshwater marsh sediments had the highest ratio of organic N:P of between 28:1 and 47:1 mol:mol, compared to 21:1 to 31:1 mol:mol in the saltmarshes, which is consistent with a trend toward P-limitation of primary production in freshwater and N-limitation in salt marshes. However, total P concentration, $24.7 \pm 11.1 \mu\text{mol P g dw}^{-1}$ (± 1 SD) averaged over the upper meter of sediment, was greatest in the freshwater marsh where bioavailability of P is apparently limited. In the freshwater marsh the greatest fraction of total P (24–51%) was associated with humic acids, while the importance of humic-P decreased with increasing salinity to 1–23% in the salt marshes. Inorganic P contributed considerably less to total sediment P in the freshwater marsh (15–40%) than in the salt marshes (33–85%). In reduced sediments at all sites, phosphate bound to aluminum oxides and clays was an important inorganic P pool irrespective of salinity. Inorganic P associated with ferric iron [Fe(III)] phases was most abundant in surface sediments of freshwater and brackish marshes, while Ca-bound P dominated inorganic P pools in the salt marshes. Thus, our results showed that particle-bound P in marsh sediments exhibited changes in chemical association along the salinity gradient of an estuarine system, which is a likely consequence of changes in ionic strength and the availability of iron and calcium.

Introduction

Some studies have shown that intertidal marsh ecosystems are sources of phosphorus (P) to adjacent estuarine and coastal waters (e.g. Wolaver et al. 1984; Jordan & Correll 1991), while others have concluded that marshes act as net sinks for P (DeLaune et al. 1981; Wolaver et al. 1983; Dame et al. 1990). Wolaver and Zieman (1984) concluded that the amount of phosphorus retained was almost sufficient to sustain annual plant production. The

importance of marsh vegetation and microorganisms in controlling sediment P storage is acknowledged (DeLaune et al. 1981), though regulation of the net storage of P must be largely regulated by the chemical and physical properties of the sediments. For example, marshes with highly oxidized surface sediments can retain dissolved reactive phosphorus (DRP), presumably through associations between P and reducible iron compounds (Scudlark & Church 1989; Chambers & Odum 1990). Differences in sediment chemical properties may account for discrepancies in wetland studies of P mass balance.

The salinity of the flood water has major effects on the chemistry of tidal marsh sediments, and the behavior of intertidal wetlands with respect to P probably varies with salinity. In freshwaters, for instance, dissolved organic carbon (DOC) forms complexes with metals such as iron (Fe) and aluminum (Al), and these complexes may sequester DRP thereby decreasing bioavailable P (Jones et al. 1993). During mixing with saltwater, DOC flocculates with associated metals and phosphate and then precipitates. This may account for non-conservative decreases in concentrations of these constituents that are commonly observed in the low salinity (0–10‰) region of estuaries (e.g. Sholkovitz 1976; Boyle et al. 1977; Fox et al. 1986). A significant fraction of river-borne P is carried to the sea on suspended particles from which a portion of the phosphate desorbs during mixing with salt water (Fox et al. 1986; Froelich 1988). Further, the composition of suspended, particle-bound P is modified in response to increased salinity and pH. Thus, approaching the sea, the contribution of iron- and aluminum-bound phosphate to total sediment P diminishes, while that of calcium-bound and easily exchangeable phosphate increase (de Jonge & Villerius 1989; Lebo 1991; Zwolsman 1994).

Differences in sediment P chemistry will be manifest in changes in distribution of the major P compounds such as iron- and calcium-bound P and DRP. The objective of this study was to quantify the distribution of major P fractions in different tidal marsh sediments and to determine controls of porewater DRP and the bioavailability of P. This was related to macrophyte P-demand. Our study was focused on intertidal marshes distributed along a salinity gradient in the Cooper River estuary (South Carolina, USA) and a tidal salt marsh that receives negligible freshwater inputs in the North Inlet estuary, South Carolina. Sediments from these marshes were characterized with respect to pool sizes of total P, Fe, and Al, the major chemical fractions of solid-phase P, DRP, and general physico-chemical characteristics of the sediments.

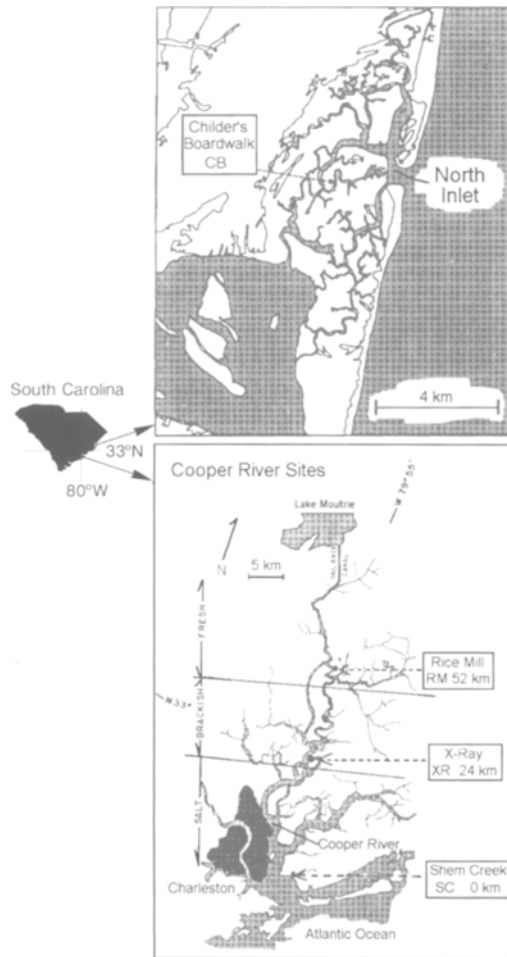


Figure 1. Geographic locations of North Inlet and Cooper River study sites.

Material and methods

Site description

The study was conducted at three sites along the Cooper River estuary, South Carolina (Figure 1). Tidal mixing creates a salinity gradient along the Cooper River extending from the mouth (22‰ salinity) to 50 km upstream (0‰ salinity) (Bradley et al. 1990). Discharge is regulated and, in an effort to reduce sedimentation in Charleston Harbor, in 1985 it was reduced by about 70% of the mean discharge that prevailed during the 1941–1985 period and now averages $130 \text{ m}^3 \text{ s}^{-1}$ (Kjerfve & Magill 1990). Sediment was sampled from

a salt marsh at the mouth of Shem Creek (SC) in Charleston Harbor, from a brackish marsh (designated XR) 24 km upstream where the salinity of river water is approximately 6‰, and from a freshwater marsh (designated RM) situated 52 km upstream. The vegetation at the salt marsh site (SC) is dominated by *Spartina alterniflora*, while *Juncus roemarianus*, *S. alterniflora*, *S. cynosuroides* and *Scirpus spp.* dominate the brackish marsh (XR). The greatest diversity of species occurs at the freshwater (RM) end of the gradient where *Peltandra virginica*, *Pontederia cordata*, *Zizania aquatica*, *J. roemarianus*, and *S. cynosuroides* are common.

To contrast the Cooper River salt marsh with a salt marsh that differs significantly in the influence of freshwater runoff and terrigenous inputs, sediments were also sampled in a mature salt marsh situated within the North Inlet estuary (Belle W. Baruch Marine Institute, Georgetown, South Carolina) at a site designated CB (Figure 1). The salinity of North Inlet creek water is approximately 32‰. At North Inlet the vegetation is a monoculture of *S. alterniflora*.

Porewater sampling and analyses

Porewater chemistry was measured monthly from December 1993–December 1995 in the Cooper River marshes and from April 1994–August 1995 in the North Inlet marsh. Every month triplicate porewater samples were collected 15 meters from the creek bank at 5 depths (10, 25, 50, 75, 100 cm) using diffusion samplers. Glass vials filled with distilled water, 25 ml volume, and screened with 45 μm mesh Nitex membranes over the mouth, were placed in the sediment and allowed to equilibrate with the porewater for 1 month. Equilibration time in water is about 95 h. Retrieved samples were transported to the lab on ice and analyzed within 24 hours for DRP (see below), Cl^- by potentiometric titration and S^{2-} by a modification (Otte & Morris 1994) of Cline's (1969) method.

Sediment sampling and analyses

Sediment was sampled during the spring 1994. In each marsh two sediment cores (1 m length \times 8 cm diameter) were collected 15 m inland from the creekbank under saturated conditions by use of a steel piston corer. Sediment compression was less than 5%. Cores were extruded and sectioned in the field in lengths of 2 cm (from 0–6 cm depth), 3 cm (from 6–15 cm), and 4 cm (from 15–27, 48–52, 73–77, and 98–102 cm). Each section was subdivided into two equal parts. One part was saved for determination of bulk density and porosity, while the other was immediately placed under a N_2 atmosphere in a ziplock plastic bag and returned on ice to the laboratory. The samples were

processed within 24 hours and carefully handled in a glove bag under a N_2 atmosphere to prevent oxidation of reduced species. At each depth, sediment sections from the two cores were pooled into one bulk sample before being passed through a 2 mm mesh sieve followed by further processing.

For determination of P pools, metals, and pH, replicate ($n = 2$) subsamples of the pooled wet sediments were weighed and placed into centrifuge tubes or serum bottles (inside a glove bag) that were then closed by airtight seals. Pooling the cores was a compromise that reduced processing time and within-site variability, while replicate measurements made on the pooled samples allowed us to assess analytical error. The disadvantage of pooling samples is that a statistical test of differences between sites is not strictly possible, because within-site variation cannot be assessed. However, differences between pooled samples were tested and then evaluated in the context of existing biogeochemical theory.

Redox potential (E_h) of the sediment was measured in the field at low tide at 10 cm intervals (to 1 m depth) with platinum and standard calomel ($E = 244$ mV) electrodes standardized against a solution of known potential (Zobell 1946). Three profiles were measured within a 1 m^2 area around the coring locations at each study site.

Bulk density and porosity were determined after drying sediment sections (60°C) to constant weight. Porosity was calculated gravimetrically. Dry weight of sieved sediment was determined after drying at 105°C to constant weight. Calculations of porosity and dry weight were corrected for porewater salinity using measured porewater Cl^- concentrations, assuming the salt to have the formula weight of NaCl. Sieved, dry sediment was ground in a porcelain mortar, and organic matter content was determined by measuring the weight loss after combustion at 550°C for 2 hours. pH was measured after extraction of 5.0 g sediment with 10.0 ml distilled water for 2 hours. All glass and plasticware was pre-washed in 5% HCl followed by a distilled water rinse.

Sediment was sequentially extracted for phosphorus-pools by use of a five step extraction scheme (Jensen & Tamdrup 1993; Paludan & Jensen 1995). A 1.5 g, wet sediment sample was treated with 37.5 ml of extraction solution and the supernatant collected after centrifugation at 5000 rpm for 15 min at 2°C . The first step in the sequence was a double extraction with deoxygenated H_2O (distilled and deionized) that removed loosely adsorbed reactive and nonreactive phosphate as well as porewater DRP and DNRP (dissolved non reactive P). The dissolved reactive fraction is referred to here as $\text{H}_2\text{O-P}$. In the analysis of brackish and salt marsh sediments, H_2O was substituted with solutions of 90 and 340 mm NaCl, respectively.

The next extraction with 0.11 M bicarbonate dithionite (BD) removed phosphate associated with reducible oxides of Fe and Mn, and the dissolved reactive fraction of this extract will be referred to hereafter as Fe-P. The efficiency of the BD extraction with respect to Fe is discussed under results. The H₂O and BD extractions were performed under a N₂-atmosphere. BD was used instead of citrate sodium-dithionate bicarbonate (CDB), because the extraction of calcium-bound P is less pronounced in BD, and BD extracts reducible Fe as efficiently as does CDB. Thus, substituting BD for CDB improves the specificity of the method for Fe-P (Psenner et al. 1984). The BD reducing reagent is also more efficient in extracting reducible iron than 0.5 M HCl, because BD dissolves crystalline and amorphous Fe oxides, while HCl dissolves only the latter. Further, NaOH is commonly used to dissolve both Fe and Al oxides. Treating the sediment with BD (second step) before NaOH (third step) specifically extracts most Fe(III) oxides. In surface sediments at the freshwater (RM) site, for example, BD extracted 45% of the total Fe pool, while a subsequent NaOH extraction yielded only an additional 4% (data not shown).

The third step, an extraction with 0.1 M NaOH, removed much of the sediment organic P together with phosphate adsorbed onto the surfaces of clays and oxides of Al. The dissolved reactive fraction of this extraction is referred to as Al-P. NaOH is commonly used to dissolve both Fe and Al oxides, though this step was preceded by a BD extraction as noted above. The supernatant, often brown because of dissolved organic matter, was acidified to pH 1 to precipitate the humic acids from solution. The humic acid precipitate was isolated by filtration, combusted at 550 °C, and the ash boiled in 1.0 M HCl (Paludan & Jensen 1995). This humic acid P fraction is here referred to as HA-P.

The fourth extraction sequence with 0.5 M HCl removed phosphate associated with calcium carbonate, and the dissolved reactive fraction of this extraction is denoted Ca-P. In the final step, the residual sediment pellet was combusted and extracted with hot 1.0 M HCl to determine P in refractory organic matter (Res-P).

Except for the last step, DNRP in the supernatants was determined as the difference between total dissolved P and DRP. These DNRP pools were assumed to represent organic compounds, and the summation of these is referred to here as Σ DNRP. However, NaOH extracts far more DNRP than any other step including some fulvic acids. At each step, DRP in the extract was determined spectrophotometrically using the ascorbic acid method (Strickland & Parsons 1972), and total dissolved P was determined by analysis of DRP after wet oxidation of the sample.

Total P (TP) in ground sediment samples from all depths was determined by the method used for HA-P determination (see above), while total organic P (P_{org}) was defined as the sum of HA-P, Res-P, and ΣDNRP . Total organic nitrogen (TKN) was determined in ground sediment samples from 0, 25, 50, 75, and 100 cm depth by the Kjeldahl method using a Kjeltec Auto Analyzer (Tecator). The contribution of ammonium to TKN in sediment by this method was considered to be negligible (Bowden 1984).

Fe was extracted from 1.0 g sediment in N_2 flushed serum bottles for 1 hour in darkness in 25.0 ml 0.5 M HCl (purged with N_2). Concentrations of $\text{Fe(II)}_{\text{HCl}}$ and total Fe_{HCl} were determined spectrophotometrically at 562 nm after adding 0.1 ml of the extract to 10 ml of non-reducing and reducing ferrozine, respectively (Stookey 1970; Phillips & Lovley 1987). Oxidized amorphous Fe [$\text{Fe(III)}_{\text{HCl}}$] was determined as the difference between total Fe_{HCl} and $\text{Fe(II)}_{\text{HCl}}$. Reducing ferrozine was also used to determine Fe in Fe-P and HA-P extracts.

Amorphous Al was extracted from 2.0 g of sediment by 15.0 ml 0.2 M ammonium oxalate (pH 3) for 4 hours, and is a measure of "free" Al oxides in soils (Blume & Schwertmann 1969). Al in these extracts as well as in the HA-P extracts was determined by atomic absorption spectroscopy (nitrous oxide acetylene flame).

The various pool sizes of sedimentary P were compared to estimates of P assimilation by the marsh macrophyte community in order to assess their ecological importance and to indicate relative turnover times. Conservative estimates of primary production of marsh macrophytes were based on collections of standing biomass taken from each site in late August. Three transects were established at each site, perpendicular to the river, and the standing vegetation was harvested from 0.0625 m^2 quadrats along each transect at 0, 10, 20, 30, and 40 m from the edge of the river, and the average standing biomass was calculated by site. Total primary production was derived by multiplying the mean standing biomass by 4 to account for leaf turnover (Morris & Haskin 1990) and belowground production (Morris 1982), assuming that these macrophytes behave similarly to the salt marsh grass *Spartina alterniflora*. Finally, plant P-demand was derived by multiplying the site-specific mean P concentration in aboveground tissue, from composited samples, by the production estimates. P concentration in plant tissues collected in October, corrected for ash weight, was analyzed after boiling the ash residue of combusted tissues in 1.0 M HCl (Paludan & Jensen 1995).

Statistics – Data means were computed by site and by sediment depth. The significance of main effects was evaluated by analysis of variance (PROC GLM of SAS) (SAS Institute 1988). Statistically significant differences among paired depths or sites were evaluated using the studentized range

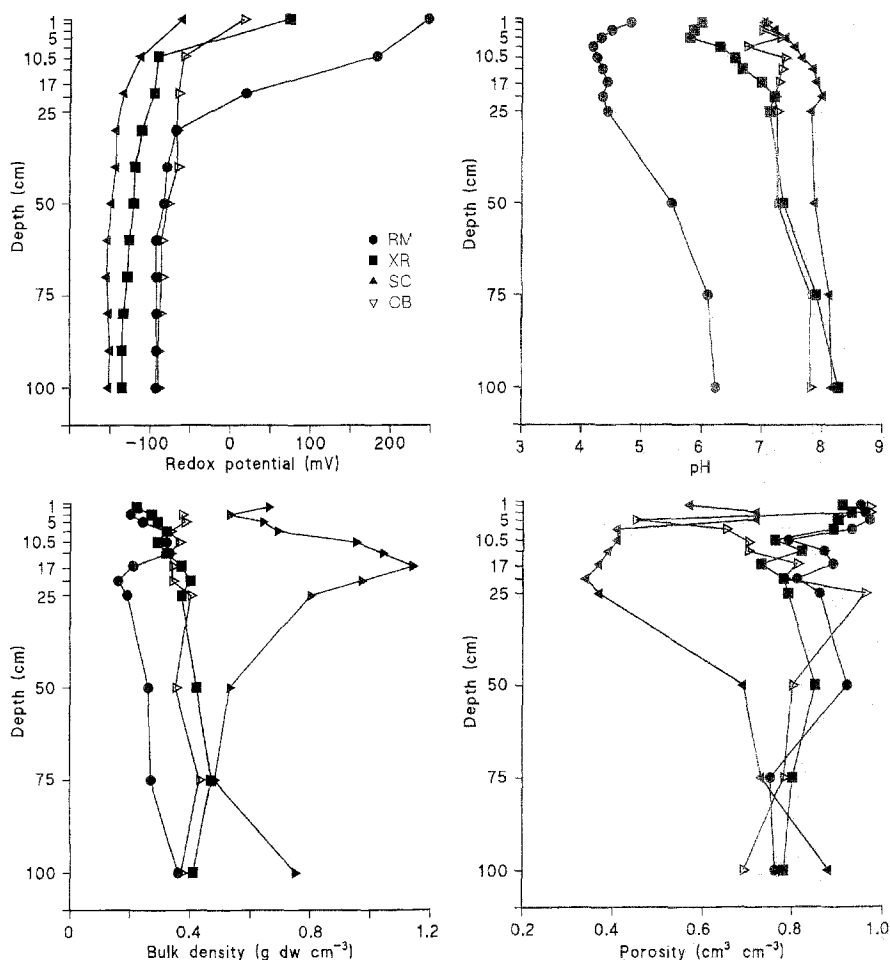


Figure 2. Depth profiles of redox potential (top left), pH (top right), bulk density (bottom left) and porosity (bottom right) in sediments from freshwater (●), brackish (■), and salt marsh (▲) sites along the Cooper River and from the North Inlet salt marsh (▽). Each curve represents the mean of 2 determinations, except for redox potential ($n = 3$).

test ($P = 0.05$). Data were normalized by log-transformation before statistical analyses. DRP, Cl^- , and S^{2-} concentrations in porewater are reported as geometric means with lower and upper 95% confidence limits.

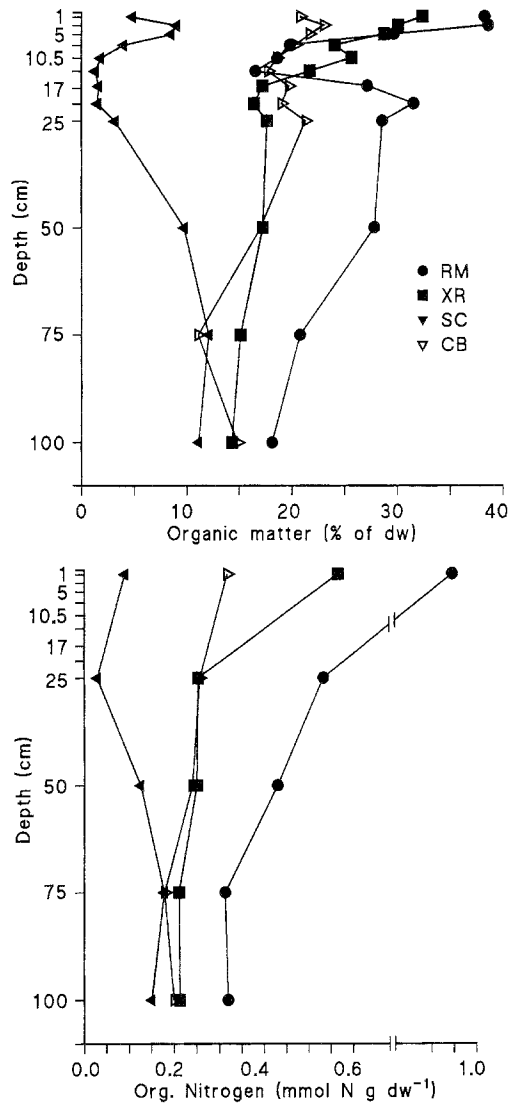


Figure 3. Depth profiles of organic matter (top) and organic nitrogen (bottom) in sediments from freshwater (●), brackish (■), and salt marsh (▲) sites along the Cooper River and from the North Inlet salt marsh (▽). Values are means of two determinations.

Results

Sediment characteristics

Sediments differed markedly in bulk density, porosity (Figure 2) and organic matter content (Figure 3) depending on location. The lowest and highest

bulk densities occurred in freshwater (RM) and salt marsh (SC) sediments, respectively, and RM and SC had the highest and lowest sediment porosity and organic matter. Brackish (XR) and North Inlet salt marsh (CB) sediments were similar with respect to these parameters, although organic matter in the XR sediment was greater than CB (Figure 3).

Redox potential decreased with depth of sediment at all sites (Figure 2). Freshwater (RM) sediments were relatively more oxidized ($E_h > 0$ mV) in the upper 20 cm than other sites, while sediments from brackish and saline marshes were reduced ($E_h < 0$ mV) throughout their profiles, except near the surface (1 cm) of XR and CB sediments.

Sediment pH was lowest at the freshwater (RM) site and highest at the salt marsh (SC) site (Figure 2). Surface sediments at the brackish (XR) site showed lower pH than the salt marshes (SC and CB), but below 25 cm depth the differences were small.

Sediment TP and TKN

There was a significant downstream decrease in concentrations of TP and TKN in sediments in the Cooper River marshes (Figures 3 and 4). Among the salt marshes, the highest TP and TKN concentrations occurred at the North Inlet salt marsh (CB). Depth profiles of TP and TKN in the freshwater (RM) and brackish (XR) marsh sediments, and to some extent CB sediments, generally showed declining concentrations with depth. The opposite generally occurred in the SC marsh, because of a sand deposit that changed bulk density, as discussed below.

The atom ratio of TKN to organic P (P_{org}) was highest in freshwater RM sediments (28:1–47:1). This ratio decreased at the brackish XR site (26:1–35:1) and still further in the salt marshes (21:1–31:1). When averaged over all sites there was no significant trend with depth in the TKN: P_{org} ratio.

Sediment P pools

The sum of all phosphorus-pools (ΣP) from the sequential extractions (Figure 4) agreed within $\pm 10\%$ with TP determined on parallel samples. Inorganic P (sum of DRP pools from the sequential extractions) was least concentrated in the freshwater marsh (RM) sediment and accounted for only 15–40% of ΣP depending on depth (Figure 4). The greatest inorganic P concentrations were found in brackish (XR) and salt marsh (CB) sediments. Averaged over all depths they were 7.2 and 7.4 $\mu\text{mol P g dw}^{-1}$, respectively. The fraction of ΣP attributable to inorganic P was greatest (46–81% depending on depth) at the Cooper River salt marsh site. Common to all profiles, the contribution of inorganic P to ΣP generally increased with depth (Figure 5).

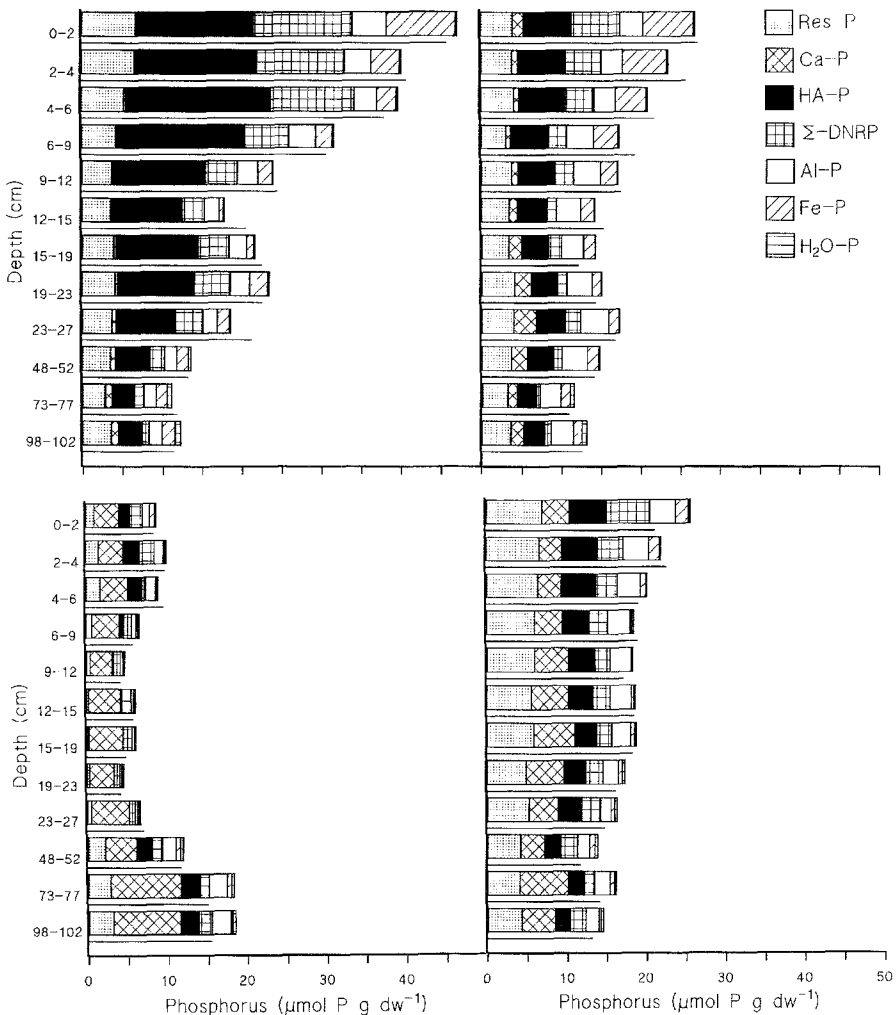


Figure 4. Concentrations of different phosphorus fractions in freshwater- (top left), brackish- (top right), and salt marsh (bottom left) sediments along the Cooper River and from the salt marsh (bottom right) at North Inlet. Lines plotted below each stacked bar show the total P concentrations determined independently on parallel samples. Each value is the mean of two determinations. Definitions of abbreviations (top right) are given in the text.

A marked decrease in concentration of inorganic P occurred in the upper 10 cm of brackish (XR) and freshwater (RM) sediments, decreasing to 6.4 from 10.8 and to 4.7 from 13.4 $\mu\text{mol P g dw}^{-1}$, respectively (Figure 5). This was largely accounted for by a decrease (4.3 and 6.8 $\mu\text{mol P g dw}^{-1}$, respectively) in concentration of Fe-P (Figure 4). Thus, phosphate associated with reducible iron was a significant P pool in the upper part of these sediments

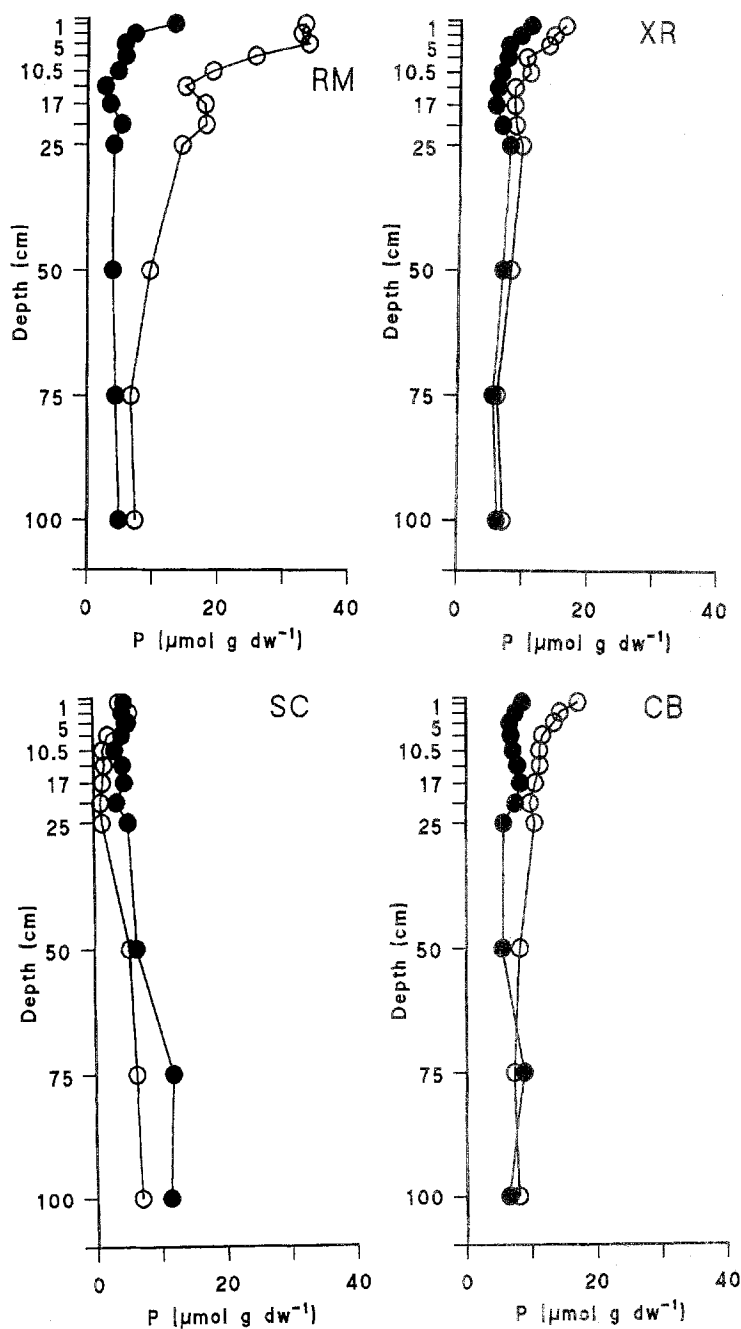


Figure 5. Concentrations of inorganic (closed symbols) and organic (open symbols) phosphorus in freshwater (RM), brackish (XR), and salt marsh (SC) along the Cooper River and from the North Inlet salt marsh (CB). Values are means from two determinations.

and accounted for as much as 24% of ΣP . In depth intervals below 10 cm the concentration of inorganic P was almost constant, and in RM sediment inorganic P was dominated by Al-P (10–14% of ΣP). Higher concentrations of Ca-P (3–16% of ΣP) at the brackish (XR) site are indicative of a greater marine influence.

The speciation of inorganic P in the salt marshes differed markedly from that in fresh and brackish marshes. Most sediment inorganic P was found in the pool of Ca-P, which accounted for 36–85% and 13–38% of ΣP in SC and CB sediments, respectively (Figure 4). The remaining inorganic P was mainly extracted as Al-P (5–15% of ΣP). In both salt marsh sediments the pool of Fe-P was insignificant, except at the sediment surface where Fe-P was 6–8% of ΣP .

The concentration of porewater DRP generally increased downstream along the Cooper River as sediment salinity and S^{2-} increased (Table 1). DRP and S^{2-} increased with sediment depth at all locations. Among the salt marsh sites, there was also a positive relation between DRP and S^{2-} . The North Inlet salt marsh site (CB) had significantly lower DRP and S^{2-} , but higher Cl^- concentrations than the SC salt marsh (Table 1).

A decline with depth of sediment organic matter (Figure 3) and organic P (Figure 5) is a common feature of depositional environments where the burial and decay of organic matter occur gradually (Morris & Bowden 1986), and this interpretation is consistent with the diminishing contribution of organic P to ΣP with increasing depth at all locations. However, this trend was not accompanied by a corresponding increase in concentration of solid-phase inorganic P (Figure 5). Thus, P in degraded organic matter is mainly released to the porewaters.

Organic P accounted for the greatest fraction of ΣP in the freshwater (RM) sediments (60–85% of ΣP), while the smallest fraction occurred in salt marsh (SC) sediment (19–54% of ΣP). The highest concentrations of HA-P (24–51% of ΣP) also occurred in RM sediment (Figure 4), and as sediment salinity increased, the concentration of HA-P and its contribution to ΣP decreased. Thus, in brackish (XR) and salt marsh (SC) sediments only 20–28% and 1–22% of ΣP was in the form of HA-P, respectively. When averaged over all sites by depth, HA-P contributed more to ΣP in the upper part (23%) than in the lower part of the sediment profile (17%).

The distribution of $\Sigma DNR P$ with depth resembled that of HA-P. When averaged over all sites $\Sigma DNR P$ contributed 23% of ΣP in surface sediments, but only 9% at the 100 cm depth. Averaged over all sites, Res-P accounted for 17% of ΣP in surface sediments and 28% at 100 cm depth.

Table 1. Time-averaged concentrations (with lower-upper 95% confidence limits) of dissolved reactive phosphorus (DRP) (μM), chloride (Cl^-) (mM), and sulfide (S^{2-}) (mM) in porewaters at the freshwater (RM), brackish (XR), and salt marsh (SC) sites along Cooper River and at the salt marsh (CB) site in North Inlet. The values are geometric means of monthly samples collected from December 1993 to December 1996 at Cooper River sites ($n = 91$ –286, depending on depth and site) and from April 1994 to July 1995 at site CB ($n = 25$ –41). Within each depth, paired means between sites that share the same superscript letters are not significantly different, and pairs that share the same superscript numbers within each site are not significantly different between depths according to Tukey's studentized range test ($P = 0.05$).

Porewater constituent and depth (cm)	Study Site							
	RM	XR	SC	CB				
DRP 10	1.0	(0.8–1.2) ^{a,1}	7.3	(6–10) ^{b,1}	13.5	(11–16) ^{c,1}	1.7	(1–2) ^{a,1}
DRP 25	1.3	(1–2) ^{a,1}	13.7	(12–16) ^{b,2}	40.4	(37–41) ^{c,2}	3.4	(3–5) ^{d,1}
DRP 50	3.5	(3–4) ^{a,2}	25.3	(22–29) ^{b,3}	59.9	(55–65) ^{c,3}	8.8	(7–11) ^{d,2}
DRP 75	6.2	(5–7) ^{a,3}	38.9	(36–42) ^{b,4}	62.4	(57–68) ^{c,3}	12.3	(9–16) ^{d,2}
DRP 100	9.5	(8–11) ^{a,3}	56.7	(54–60) ^{b,5}	64.3	(61–68) ^{b,3}	14.7	(10–21) ^{c,2}
Cl [−] 10	<1		92	(87–98) ^{a,1}	397	(387–407) ^{b,1}	546	(515–578) ^{c,1}
Cl [−] 25	<1		102	(96–108) ^{a,1,2}	402	(390–414) ^{b,1}	553	(522–586) ^{c,1}
Cl [−] 50	<1		108	(103–114) ^{a,2}	391	(379–404) ^{b,1}	545	(518–575) ^{b,1,2}
Cl [−] 75	<1		106	(100–112) ^{a,2}	383	(371–396) ^{b,1}	522	(500–545) ^{c,1,2}
Cl [−] 100	<1		101	(95–108) ^{a,1,2}	350	(340–361) ^{b,2}	473	(452–496) ^{c,2}
S ^{2−} 10	2.1	(2–3) ^{a,1}	15.3	(11–22) ^{b,1}	276.8	(214–356) ^{c,1}	27.3	(15–49) ^{b,1}
S ^{2−} 25	4.2	(3–6) ^{a,2}	85.0	(60–121) ^{b,2}	1517	(1338–1720) ^{c,2}	204	(139–300) ^{d,2}
S ^{2−} 50	15.6	(12–21) ^{a,3}	530.3	(452–623) ^{b,3}	3666	(3405–3947) ^{c,3}	441	(325–599) ^{b,3}
S ^{2−} 75	17.5	(13–24) ^{a,3}	1056	(948–1176) ^{b,4}	4530	(4252–4826) ^{c,3}	780	(680–894) ^{b,3,4}
S ^{2−} 100	18.1	(13–25) ^{a,3}	1671	(1521–1836) ^{b,4}	4837	(4622–5062) ^{c,3}	988	(849–1149) ^{d,4}

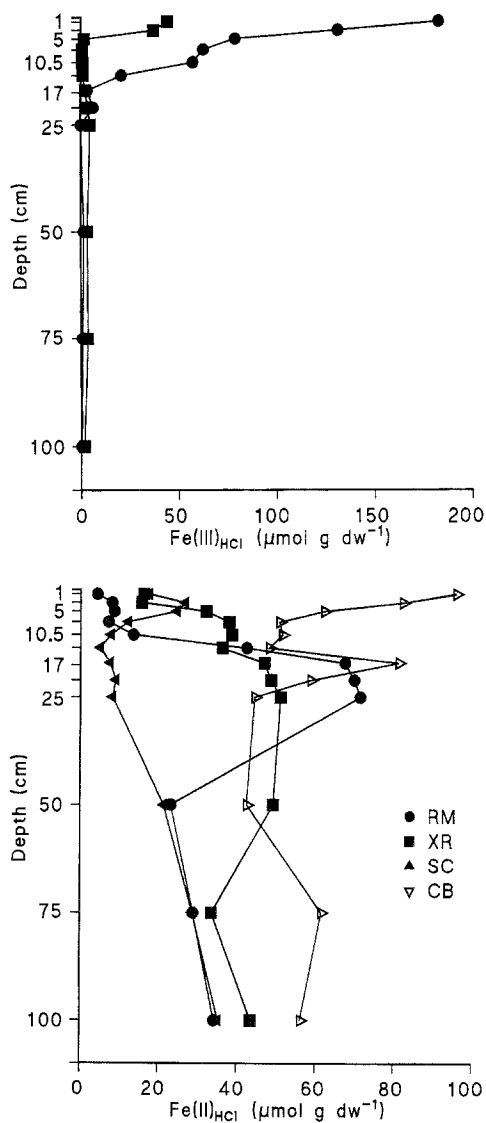


Figure 6. Depth profiles of iron as extracted by 0.5 M HCl and separated into Fe(III) (top) and Fe(II) (bottom) in sediments from freshwater (●), brackish (■), and salt marsh (▲) sites along the Cooper River and from the North Inlet salt marsh (▽). Fe(III) was only detectable in freshwater and brackish sediments. Values are means of two determinations.

Sediment Fe and Al pools

Fe(III)_{HCl} was present in significant concentrations in the surface sediments at the freshwater (above 15 cm at RM) and brackish (above 5 cm at XR) sites, but below these depths, Fe(III)_{HCl} disappeared as concentrations of extractable Fe(II)_{HCl} increased (Figure 6). The Fe distribution was different in the salt marshes where Fe(III)_{HCl} was not detected at any depth and where Fe(II)_{HCl} was relatively high at the surface. However, the BD reducing agent, which extracts reducible Fe more efficiently than 0.5 M HCl, extracted reactive Fe ($13\text{--}53\ \mu\text{Fmol Fe g dw}^{-1}$) in the salt marsh CB sediment (0–6 cm), but not in salt marsh SC sediment. The two salt marshes also differed in concentration of Fe(II)_{HCl}, which was up to 5 times higher in North Inlet CB than in Cooper River SC sediments.

Concentrations of iron associated with humic acids (HA-Fe) and of humic acid-bound aluminum (HA-Al) were greatest in the freshwater site and least in the salt marshes (Figure 7). In all locations concentrations of HA-Al far exceeded concentrations of HA-Fe, with the molar ratio of HA-Al:HA-Fe typically between 4:1 and 7:1. HA-Al was 5–10 times more concentrated than the pool of amorphous Al (data not shown).

Ratios of HA-metal:HA-P increased significantly ($P = 0.001$) with increasing pH across sites (Figure 8). Contrary to these results, as pH increases, the acidic groups of humic acids should dissociate and increase the complexation with metal oxides and adsorption of phosphate (Gerke & Hermann 1992; Jones et al. 1993). Our results indicate that, across sites, P-saturation of the humic acid-metal association was probably dominated by salinity, because salinity and pH were positively correlated. Thus, ratios of HA-metal:HA-P increased with increasing salinity across sites (Figure 8), while the concentrations of HA-Fe and HA-Al decreased (Figure 7). Thus, the HA-metal complex loses its tendency to bind P as salinity increases.

Available P and Macrophyte P demand

The P pools identified in this study differ in their bioavailability. Moreover, the bioavailability of a given pool is likely to vary temporally and spatially depending on sediment chemistry. We define the *potentially* bioavailable P pool as the sum of H₂O-P, Fe-P, Al-P and ΣDNRP . These are the pools that are not refractory to the chemical extraction procedure and that have the potential to be mineralized or rendered available by some means. By this definition, among the river-dominated sites, P was least bioavailable (per volume of sediment to a depth of 1 meter) in freshwater (RM) and most bioavailable in brackish (XR) sediments (Table 2) in the vicinity of the turbidity maximum.

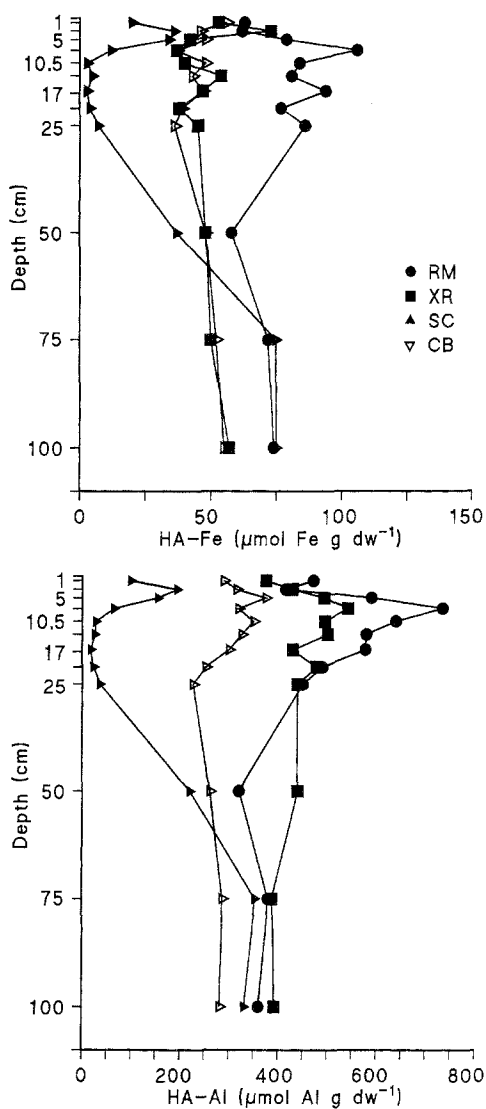


Figure 7. Depth profiles of iron (Fe) (top) and aluminum (Al) (bottom) extracted together with humic acid bound P in sediments from freshwater (●), brackish (■), and salt marsh (▲) sites along the Cooper River and from the North Inlet salt marsh (△). Values are means of two determinations.

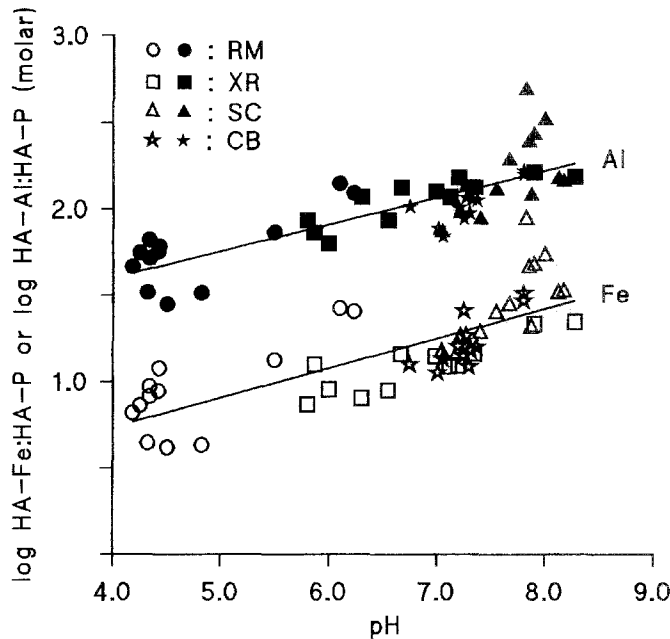


Figure 8. Linear regression of sediment pH as a function of the ratio between humic acid bound-metals (HA-Fe or HA-Al) and humic acid bound-P (HA-P) across sites [symbols denote freshwater (RM), brackish (XR), and salt marsh sites (SC and CB)]. Fe: $Y = 0.172X + 0.05$ ($n = 48$, $r^2 = 0.59$, $P < 0.001$). Al: $Y = 0.155X + 0.98$ ($n = 48$, $r^2 = 0.64$, $P < 0.001$).

Table 2. Potentially bioavailable ($\text{mol P m}^{-2} \text{ m}^{-1}$) P pools ($\text{H}_2\text{O-P}$, Fe-P, Al-P, ΣDNRP) per volume of sediment to a depth of 1 meter at the freshwater (RM), brackish (XR), and salt marsh (SC) sites along Cooper River and at the salt marsh (CB) site in North Inlet. Calculation of macrophyte P demand (mol P yr^{-1}) is explained in the text. The turn-over time (yr) is calculated as the ratio of potentially bioavailable P to macrophyte P demand.

	Study Site			
	RM	XR	SC	CB
Potential bioavailable P	1.69	2.40	1.98	1.66
Macrophyte P demand	0.107	0.174	0.119	nd
Turn over time	15.8	13.8	16.6	nd

Among the river-dominated sites, potentially bioavailable P and macrophyte P demand were positively correlated (Table 2). Macrophyte P-demand was greatest in the brackish (XR) marsh and least in the freshwater (RM) marsh. Potentially bioavailable P in the upper 1 m of sediment has a turnover time of about 15 years (Table 2). The P concentration in aboveground living biomass was independent of bioavailable P pool-size and averaged $0.08\text{--}0.09 \pm 0.01\%$ of ash free dw (± 1 SD) irrespective of site. However, absolute differences among sites in potentially bioavailable P were small.

Discussion

Insights into the regulation of P storage and diagenesis in intertidal marsh sediments can be achieved by considering the composition of solid phase P together with other sediment physico-chemical parameters. Our results show that the speciation of solid phase P in vegetated, tidal marsh sediments can vary along salinity gradients due to changes in ionic strength and availability of iron and calcium. The ability, for example, of sediment humic acids to bind P decreases in response to increasing salinity. Concentrations of solid phase P also varies among marshes of similar salinity, indicating that local effects are important as well.

TP concentrations decreased markedly with depth at all locations except the Cooper River salt marsh (Figure 4). Similar TP concentrations have been reported from other marshes of varying salinity (e.g. Bowden 1984; Craft et al. 1988). Sediment profiles at SC have been affected by changes in Cooper River discharge and sedimentation. A period of high river discharge between 1941–1985 (Kjerfve & Magill 1990) changed the pattern of sediment deposition in Charleston Harbor (Nieuwenhuise et al. 1978) and is consistent with the discontinuities in bulk density and porosity profiles (Figure 2). There is generally a negative correlation between particle size and concentrations of inorganic and total P (McGlathery et al. 1994), and the presence of sandy sediments in the upper SC profile probably explains the inverted P-profile at this site.

Bioturbation also can influence depth profiles of chemical constituents in marsh sediments. This is especially significant in salt marshes where the greatest activity occurs in the upper 10 cm of sediment (Sharma et al. 1987). Bioturbation is less important in freshwater marshes (Chambers & Odum 1990).

As shown by the importance of Fe-P in surface sediments at the freshwater and brackish (RM and XR) sites (Figure 4), the reaction between ferric iron and phosphate is another important regulatory mechanism of P in surface sediments. DRP generated at depth by the reduction of Fe(III)-P or by microbial

decomposition processes should diffuse to the surface, down gradient (e.g. Table 1), where it will combine with Fe(III) in the oxidized layer (Moore & Reddy 1994). The Fe(III) layer at the sediment surface acts as a sink for DRP and inhibits the diffusion of porewater DRP out of the sediment (Scudlark & Church 1989; Chambers & Odum 1990; De Groot & Fabre 1993). The low DRP concentrations (Table 1) and relatively large pools of Fe-P (Figure 4) and Fe(III)_{HCl} (Figure 6) that we observed in surface sediments at the freshwater and brackish sites are consistent with this interpretation.

In anoxic sediments where the availability of Fe(III) is limited, such as the salt marsh sites (Figure 6), other P pools assume an important regulatory role over DRP. For instance, calcium carbonate is important in reduced calcareous lake sediments (Moore & Reddy 1994), though its importance may depend on the availability of dissolved organics that can bind with calcium carbonate and reduce its adsorption of phosphate (Krom & Berner 1980; Lahann & Cambell 1980). In more acidic wetland sediments control of porewater DRP concentrations could be from Al oxides (Richardson 1985). As our results indicate, a large fraction of sediment Al and Fe oxides in fresh and brackish marsh sediments interact with HA, and the ability of these metal oxides to adsorb DRP from the porewaters therefore seems partly controlled by the diagenesis of sediment organic matter. Thus, with increasing age of the sediments the concentration of organic-P as well as the relative contribution of HA-P and Σ DNRP to TP decreased (Figure 4).

In the salt marsh sediments Fe-P was present only in the upper 2 or 6 cm of the sediment (Figure 4), and Fe(III)_{HCl} was below detection (Figure 6). Fe(III)_{HCl} availability is a function of sediment redox potential (Figure 2), and the Fe(III) concentration in salt marsh sediments may cycle seasonally due to an Fe-sink imposed by microbial sulfate reduction and the production of pyrite (FeS₂) and iron monosulfides (FeS), alternating with a season of net oxidation. Fe(III) oxides and Fe(II) are consumed during formation of FeS₂ (Giblin & Howarth 1983; Oenema 1990), which can sequester a large fraction of sediment Fe (Lord & Church 1983), and limit the availability of Fe(III) oxides in sediments (Carignan & Tessier 1988). Fe(III) is considered to be the primary oxidant of reduced sulfur species in salt marsh sediments (Luther et al. 1991). The importance of this Fe-S interaction was greatest in salt marsh (SC) sediment, where the extractable pools of Fe(III)_{HCl}, Fe(II)_{HCl} (Figure 6) and BD-extractable Fe were almost exhausted, and where the greatest dissolved S²⁻ concentrations were measured (Table 2). Thus, the P-Fe interactions seen in typical freshwater systems can be disrupted in marine sediments with significant sulfate reduction.

The binding of P to metal oxides is also influenced by pH and competition from competing anions. Metal oxides (e.g. of Fe(III) and Al) have variably

charged surfaces that generally carry a net positive charge at low pH and a net negative charge at high pH, though this trend is counteracted by increased electrolyte concentrations (e.g. NaCl) (Barrow et al. 1980). Thus, associations between metal oxides and anions such as phosphate are facilitated in freshwater at low pH (Hawke et al. 1989). However, anions such as sulfate compete with phosphate for adsorption sites (Hawke et al. 1989), and in estuarine waters the net effect of increased pH and electrolyte concentration on phosphate adsorption onto suspended particles is a decrease in the amounts of P associated with Al and Fe(III) (Lebo 1991; Zwolsman 1994). Indeed, Fe-P were more important in fresh- and brackish water sediments (Figure 4).

Unlike Fe-P, Al-P was in an important inorganic P reservoir irrespective of sediment depth in all the marshes (Figure 4). Al is insensitive to changes in redox potential, while the stability of Fe(III) increases with Eh (Gotoh & Patrick 1974). As the pool of Fe(III) is reduced in waterlogged sediments, the relative importance of associations between phosphate and Al oxides will increase (Richardson 1985).

The high Fe and Al content in the HA-P fraction (Figure 7) is consistent with the interpretation that oxides of Fe and Al form complexes with dissociated and negatively charged surfaces of humic acids, and phosphate may bind to these complexes by ligand exchange on the oxide surfaces (Gerke & Hermann 1992). In freshwater environments phosphate seems to react preferentially with organic-metal complexes of large molecular size (Jones et al. 1993). However, in the presence of excess Ca^{2+} , phosphate is inhibited from bonding with dissolved organics due to competition between metal oxides and Ca^{2+} for binding sites on organic macromolecules (Stewart & Wetzel 1982). Also, association between P and complexes of metal oxides and humic acids should be suppressed in saline environments because the binding of P to metal oxides is disrupted under high electrolyte concentrations as discussed above.

The concentration of Ca-P was significantly higher in salt marsh sediments in comparison to lower salinity sites (Figure 4). Availability of solid calcium carbonates is governed by salinity and pH (de Jonge & Villerius 1989; Huanxin et al. 1994). Thus, calcium and carbonate carried into estuaries precipitate due to decreasing salinity and will fail to reach freshwaters. Low pH sediments are poor in solid calcium carbonate because it dissolves and leaches from the sediments. In contrast seawater is a rich source of calcium carbonate, and Ca-P contributes substantially to TP in marine sediments. Concentrations of Ca-P in sediments were nearly equal at both salt marsh sites (Figure 4), while pools of extractable iron differed (Figure 6). This suggests that Fe availability in the salt marsh sediments tested here had little influence on

adsorption of phosphate by calcium carbonate through coatings as has been proposed (Sherwood et al. 1987).

Bioavailability of solid phase inorganic P-reservoirs depends on their solubility and exchangeability in porewater. By use of radiolabeled P, Jensen and Thamdrup (1993) showed that Fe-P is the most important exchangeable P pool in marine sediments. H₂O-P and Al-P pools also exchange with porewater while the exchange of Ca-P is almost insignificant. P in organic matter is another important potentially bioavailable P pool (e.g. Tate et al. 1991). Our results indicate that some fraction of the organic P pool in marsh sediments is bioavailable through mineralization. That is, Σ DNRP contributed less to TP with increasing sediment depth (Figure 4) and released P was not converted to inorganic solid fractions (Figure 5).

There is a tendency toward nitrogen limitation of primary production in salt marshes (Valiela & Teal 1974; Morris 1988), and higher N to P ratios of both particulate matter and of dissolved phases in freshwaters suggest that net primary production in freshwater systems is most often limited by P (Howarth 1988; Hecky et al. 1993). This is consistent with the distribution of porewater DRP, TKN:P_{org} ratios and potential bioavailability of solid P in sediments along the Cooper River. P-speciation clearly differed between freshwater and saltwater end-members, while total P concentration was actually greatest in freshwater sediments (Figure 4). The relative importance of these pools as stable sinks and their bioavailability must have a bearing on the nutrient limitations imposed on primary producers. One difference between freshwater and marine systems may be a function of the availability of sulfate and its control of P release (Caraco et al. 1990), though differences in porewater DRP, porewater S²⁻, and P-speciation among the two salt marshes indicate that sulfate availability alone is not the sole determinant of sedimentary P dynamics. A higher total Fe concentration in North Inlet CB sediment compared to SC sediment (data not shown) points to the fact that CB sediment has the greatest capacity to precipitate metal sulfides, but also the largest potential to maintain a pool of reactive Fe which, at least in the upper sediment profile, may control porewater DRP.

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