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Al and Fe biogeochemistry in a floodplain forest: Implications for P retention

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Abstract. We examined spatial and temporal variations in soil chemistry in a floodplain forest landscape to determine the effects of flooding on aluminum (Al) and iron (Fe) oxide biogeochemistry and inorganic phosphorus (P_i) sorption capacity. When previously sorbed P_i was considered, the sorption capacities of floodplain and adjacent upland soils were comparable, suggesting that floodplain soils represent a second line of defense protecting downstream aquatic ecosystems from agricultural run-off. P_i sorption capacity was highly correlated with oxalate-extractable Al (Al_o) ($r_s = 0.78$); Al_o and percent organic matter (OM) were also highly correlated ($r_s = 0.72$), suggesting the importance of OM-Al complexes in these soils. The correlation of oxalate-extractable Fe (Fe_o) with OM ($r_s = 0.64$) was improved ($r_s = 0.80$) by removing lower elevation (swale) soils, suggesting that flooding inhibits the association of Fe_o with OM. Fe oxide crystallinity decreased during seasonal flooding, but total extractable Fe did not change significantly. Fe solubilized during flooding was either replaced by sediment deposition (252 ± 3 mmol kg^{-1} yr^{-1}), and/or reprecipitated locally. Al oxide crystallinity also decreased during flooding due to a significant decline in NaOH-extractable Al (Al_N). Al_N concentrations subsequently returned to pre-flooding levels, but sediment Al inputs (57 ± 3 mmol kg^{-1} yr^{-1}), were insufficient to account for this recovery. Observed Fe transformations suggest the importance of flooding-induced declines in soil redox potential to Fe biogeochemistry; observed Al transformations suggest the importance of complexation reactions with soil OM to Al biogeochemistry in this floodplain forest.

Abbreviations: Al – aluminum; Al_N – NaOH minus oxalate-extractable Al; Al_O – oxalate-extractable Al; Al_{ox} – Al oxides and oxyhydroxides; Al_T – Al_O plus Al_N; DCB – dithionite-citrate-bicarbonate; Fe – iron; Fe_D – DCB minus oxalate-extractable Fe; Fe_O – oxalate-extractable Fe; Fe_{ox} – Fe oxides and oxyhydroxides; Fe_T – Fe_O plus Fe_D; OM – organic matter; P – phosphorus; P_i – inorganic P; PSI – P sorption index

Introduction

Aluminum (Al) and iron (Fe) oxides and oxyhydroxides (Al_{ox} and Fe_{ox}, respectively) are known to be important in controlling the retention of dissolved inorganic phosphorus (P_i) in wetland soils. It is widely believed that adsorption and precipitation with these mineral oxides (P sorption, *sensu* Scheidegger & Sparks 1996) are the dominant mechanisms associated with the long-term retention of dissolved P_i in wetlands that develop over acid substrates (Richardson & Marshall 1986; Brinson 1990; Brinson 1993; Walbridge 1993; Walbridge & Lockaby 1994). Adsorption is a two-dimensional process, ranging from weak physical bonding to chemical interactions, including ligand exchange, that occurs at low P_i concentrations (Scheidegger & Sparks 1996). Precipitation of Al and Fe phosphates is a three-dimensional process that is believed to occur at higher P_i concentrations (He et al. 1991; Scheidegger & Sparks 1996).

P_i sorption capacities often have been found to be significantly positively correlated with concentrations of oxalate-extractable (noncrystalline) iron (Fe_o) (Willett et al. 1978; Kuo & Mikkelsen 1979, Sah & Mikkelsen 1986) and aluminum (Al_o) (Richardson 1985; Richardson et al. 1988; Walbridge & Struthers 1993; Lockaby & Walbridge 1998) in wetland soils. Richardson (1985) identified Al_o as the best single predictor of P_i sorption capacity in a variety of bog, fen, and swamp soils. A similar relationship has been observed in some upland soil types (e.g., Borggaard et al. 1990; Walbridge et al. 1991). These results have led to speculation that amorphous inorganic Al_{ox} and Fe_{ox} minerals, which have larger sorption capacities than more crystalline forms due to their larger surface area per unit soil volume (Parfitt & Childs 1988; Parfitt 1989), control P_i sorption in many wetland soils.

Because ferric Fe phosphates are solubilized when Fe(III) is reduced to Fe(II) under anaerobic conditions, such as occurs during soil flooding (cf., Ponnamperuma 1972, Gambrell & Patrick 1978), it seems logical that Al_{ox} might be particularly important as an agent of dissolved P_i retention in wetland soils. However there is some evidence to suggest that flooding can also cause the transformation of crystalline Fe_{ox} to amorphous (noncrystalline) oxide forms (cf., Wang et al. 1991), increasing P_i sorption capacity due to the concomitant increase in the surface area of P_i sorbing minerals (per unit soil volume). Increases in Fe_o concentrations, with concomitant increases in P_i sorption capacity, have been observed in upland soils artificially flooded for rice cultivation (Willett et al. 1978; Kuo & Mikkelsen 1979; Sah & Mikkelsen 1986), but with the exception of Darke et al. (1997), these effects have been little studied in natural wetland soils.

The valence state of Al is not affected by changing soil redox potentials, nor does soil anaerobiosis cause the solubilization of Al phosphates. Soil Al chemistry thus should be less affected by flooding than Fe chemistry. However, the fact that Al_o concentrations are often highly correlated with P_i sorption capacity in wetland soils (Richardson 1985; Richardson et al.

1988; Walbridge & Struthers 1993; Lockaby & Walbridge 1998) suggests that there may be some mechanism that favors Al_o formation and/or persistence in these soils. Because the anaerobic conditions associated with flooding impede decomposition (cf., Kuo & Baker 1982), organic matter (OM) also tends to accumulate in wetland soils. Free Al^{3+} in solution can bind with OM to form an OM-Al complex, preventing the precipitation of an amorphous mineral oxide (Velbel 1984, 1985). Organic anions also can reduce the P_i sorption capacity of existing oxides by competing with phosphate ions for binding sites (Easterwood & Sartain 1990; Espejo & Cox 1992). Finally, OM can inhibit the crystallization of preexisting amorphous Al and Fe oxide minerals (Kodama & Schnitzer 1979, 1980), enhancing P_i sorption capacity (Borggard et al. 1990). In sandy Danish soils, Borggaard et al. (1990) found that OM inhibited the crystallization of soil Al_{ox} to a greater extent than Fe_{ox}, resulting in poorly crystalline Al_{ox} that adsorbed nearly twice as much phosphate as Fe_{ox}.

Flooding has the potential to affect the biogeochemistry of both Al and Fe in wetland soils. Flooding could be particularly important in determining the P_i retention capacities of forested floodplains in the southeastern United States, because these wetlands have strong seasonal hydrologic cycles in which comparatively dry summers and autumns alternate with winter and spring flooding (Williams 1998). The effects of flooding on Al and Fe oxide biogeochemistry are likely to vary spatially as well as temporally in floodplain forests. Floodplain surfaces represent a microtopographical mosaic of lower elevation (swale) and higher elevation (ridge) microsites, the former characterized by more frequent flooding and longer hydroperiods than the latter. The effects of overbank flooding also should decrease laterally across the floodplain with increasing distance from the river channel, while hydrologic and material inputs associated with upland groundwater discharge (riparian transport, *sensu* Brinson 1993) should increase along this same gradient. Because floodplain forests can receive dissolved P_i inputs from both upstream and upslope sources, and commonly either remove them from the water column or convert them to less harmful organic forms, they have the potential to affect downstream water quality (Brinson 1993; Mitsch et al. 1995; Lockaby & Walbridge 1998; Weller et al. 1998). Yet the biogeochemical processes controlling dissolved P_i retention and transformation in floodplain forests subject to repeated natural flooding and draining cycles are poorly understood.

In an earlier study of this floodplain forest along the Ogeechee River, near Savannah, GA, we used an *in situ* field experiment to examine the effects of flooding on Al and Fe biogeochemistry and P_i sorption capacity (Darke et al. 1997). In this subsequent study, we examined spatial and

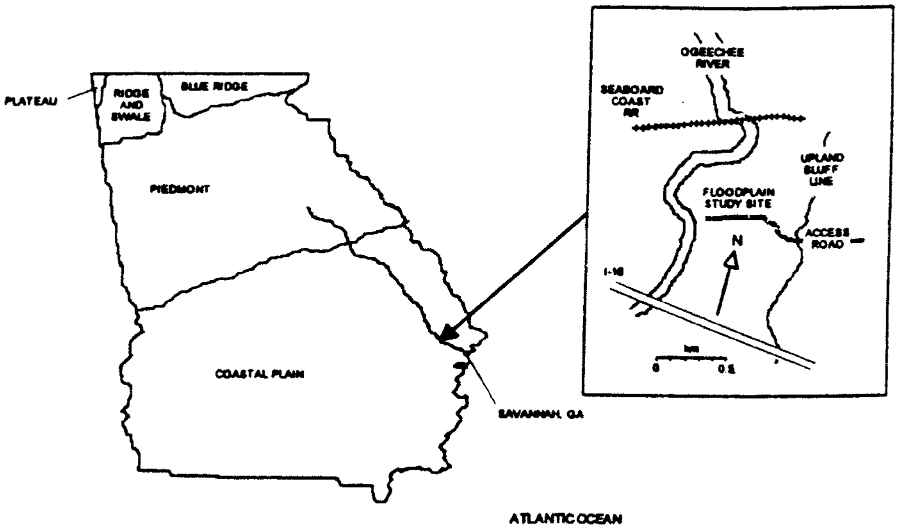

Figure 1. Study site on the east bank of the Ogeechee River near Savannah, GA.

temporal variation in soil chemistry coincident with natural hydroperiod fluctuations to determine the effects of seasonal flooding on soil Al and Fe oxide biogeochemistry and P_i sorption capacity in this same floodplain. We hypothesized that flooding would result in increases in soil noncrystalline (oxalate-extractable) Al_{ox} and Fe_{ox} and, concomitantly, P_i sorption capacity. Thus, P_i sorption capacity would be directly related to hydroperiod within the floodplain, and higher in floodplain soils than in upland soils. Short-term flooding effects were determined by examining seasonal changes associated with natural hydroperiod variations; long-term effects were assessed by comparing the chemistries of swale (lower elevation) and ridge (higher elevation) soils, assuming an inverse relationship between microsite elevation and hydroperiod. Estimates of sediment deposition and changes in soil chemical parameters with increasing distance from the river channel were used to assess the influence of overbank flooding on spatial and temporal variation in soil chemistry.

Site description

The study site (Figure 1) is located in Effingham County, GA, along the east floodplain of the Ogeechee River, approximately 63 km from its mouth (Carlough & Meyer 1991). At this point, the Ogeechee is a meandering, low gradient, alluvial river with a mean channel width of 33 m and an average annual discharge of 68 m^3/s (Cuffney & Wallace 1987). Commonly referred to as a blackwater stream (e.g., Meyer & Edwards 1990), the Ogeechee actually arises in the Piedmont, close to the Piedmont/Coastal Plain boundary. The watershed contains a mixture of agricultural and forest land (Meyer & Edwards 1990).

The floodplain is 1–2 km wide at the study site, and is heavily forested with baldcypress (*Taxodium distichum* L.), sweetgum (*Liquidambar styraciflua* L.), water oak (*Quercus nigra* L.), black gum (*Nyssa sylvatica* Marsh), water tupelo (*Nyssa aquatica* L.), willow (*Salix* spp.) and pines (*Pinus* spp.) (Cuffney & Wallace 1987). The site is classified primarily as palustrine, forested, broad-leaved deciduous, seasonally flooded wetland (PFO1C), interspersed with threads of palustrine, forested, deciduous, semipermanently flooded wetland (PFO6F) (National Wetlands Inventory 1988). Soils are Chastain series (Typic Fluvaquent) and Tawcaw series (Fluvaquentic Dystrochrept) (M. Thomas, Soil Scientist, USDA Natural Resources Conservation Service, Effingham County, GA).

Methods

Soil collection

Initial survey, January 1992: In this preliminary study, surface (0–15 cm) mineral horizon soils were collected at 7 sites in both the floodplain and the adjacent upland for initial characterization of soil properties. Twenty 4 × 8 m plots were established: two in the upland adjacent to the floodplain; two in each of three pairs of concave and convex microsites, evenly spaced at 0.3 km intervals along a 1.0 km riverside to upland transect; four on the levee adjacent to the river channel, and two in a slough (depression) near the levee. Soil cores ($n = 4$ per site) were taken from random locations in each plot and composited in polyethylene bags. Additionally, a 20 × 40 m plot in a fairly level area near the river was sampled intensively ($n = 20$). Portions of this data set have been reported previously in Darke and Walbridge (1994) and Darke et al. (1997). In this paper, data from this preliminary study are used solely for specific correlational analyses, and are clearly identified as “1992 data” on appropriate figures and tables.

Seasonal study, May 1993–June 1994: Because seasonal changes in water table elevation were critical to our analysis of soil chemical dynamics in response to natural flooding and draining cycles, we established three randomly located 5 × 10 m sample plots at each of 10 hydrologic monitoring stations in the floodplain. These monitoring stations were established the previous year by T. M. Williams, Belle W. Baruch Forest Science Institute, SC, as pairs of high and low elevation microsites (identified by visual inspec-

Table 1. Approximate ground elevations of low and high elevation microsites along a riverside to upland gradient. Values represent means with S.D. in paretheses, $n = 2$. Data from T. M. Williams (unpublished).

Gradient position (River to upland)	Elevation (cm above MSL*)	
	Low	High
1	923.1 (3.5)	936.5 (3.2)
2	872.7 (3.1)	934.7 (4.1)
3	911.4 (3.7)	913.5 (0.9)
4	879.8 (12.3)	940.9 (4.9)
5	879.2 (2.0)	923.7 (5.3)

*Mean sea level.

tion, including vegetational differences) at five points (designated landscape gradient positions 1–5) along a 1 km transect from the river margin to the upland. Three randomly located 5 × 10 m plots also were established in the adjacent upland, near the upland/wetland boundary. These plots were located near (but not adjacent to) an eleventh hydrologic monitoring station.

Subsequent analyses revealed that elevational differences between low and high elevation microsites at landscape positions 1 and 3 were small ($<$ 15 cm) in comparison with those at landscape positions 2, 4 and 5 ($>$ 45 cm) (Table 1). Because we were concerned that the small elevational differences at landscape gradient positions 1 and 3 might obscure the hydroperiod/soil chemistry relationships we were interested in studying, we analyzed the data in two ways: (1) averaging all sites together by microsite elevation; and (2) focusing solely on those landscape positions (2, 4, 5) that exhibited large (i.e., $>$45 cm) elevational differences. We use the terms "low" and "high" elevation microsites when referring to the average of all landscape positions, 1–5 inclusive, and the terms "swale" and "ridge" when referring solely to averages of landscape positions 2, 4 and 5. Similar trends were generally observed for both comparisons, but were more frequently statistically significant in comparisons of swales *vs*. ridges.

Soil samples were collected at approximately monthly intervals, from May 1993 through June 1994. Soil cores (0–10 cm) were collected at random locations from each subplot ($n = 4$ per subplot), using a bulb planter, and composited in polyethylene bags.

General analyses

All soils were stored intact on ice during the 9.5 hr return trip to the laboratory, where they were stored at 4 °C. Prior to analysis, each sample was mixed thoroughly by hand, and coarse root material was removed. Analyses were begun within 10 hr of returning to the lab. P_i sorption equilibrations, oxalate extractions and pH determinations were completed within 6 da of soil collection; dithionite-citrate bicarbonate (DCB) and NaOH extractions were completed within 8 da of soil collection.

Soil pH was determined by pH electrode in a 1:2 slurry of soil:deionized water. Exchangeable base cations and exchangeable acidity were determined by the method of Qiu and Zhu (1993); supernatant Ca, Mg, Na and K concentrations were analyzed using a Perkin-Elmer Model 2380 atomic absorption spectrophotometer (Perkin-Elmer 1982). Soil texture was determined by the Bouyoucos method (Day 1965). Four 5.2 cm diameter cores per subplot of surface soil (0–10 cm), collected with sections of pvc pipe sharpened on one end, were used to estimate soil bulk density. Soil organic matter was estimated by mass loss on ignition in a muffle furnace at 500 °C for 8 hr. Percent moisture content was determined gravimetrically by drying 15–35 g aliquots of each bulk sample to a constant mass at 80 °C.

P_i sorption

P_i sorption capacities of sterilized and nonsterilized soils were determined using the method of Walbridge et al. (1991), to estimate geochemical and geochemical plus microbial immobilization of P_i, respectively. Analyses were performed on soils collected in January 1992 (nonsterilized soils only), September 1993, and February and June 1994. We used 2.0 g dry weight equivalent (dwe) soil aliquots and 25 mL 0.01 M $CaCl_2$ containing 0.5, 1.1, 4.2 and 8.4 mmol P/L as KH_2PO_4 with $n = 4$ per sample per treatment. We added 0.5 mL of liquid $CHCl_3$ to half of the replicates prior to $CaCl_2$ addition to suppress microbial P_i uptake. Additional P released by $CHCl_3$ treatment was estimated by extracting a set of $CHCl_3$-treated soil samples ($n = 2$) with 0.01 M $CaCl_2$ immediately after $CHCl_3$ addition. The P_i measured in these extracts was included as “added P” when calculating P_i sorbed in sterilized soils. Orthophosphate concentrations of supernatants were analyzed colorimetrically using a Technicon II Autoanalyzer (Technicon 1983).

P_i sorption isotherms were used to characterize each soil’s capacity to remove dissolved P_i from solution (Richardson 1985; Walbridge & Struthers 1993). Isotherms, prepared by plotting mmol PO_4^{-3}-P adsorbed or precipitated per 100 g soil as a function of μM P remaining in solution after equilibration (24 hr) at a constant temperature with 0.5, 1.1, 4.2 and 8.4 mmol P/L, resulted in curvilinear plots which were useful for describing P_i sorption over this range of concentrations. The P_i sorption isotherms were used as graphical tools for visual comparison of soil sorption relationships as a function of landscape position and time.

The P_i Sorption Index (PSI) for each soil was calculated as x/log C, where x is mmol P adsorbed or precipitated/100 g soil and C is μmol P remaining in solution after a 24 hr laboratory equilibration with 4.2 mmol P/L (Bache & Williams 1971). This index was used for analyzing correlative relationships between P_i sorption capacity and other soil variables. Total P_i sorption capacity (including initially sorbed P_i) was estimated as the sum of soil NaOH-extractable P (Wright 1998) plus mmol P sorbed/100 g soil during a 24 hr equilibration with 4.2 mmol P/L. NaOH-extractable P and sorbed P_i were determined for aliquots of identical soil samples.

Theoretical P sorption maxima (P_{max}) were calculated using the y-intercept of the plot of x as a function of $(x/C)^{1/2}$. This modified Langmuir equation takes into account the decreasing energy of adsorption with increasing surface coverage (Kuo 1988). For each sample point, P_{max} values for the upper 10 cm of soil were calculated using the average of values for September 1993, February 1994 and June 1994.

Al_{ox} and Fe_{ox} fractions

Soil Al_{ox} and Fe_{ox} fractions were analyzed using the procedure of Darke and Walbridge (1994). In this procedure, noncrystalline Al_{ox} and Fe_{ox} are estimated by extraction with 0.2 M acid ammonium oxalate (pH 3) (McKeague & Day 1966; USDA 1972). A sequential 0.1 M NaOH extraction (Hsu 1991) is used to estimate crystalline Al_{ox}. Noncrystalline plus crystalline Fe_{ox} is estimated by a separate DCB extraction (Boero & Schwertmann 1989). Crystalline Fe_{ox} is estimated by difference. To identify crystallinity changes within the noncrystalline pool (May 1993–June 1994), the least crystalline part of this pool was extracted using 0.2 M acid ammonium oxalate adjusted to pH 6 (Sah et al. 1989), in addition to the more common extraction at pH 3, as described above. Supernatants were analyzed for Al and/or Fe concentrations using a Perkin-Elmer Model 2380 atomic absorption spectrophotometer (Perkin-Elmer 1982).

In this paper, we use the terms Al_O and Fe_O to refer to Al and Fe extracted by acid ammonium oxalate at pH 3; Al_O (pH 6) and Fe_O (pH 6) refer to Al and Fe extracted by ammonium oxalate at pH 6; Al_N refers to the remaining Al extracted by NaOH following oxalate extraction; Fe_D refers to DCB-extractable minus oxalate-extractable Fe; Al_T equals Al_O plus Al_N; Fe_T equals Fe_O plus Fe_D.

Sediment deposition

Sediment traps (n = 2 per plot) were used to estimate sediment deposition during the period October 1993 to May 1994. Traps consisted of 14.2 cm diameter Gelman Versapor 450 filters, clipped to 15 × 15 × 2 cm plastic frames covered with plastic mesh screening material and staked to the ground with plastic surveyor's flags. Because of the small total mass, sediment samples (n = 24) were composited prior to analysis for Al_T and Fe_T as described above.

Water table

Average 30-da water table elevation estimates were based on intermittent biweekly piezometer pressure measurements (n = 5 for low and high elevation microsites and n = 1 for the upland) (T. M. Williams, unpublished data). Missing values were estimated using surface water measurements or measurements from piezometers with continuous recorders (n = 2 for low and high elevation microsites) (T. M. Williams, unpublished data).

Statistical analyses

Normal probability plots (GB Stat, Version 5.4 1995) revealed that data distributions were somewhat nonnormal. Because of this, we restricted our use of statistical techniques either to nonparametric methods or to parametric methods that are robust for somewhat non-normal distributions, such as two-way analysis of variance. Seasonal and microsite variation in floodplain soil properties were evaluated by two-way analysis of variance with fixed effects, followed by Fisher's LSD when the overall ANOVA was significant at $p < 0.05$ (GB Stat, Version 5.4 1995). Significant differences between landscape positions within the floodplain and between floodplain and upland were determined using the Mann-Whitney U Test at $p < 0.05$ (GB Stat, Version 5.4 1995). Differences in upland soil properties across time were tested using Kruskal-Wallis one-way ANOVA, followed by a multiple comparison test when the overall ANOVA was significant at $p < 0.05$ (BMDP Statistical Software, Inc. 1993).

Relationships between soil properties were examined using Spearman's Rho correlation analysis (GB-Stat, Version 5.4 1995). Correlations between geochemical P_i sorption capacity and other soil variables were determined using data collected in January 1992 (nonsterilized soils) and June 1994 (sterilized soils), months when all soil variables were estimated.

Table 2. General characteristics of Ogeechee floodplain and upland soils. Values represent means, with S.E. in parentheses, of soils collected in June 1994, with the exception of pH which is an annual average, and % organic matter (OM) and NaOH-extractable P, which are averages of September 1993, February 1994 and June 1994. N = 3 for swale, ridge and uplands soils; n = 10 for floodplain soils.

	Loss on ignition %OM	Soil texture			Bulk density g/cm^3	pH	Exchangeable bases				Exchangeable acidity cmol/kg	NaOH-extractable mmol/100 g
		Sand %	Silt %	Clay %			Ca	Na	K	Mg		
							cmol/kg					
Floodplain[2,3]	8.60*	67.48*	15.08*	17.44*	0.65*	4.95*	3.43*	0.16	0.05*	0.30*	7.85*	0.14*
	(0.91)	(4.08)	(1.98)	(2.41)	(0.04)		(0.43)	(0.04)	(0.01)	(0.04)	(0.71)	(0.02)
Swale[4,5]	10.26	71.23	11.81	16.96	0.51	4.85	4.40	0.18	0.06	0.35	9.01	0.14
	(1.22)	(2.74)	(1.02)	(1.73)	(0.04)		(0.72)	(0.06)	(0)	(0.07)	(0.65)	(0.03)
Ridge[4]	5.89	75.23	14.37	10.39	0.77	4.97	2.12	0.10	0.01	0.19	5.67	0.08
	(0.78)	(5.53)	(2.92)	(2.75)	(0.08)		(0.54)	(0.02)	(0.01)	(0.05)	(0.80)	(0.08)
Upland	3.16	95.06	2.18	2.89	1.16	5.72	1.16	0.09	0.27	0.13	2.02	0.44
	(1.02)	(0.58)	(0.41)	(0.90)	(0.08)		(0.25)	(0.01)	(0.02)	(0.03)	(0.08)	(0.10)

[1] Data from Wright (1998). Soil samples were identical to those analyzed for other variables.
[2] Averages of both low and high elevation microsites at landscape positions 1–5 (see Methods, p. 9).
[3] * indicates significant difference between floodplain and upland at $p < 0.05$.
[4] Averages of low (swale) or high (ridge) elevation microsites at landscape positions 2, 4, and 5 only (see Methods, p. 9).
[5] No significant differences between swales and ridges at $p > 0.05$.

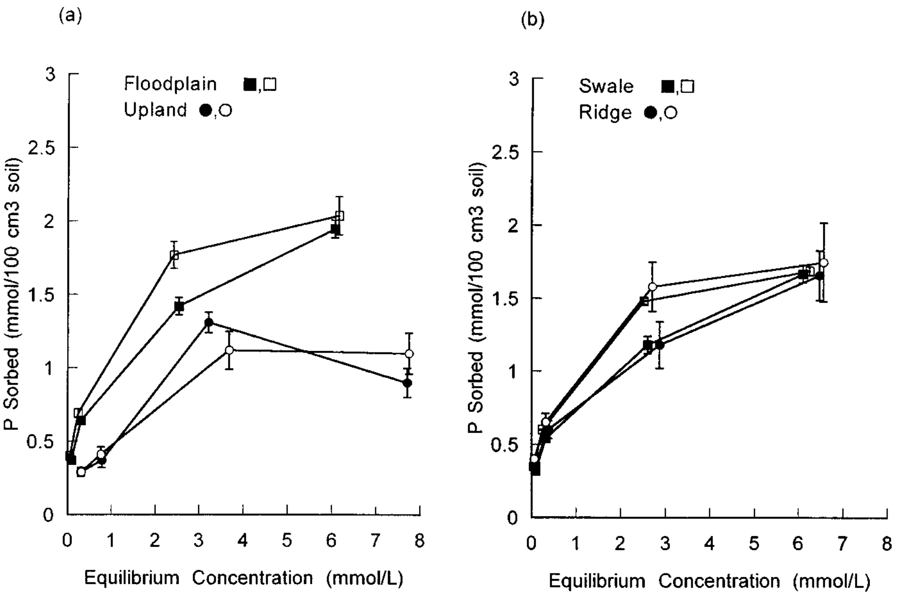

Figure 2. Effect of microtopography on P_i sorption isotherms for (a) the Ogeechee River floodplain (averages of both low and high elevation microsites at landscape positions 1–5) and adjacent upland soils, and (b) floodplain swale and ridge soils (averages of low [swale] and high [ridge] elevation microsites at landscape positions 2,4 and 5 only). Closed symbols (■, ●) indicate nonsterilized soils; open symbols (□, ○) indicate sterilized soils. Values are means with S.E., $n = 3$.

Results

General soil characteristics

Ogeechee floodplain soils exhibited textural characteristics of sandy loams (cf., Brady 1990), with lower pH's and bulk densities than adjacent upland soils (Table 2). Silt, clay and organic matter concentrations were all significantly higher and NaOH-extractable P was significantly lower in floodplain soils than in upland soils.

P_i sorption capacity

In the top 10 cm of soil, the estimated maximum P_i sorption potential (P_{max}) of the Ogeechee floodplain was 21.8 (S.E. 1.7) kmol PO_4-$^{3-}$P/ha, based on the average of sterilized and nonsterilized soils, which were not significantly different ($p > 0.05$). Based on visual comparisons, bulk density corrected P_i sorption capacities were higher in floodplain vs upland soils, but similar in swale and ridge soils (Figure 2). When we accounted for previously sorbed

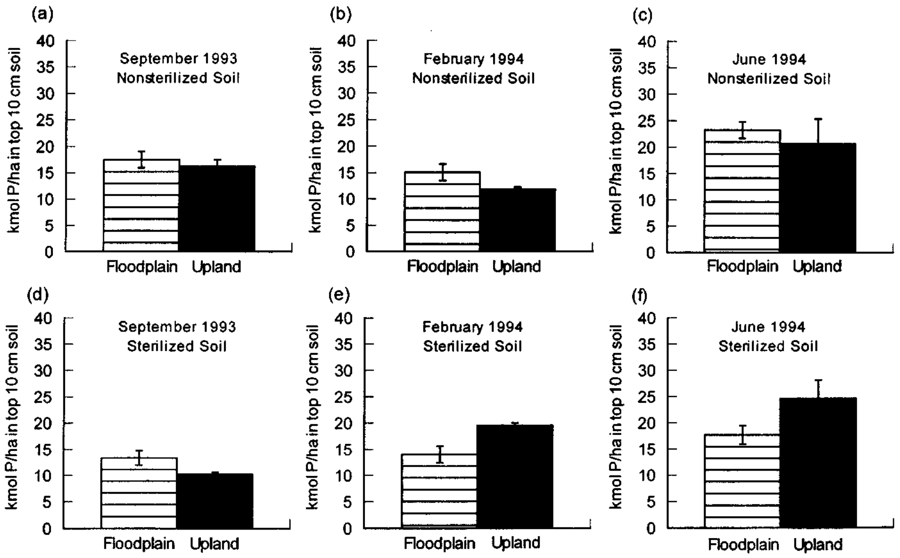

Figure 3. Total P_i sorption capacities of (a–c) nonsterilized and (d–f) sterilized floodplain and upland soils. Total sorption capacities were estimated as the sum of NaOH-extractable P_i and P_i sorbed after a 24 hour laboratory equilibration with 4.2 mmol PO_4^{-3}-P/L. NaOH-P_i data, from Wright (1998), and sorbed P_i data were determined for aliquots of identical soil samples. Values are means with S.E., $n = 10$ for floodplain, $n = 3$ for upland. No floodplain-upland differences are statistically significant at $p < 0.05$.

P_i, sorption capacities of floodplain and upland soils were not significantly different (Figure 3). Based on visual comparisons, P_i sorption capacities for both sterilized and nonsterilized floodplain soils were higher in June than in September and February (Figure 4(a) and (b)).

Factors controlling P_i sorption capacity

P_i sorption was most highly correlated with the sum of $Al_O + Fe_O$ (Table 3), with a stronger correlation for Al_O than Fe_O. P_i sorption was more highly correlated with Al_O than Al_T, but more highly correlated with Fe_T than with Fe_O. Correlations (1993/1994 soils) were similar whether oxalate extractions were carried out at pH 3 or pH 6 (0.917 vs 0.938 for Al_O; 0.919 vs 0.887 for Fe_O ($p < 0.0001$; Darke 1997). Both OM and clay also were highly correlated with P_i sorption.

Al_O was strongly correlated with OM in floodplain soils (Figure 5(a)). Fe_O was also positively, though less strongly, correlated with OM (Figure 5(b)). Fe_O exhibited a different relationship with OM in swale vs nonswale soils. The relationship between Fe_O and OM in swales was not statistically significant; in non-swales Fe_O and OM were significantly positively correlated.

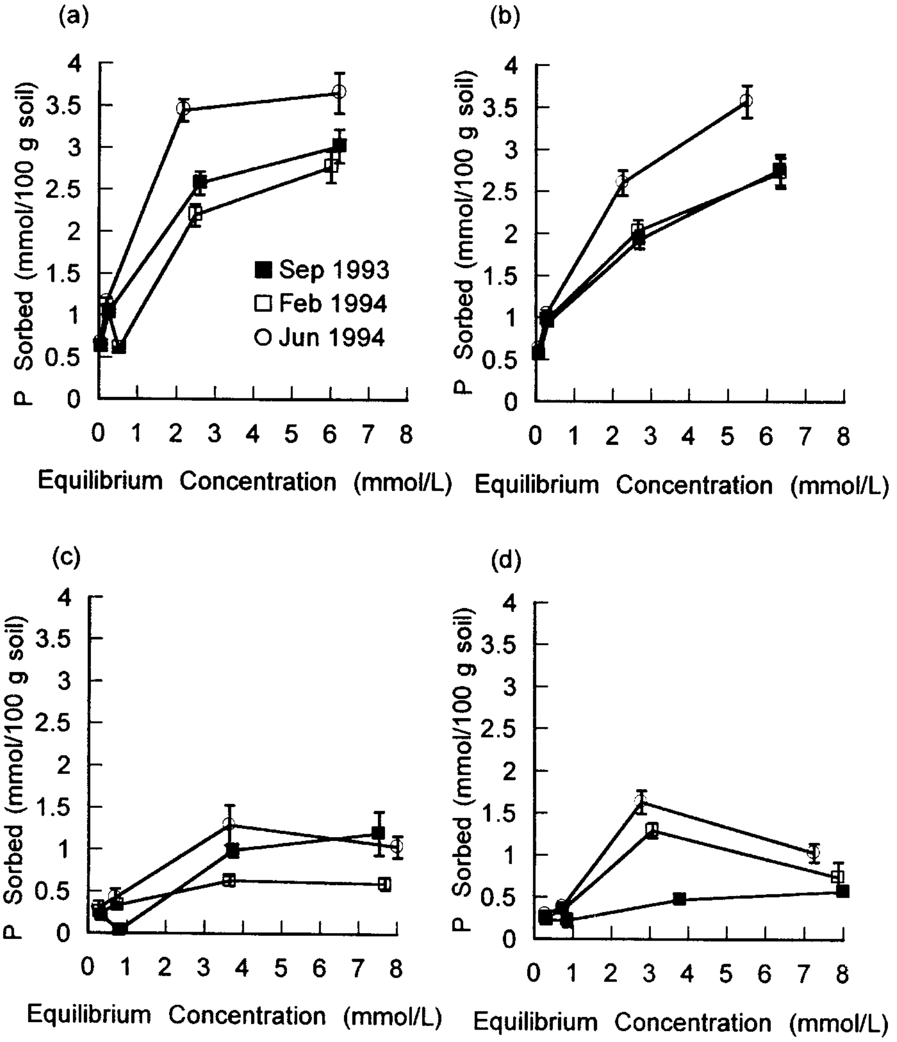

Figure 4. Seasonal changes in P_i sorption isotherms for (a) nonsterilized floodplain, (b) sterilized floodplain, (c) nonsterilized upland, and (d) sterilized upland soils. Values are means with S.E., n = 10 for floodplain, n = 3 for upland.

Spatial variation in soil chemistry

Patterns of spatial variation in clay, OM, Al_{ox} and Fe_{ox} fractions, and P_i sorption were similar along the landscape gradient from riverside to upland (Figure 6). There was a general decline in all forms of Fe_{ox} with increasing distance from the river channel margin, with a somewhat weaker trend for Al_{ox}.

Table 3. Relationship between soil P_i sorption index (PSI) and floodplain soil characteristics. Values are Spearman's Rho Correlation Coefficients. Soil samples were Collected in January 1992 (*n* = 38) and June 1994 (*n* =30).

	Spearman's Rho	*p* Value
$Al_O + Fe_O$	+0.879	<0.0001
% OM	+0.836	<0.0001
% Clay	+0.832	<0.0001
Al_O	+0.782	<0.0001
Fe_T	+0.709	<0.0001
Fe_O	+0.686	<0.0001
Al_T	+0.647	<0.0001
pH	+0.062	0.1321

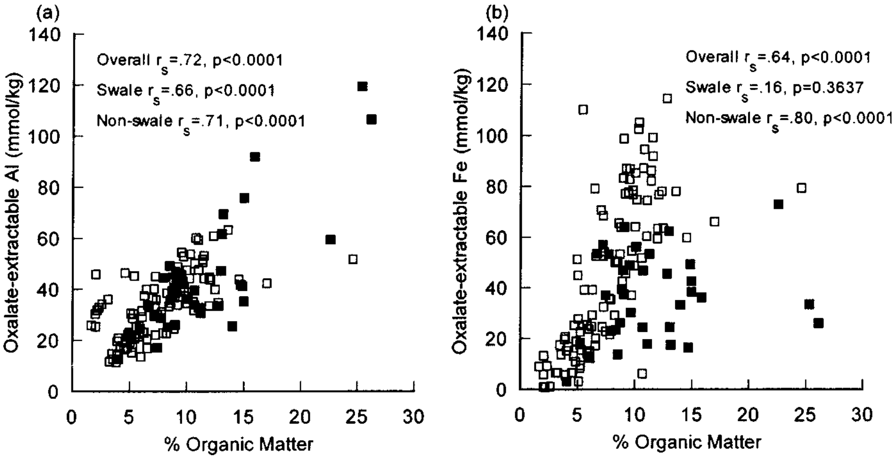

Figure 5. Effect of landscape microtopography (swale *vs.* non-swale) on the relationship between percent organic matter and oxalate-extractable (a) Al and (b) Fe. Closed squares (■) are swale and open squares (☐) are nonswale microsites. Spearman's Rho correlation coefficient = r_S. Soil samples were collected in January 1992 (*n* = 38) and June 1994 (*n* = 30).

Noncrystallinity ratios (Al_O/Al_T and Fe_O/Fe_T) suggest that the relative proportions of soil metal fractions differ as a function of microtopography. Based on annual averages, Al_{ox} was significantly more crystalline in low (0.29 ± 0.02) vs high (0.36 ± 0.01) elevation microsites ($p < 0.05$), and Fe_{ox} was significantly less crystalline in low (0.95 ± 0.02) vs high (0.86 ± 0.02) elevation microsites ($p < 0.05$).

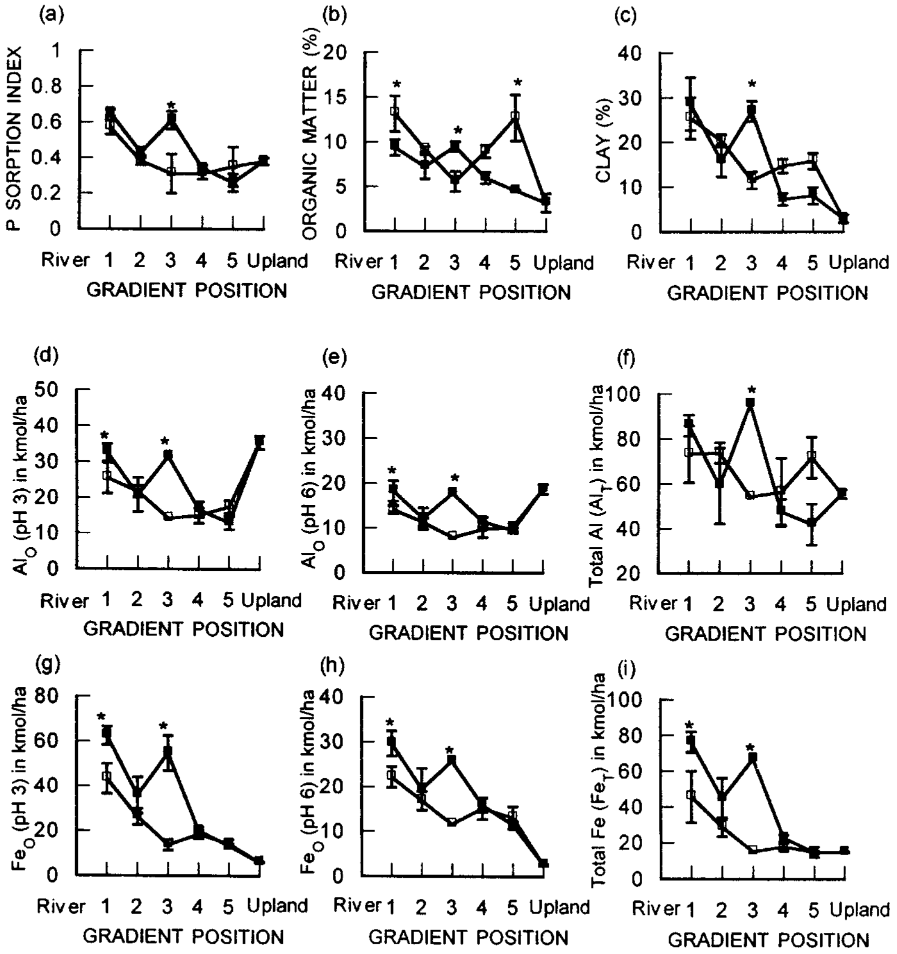

Figure 6. Changes in: (a) mean bulk density adjusted P_i sorption index and (b) mean percent organic matter for September 1993, February and June 1994; (c) percent clay for June 1994; and annual average for (d) oxalate (pH 3) extractable-Al (Al_O), (e) oxalate (pH 6)-extractable-Al (Al_O (pH 6)), (f) oxalate plus NaOH-extractable Al (Al_T), (g) oxalate (pH 3)-extractable-Fe (Fe_O), (h) oxalate (pH 6)-extractable-Fe (Fe_O (pH 6)), and (i) DCB-extractable Fe (Fe_T) along a riverside to upland gradient. Open squares (□) are low and closed squares (■) are high elevation microsites. Values are means with S.E., $n = 3$. Asterisks indicate significant differences between low and high elevation microsites, $p < 0.05$. All landscape gradient position 1 vs 5 differences are statistically significant at $p < 0.05$, except for low elevation microsite percent organic matter and Al_T (Darke 1997).

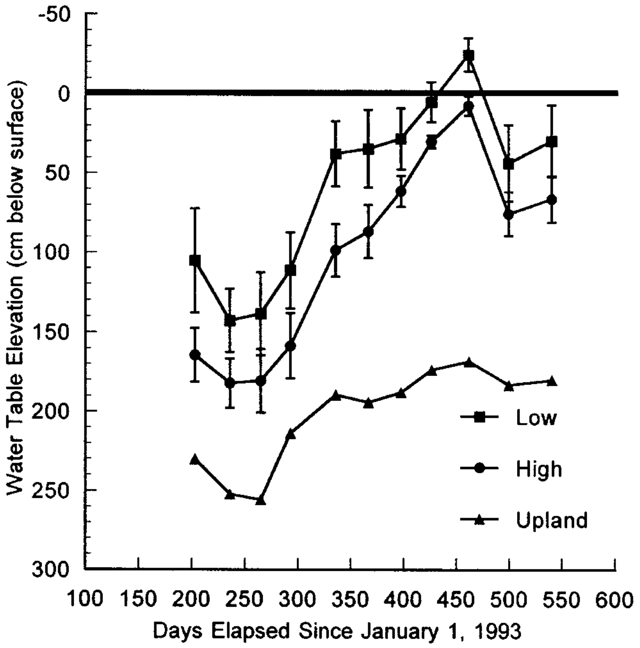

Figure 7. Estimated average monthly water table elevation in Ogeechee floodplain low and high elevation microsites, July 1993–June 1994. The adjacent upland is shown for reference. The thick solid line indicates surface of land. Values represent means and S.E., n = 5 for low and high elevation microsites and n = 1 for the upland. Water table data are from T.M. Williams (unpublished). For significant differences not given in text, see Darke (1997).

Temporal variation in soil chemistry

The floodplain water table rose significantly between October and December 1993, with surface flooding greatest in April 1994, and dropped significantly between April and May in both low and high elevation microsites (Figure 7, Darke 1997).

Soil pH in low elevation microsites rose significantly during winter-spring flooding (Figure 8, Darke 1997), peaking in April and remaining elevated through June 1994. The seasonal pH range was greater for the low than for the high elevation microsites. There were no significant seasonal differences in floodplain %OM (Table 4).

There were no seasonal differences in Fe_T content of either low elevation/swale or high elevation/ridge microsites (Table 5, Figure 9(a), Darke 1997), although there was a general trend for gradually declining Fe_O concentrations in all microsites during the dryer summer and autumn months. Fe_O concentrations reached a minimum in January, when the water table was still approximately 40 cm below the surface in low and 90 cm below the surface in

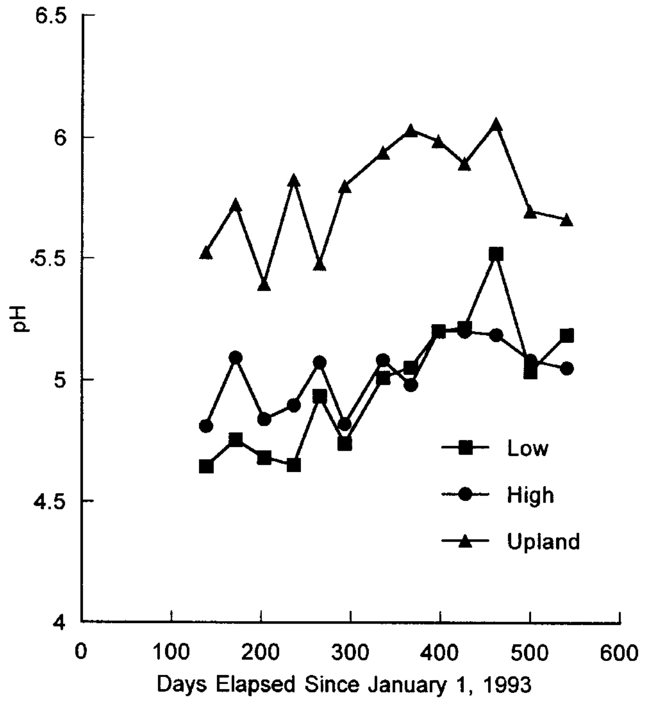

Figure 8. Seasonal pH changes in Ogeechee floodplain low and high elevation microsites, May 1993–June 1994. The adjacent upland is shown for reference. Values represent means, $n = 5$ for low and high elevation microsites and $n = 3$ for upland. For significant differences not given in text, see Darke (1997).

Table 4. Seasonal changes in percent organic matter (OM). Values represent means with S.E. in parentheses, $n = 5$ for low and high elevation microsites, $n = 3$ for upland. Lower case letters indicate significant differences between landscape positions at $p < 0.05$. There were no significant seasonal differences.

	September 1993	February 1994	June 1994
		% OM	
Floodplain Low Elevation Microsites	10.69 (18.5) a	8.41 (1.10) a	10.6 (1.15) a
Floodplain High Elevation Microsites	7.22 (0.83) a	6.98 (0.95) a	7.72 (1.21) a
Upland	5.25 (2.72) a	2.25 (0.16) b	2.00 (0.19) b

Table 5. Seasonal changes in water table and Al oxide and Fe oxide fractions in swale and ridge microsites, May 1993–June 1994. Values represent means with S.E. in paretheses, $n = 3^1$.

	May	Jun	Jul	Aug	Sep	Oct	Dec	Jan	Feb	Mar	Apr	May	Jun
Water table^2 (cm from surface)													
Swale	N.A.	N.A.	58.66 (22.88) bcz	1115.26 (13.17) az	104.76 (20.88) abz	79.58 (22.72) abz	10.80 (10.27) cdz	3.31 (13.10) dz	2.95 (9.36) d	–12.68 (5.91) d	–39.43 (7.52) d	10.78 (14.27) cd	–0.10 (4.28) dz
Ridge	N.A.	N.A.	151.04 (19.46) ay	174.15 (24.12) ay	167.10 (28.68) ay	150.95 (35.25) ay	96.89 (29.99) by	79.33 (25.78) bcy	54.04 (9.34) bcd	28.43 (6.33) cd	12.89 (8.93) d	59.78 (11.87) bcd	55.27 (15.45) bcdy
Total Al oxide (AlT) (kmol/ha)													
Swale	98.12 (15.93) ay	61.07 (4.69) bcy	62.25 (12.13) bc	65.61 (5.21) bc	67.53 (3.65) bcy	66.64 (8.59) bc	68.60 (4.57) bc	73.37 (10.50) b	49.85 (8.01) c	52.22 (3.82) bc	68.62 (9.24) bcy	68.45 (10.31) bc	71.49 (6.18) bc
Ridge	60.07 (14.12) z	40.48 (4.23) z	51.87 (4.10)	51.55 (7.65)	44.85 (5.27) z	48.15 (5.23)	56.91 (7.80)	56.00 (6.33)	39.47 (5.13)	41.18 (3.78)	44.90 (4.02) z	52.89 (3.34)	54.18 (12.32)
Crystalline Al oxide (AlN) (kmol/ha)													
Swale	76.40 (13.68) ay	46.80 (5.47) bcd	44.16 (7.56) bcd	46.46 (4.68) bcd	47.39 (3.70) bcdy	48.86 (6.18) bcdy	50.24 (3.20) bc	52.02 (7.13) bc	32.59 (5.68) d	36.73 (3.10) cd	54.09 (8.35) by	50.41 (9.19) bc	53.66 (4.15) b
Ridge	36.92 (8.97) z	27.17 (2.01)	34.97 (2.36)	35.67 (6.06)	27.71 (3.26) z	33.41 (3.68) z	40.98 (5.46)	38.14 (4.63)	23.86 (2.65)	25.25 (1.63)	27.29 (2.36) z	35.88 (1.73)	37.66 (8.78)
Noncrystalline Al oxide (AlO pH 3) (kmol/ha)													
Swale	21.72 (2.37)	14.27 (1.64)	18.09 (4.57)	19.15 (0.71)	20.14 (0.17)	17.78 (2.42)	18.37 (2.02)	21.36 (3.41)	17.26 (3.56)	15.48 (1.44)	14.53 (2.19)	18.04 (1.78)	17.83 (2.10)
Ridge	23.16 (5.25)	13.31 (2.22)	16.90 (1.79)	15.88 (1.94)	17.14 (2.08)	14.75 (2.09)	15.93 (4.02)	17.85 (3.02)	15.62 (2.51)	15.93 (2.15)	17.61 (1.77)	17.02 (1.82)	16.51 (3.56)
Noncrystalline Al oxide (AlO pH 6) (kmol/ha)													
Swale	11.80 (1.80)	8.98 (0.54)	12.40 (2.07)	12.80 (0.47)	11.49 (1.12)	9.53 (1.49)	11.31 (1.11)	11.07 (0.78)	8.36 (0.80)	9.78 (1.79)	8.25 (0.65)	8.40 (1.30)	10.33 (0.86)
Ridge	11.89 (2.38)	11.91 (1.16)	12.26 (1.69)	9.80 (0.82)	11.24 (0.67)	10.74 (0.60)	10.82 (0.45)	11.02 (0.69)	9.99 (0.86)	10.41 (1.32)	10.95 (1.02)	10.47 (1.01)	10.79 (1.26)
Al oxide nocrystallinity ratio (AlO/AlT)													
Swale	0.23 (0.01) cdz	0.25 (0.04) bcdz	0.29 (0.01) bc	0.30 (0.02) ab	0.30 (0.02) abz	0.27 (0.00) bcd	0.27 (0.02) bcd	0.29 (0.01) b	0.35 (0.05) a	0.31 (0.02) abz	0.22 (0.03) dz	0.28 (0.03) bc	0.25 (0.01) bc
Ridge	0.40 (0.01) ay	0.33 (0.02) by	0.33 (0.01) b	0.33 (0.02) b	0.40 (0.01) ay	0.31 (0.02) b	0.28 (0.04) b	0.32 (0.04) b	0.41 (0.02) a	0.39 (0.02) ay	0.39 (0.01) ay	0.34 (0.02) ab	0.31 (0.01) b
Total Fe oxide (FeT) (kmol/ha)													
Swale	22.13 (2.91)	17.91 (4.09)	21.56 (8.14)	21.05 (3.59)	24.08 (2.16)	18.93 (4.06)	18.49 (3.44)	19.20 (3.68)	17.40 (4.36)	21.02 (7.03)	17.22 (6.76)	22.52 (2.860	23.61 (4.16)
Ridge	37.50 (12.96)	23.06 (7.87)	24.28 (7.73)	23.20 (7.03)	31.70 (13.20)	25.97 (9.36)	25.55 (8.85)	24.29 (7.50)	29.83 (12.75)	26.48 (8.83)	24.35 (8.09)	27.95 (8.62)	30.56 (12.23)

Table 5. Continued.

	May	Jun	Jul	Aug	Sep	Oct	Dec	Jan	Feb	Mar	Apr	May	Jun
							Cystalline Fe oxide (FeD) (kmol/ha)						
Swale	0.84 (0.84) c	0.75 (0.56) c	0.76 (0.60) c	0.40 (0.40) c	1.40 (1.40) c	0.73 (0.38) c	4.11 (0.65) bc	8.73 (1.52) a	4.75 (0.39) abc	1.61 (1.02) c	4.16 (1.32) bc	7.74 (1.26) ab	1.29 (1.29) c
Ridge	1.65 (1.65) b	0.97 (0.37) b	0.52 (0.33) b	0.38 (0.20) b	7.02 (5.42) b	2.58 (1.11) b	8.34 (2.53) b	11.87 (0.59) a	11.76 (5.52) ab	4.97 (2.45) b	7.49 (1.75) b	7.17 (2.44) ab	5.33 (2.68) b
							Noncrystalline Fe oxide (FeO pH 3) (kmol/ha)						
Swale	24.53 (1.75) ab	19.86 (4.44) ab	24.86 (6.30) ab	26.94 (2.17) a	24.95 (2.17) a	19.80 (3.32) ab	14.84 (4.46) ab	10.47 (4.61) b	12.66 (4.68) ab	20.34 (5.87) ab	14.90 (7.66) ab	14.77 (2.28) ab	25.90 (2.09) a
Ridge	41.58 (14.16) a	23.03 (8.10) ab	26.67 (6.34) ab	24.29 (7.10) ab	24.99 (7.65) ab	24.69 (8.03) ab	17.38 (6.30) b	12.42 (7.93) b	18.07 (7.31) b	21.82 (6.22) b	16.86 (6.66) b	21.29 (6.04) ab	26.52 (9.10)
							Noncrystalline Fe oxide (FeO pH 6) (kmol/ha)						
Swale	16.34 (1.72) b	11.88 (1.92) bc	15.18 (1.92) bc	14.82 (1.15) bc	13.79 (0.95) bc	11.03 (0.53) bc	15.18 (2.12) bc	13.81 (0.90) bc	9.61 (0.30) c	10.00 (2.96) c	12.28 (1.09) bc	16.91 (1.81) b	33.85 (5.07) ay
Ridge	19.53 (5.63) b	13.42 (2.67) bcd	18.06 (1.51) bc	14.18 (1.44) bcd	13.86 (2.38) bcd	14.34 (1.72) bcd	15.65 (3.95) bcd	13.54 (2.07) bcd	11.44 (1.38) cd	9.89 (3.07) d	13.13 (1.75) bcd	17.40 (2.06) bcd	27.94 (4.89) az
							Fe oxide noncrystallinity ratio (FeO/FeT)						
Swale	1.00 (0.08) ab	1.00 (0.02) ab	1.00 (0.13) ab	1.00 (0.18) a	1.00 (0.12) ab	1.00 (0.03) ab	0.76 (0.08) cd	0.51 (0.13) d	0.65 (0.09) d	0.98 (0.06) bc	0.77 (0.16) cd	0.65 (0.03) d	1.00 (0.13) ab
Ridge	1.00 (0.21) a	1.00 (0.03) abcd	1.00 (0.11) ab	1.00 (0.01) abc	0.91 (0.07) bcde	0.98 (0.05) abcde	0.68 (0.01) ef	0.39 (0.14) g	0.62 (0.05) fg	0.87 (0.06) cdef	0.67 (0.04) efg	0.76 (0.05) def	0.97 (0.11) abcd

[1] a–g indicate significant differences between months.
y–z indicate significant differences between swale and ridge microsites.
[2] Water table data from T. William (unpublished).

high elevation microsites (Figure 9(c), Figure 7). $\mathrm{Fe_O}$ concentrations gradually increased during late winter/spring, when the water table reached a maximum. The decrease from late summer to winter and the increase from winter to early summer were significant in swales (Table 5).

As $\mathrm{Fe_O}$ concentrations decreased, $\mathrm{Fe_D}$ concentrations increased (Figure 9(b) and 9(c)). This increase was significant in ridges and swales in January 1994 vs summer/autumn 1993 values (Table 5). $\mathrm{Fe_D}$ concentrations in upland soils also increased significantly between May 1993 and January 1994, paralleling the decrease in $\mathrm{Fe_O}$ (Figure 9(b), Darke 1997).

$\mathrm{Fe_{ox}}$ noncrystallinity (i.e., $\mathrm{Fe_O/Fe_T}$) decreased significantly during autumn and early winter, and then increased significantly as the water table approached the land surface in late winter and early spring (Table 5, Figure

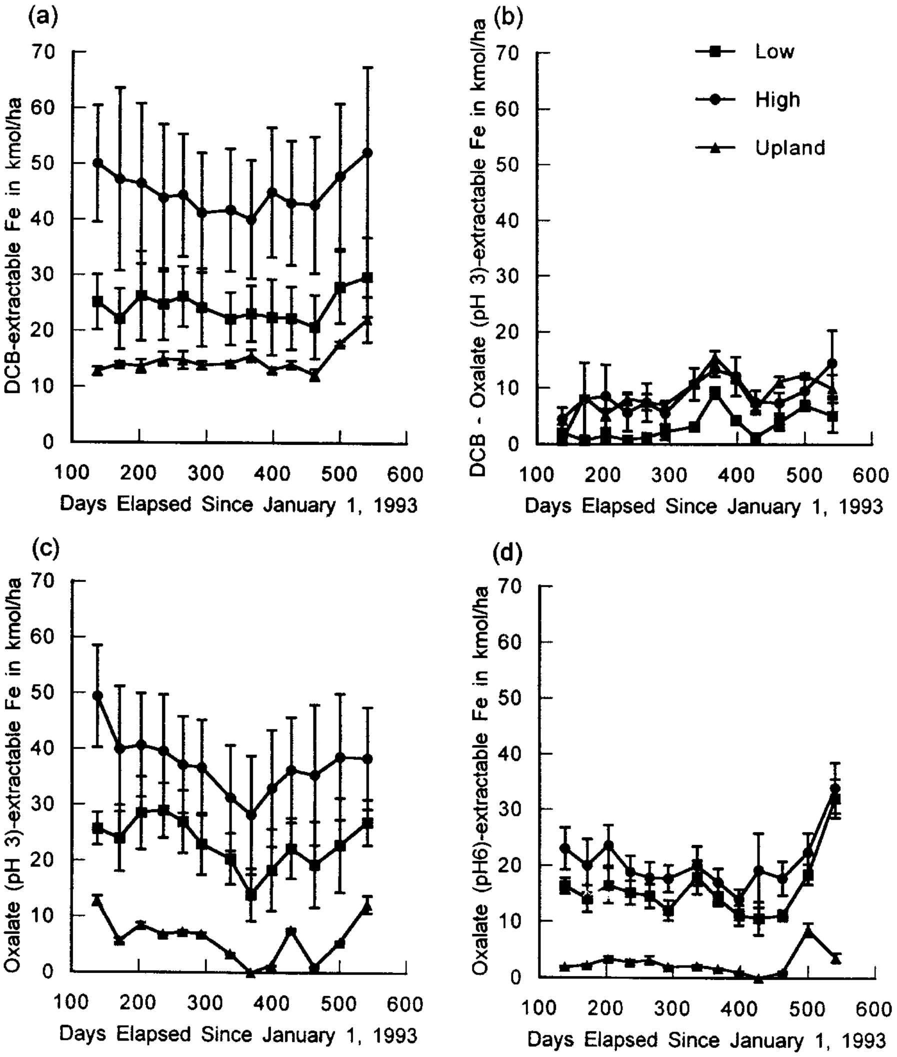

Figure 9. Seasonal changes in Fe oxide fractions in floodplain low and high elevation microsites, May 1993–June 1994. The adjacent upland is shown for reference. Fractions are: (a) DCB-extractable Fe (Fe_T); (b) DCB minus oxalate (pH 3)-extractable Fe (Fe_D); (c) oxalate (pH 3)-extractable Fe (Fe_O), and (d) oxalate (pH 6)-extractable Fe (Fe_O (pH 6)). Values represent means with S.E., $n = 5$ for floodplain low and high elevation microsites, $n = 3$ for upland. For significant differences not given in text, see Darke (1997).

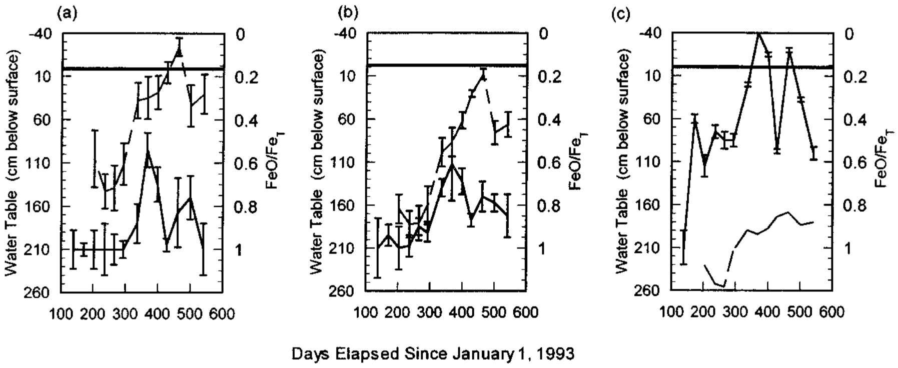

Figure 10. Seasonal changes in Fe oxide crystallinity and water table elevation for floodplain (a) low and (b) high elevation microsites, and for (c) the adjacent upland, May 1993–June 1994. The noncrystallinity ratio equals oxalate-extractable Fe divided by DCB-extractable Fe (crystallinity increases as the ratio decreases). Broken line (- -) indicates water table, thin solid line (–) indicates noncrystallinity ratio, and thick solid line (——) indicates land surface. Values represent means with S.E., $n = 5$ for low and high elevation microsites, $n = 3$ for upland noncrystallinity ratio, and $n = 1$ for upland water table. For significant differences not given in text, see Darke (1997).

10, Darke 1997). The estimated average annual depth of the water table below the surface was significantly negatively correlated with final (June 1994) Fe_{ox} noncrystallinity ratios ($r_s = -0.742$, $p < 0.05$), suggesting that the closer the average annual water table was to the surface at any location, the less crystalline Fe_{ox} ultimately became. This relationship was very strong in more frequently flooded microsites ($r_s = -0.975$, $p = 0.0048$ for low vs $r_s = -0.500$, $p = 0.391$ for high elevation microsites). Based on annual averages, Fe_{ox} was significantly less crystalline in low/swale microsites than high/ridge microsites ($p < 0.05$). Because Fe_T concentrations remained constant (Figure 9(a)), variations in crystallinity were likely due to seasonal changes in the proportions of Fe_O and Fe_D (Figure 9(b) and (c)). Upland Fe_{ox} crystallinities were highly variable over time and difficult to interpret, although Fe_{ox} crystallinity did increase significantly in upland soils between May 1993 and January 1994 (Figure 10(c), Darke 1997).

An overall decline in Al_T in February (Figure 11(a)) was significant in swales (Table 5). This late winter loss of Al_T reflected changes primarily in the Al_N fraction, which declined significantly between January and February, and then increased significantly in April in swales (Table 5). There were no significant seasonal differences in Al_O (pH 3 or pH 6) (Table 5, Figure 11(c) and (d), Darke 1997).

Like Fe_{ox}, Al_{ox} noncrystallinity (Al_O/Al_T) also increased significantly in late winter-early spring as the water table rose, and then decreased in late

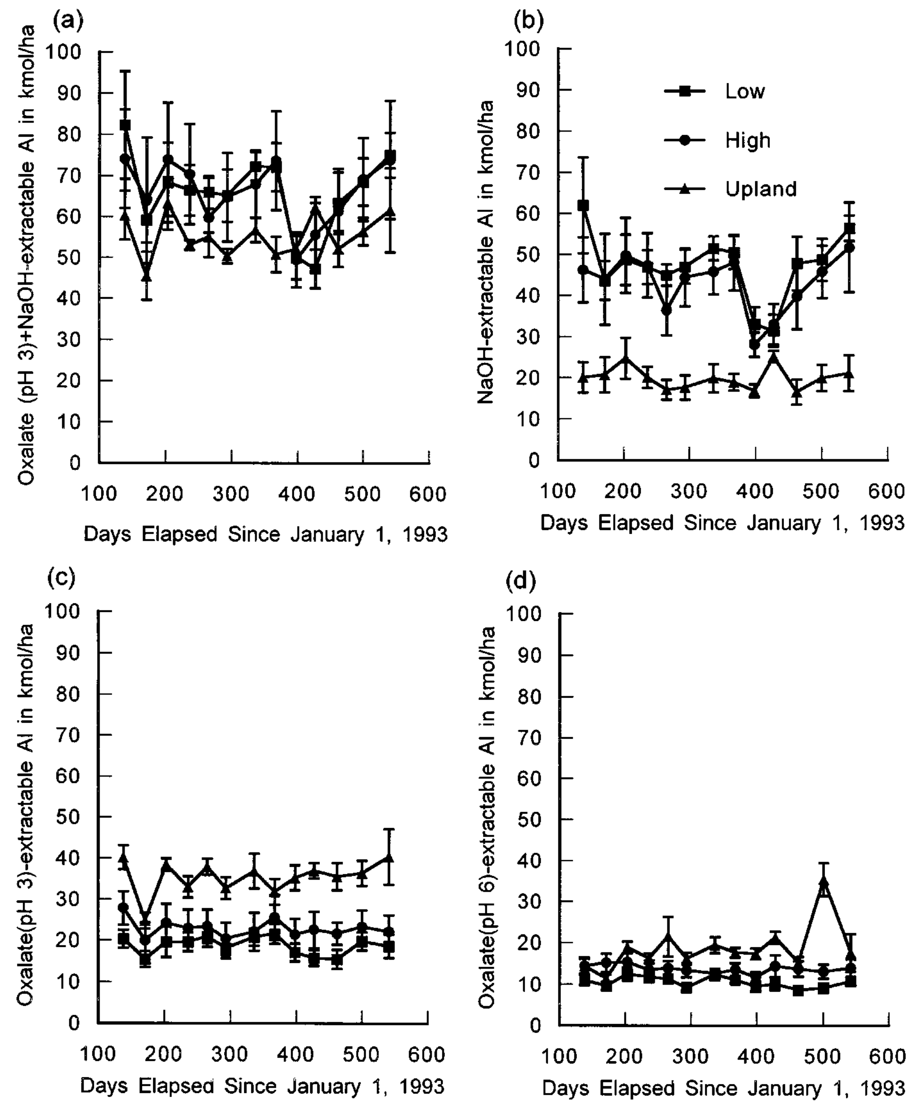

Figure 11. Seasonal changes in Al oxide fractions in floodplain low and high elevation microsites, May 1993–June 1994. The adjacent upland is shown for reference. Fractions are: (a) oxalate (pH 3) plus NaOH-extractable Al (Al_T); (b) NaOH-extractable Al (Al_N); (c) oxalate (pH 3)-extractable Al (Al_O), and (d) oxalate (pH 6)-extractable Al (Al_O (pH 6)). Values represent means with S.E., $n = 5$ for low and high elevation microsites, $n = 3$ for upland. For significant differences not given in text, see Darke (1997).

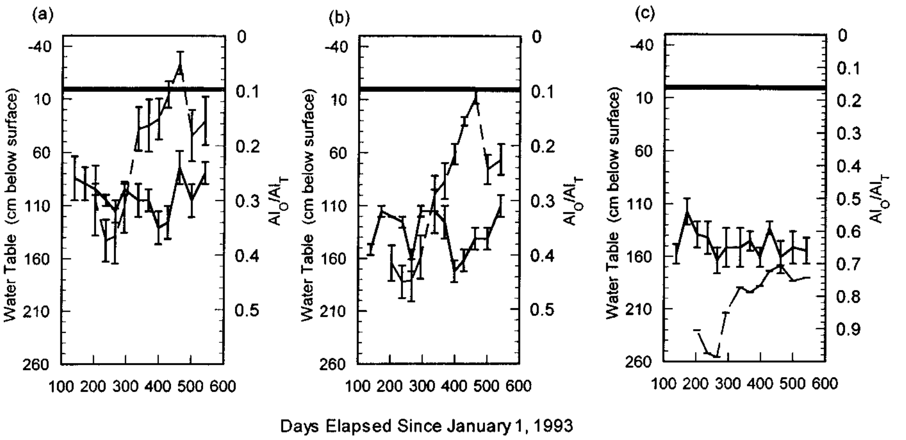

Figure 12. Seasonal changes in Al oxide crystallinity and water table elevation for floodplain (a) low and (b) high elevation microsites, and for (c) the adjacent upland, May 1993–June 1994. The noncrystallinity ratio equals oxalate-extractable Al divided by oxalate plus NaOH-extractable Al (crystallinity increases as the ratio decreases). Broken line (- -) indicates water table, thin solid line (–) indicates noncrystallinity ratio, and thick solid line (–) indicates land surface. Values represent means with S.E., $n = 5$ for low and high elevation microsites, $n = 3$ for upland noncrystallinity ratio, and $n = 1$ for upland water table. For significant differences not given in text, see Darke (1997).

spring in all floodplain microsites (Table 5, Figure 12, Darke 1997). Unlike Fe_{ox}, however, short-term changes in Al_{ox} crystallinity were driven primarily by losses from the crystalline fraction (Figure 11(b)). Based on annual averages, Al_{ox} was significantly more crystalline in low/swale than in high/ridge microsites ($p < 0.05$).

Sediment deposition

Mean sediment deposition in the floodplain during the winter-spring flood season was 312 ± 31 kg/ha, an estimate that includes sediments brought into the floodplain by floodwaters as well as those generated locally by resuspension. Fe_T concentration of the sediment (252 ± 3 mmol/kg) was four times that of Al_T (57 ± 3 mmol/kg).

Discussion

Floodplain P_i retention

The P_i retention capacities of freshwater wetland soils are known to vary considerably (Richardson 1985). If we assume uniformity with depth in surface (0–15 cm) soils, the theoretical P_i sorption maximum for the upper 10 cm of Ogeechee floodplain soils, 21.8 kmol/ha, is more than twice the 13.5 kmol/ha estimated for the upper 15 cm of a forested wetland in the North Carolina Coastal Plain (Richardson et al. 1988), and eight times the 1.2 kmol/ha estimated for the upper 5 cm of a fen peatland at Houghton Lake, Michigan (Richardson & Marshall 1986). The magnitude of the estimated P_i sorption maximum suggests the potential importance of this floodplain in removing inorganic P inputs from both floodwaters and runoff.

Soil P_i sorption capacity varied seasonally (Figures 4(a) and (b)), peaking in late spring/early summer, during the period of maximum expected runoff from agricultural fertilizers (i.e., following spring application). This was related to higher concentrations of Fe_{ox} and Al_{ox} fractions in June vs September and January (Figures 9 and 11), which may be a post-flooding response to the deposition of fresh Fe_{ox} and Al_{ox}, and/or a function of flood-induced changes in Fe_{ox} and Al_{ox} chemistry. P_i immobilization by seasonally larger or more active microbial populations also may be important. Seasonal microbial immobilization is known to occur for nitrogen (N), and has been found to be the most important mechanism retaining N in northern hardwood forests in the spring prior to canopy development (Zak et al. 1990).

We had expected spatial variability in biogeochemical processes to occur at the microsite level – e.g., P_i sorption capacities would be higher in swale vs ridge soils – affecting the overall P_i retention capability of the floodplain. However, after adjusting for bulk density differences, P_i sorption capacities did not differ between swales and ridges (Figure 2). Both swale and ridge microsites, however, had higher P_i sorption capacities than upland soils, despite their lower bulk densities (Table 2).

The apparent greater maximum P_i sorption capacity of Ogeechee floodplain *vs*. upland soils is attributable to higher concentrations of previously sorbed P_i in upland soils (Table 2). When previously sorbed P_i was accounted for, the P_i sorption capacities of floodplain and upland soils were nearly identical (Figure 3). At the landscape level, the Ogeechee floodplain appears to function as a second line of defense, protecting water quality from P_i inputs that are not retained in the more heavily loaded uplands. The importance of this function may increase with time, as loadings to upland soils increase, because the amount of P_i lost to surface waters tends to increase with increasing soil P content (Carpenter et al. 1998). The role of floodplain forests may be particularly significant in Coastal Plain agricultural watersheds, where non-point source P_i inputs may be high relative to the sorption capacities of both sandy floodplain and upland soils (Walbridge 1993).

Factors affecting P_i sorption capacity

Al_O was more strongly correlated with P_i sorption capacity than Fe_O (Table 3). Borggaard et al. (1990) found that on a per mole basis, Al_O adsorbs nearly twice as much phosphate as Fe_O. However, the sum of $Al_O + Fe_O$ was a better predictor of P_i sorption capacity than either Al_O or Fe_O alone (Table 3). Borggaard et al. (1990) and Freese et al. (1992) found that both Al_O and Fe_O concentrations were important predictors of soil P_i sorption capacity in clayey, peaty and sandy soils. Our observed relationships were similar regardless of whether oxalate extractions were carried out at pH 3 or pH 6 (the latter extracting the least crystalline subfraction of the noncrystalline fraction), in contrast with Sah et al. (1989) who found that in agricultural soils managed for rice cultivation, P_i sorption was more highly correlated with changes in the Fe_O (pH 6) subfraction.

Clay and OM content of Ogeechee soils also were highly correlated with P_i sorption capacity (Table 3), similar to the organic forest soils investigated by Nakos (1987). In acid mineral soils, Al and Fe oxides should be associated primarily with the soil clay fraction, so the clay-P_i sorption relationship is not surprising. However, a strong relationship between OM and P_i sorption capacity is not commonly reported in acid mineral soils, and contrasts with Borggaard et al. (1990) who found that removal of OM had no direct influence on P_i sorption capacity in sandy Danish soils.

Both Al_O and Fe_O were positively correlated with soil OM (Figure 5), suggesting that organic matter-metal (Al, Fe) complexes, which are also extracted by acid ammonium oxalate at pH 3, may provide an important component of the P_i sorption capacity of Ogeechee floodplain soils. Gerke and Jungk (1991) made a similar observation in sandy soils, suggesting that humic Fe and Al complexes provide important P_i sorbing sites (i.e., PO_4^{3-} was bound to the organic matter via Al or Fe ligands). Fe freshly complexed with humic substances can sorb 10 times more P_i than noncrystalline Fe_{ox} (Gerke & Hermann 1992). Thus, the presence of OM-metal complexes could significantly increase the P_i sorption capacity of floodplain soils.

Differences in Al vs Fe biogeochemistry

In the Ogeechee floodplain, the biogeochemistries of Al_{ox} and Fe_{ox} appear to be controlled by separate processes that respond differently to flooding. Our results suggest that Al biogeochemistry is strongly influenced by complexation reactions with OM, while Fe biogeochemistry is more strongly influenced by flooding-induced changes in crystallinity, suggesting the importance of redox reactions.

Short and long-term changes in soil Al_{ox} and Fe_{ox} fractions: As hypothesized, Fe_{ox} crystallinity increased during the relatively dry summer and autumn, and decreased as the water table rose during the late winter and early spring (Figure 10). The strong relationship between flooding and Fe_{ox} crystallinity suggests that hydroperiod plays an important role in these crystallinity changes. Because Fe_T concentrations did not change significantly during the seasonal cycle (Figure 9(a)), observed changes in crystallinity suggest either flooding-induced conversion of crystalline Fe_{ox} to noncrystalline forms (local reprecipitation of solubilized Fe^{3+} at oxic/anoxic interfaces), and/or balancing of Fe_{ox} losses with fresh floodwater Fe_{ox} inputs of lower crystallinity. The spatial distribution of soil Fe_{ox} (Figure 6) suggests the importance of long-term Fe inputs to the system via floodwaters, with Fe_{ox} concentrations decreasing with increasing distance from the river. Sediment deposition, accounting for Fe_{ox} inputs of 0.14 kmol/ha, can explain only a small fraction of the crystallinity decrease during winter-spring flooding. However, precipitation of soluble floodwater Fe inputs is also a potential source of relatively noncrystalline Fe_{ox} to the floodplain.

Although as hypothesized, Fe_{ox} became more crystalline over time following drainage, natural flooding appears to result in the long-term accumulation of noncrystalline Fe_{ox}. This is suggested by the fact that, unlike upland soils, the majority of floodplain Fe_{ox} is noncrystalline (Figure 9), and that Fe_{ox} is significantly less crystalline in more frequently flooded low/swale vs high/ridge microsites. A similar effect of flooding on Fe_{ox} crystallinity has been observed in upland soils flooded for rice cultivation (Willet & Higgins 1980).

Flooding appeared to cause a seasonal decline in soil Al_T, but not in soil Fe_T (Figures 9(a) and 11(a)). While the 36 mmol/kg Al loss seems large, fluxes of this magnitude can occur in some forest ecosystems. For example, Fox and Comerford (1992) calculated an annual Al loss of 19 mmol/kg in response to potential annual oxalate loading rates in the rhizosphere of a slash pine forest. The loss of Al we observed in the Ogeechee floodplain may have occurred via the suspension of particulates from the floodplain surface by the action of floodwaters, and/or by the solubilization of soil Al, with subsequent export from the system. Solubilization might occur via some form of dissolution weathering of soil Al minerals (Schlesinger 1991), or complexation reactions involving dissolved OM (cf., Fox & Comerford 1992). Dissolved OM concentrations are high in the Ogeechee River (Meyer & Edwards 1990), and Al is known to complex readily with OM (Borggaard et al. 1990; Qualls & Haines 1991). Cuffney (1988) reported net OM exports from this floodplain to the Ogeechee River; our results suggest that these exports may include OM-Al complexes.

Flooding induced changes in soil pH could favor both the formation and solubilization of humic-Al complexes. Typically, pH's range from 4.5–5.0 in non-flooded Ogeechee soils, and increase to 5.5–5.6 in flooded soils (Figure 8). Both complexation of Al with organic matter (Hargrove & Thomas 1982; Lindsay & Walthall 1996) and amounts of P coprecipitated with humic acids (Bedrock et al. 1997) increase with increasing pH in the range pH 2–5, while the solubility of humic-Al complexes increases significantly above pH 5.4 (Gerke 1997). Thus ambient pH's of non-flooded Ogeechee soils are in the range favoring the formation of OM-Al-P_i complexes, and flooding-induced increases in soil pH at the Ogeecheee would be of sufficient magnitude to solubilize these OM-Al-P_i complexes.

By late spring, Al concentrations had returned to pre-flooding levels. The spatial distribution of soil Al_{ox} in the floodplain (Figure 6(f)), and the small amount deposited in sediments, suggest sources in addition to particulate Al_{ox} inputs in floodwaters. These could include inputs of dissolved forms of Al in floodwaters, and/or the discharge of Al via upland groundwaters. Fertilization is known to cause mobilization of Al in acid soils (Egli & Fitze 1995). Upland soils adjacent to the Ogeechee are used for pasturing cattle and are fertilized at least twice each year. Alternatively, the loss of free Al during flooding could stimulate weathering of Al minerals *in situ*.

In contrast to Fe_{ox}, flooding may cause a long-term decline in noncrystalline Al_{ox}. Unlike in upland soils, the majority of floodplain Al_{ox} was in crystalline form (Figure 11), and Al_{ox} was significantly more crystalline in more frequently flooded low/swale vs high/ridge microsites.

Significance of OM-metal complexes: The strong correlative relationship between Al_O and OM (Figure 5(a)) suggests that OM may play an important role in controlling Al biogeochemistry in this floodplain forest. Simple aliphatic acids, hydroxamate siderophores, and phenols, including complex polymeric forms, are among the soil organic compounds that are known to form stable complexes with Al (Stevenson & Vance 1989). Higher molecular weight organic compounds also can form complexes with Al. Although generally considered recalcitrant, humic substances can form both soluble and insoluble complexes with Al; fulvic acid-Al complexes are generally more soluble than humic acid-Al complexes (Stevenson & Vance 1989).

Formation of OM-Al complexes has potentially important implications for soil P_i sorption capacity. Bowman and Cole (1978) suggested that a significant portion of soil organic P may be bound to OM by metal ligands, rather than as part of defined organic compounds. Phosphate may be released when OM-Al complexes are solubilized, although some OM-Al-PO_4 complexes that occur in soil solution and leachate waters are soluble (Stevenson &

Vance 1989). The formation of OM-Al-PO_4 complexes in this floodplain has important water quality implications, increasing soil retention of inorganic PO_4^{3-} inputs, and slowing the release of exported PO_4^{3-} to aquatic organisms downstream, thereby reducing the likelihood of nuisance blue-green algal blooms (cf., Elder 1985), which are largely P-limited (Soranno et al. 1996).

For Fe_O, the correlative relationship with OM was weaker than for Al_O because the relationship broke down in more frequently flooded swales (Figure 5(b)). Despite a higher percentage of OM in swales (Table 2), flooding appears to operate against the OM-Fe relationship. Fe biogeochemistry in swales is likely controlled by redox processes, with Fe reduction working against the formation of OM-Fe complexes.

Spatial distribution of P-sorbing (Al_{ox}, Fe_{ox}) minerals

Changes in soil chemistry within the floodplain were more complex than can be explained by a simple riverside to upland gradient (Figure 6). It has been suggested that much of the complexity in biogeochemical processes in floodplain forests may result from hydrologic linkages with adjacent streams and uplands (Lockaby & Walbridge 1998). In the Ogeechee floodplain, these linkages appear to affect Al and Fe differently. In general, Fe appears to be dominated by floodwater inputs; Al may be more influenced by riparian transport (Figure 6). However, our overall observations suggest a distributional mosaic that likely results from a diversity of factors including levee breaks, spatially variable overbank flooding, spatial variability in soil permeability, and differential groundwater inputs from the upland.

Conclusions

Floodplain forests like the Ogeechee can play an important role in maintaining the water quality of stream ecosystems that are located in agricultural watersheds. They can function as a second line of defense that shields the downstream aquatic ecosystem from excess fertilizer or manure phosphates exported from uplands by surface runoff or groundwater discharge. Both Al and Fe are important in controlling P_i sorption capacity in this forested floodplain, and their dynamics are linked to seasonal flooding cycles. However, different processes appear to control the biogeochemistries of these elements. Fe transformations appear largely controlled by flooding-induced declines in soil redox potential. Al dynamics appear linked to the tendency of Al to form complexes with soil OM. Al losses that occur during seasonal flooding, presumably by solubilization of OM-Al complexes, are not balanced by sediment Al inputs alone, but by unidentified sources. Correlations between Al_O

and P_i sorption frequently have been observed in wetland soils. In the Ogeechee floodplain, OM-Al complexes, rather than amorphous inorganic Al_{ox} minerals, appear be the dominant form of Al controlling P_i sorption.

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