Porewater oxidation, dissolved phosphate and the iron curtain
Iron-phosphorus relations in tidal freshwater marshes

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Abstract. The process of dissolved phosphate removal from aqueous solution, which occurs during oxidation of soluble ferrous compounds to insoluble ferric forms, was examined in soils of two tidal freshwater marshes. Sites of amorphous iron deposition and sorption or co-precipitation of phosphate were found to be in surface soils and along creekbanks, where both ion diffusion and porewater advection move dissolved iron and phosphate from reduced to oxidized regions. Profiles of extractable iron and total phosphorus from creekbank and interior soils were consistent with hypothesized differences between a high and a low marsh. Porewater concentrations of dissolved phosphate were higher in creekbank soils of the high marsh, compared with water actually discharging from the creekbank during tidal exposure. We propose that an iron curtain of ferric hydroxides functions as a barrier to diffusive and advective movement of dissolved phosphate along surfaces of tidal freshwater marshes, and has important implications for the distribution and availability of phosphorus in other types of wetlands and aqueous systems.

Introduction

Many oxidized iron minerals are unstable in saturated environments where redox potentials vary. Whether by direct microbial or indirect chemical transfer of electrons (Lovley & Philips 1986a; Bell et al. 1987; Jansson 1988; LaKind & Stone 1989), ferric iron oxides are reduced in regions where Eh falls below + 200 mV (Gotoh & Patrick 1974). Although some microbes exploit the energy associated with ferric iron formation (Lovley 1987), oxidation can proceed chemically at a circumneutral pH range (Davison & Seed 1983). The processes of biological and chemical oxidation/reduction of iron compounds have been examined extensively in studies of hypolimnetic development (Nurnberg 1985), deep sea sediment geochemistry (Sundby et al. 1986), and organic matter decomposition (Bell et al. 1987).

Oxidations of soluble ferrous compounds to insoluble ferric forms are coupled tightly with the sorption of dissolved phosphate (McQueen et al. 1986). When iron oxides precipitate from solution, they scavenge strongly electronegative species like phosphate, a process exploited by waste-water treatment facilities to reduce phosphorus loading in their effluent (Hearn 1984). In natural systems such as wetlands, the sorption mechanism limits phosphate's mobility and perhaps its availability to plants and animals (Odum 1988). Reduction of

ferric oxides, on the other hand, not only solubilizes iron, but also releases sorbed phosphate. In environments where both oxidation and reduction events occur, phosphate participates in reversible sorption and desorption reactions with iron (Lijkleme 1977). The cyclical nature of the exchange mechanism is used to explain the function of 'ferrous wheels' and 'phosphate shuttles', which employ iron and manganese as carriers of phosphate across redox discontinuities in lake waters (Mayer et al. 1982) and in ocean sediments (Shaffer 1986).

The concentration of dissolved phosphate in saturated wetland soils usually is much higher than in the overlying water, so there is a vertical diffusion gradient out of the soil. Fickian diffusion models can predict the amounts of dissolved phosphate which should be released to overlying water from nutrient-rich soils, but these calculations ignore the possibility of biological fixation of phosphorus (Gachter et al. 1988) and of geochemical sorption of phosphate to oxidized iron (Aller 1980; Sundby et al. 1986; Froelich 1988). In fact, sorptive processes occurring in oxidized surfaces atop reduced sediments generally decrease the diffusion of phosphate into the overlying water column (Patrick & Henderson 1981; Callendar 1982; Richardson 1985; Jaynes & Carpenter 1986; Scudlark & Church 1989). Even though diffusive export of phosphate may contribute substantially to the total phosphorus budgets of some wetlands (Gardner 1975), in many environments the release of phosphate is likely inhibited by iron oxides on the soil surfaces.

Besides vertical diffusive export, a second and potentially more important method of phosphorus movement through soils is via porewater advection. Solutes like phosphate can move only short distances over fairly long time scales via molecular diffusion, but advection of reduced porewater to surface water facilitates more rapid and extensive solute movement. This phenomenon occurs where piezometric pressure differences create a potential for discharge to subsurface water. While common along wetland creekbanks, the actual advection of water from reduced subsurface zones to oxidized surface waters has been addressed only recently (Jordan & Correll 1985; Yelverton & Hackney 1986; Harvey et al. 1987). These current estimates of water and nutrient export from different wetland creekbanks use creekbank concentrations of dissolved nutrients in their calculations and do not include possible sorptive-desorptive reactions occurring at the sites of porewater export. We have calculated that subsurface export of nutrients via creekbank seepage is nearly half as large as net surface import measured in a mesohaline tidal marsh (unpub. data; Wolaver et al. 1983), so many of the nutrients sequestered on the surface of wetlands may actually be released by porewater advection. On the other hand, the oxidation of reduced iron compounds and subsequent sorption of dissolved phosphate could inhibit this transport and lead to an increase in total sorbed phosphorus concentrations within creekbanks. Compared to interior marsh areas, iron oxidation/reduction cycles and increased primary production might be expected to be associated with creekbanks, where higher concentrations of iron oxyhydroxides and total phosphorus are hypothesized.

The precipitation of iron during oxidation, which can account for the removal

of a large percentage of dissolved phosphate found in wetland porewaters, is the functional basis of a phenomenon we call the 'iron curtain'. In this paper, we demonstrate the effect and consequence of this process in surficial soils and along creekbanks of tidal freshwater marshes, where the amounts of acid-extractable iron are higher than in interior marsh sites. Preferential deposition of iron occurs in creekbanks, the source material coming both from suspensions in surface waters and from precipitation of ferric iron in advecting, oxidized groundwater. Further, our analysis of creekbank soils relative to interior wet-land areas suggests that formation of amorphous iron oxyhydroxides, sorption surfaces for phosphate, occurs there. This hypothesis is supported by profiles of total phosphorus in marsh soils, which exhibit phosphorus enrichment in a high marsh creekbank. Finally, a comparison of dissolved phosphate concentrations in seepage collectors and porewater samplers in creekbanks demonstrates the decrease in phosphate as water advects from wetland soils. The importance of the proposed 'iron curtain' as a phosphate retention process is discussed with respect to different types of wetlands where discharge of subsurface water occurs.

Methods

The wetlands we studied are tidal freshwater marshes located along the Chickahominy River, a tributary of the James River in Virginia (Fig. 1). Tidal range is 0.8 m; river salinities annually average less than 0.5 ppt (Odum et al. 1984). Two marshes of different geomorphology were studied during summer 1988: Eagle Bottom, a frequently flooded low marsh with a sloping topography and seldom-exposed creekbank; and Parsons Island, a less frequently flooded high marsh with a flat surface topography and pronounced creekbank (Fig. 1). Preliminary results of modeling subsurface water flow indicated that creekbanks are important sites of porewater discharge in both marshes (Harvey & Odum 1988).

Phosphate sorption by ferric iron compounds

To demonstate that phosphate sorbs and/or co-precipitates with oxidizing iron, a series of water samples was collected from reduced soils with suction lysimet-ers, or 'sippers', modified after a design by Montgomery et al. (1979). The sippers were constructed of lengths of $1\frac{1}{2}$ inch PVC pipe fitted on one end with fritted polyethylene (70 μm pore size). A butyl-rubber stopper with two luer-locking ports was pushed tightly into the other end of the pipe. Tygon tubing was attached to one port and run inside the length of the pipe to the frit. The lysimeter was pushed or cored into the marsh so that the frit was located at the depth desired for sampling. Nitrogen was used to flush the lysimeter of water which had collected from previous sampling intervals. The inert gas also dis-placed any residual air and maintained anoxic conditions while the porewater
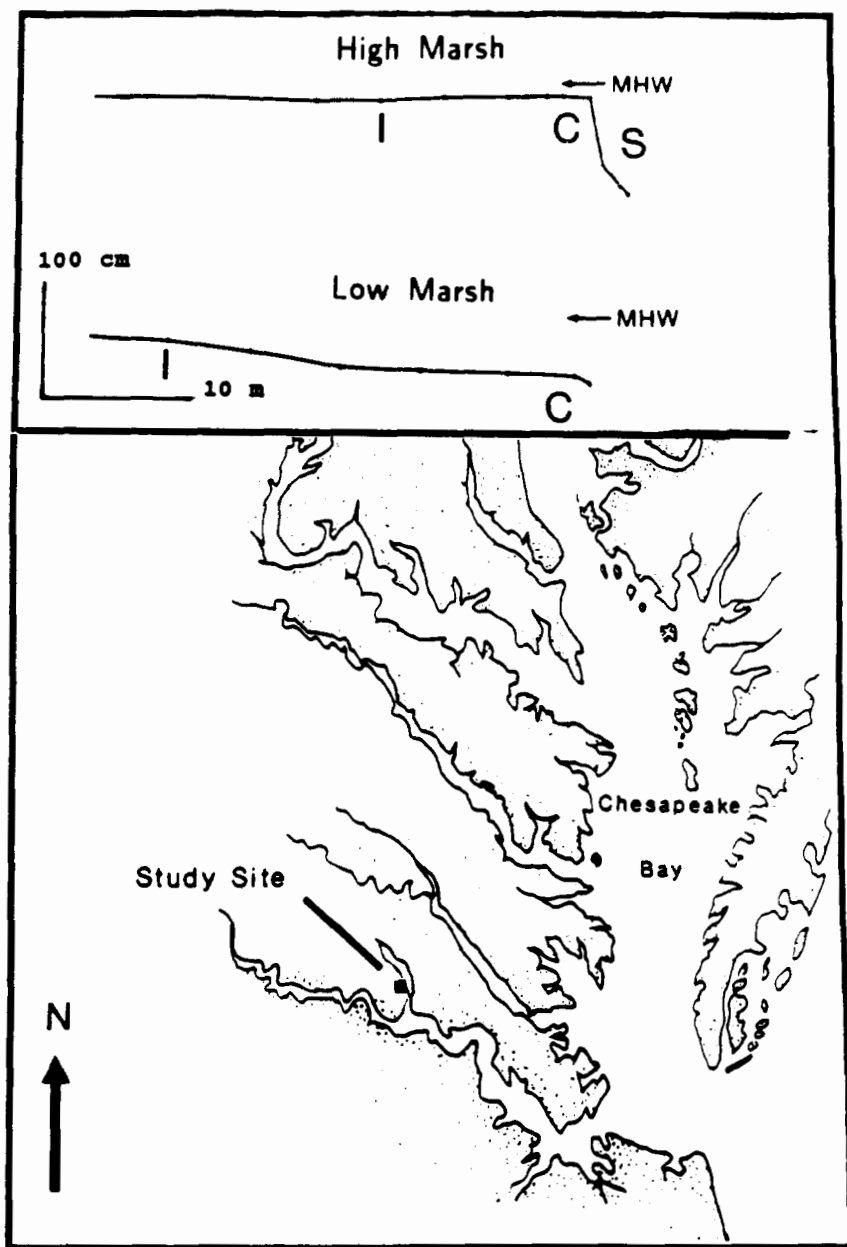
Fig. 1. Map of study site. Inset: Morphological profiles of high marsh (Parsons Island) and low marsh (Eagle Bottom) relative to mean high water (MHW). General sites of interior (I), creekbank (C) and seepage (S) water sampling are shown.

was sampled. A hand-held pump, used to create suction inside the lysimeter, speeded up the collection process. When enough water had entered the sipper, it was removed by syringe and immediately transferred to an evacuated tube.

During a single low tide, porewater was collected under nitrogen from a total of 52 sippers located both at creekbank and interior marsh sites, from different sampling depths 10–50 cm into the soil (Fig. 1). The water from each sipper was filtered (0.45 μm) and divided into two treatments based on preservation in 6 N HCl or chloroform. Dissolved iron in the chloroform-preserved samples precipitated from solution as ferrous iron was oxidized. Ferric iron was stabilized in solution in the acid-preserved samples. After 24 h, dissolved iron (Gibbs 1979) and dissolved phosphate (Parsons et al. 1984) were determined for all samples. The amounts of precipitated iron and sorbed phosphate were calculated by subtraction of the choloroform-preserved from the acid-preserved samples, then plotted.

Soil chemistry

We hypothesized that iron oxidation along creekbanks would be verified by the presence of high concentrations of amorphous iron oxyhydroxides in the soil. To compare creekbank soils with permanently saturated interior marsh soils where oxyhydroxide formation was less likely to occur, three cores from creekbank and interior areas in each of the two marshes were taken. These cores were sub-sampled at depths of 0, 2, 8, 12, 20, 28, and 36 cm by pushing a modified 10 ml plastic syringe into pre-drilled holes in the sides of the corer. This procedure minimized the exposure time of the soils to the atmosphere. Approximately 0.2 g soil samples from each depth were placed in extraction solutions for chemical determinations of iron (Lovley & Philips 1987). HCl-extractable iron was determined by extraction in 10 ml of 0.5 N HCl; HCl- and hydroxylamine-extractable iron was determined by extraction with 10 ml of 0.25 N HCl and 0.25 N hydroxylamine HCl. After 24 h, the extraction solutions were analysed for dissolved iron, and the soils were collected on a filter, dried, and weighed. Hydroxylamine-extractable ferric iron, expressed as μmoles Fe per g dry weight of soil, was calculated by subtraction of the results of the two extractions. This represented the amount of recently precipitated amorphous Fe(III) oxyhydroxides present in the soils (Lovley & Philips 1987). As a check, the chemical speciation program WATEQF (Plummer et al. 1976) was used to calculate the state of saturation of reduced and oxidizing porewater with respect to amorphous iron oxides. Input to the program were pH and total dissolved iron and phosphate concentrations measured in creekbank porewater under reducing and oxidizing regimes to determine thermodynamically which iron species would be likely to dissolve or precipitate in creekbank soils.

In January 1989, a second set of 4 large soil cores was collected from each creekbank and interior marsh site for total extractable phosphorus determinations. The cores were brought back to the lab for sectioning at 5 cm intervals to 40 cm, freeze-drying, and milling. After processing, total phosphorus in ashed,

Table 1. Mean concentrations of dissolved iron and phosphate in soil ($N = 12$), seepage ($N = 27$) and surface waters ($N = 12$). Standard errors in parentheses.

	μM Iron	μM Phosphate
High Marsh Soils		
Interior	522 (19)	17 (3)
Creekbank	658 (57)	30 (4)
Seepage water	319 (56)	8 (2)
Low marsh soils		
Interior	64 (9)	7 (2)
Creekbank	1004 (106)	56 (7)
Surface water	21 (4)	0.9 (0.3)

0.2 g soil samples from different depths was extracted in hot, concentrated HCl for 8 h (Meixner & Singer 1985), then measured as dissolved phosphate.

Comparison of creekbank porewater with seepage water

Twenty sippers were placed in the creekbanks of the two marshes, nested in pairs at depths of 10, 20, 30, 40, and 50 cm (Fig. 1). On 20 July 1988, soil porewater was sampled and preserved in 6 N HCl. Also, 27 seepage collectors were installed at various heights along a 50 m section of creekbank of the high marsh by carefully pushing the lip of a thin, plastic, 60 ml reservoir into the soil surface exposed during low tide (Fig. 1). Water discharging from the creekbank ponded in the collector, which was installed to minimize disturbance to the seepage face. The low marsh had such a small and infrequently-exposed creekbank that collectors could not be installed there, and subsurface seepage collection was not attempted. The rate of export of porewater from creekbank seeps was not quantified, but appeared to vary by site and decreased with time after tidal exposure. After 30–60 minutes, water from collectors was filtered and preserved, then brought to the lab for analysis of iron and phosphate.

Results

Porewaters from soils of the tidal freshwater marshes of the Chickahominy River are neutral to slightly acidic, with a pH range from 6.0 to 6.6. No differences between creekbank and interior soils are evident, but a pH minimum occurs in the top few cm (6.0), and surface water pH is slightly higher (6.7–7.1). Because of the presence of high concentrations of dissolved iron, an electroactive species, the electrical potential of reduced porewaters at depths to 100 cm is poised by the ferrous/ferric couple at an average of + 160 mV (unpubl. data).

Depth-averaged dissolved iron and phosphate concentrations in pore water from July, 1988 varied significantly by site in both marshes (creekbank vs. interior comparisons, *t*-tests, $\alpha = 0.05$), at levels much higher than surface waters (Table 1). In the low marsh, creekbank iron concentrations were more
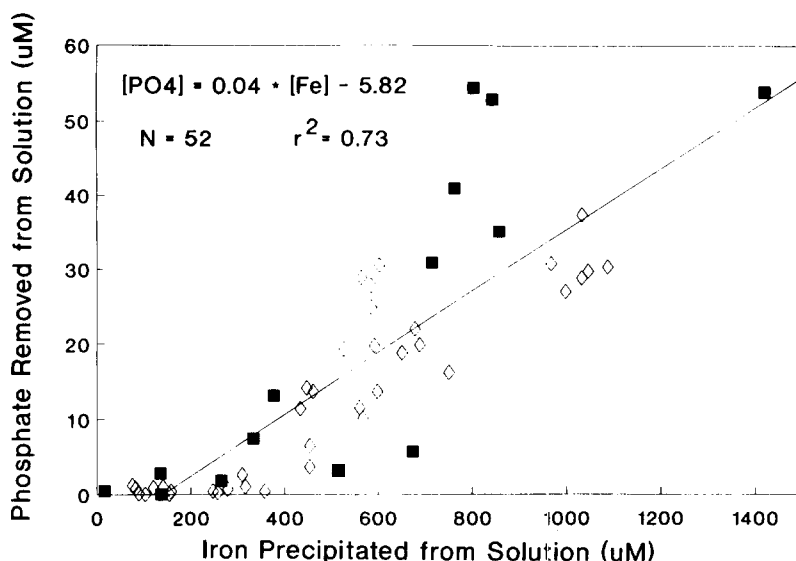
Fig. 2. Plot of phosphate removal from oxidized porewaters of high (◇) and low (■) marsh soils as a function of iron precipitation from solution.

than an order of magnitude greater than those in interior porewaters or in surface waters. In the high marsh, creekbank concentrations of dissolved iron were slightly higher than the interior. Similarly, phosphate concentrations were higher in creekbank than interior porewaters, with the larger differences found between creekbank and interior soils of the low marsh (Table 1).

The phosphate sorption experiment demonstrated that iron precipitation was positively correlated with the disappearance of dissolved phosphate from oxidizing porewater (Fig. 2). The regression line relating the amounts of dissolved iron precipitated from solution with the reduction in dissolved phosphate in oxidized porewater samples from the high and low marsh accounted for 73% of the variance in the data ($N = 52, p < 0.01$). From the slope of this line, the molar ratio of iron precipitated to phosphate sorbed is roughly 25:1.

The amounts of hydroxylamine–HCl extractable iron in the freshwater marsh soils were higher in creekbanks than interior regions (Fig. 3), consistent with the hypothesis that creekbanks are sites of iron deposition. This effect was more pronounced in shallower soils (< 20 cm depth), and more pronounced in the low marsh. Both interior sites averaged approximately 200 μmoles iron/g dry weight of soil throughout the soil column. In contrast, the creekbank soils of the two marshes had larger variation in extractable iron with depth, with average concentrations up to 940 μmoles iron/g soil.

The differences in extractable iron between creekbank and interior sites were further elucidated in a plot of amorphous ferric iron (Fig. 4). Data from both marshes were grouped because of similar information: the amounts of poorly crystalline, amorphous oxyhydroxides were higher in creekbank soils, and
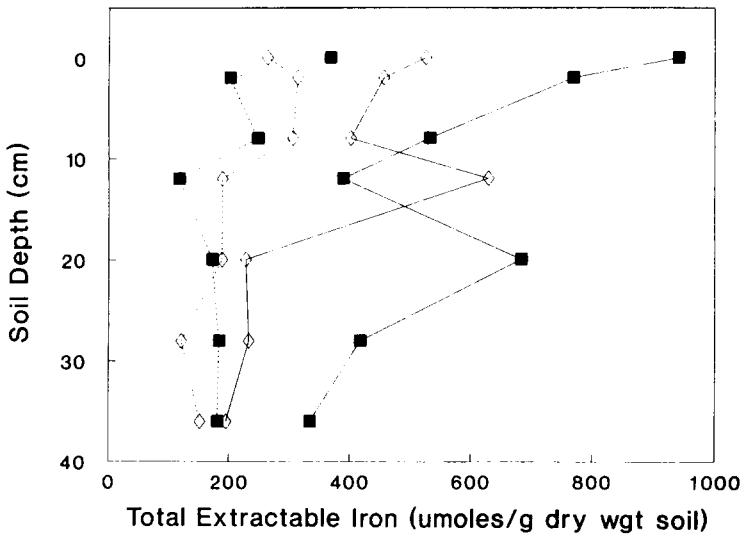
Fig. 3. Total iron profiles in high (◇) and low (■) marsh soils. Each point represents a mean of 4 samples from creekbank (solid lines) and interior (dashed lines) sites.

higher at shallow depths. The difference was diminished deeper than 30 cm, but near the surface there was more than 6 times more reducible iron in creekbank soils than in interior soils. By operational definition this extraction represented a class of ferric iron compounds which were temporally unstable, mostly free oxyhydroxides and oxyhydroxides sorbed to clays (Lovley & Philips 1987). Further, the chemical speciation program WATEQF calculated that creekbank porewaters, when exposed to oxic conditions, were over-saturated with numerous iron minerals, including amorphous iron oxyhydroxides, known to form rapidly in natural waters (Davison & Seed 1983). The presence of an oxidized iron zone in creekbanks suggests its potential importance in retarding the movement of dissolved phosphate with water discharging through creekbank soils.

Total extractable phosphorus concentrations from creekbank and interior sediments of both marshes decreased with depth in the soil (Fig. 5), and were greater in the high marsh at all depths below 2.5 cm. In surface soil from every site, the amounts of phosphorus were between 0.16 and 0.17% P by weight, but dropped roughly 50% at 25 cm depth. Profiles from both sites in the low marsh and the interior site in the high marsh were characterized by the largest decreases in total P in the top two soil layers. In contrast, the profile of total P in the high marsh creekbank exhibited no sharp decrease to a depth greater than 20 cm into the soil column. Profiles of amorphous iron were similar for the creekbanks of both high and low marshes (Fig. 4), but soils of the low marsh creekbank contained less total phosphorus than the high marsh creekbank.

Porewater seeping from the high marsh creekbank during tidal exposure was
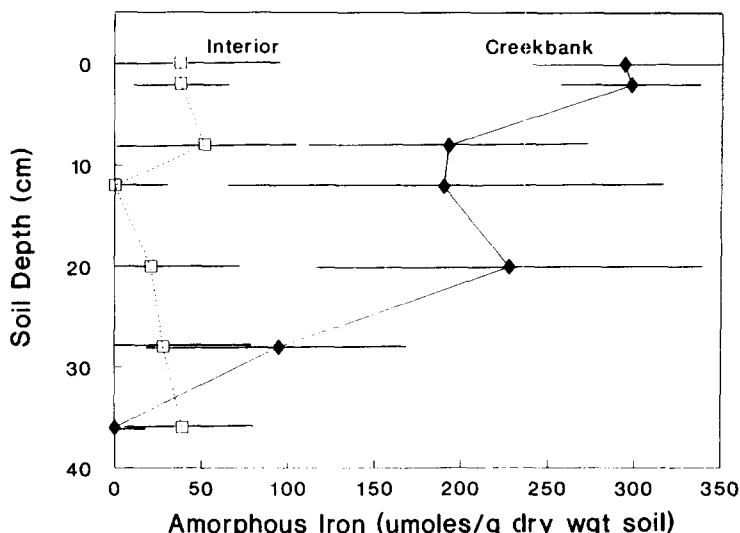
Fig. 4. Amounts of extracted amorphous iron from creekbank (◆) and interior (□) marsh soils, high and low marsh data grouped. Each point represents a mean ± s.e. of 6 samples.

low in dissolved iron and phosphate, compared with concentrations found in porewater from creekbank sippers (Table 1). Whereas phosphate concentrations in creekbank porewater averaged 30 μM, seepage water averaged 8 μM, and of 27 seepage areas, 18 had phosphate concentrations < 5 μM (Fig. 6). The range of values was between 0.1 and 40 μM. The water collected on the oxidized seepage face of the creekbank was characterized by average dissolved iron and phosphate concentrations roughly 50 and 75%, respectively, less than porewaters in the reduced section of the creekbank.

It is unclear whether the collected water exiting the creekbank above the water level of the falling tide was representative of porewaters discharging below it, which were not sampled. We have observed, however, that the oxidation of iron produced a somewhat uniformly orange soil in the high marsh creekbank where water flowed out from soil pores to surface water. The orange, supposed oxidized nature of the soils was maintained even during tidal submergence. In the low marsh, where a significant creekbank was absent, this effect was much less distinct, and oxidized soils were found associated only with old root channels.

Discussion

As found in many other aquatic environments (Khalid et al. 1977; Callender & Hammond 1982; Strom & Biggs 1982; Gachter & Mares 1985), iron oxyhydroxides sorb dissolved phosphate in oxidized porewaters of tidal freshwater
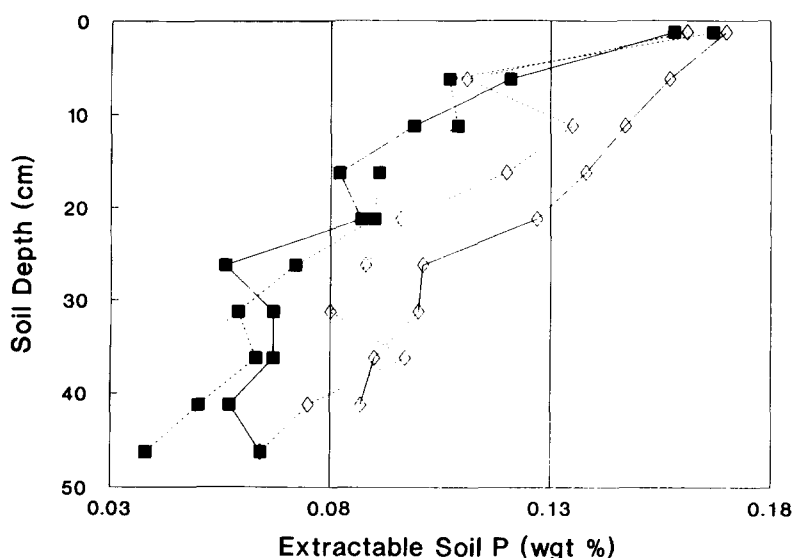
Fig. 5. Total phosphorus profiles in high ($\diamond$) and low ($\blacksquare$) marsh soils. Each point represents a mean of 4 samples from creekbank (solid lines) and interior (dashed lines) sites.

marshes (Fig. 2). This effect is especially pronounced in the creekbank of the high marsh studied, where porewater concentrations of dissolved iron and phosphate are high in the reduced soils, but much lower in the oxidized water collected from seeps (Table 1). The observed patterns of high dissolved phosphate in creekbank porewaters and high total phosphorus in regions of soil oxidation (Fig. 5) are consistent with the iron curtain phenomenon, which we use to describe conditions of phosphate retention in soils containing oxidized iron compounds. Although aluminum oxides have been shown to control the solubilities of phosphate in some wetland soils (Richardson 1985), unlike iron, aluminum is not electroactive. Aluminum compounds are not sensitive to changes in oxidation state, so that their solubilities and sorptive capacities do not change significantly with the changes either in pH or soil redox measured in this study. Some phosphate is certainly bound by aluminum hydroxides in these marsh soils, but the phenomenon of phase change from soluble to solid and phosphate sorption during oxidation is restricted to electroactive species like iron.

Total extractable phosphorus concentrations in surface soils (0–2.5 cm) were higher than any other depth in soil profiles from interior and creekbank locations of both marshes studied (Fig. 5). Throughout the marshes, phosphorus is retained in surface soils, and sorption to iron minerals is at least partly responsible for this enrichment. Across the expanse of marsh away from the influence of creekbank drainage (> 5 m), higher total phosphorus in oxidized surface soils results from upward diffusion of phosphate from reduced porewater, from deposition of $FeOOH–PO_4$ complexes from the tidal water column and perhaps
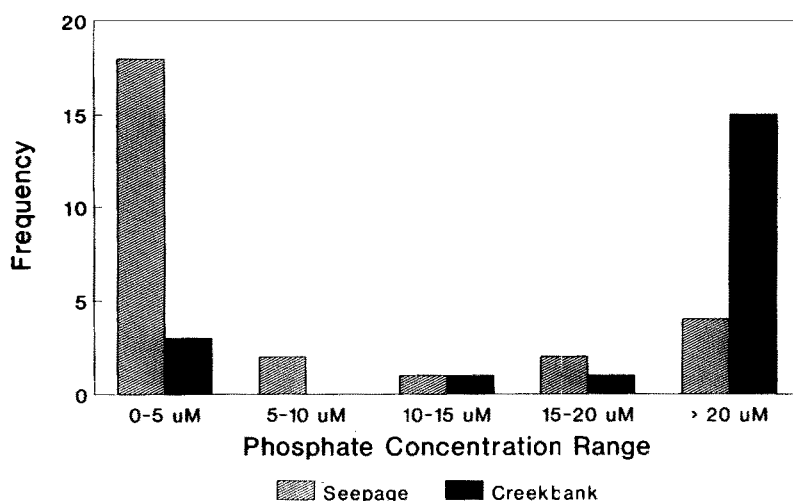
Fig. 6. Frequency histogram of seepage (*N* = 27) and creekbank (*N* = 20) porewater samples, grouped by phosphate concentration range.

from root uptake at depth and translocation to the surface environment (Booth 1989). Simpson et al. (1983) found no differences in total phosphorus by soil depth in tidal freshwater marshes in New Jersey, but Bowden (1984) reported a phosphorus profile similar to ours for organic sediments in a Massachusetts tidal freshwater marsh. He hypothesized the increased phosphorus in aerobic surface sediments was supplied by deposition from tidal water and by upward phosphorus mobilization from deep soils and precipitation in aerobic surface sediments. Although recent anthropogenic inputs could lead to increases in surface phosphorus concentrations, much older soils down to 25 cm were enriched with phosphorus relative to deeper soils, suggesting that other processes such as iron-phosphorus complex formations may help shape the observed total P profile (Bowden 1984; Fig. 5). Bioturbation probably does not contribute significantly to the distribution of iron and phosphorus in these soils since, unlike salt marshes, polychaete and fiddler crab populations are not extensive in tidal freshwater marshes, and there are no obvious signs of extensive soil bioturbation by other organisms.

In and along creekbanks, reduced porewater discharges laterally to surface waters through oxidized soils, sites of iron oxidation, amorphous iron precipitation (Figs. 3, 4), and phosphate sorption (Fig. 2). The subsequent fate of phosphorus seems to depend on the extent of oxidation of the creekbank soils since, relative to the high marsh, low marsh creekbank soils are enriched in dissolved phosphate but not total phosphorus (Table 1; Fig. 5). Generally, iron oxidation and phosphate sorption occur during tidal exposure and porewater drainage; iron reduction and phosphate release occur during tidal submergence and porewater flooding. In the high marsh, where water table drawdowns and

oxygen infiltration occur almost every tidal cycle, both dissolved and total phosphorus concentrations are built up behind a creekbank curtain of recently precipitated and more stable iron/phosphorus complexes (Froelich 1988). Porewater advects from the creekbank during exposure, but reduced iron and soluble phosphorus are immobilized by oxidation. The high marsh creekbanks are exposed for longer periods of time relative to low marshes, so there is a greater opportunity for dissolved phosphate to sorb to precipitating iron oxides. The oxides apparently are not entirely re-reduced during flooding, nor is all the desorbed phosphate transported out of the creekbank, since at this time of the tidal cycle no gradient for subsurface water flow exists. The short exposure time of the low marsh creekbank may limit the persistence of oxidized iron/phosphorus complexes, thus maintaining low total P in the soils but high dissolved iron and phosphate. Relative to high marsh creekbanks, then, there is greater opportunity for porewater export of dissolved phosphate from creekbanks which are oxidized less extensively, a conclusion reached independently by calculations of porewater export (Jordan & Correll 1985; Harvey et al. 1987).

The extent to which water from seepage collectors in the high marsh creekbank (Table 1) is representative of all water discharging from soil pores is unknown. The visually-determined distribution of oxidized iron in soils suggests the presence of macropores, which are preferred flow paths for water (Beven & Germann 1982). Porewaters move through these macropores at greater velocities than water occupying other smaller, perhaps unconnected pores in the soil matrix, and thus experience shorter residence times exposed to oxidized conditions in the creekbank. Seepage collectors may preferentially sample waters from macropores, and these have redox and solute characteristics different from matrix water (J. Harvey, pers. comm.). Further, estimates of seepage from creekbanks are obtained by modelling the discharge of porewater at or below the water table (e.g. Harvey et al. 1987), but all seepage samples in the current study were collected above the falling water table (Fig. 1). Some of this water might consist of recently infiltrated surface water, which by dilution and oxidation would lower dissolved phosphorus concentrations in seepage water. Porewater draining below the water table is not exposed such extensive oxidation, although the presence of iron oxyhydroxides and high total phosphorus levels to at least 20 cm depth in the high marsh creekbank indicates a persistence of a phosphorus-retention effect even under saturated conditions. Inferred reductions in dissolved phosphate concentrations of porewater discharging above the water table, however, may not be as large for discharge below the water table.

The establishment of an oxyhydroxide 'iron curtain' is important because of its demonstrated capacity to remove dissolved phosphate from porewaters discharging from a high marsh creekbank, and because of its dynamic nature. The sorption 'sites' on iron oxyhydroxide molecules would saturate rapidly in a system in which phosphate alone was continually delivered during porewater advection. Along creekbanks, however, porewater draining from the interior of the marsh carries not only dissolved phosphate but dissolved iron as well. The oxidation of this reduced iron increases the sorptive capacity of the soils for

removing dissolved phosphate from solution. Results of the phosphate sorption experiment (Fig. 2) demonstrated no saturation of sorptive sites, because the sorption curve was linear over the natural range of phosphate and iron concentrations examined. The molar ratio of iron:phosphate removal (25) is larger than the range of 6–10 observed for other natural waters (Khalid et al. 1977; McQueen et al. 1986; Lovley & Philips 1986b), all of which are larger than the theoretical removal ratio of two iron oxyhydroxide molecules coordinating with each H_2PO4^- ion (Lijkleme 1977). Dissolved phosphate is thus removed from discharging porewater by sorption to stable oxidized iron compounds in creekbank soils, and to amorphous iron oxyhydroxides as they precipitate from solution.

The establishment and maintenance of the iron curtain in tidal freshwater marshes relies on the association between iron and phosphate in both dissolved and particulate phases. Its importance in other types of aquatic environments may not be as great. In salt marsh soils, chemical oxidation of iron proceeds more rapidly at the high pH typical of seawater (Davison & Seed 1983), but the effect of an iron curtain may be diminished where sulfate competes for sorptive sites with phosphate, and where iron sulfide precipitation creates low dissolved iron concentrations in porewater (Caraco et al. 1989). Since oxic conditions are required for the establishment of an iron oxyhydroxide curtain, however, an iron curtain effect is evident in the sediments of some well-drained, high salt marshes (Scudlark & Church 1989), where a seasonally dynamic oxidized/reduced cycling of iron has been described (Giblin & Howarth 1984). In low marshes, water discharges or phosphate diffuses through a surface layer of sediment which is reduced, and no phosphate sorption to oxidizing iron compounds can occur. Also, the seasonal cycles of phosphate retention and release from lake bottoms are in part a consequence of changing redox conditions in the iron-rich sediments of hypolimnia (Gachter et al. 1988).

Subsurface waters in marshes typically contain dissolved concentrations of nutrients many times that of surface waters (Agosta 1985; Jordan & Correll 1985; Table 1), suggesting that discharge of even small volumes of water through creekbanks or other seepage faces could be an important pathway for nutrient export from marshes. Porewater seepage has been calculated to be in excess of 10 liters per meter of creekbank per tidal cycle in a variety of tidal wetlands (Jordan & Correll 1985; Yelverton & Hackney 1986; Harvey et al. 1987). It is more difficult, however, to model the solute characteristics of discharging water since biogeochemical changes occur as the water moves from reducing to oxidizing conditions. Results from this study indicate that relative to low marsh creekbanks, subsurface waters actually are much more depleted in phosphate as they discharge from high marsh creekbanks (Table 1). Greater phosphate losses are predicted from frequently flooded low marshes, where no enrichment in total phosphorus was noted (Fig. 5). Higher total phosphorus concentrations in the geomorphologically mature, high marsh, where tidal subsidies of nutrients are less, suggest that phosphorus cycles more tightly there than in the younger, low marsh.

King et al. (1982) hypothesized that in salt marshes the formation of iron monosulfides in creekbanks lowers the toxic concentrations of the by-products of sulfate reduction, facilitating growth of *Spartina alterniflora.* Unlike salt marshes, however, sulfide concentrations in tidal freshwater marshes are low enough to be non-toxic, so that higher plant productivity on creekbanks (pers. observ.) must be due to other factors. More recently, the high productivity of marsh vegetation in salt marshes has been explained by the synergistic effects of oxidation and nutrient availability associated with frequent porewater turnover (Dacey & Howes 1984; Agosta 1985; Howes et al. 1986). The iron curtain hypothesis further develops the notion of increased nutrient availability to creekbank vegetation in freshwater marshes, because iron reduction and oxidation cycles concentrate dissolved phosphate in the porewaters of creekbank soils. Nutrient subsidies to creekbank vegetation of tidal freshwater marshes, therefore, come both from flooding tidal waters and from water discharging from the marsh interior.

The cyclical reduction and oxidation of iron in natural aquatic systems can create sites of release and retention of dissolved phosphate. In tidal freshwater marshes, iron oxyhydroxide formation functions as a barrier to diffusive movement of phosphate (on marsh surfaces), and to advective movement of phosphate in discharging porewater (in creekbanks). The implications of phosphate sorption to iron oxyhydroxides relate to the ability of wetlands to retain nutrients and to our understanding of wetlands as nutrient processors.

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