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Groundwater-induced redox-gradients control soil properties and phosphorus availability across four headwater wetlands, New York, USA

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Abstract Hydrochemical patterns across groundwater-fed wetlands, especially carbonate and redox gradients, can influence phosphorus (P) availability by controlling its distribution among different soil pools. We explored these linkages by comparing shallow (5–20 cm) soil properties along groundwater flowpaths in two rich fens, a marl fen, and a poor fen. Organic matter content, bulk density, and total elemental content varied more with depth to underlying drift materials than with water table fluctuation, but also were influenced by groundwater discharge, which stabilized water table elevations and controlled redox conditions. Total sulfur and calcium content increased where pore-water chemistry indicated active iron and sulfate reduction. Calcium mineral dynamics, however, did not appear to influence P availability: first, calcium carbonate ($CaCO_3$) accounted for <2% of the soil composition, except in the marl fen where it accounted for 20–25% of the soil composition. Second, Ca-bound P pools, determined from hydrochloric extraction of wet soil samples, accounted for <25% of the inorganic soil P pool. In contrast, iron-bound P determined from bicarbonate-buffered dithionite solution, accounted for 50–80% of the inorganic soil P, and increased where there was evidence of groundwater mixing, as did P release rates inferred from incubated anion resin bags. The total carbon and phosphorus content of organic-rich soils as well as available and labile P pools were strongly correlated with pore-water iron and alkalinity concentrations. Groundwater discharge and resulting hydrochemical gradients explained significant variation in soil composition and P availability across each site. Results highlight the importance of conducting biogeochemical studies in the context of a site's shallow geologic setting and suggest mechanisms supporting the diverse plant species unique to groundwater wetlands.

Keywords Alkalinity · Calcium carbonate · Iron · Plant nutrient availability · Sulfate

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Introduction

Although we have made much progress in understanding the role of groundwater in regulating the development of wetland soils (Almendinger and Leete 1998a; Giesler et al. 1998), interactions between nutrient availability, soil mineralization, and water chemistry remain uncertain (Axt and Walbridge 1999; Kellogg and Bridgham 2003; Moore et al. 2007). Hydrologic studies suggest that wetland soil development is closely related to biogeochemical reactions regulated by hydrologic fluxes across a wetland complex (Lucassen et al. 2000; McNamara et al. 1992). For example, in four headwater wetlands, geochemical reactions depended on by-products of redox reactions associated with groundwater supply of terminal electron acceptors to the organic-rich substrates (Boomer and Bedford 2008). Alkalinity and dissolved iron gradients were significant enough to differentially influence carbonate- and iron-mineral equilibria across each site. These results were consistent with experimental laboratory incubations (Lamers et al. 2001; Lucassen et al. 2004a, b) and field studies in highly managed wetlands across northern Europe (Smolders et al. 2006), but had not been reported for relatively pristine sites typical of North America. These linkages may explain why, historically, wetland plant communities have been associated with hydroperiod (i.e., timing, magnitude, and duration of flooding), pH or alkalinity gradients, and nutrient (nitrogen and phosphorus) availability (Vitt 1994).

Groundwater-fed wetlands (i.e., fens) offer an ideal setting for investigating linkages between soil composition, nutrient status, and pore-water composition because there is minimal variation in the flood regime (Bedford and Godwin 2003). Water table elevations consistently occur within 10 cm of the land surface, and therefore soils remain saturated but not flooded (Almendinger and Leete 1998b; Amon et al. 2002). These conditions result in formation of carbon-rich soils with more than 50% organic matter content (Verhoeven et al. 1996), except where the soils consist predominantly of calcium carbonate precipitates (Bedford and Godwin 2003). Fens that have not been impacted by humans often host a diversity of plant species, many of which are locally or globally rare (Amon et al. 2002; Johnson and Leopold 1994). Our previous work relating nutrient limitation to wetland plant diversity (Bedford 1999; Drexler and Bedford 2002; Drexler et al. 1999) suggested that groundwater might influence plant diversity, in particular, through effects on soil phosphorus (P) availability.

Without surface water flow across the fens, sediment-sorbed P is restricted to edge areas receiving over-land flow; P availability is regulated primarily by internal biogeochemical processes (Kellogg and Bridgham 2003; Reddy et al. 1999). In acidic wetland soils, P sorption is closely related to hydrogen ion activity, organic matter content, and subsequent effects on amorphous (non-crystalline) aluminum and iron dynamics (Axt and Walbridge 1999; Richardson 1985). In alkaline, reduced environments, co-precipitation with calcium minerals reduces P availability (Moore and Reddy 1994). Under circumneutral conditions (pH range 5.5–7.4; Sharpley 1995) typical of fens in glaciated regions of the US (Almendinger and Leete 1998b; Amon et al. 2002; Komor 1994), both mechanisms could influence P availability, but the relative importance of each mechanism remains uncertain. Elevated alkalinity (Drever 1988) and carbon dioxide (CO_2) degassing at the land surface in discharge areas (Boyer and Wheeler 1989; Komor 1994) has been observed to enhance calcium carbonate precipitation in fens (Almendinger and Leete 1998a; Futyma and Miller 2001). The frequent association of rich fen vegetation with calcium (Ca^{2+})-rich groundwater and P limitation (Bedford and Godwin 2003) further suggests that Ca–P co-precipitation may be more important to controlling P availability (Boyer and Wheeler 1989; Richardson and Marshall 1986).

Buffered redox conditions sustained by groundwater supply of terminal electron acceptors (Drever 1988; Boomer and Bedford 2008) and consequent effects on iron–sulfur reactions could play a more prominent role than pH-controls in regulating P availability across fens (Carlyle and Hill 2001; Lamers et al. 2002; Lucassen et al. 2005; Smolders et al. 2006). In particular, influx of sulfate (SO_4^{2-})-enriched water to organic-rich wetlands and subsequent reduction processes can enhance ferric iron (Fe^{3+}) reduction to soluble ferrous iron (Fe^{2+}), simultaneously releasing P (Roden and Edmonds 1997). Sulfate reduction also promotes P mobilization by inducing formation of more stable iron–sulfide minerals which do not bind P (Caraco et al. 1989; Smolders and Roelofs 1993). Further, alkalinity generated as a by-product of reduction–oxidation reactions can increase P availability by stimulating mineralization and increasing internal nutrient release rates (Brouwer et al. 1999; Curtis 1989; Lamers et al. 2001; Lucassen et al. 2004a; Roelofs 1991). This effect has been attributed to pH buffering (Lamers et al. 1998a; Smolders et al. 2003) and inhibition of P sorption onto iron oxides in sediments (Hawke et al. 1989; Moore and Reddy 1994). These processes co-occur and therefore have a strong potential to significantly influence the inorganic P pool.

Previously, we reported that sequential changes in NO_3^-, Fe^{2+}, SO_4^{2-}, and HCO_3^- concentrations indicated that meter-scaled horizontal redox gradients paralleled groundwater flowpaths (Boomer and Bedford 2008). Geochemical modeling indicated that sulfate reduction significantly influenced iron mineral chemistry. Here we sought to confirm results from these hydrologic studies and assess the importance of groundwater delivery to soil nutrient status by investigating linkages between measured soil properties and hydrochemical patterns. Specifically, we hypothesized the following spatial patterns:

1. Where groundwater discharge maintained suboxic conditions, we expected enhanced decomposition would result in organic soils with lower carbon content, increased mineral content, and increased bulk density. We use the term "suboxic" to refer to intermediate conditions along a reduction–oxidation gradient, where ferric iron and sulfate reduction processes predominate (Li et al. 2006; Murray et al. 1989).
2. Due to circumneutral conditions typical of fens in the glaciated US region, we did not expect to see strong trends between noncrystalline (amorphous) iron and aluminum and hydrochemical patterns or organic matter content. We also did not expect clay-bound P pools to contribute significantly to the soil inorganic P pool.
3. If calcium-mineral dynamics controlled P-availability by promoting co-precipitation with Ca minerals, we expected to find a higher proportion of Ca-bound inorganic P closely related to soil $CaCO_3$ and total calcium (Ca_{total}) content. Alternatively, if groundwater delivery of terminal electron acceptors, notably SO_4^{2-}, controlled P-availability by regulating iron–sulfur redox chemistry, then formation of iron–sulfide and iron–carbonate precipitates would increase Fe_{total} and S_{total} soil concentrations. The inorganic soil P pools would consist primarily of Fe-bound P.
4. P-release rates would reflect the dominant biogeochemical process regulating P availability; relatively lower rates would co-occur with Ca–P mineral co-precipitation whereas higher release rates would co-occur where redox chemistry primarily influenced soil P dynamics.

We expected to find close linkages between soil properties and ground water fluxes characterized by pore-water chemistry and water table dynamics. More specifically, we expected to see evidence that calcium or iron-mineral dynamics controlled P availability in the organic-rich soils. Although inorganic P may constitute as little as 10% of the total P in the organic-rich soil, its rapid cycling rate and response to environmental conditions makes this pool biologically important (Darke and Walbridge 2000).

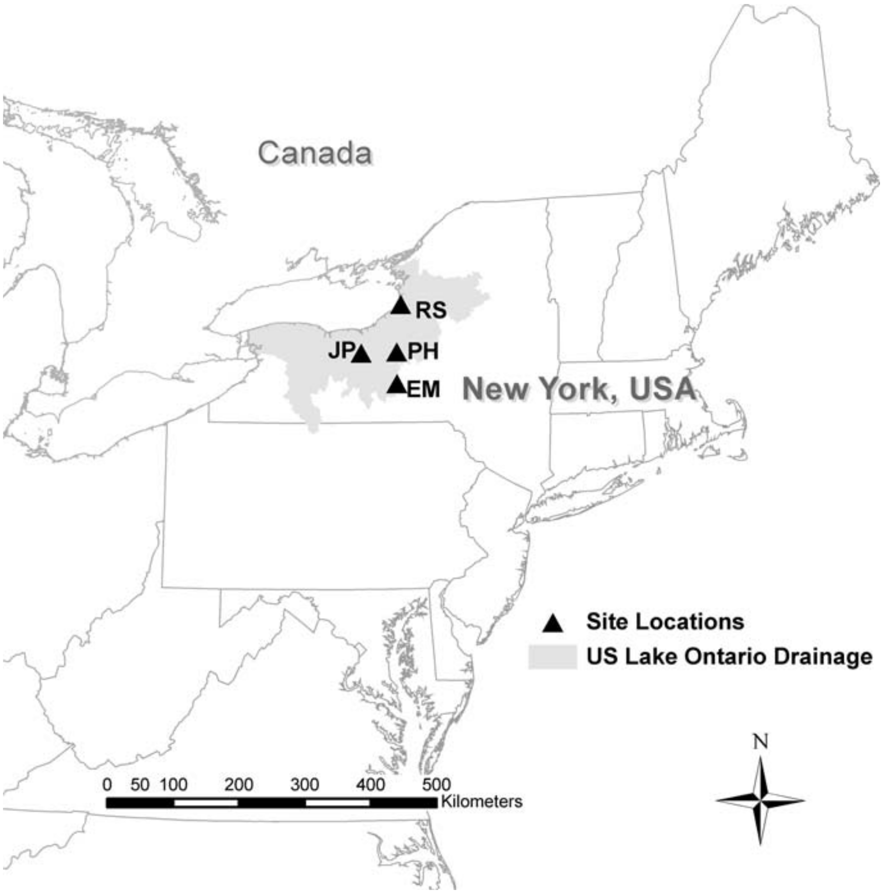
Methods

Study area descriptions

We investigated linkages between soil composition and hydrochemical gradients in four headwater wetlands within the southern Lake Ontario drainage basin in New York (Fig. 1). The study sites included two base-rich fens (East Malloryville fen (EM): 42.536°N, 76.292°W; WGS84; and Pumpkin Hollow fen (PH): 42.964°N, 76.287°W), a marl fen (Junius Pond fen (JP): 42.956°N, 76.949°W), and a mineral-poor fen (Rainbow Shores fen (RS): 43.616°N, 76.195°W). Soils in the rich fens and marl fen mainly included euic, mesic, typic medisaprists, and in the poor fen, medifibrists (U.S. Department of Agriculture 1998). Our classification of fen type was based on Reschke (1990) and vegetation surveys by Olivero (2001).

In the two rich fens and the marl fen, discharge from nested groundwater systems results in stable water table elevations that occur within 10 cm of the land surface and distinct hydrochemical gradients that extend across each site (Boomer and Bedford 2008). In the poor fen, influence by deeper groundwater is limited by a thick lacustrine clay layer (Bailey 2006). Water table fluctuations primarily respond to seasonal and short-term weather events throughout the growing season and range over 50 cm from the land surface. Shallow groundwater inflow from the edge and aeration of the shallow peat soil predominantly influence spatial patterns across the site. Because of the strong hydrochemical gradients observed in the base-rich sites, sampling points were set approximately every 10 m. In the poor fen, sampling locations were set approximately every

Fig. 1 Location of the four New York fen study sites: East Malloryville rich fen (EM), Pumpkin Hollow rich shrub fen (PH), Junius Pond marl fen (JP) and Rainbow Shores poor fen (RS)



20 m. Site features and sampling information are summarized in Table 1.

Groundwater collection

Shallow pore-water chemistry was characterized by sampling PVC lysimeters, installed 5–20 cm below the land surface near existing sampling locations. Water samples were also collected from nested observation wells ranging 0.5–3.0 m in depth. Additional information describing the hydrologic monitoring, water sample collection and analytical procedures are described in Bailey (2006). Briefly, one-day sampling events were conducted within 24 h of purging observation wells at each site during the 2002 growing season. Samples were stored on ice and filtered by vacuum pressure using 47 mm 0.45 µm millipore membrane filters within 24 h of collection. Bicarbonate alkalinity was determined on filtered samples as mg $CaCO_3$ based on titration to pH 4.5 (AWWA Method 2320B) (American Water Works Association (AWWA) 1998). A sub-sample of filtered water was acidified with nitric acid to $pH < 2$ and analyzed for total dissolved Ca^{2+} and Fe^{2+} by mass spectroscopy (US-EPA Method 3020) (U.S. Environmental Protection Agency 1998); all measured iron was assumed to be in its soluble, reduced form. Nitrate (NO_3^-) and SO_4^{2-} were analyzed using a Dionex 4000 ion chromatograph (AWWA Method 4110B) (1998).

Soil sample collection

During August 2002, six soil cores were collected adjacent to each lysimeter from a depth of 5–20 cm below the land surface (i.e., below the zone affected by atmospheric oxygen diffusion and corresponding to the lysimeter depths). The cores were collected with minimal disturbance to the substrate using a PVC cylinder with a cutting edge. After cutting through the surface root mat with a stainless steel bread knife, the corer was driven to the desired depth,

Table 1 Study site features

Site	Fen type[a]	Dominant plant species	Relief (m)	Water table gradient (m/m)	Transect length (m)	Number of sampling points
East Malloryville fen (EM)	Rich, graminoid	*Cornus sericea*, *Dasiphora floribunda*, *Carex prairea*, *C. flava*, *C. stricta*, *C. aquatilis*, *Campylium stellatum*, *Climacium dendroides*, *Plagiothecium laetum*	1.5	0.03	75	7
Pumpkin Hollow fen (PH)	Rich, shrub	*Thuja occidentalis*, *Alnus incana*, *Cornus sericea*, *Dasiphora floribunda*, *Carex prairea*, *C. flava*, *C. stricta*, *C. aquatilis*, *Campylium stellatum*, *Climacium dendroides*, *Plagiothecium laetum*	1.5	0.01	85	10
Junius Pond fen (JP)	Rich, shrub/marl	*Apios Americana*, *Lindera benzoin*, *Toxicodendron vernix*, *Dasiphora floribunda*, *Eleocharis rostellata*, *Campylium stellatum*	0.8	0.005	130	11
Rainbow Shores fen (RS)	Inland poor	*Alnus incana*, *Acer rubrum*, *Chamaedaphne calyculata*, *Photinia malanocarpa*, *Vaccinium oxycoccos*, *Woodwardia virginica*, *Sphagnum* spp.	0.25	0.01	105	5

[a] Reschke (1990), Olivero (2001)

capped to create suction, and pulled from the ground. Samples were sealed in airtight plastic bags and returned to the laboratory on ice.

Soil analyses

Three intact cores were dried at 105°C to a constant weight to estimate dry bulk density (Elliott et al. 1999). Dried samples were homogenized for additional soil analyses by grinding with a mortar and pestle and passing the soil through a 2 mm sieve to exclude roots. Organic matter content was estimated by mass loss-on-ignition after combustion in a muffle furnace at 520°C for 2 h (Carter 1993) assuming that the relatively low temperature oxidized only organic carbon (Bisutti et al. 2004). Total elemental content was determined by hydrofluoric digestion and subsequent analysis by inductively-coupled plasma atomic emission spectrometry (US-EPA Method 3052) (U.S. Environmental Protection Agency 1996).

Non-crystalline or amorphous Al and Fe were determined by extraction with 0.2 M acid ammonium oxalate (pH 3) (Axt and Walbridge 1999; Darke and Walbridge 2000). Five grams of sample and 25 ml of extractant were shaken for 4 h in darkness. Supernatants were analyzed for Al and Fe using a Perkin-Elmer atomic absorption spectrometer. Soil carbonate content was determined gravimetrically after acidifying with 3 M hydrochloric acid (Loeppert and Suarez 1996).

The remaining three wet samples were combined to estimate inorganic P pools using a modified sequential fractionation scheme (Paludan and Jensen 1995). Within 24 h of sample collection, the composite sample was passed through a 2-mm mesh sieve under a N_2 atmosphere. A 5–10 g sub-sample was collected in an airtight container for mass measurement and subsequently returned to the glove box for the first two of the four extractions outlined here: (1) water-soluble, available P was extracted from the pre-weighed soil samples using two sequential treatments of 50 ml deionized and deoxygenated water, shaken for 1 h. After the second treatment, the samples were centrifuged (20 min; 1,200 rpm) and filtered (Gelman C membrane filters). Extracts were combined and acidified with 1.2 ml 1 M H_2SO_4 (added to prevent phosphate precipitation with Fe and Mn) before storing at 4°C for later analysis. (2) To estimate labile P associated with oxidized Fe and Mn, soil pellets remaining from the water-soluble P extractions were extracted with 50 ml of bicarbonate-buffered dithionite (BD) solution (0.11 M $NaHCO_3$ and 0.11 M $Na_2S_2O_4$) and shaken for 1 h. Soil residues were rinsed by shaking with 50 ml deionized and degassed water. The BD and water extracts were combined, centrifuged, and filtered, then acidified with 5.6 ml 1 M H_2SO_4. (3) Non-labile P associated with aluminum oxides or clay and organic matter was extracted with 50 ml of 0.1 M sodium hydroxide (0.1 M NaOH) and a subsequent rinse with 50 ml degassed and deionized water. Combined supernatants were centrifuged and filtered, then stored for 1 month to allow sulfur precipitation to occur prior to analysis. (4) Recalcitrant P associated with Ca minerals was extracted and rinsed from the sample pellets with hydrochloric acid (50 ml 1 M HCl) and 50 ml degassed and deionized water, shaken for 1 h. Combined supernatants were centrifuged and filtered. Extracts were analyzed for total P using the phenate method (Murphy and Riley 1962) on an Orion Instruments autoanalyzer.

Because of the difficulty in measuring available P, we also used a standard dry extraction technique to estimate labile P. Twelve to fourteen grams of sample were extracted with 50 ml of 0.5 M $NaHCO_3$ (pH 8.5) and shaken for 20 min at 120 rpm (Carter 1993). Resulting supernatants were analyzed similarly to the wet soil extracts. Aerobic conditions which develop with drying can induce the transformation of "available" P to insoluble Fe^{3+} phosphate and lead to underestimating labile P.

P release rates

A set of three nylon-mesh bags filled with anion-exchangeable resin was deployed at each sampling location to estimate P release rates during the growing season (Lajtha 1988). Each bag contained 10 g of wet anion resin (Dowex 1-X8) activated prior to deployment by soaking in 0.5 M $NaHCO_3$. The bags were removed after 3 months (early June through mid-September 2002), dried, and consolidated. All in-grown roots were removed prior to extraction. Cumulative available phosphate was measured by rinsing the resin with 0.5 M HCl for 1 h. Extracts were analyzed using the phenate method on an Orion Instruments auto-analyzer.

Data analysis

Linkages between soil characteristics and P-availability were based on Pearson correlation coefficients. Patterns in soil composition were similarly related to site characteristics including peat depth, water table fluctuation, and pore water chemistry.

Results

Soil composition

Organic-rich peat soils occurred at all sites; however the C-content varied widely along the sampling transects set at the two rich fen and marl fen study sites. In the two rich fens (EM and PH), organic matter content (%LOI) ranged from 15% near the upland–wetland interface to 75% in interior, hydrologically down-gradient areas (Fig. 2). In the marl fen (JP), organic matter increased from the upland–wetland edge to 66% LOI, but then decreased to <30% LOI in the open marl area. In the poor fen (RS), organic matter content was greater (85–95% LOI) than the other three sites and more similar among its sampling points. Among all sites, organic matter content was closely related to soil C-content ($r = 0.96$; $P < 0.001$; Table 2; Fig. 2a) and inversely related to bulk density ($r = -0.83$; $P < 0.001$). Water table fluctuations did not explain the variation in organic matter content ($r = 0.16$; $P = 0.39$; Fig. 2b); instead it related more closely with total peat depth (Pearson $r = 0.73$; $P < 0.001$; Fig. 2c). This was especially evident at PH where undulations in the peat depth along the sample transect corresponded with changes in organic matter content; LOI estimates increased from 17% near the upland–wetland interface to 76% in the interior areas (PH8: 76%), but decreased at intermediate locations with more shallow peat depths (e.g., PH5, peat depth: 0.5 m; 27% LOI). At the marl fen (JP), organic matter content increased from the wetland edge (JP1 22% LOI) to the interior (JP5 66% LOI) but decreased in the down-gradient, open fen area, where carbonate precipitates contributed significantly to the soil composition (JP6–JP11: 16–40% LOI).

Elemental content generally increased with proximity to the wetland–upland interface or shallow peat depths. Soil Al_{total} and Fe_{total} were closely related to organic matter or C-content (Fig. 3a, b, respectively). Elevated calcium and sulfur concentrations, however, correlated significantly with lower water table fluctuation ranges (Ca_{total}: $r = -0.37$; $P = 0.05$; S_{total}: $r = -0.49$; $P = 0.005$; see Table 2). Although there

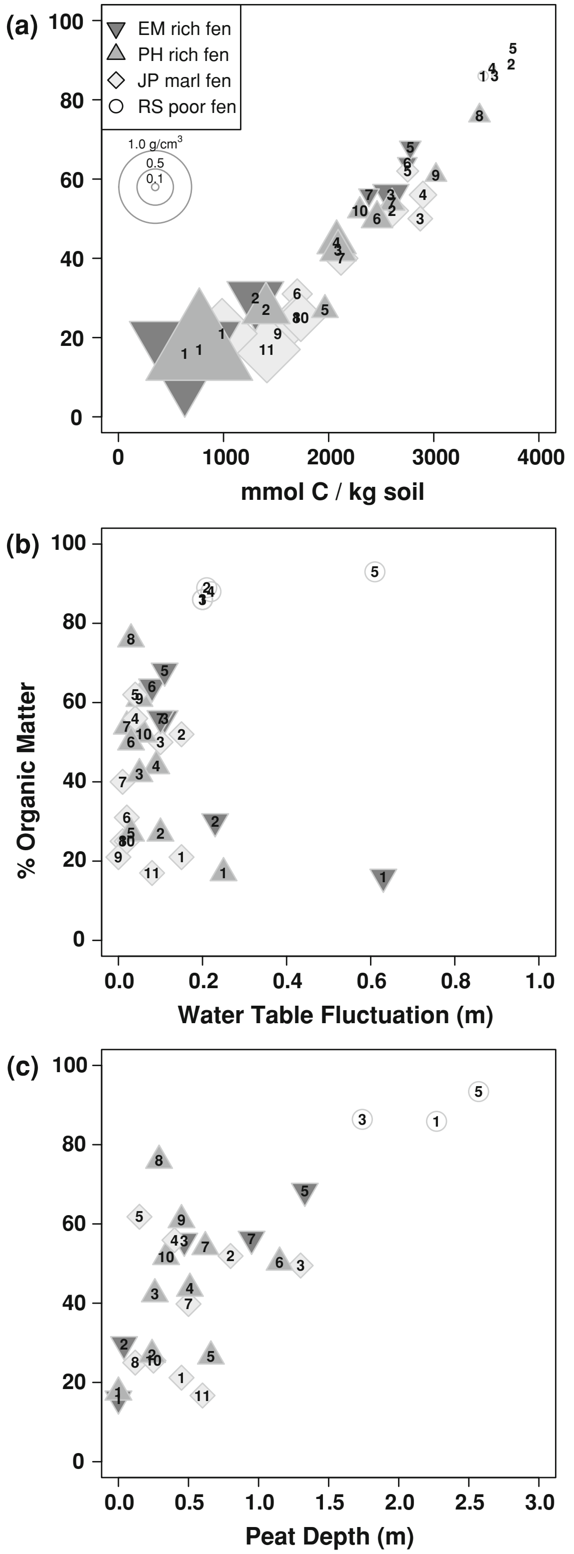


Fig. 2 Shallow soil (5–20 cm depth) organic matter content in ▶ relation to **a** soil carbon (C) content and bulk density, which is indicated by *size of the symbol*. The barely visible symbols in the upper right corner of the figure are RS samples with bulk densities <0.1 g/cm^3. **b** water table fluctuation; and **c** peat depth. *Numbers* indicate position along the hydrologic gradient with one furthest up-gradient and nearest the upland–wetland interface. Sites include East Malloryville rich fen (EM), Pumpkin Hollow rich shrub fen (PH), Junius Pond marl fen (JP), and Rainbow Shores poor fen (RS)

was no correlation between C-content and Ca_{total} ($r = -0.03$; $P = 0.39$) or S_{total} ($r = 0.23$; $P = 0.16$), positive trends were evident if the poor fen data were excluded (Fig. 3c, d, respectively). In the poor fen (RS), total elemental content was much lower and concentrations consistently decreased as C and %OM content increased along the sample transect. Estimates of soil S_{total}, content were comparable to other sites, but the highest measurements occurred at the up-gradient locations (i.e., RS1 and RS2). Among all sites, elemental P_{total} ranged between 5 and 45 mmol/kg soil and was closely correlated with soil Fe_{total} ($r = 0.52$; $P = 0.002$), Al_{total} ($r = 0.72$; $P < 0.001$), and Ca_{total} ($r = -0.70$; $P < 0.001$). The latter negative correlation was imposed by the elevated Ca_{total} and low P_{total} concentrations (5–7 mmol P/kg soil) observed in the marl fen (JP) where secondary precipitates of calcium carbonate contributed significantly to the soil composition. In the poor fen, total soil P was similar among all sample locations, ranging from 17 to 21 mmol P/kg soil. There was a weak, but non-significant trend suggesting that more permanently saturated organic soils had relatively higher soil P_{total} ($r = -0.23$; $P = 0.20$).

Amorphous (non-crystalline) aluminum (Al_{ox}) and iron (Fe_{ox}) contributed <1% of the soil composition and did not relate to soil organic matter content (Pearson $r = -0.26$; $P = 0.15$), but measures were closely related to total soil aluminum and iron (see Table 2). Slight increases in Fe_{ox} occurred near the wetland edge and at interior locations under sub-oxic conditions (i.e., where dissolved iron concentrations increased and SO_4^{2-} concentrations decreased). Variation in Al_{ox} and Fe_{ox} was most evident in the marl fen (JP; see Fig. 4c); in the up-gradient area where organic-rich soils occurred, Fe_{ox} and Al_{ox} contents were similar to measures at EM and PH (Al_{ox} range 0–0.02%; Fe_{ox} range 0.05–2%). In the

Table 2 Correlation coefficients of site physical characteristics, soil chemistry, and pore water chemistry with $P \leq 0.05$

	Peat depth	WT depth	WT range	% OM	BDensity	Soil C_{total}	Soil Al_{total}	Soil Fe_{total}	Soil Ca_{total}	Soil S_{total}	Soil P_{total}	% Soil Al_{ox}	% Soil Fe_{ox}	% $CaCO_3$	% H_2O P_{ext}	% BD P_{ext}	% NaOH P_{ext}	% HCl P_{ext}	% HCO_3^- P_{ext}	Aqueous Fe^{2+}	Aqueous SO_4^{2-}	Aqueous HCO_3^-
Peat depth (m)																						
Water table (WT) depth (m)	*																					
Water table (WT) fluctuation range (m)	*	*																				
% Organic matter (OM)	0.73	*	*																			
Bulk density (BD) (g/cm^3)	−0.59	*	*	−0.83																		
Soil C_{total} (mmol/kg)	0.69	*	*	0.96	−0.90																	
Soil Al_{total} (mmol/kg)	−0.45	*	*	−0.54	0.53	−0.62																
Soil Fe_{total} (mmol/kg)	−0.42	*	*	−0.48	0.61	−0.56	0.81															
Soil Ca_{total} (mmol/kg)	*	*	−0.37	*	*	*	−0.49	−0.36														
Soil S_{total} (mmol/kg)	*	*	−0.49	*	−0.40	*	−0.40	−0.40	*													
Soil P_{total} (mmol/kg)	*	*	*	*	*	*	0.72	0.52	−0.70	*												
% Amorphous Al (Al_{ox})	*	*	*	*	*	*	0.66	0.64	*	*	0.50											
% Amorphous Fe (Fe_{ox})	−0.41	*	*	*	*	*	0.39	0.63	*	*	*	0.50										
% Calcium carbonate ($CaCO_3$)	*	*	*	−0.46	*	*	*	*	0.41	*	*	−0.55	*									
% H_2O extractable P (H_2O P_{ext})	*	*	*	0.44	−0.39	0.41	*	*	*	*	*	*	*	*								
% BD extractable P (BD P_{ext})	*	*	*	0.36	−0.35	*	*	*	*	*	*	*	*	*	0.83							
% NaOH extractable P (NaOH P_{ext})	*	*	*	*	*	*	*	*	*	*	*	*	*	−0.54	0.63	0.75						
% HCl extractable P (HCl P_{ext})	*	*	*	*	0.38	−0.39	*	0.49	*	*	*	0.43	0.69	*	*	*	*					
% HCO_3 extractable P (HCO3 P_{ext})	0.82	*	*	0.89	−0.72	0.86	−0.53	−0.47	*	*	*	*	−0.37	−0.36	0.38	*	*	*				
Aqueous Fe^{2+} (mmol/l)	0.62	*	*	0.65	−0.50	0.61	−0.56	−0.44	*	*	−0.38	*	*	*	*	*	*	*	0.74			
Aqueous SO_4^{2-} (mmol/l)	*	*	*	*	0.35	−0.38	*	0.38	*	*	*	*	*	*	*	*	*	*	*	−0.39		
Aqueous HCO_3^- (mmol/l)	−0.78	*	−0.50	−0.71	0.43	−0.65	0.50	0.38	*	*	*	*	*	0.37	*	*	*	*	−0.74	−0.60	*	
Aqueous Ca^{2+} (mmol/l)	−0.78	*	−0.42	−0.74	0.51	−0.71	0.60	0.50	*	*	0.42	0.38	*	*	*	*	*	*	−0.78	−0.61	*	0.98

An asterisk indicates non-siginificant correlation down-gradient, open fen area where marl deposits significantly contributed to the soil matrix, Al_{ox} and Fe_{ox} decreased to near detection limits and were more similar to measures in the poor fen (<0.01% Al_{ox} and 0–0.05% Fe_{ox}). Soil $CaCO_3$ content contributed <2% of the soil composition in the peat soils with greater than 50% LOI (Fig. 4a–d). Only in the marl fen did $CaCO_3$ content increase to 25% (see Fig. 4c).

Inorganic soil P pools varied with hydrochemical gradients across each site. At the two rich fens and the marl fen, inorganic soil P pools constituted a larger proportion of the total soil P content near the upland–wetland interface, but also at locations under sub-oxic conditions (e.g., EM5–6, PH9, JP4–JP8; Fig. 5a–c). Water-extractable ("available") P pools accounted for <3% of the inorganic soil P content of all soil samples, and concentrations were too low to distinguish trends among sampling locations or sites (range 0.00–0.25 mmol H_2O_{ext}-P/kg soil). Instead, variation in BD_{ext}-P ("Fe-bound P") pool, ranging from 2 to 25%, largely accounted for changes in the soil inorganic P content. In the rich fens (EM and PH), BD_{ext}-P increased to as much as 8 mmol BD_{ext}-P/kg soil in sub-oxic zones of each rich fen site (Fig. 5a, b). In the marl fen (JP), BD_{ext}-P contributed to relatively smaller soil inorganic P pools than organic soil samples collected either from up-gradient locations or from other sites (Fig. 5c). In the poor fen, where the highest total dissolved Fe^{2+} concentrations were observed, BD_{ext}-P ranged from 0.7 to 1.1 BD_{ext}-P/kg soil, accounting for more than 80% of the inorganic soil P pool but only 3–6% of the total soil P pool (Fig. 5d). Across all sites, variation in the clay-bound P ($NaOH_{ext}$-P) was consistent with that of the BD_{ext}-P pool, though generally much smaller, accounting for 10–20% of the soil inorganic P pool and <5% of the total soil P pool. Ca-bound P pools, as determined from 1 M HCl extraction of wet soil samples, were similarly low among all samples including those from the poor fen (range 0.01–4 mmol HCl_{ext}-P/kg soil) except where $CaCO_3$ precipitates visibly formed in the marl fen (JP); at these sampling locations, HCl_{ext}-P accounted for as much as 30% of the inorganic soil P pool and 10% of the soil total P pool.

P release rates

The anion resin bag incubation indicated that the highest soil P release rates consistently occurred near the upland–wetland edge (range 1.9–2.9 μg/bag/day). In interior areas of the rich fens and marl fen under sub-oxic conditions, P release rates also increased to more than 2 μg/bag/day (e.g., EM5, PH6–PH9, and JP5). Lower release rates (range 0.0–0.9 μg/bag/day) were estimated for areas in-between the upland–wetland interface and sub-oxic zones. In the marl fen (JP); release rates in the up-gradient, organic-rich locations ranged between 1.8 and 2.9 μg/bag/day but decreased to <0.1 μg/bag/day where $\%CaCO_3$ increased substantially. Phosphorus release rates in the poor fen (RS) decreased along the sample transect from 1.9 to <0.7 μg/bag/day.

Assessment of soil and pore-water effects on P-availability

Soil C_{total} and P_{total} contents were closely related to pore-water alkalinity (Fig. 6a, b, respectively). Excluding sampling locations where marl formation predominantly influenced soil composition and Ca_{total} exceeded 7 mmol Ca/kg soil, soil P content increased with alkalinity ($r = 0.77$; $P < 0.001$) and decreased with dissolved iron concentrations ($r = 0.74$; $P < 0.001$). Labile ($NaHCO_3$ extractable) P was strongly correlated with dissolved iron ($r = 0.74$; $P < 0.001$) and negatively correlated with alkalinity ($r = -0.74$; $P < 0.001$) and Ca^{2+} ($r = -0.78$; $P < 0.001$) concentrations. Water-extractable P measures followed similar but non-significant trends.

Discussion

Our results highlight the importance of advective groundwater flow to regulating biogeochemical processes which influence the development of organic-rich soils in headwater wetlands. The close correlation between soil composition, P-availability, and pore water chemistry along hydrologic gradients indicated that significant, non-random variation in soil properties occurred in response to the groundwater influence and suggested the importance of microbially-mediated biogeochemical reactions to controlling soil nutrient status. Previous hydrologic studies showed that stable water table elevations are sustained by discharge from multiple groundwater systems (Almendinger and Leete 1998b; Boomer and Bedford 2008). Equally important, we found that

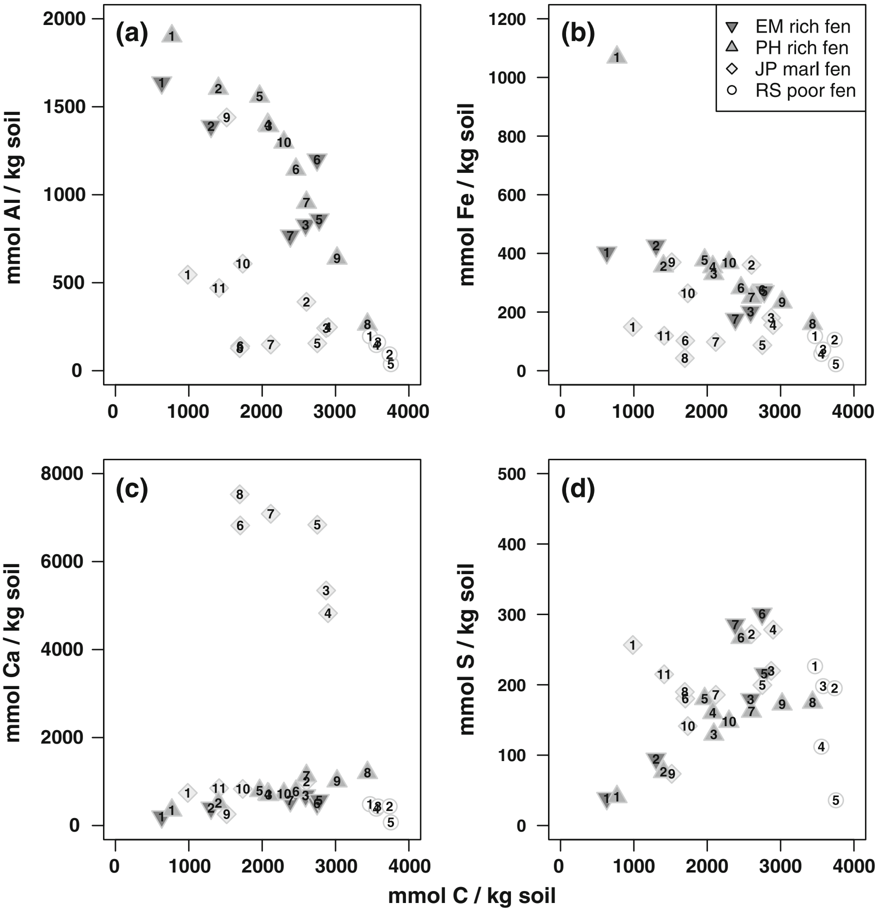


Fig. 3 Total elemental content of shallow (5–20 cm depth) soil samples, including **a** aluminum (Al), **b** iron (Fe), **c** calcium (Ca), and **d** sulfur (S), in relation to soil carbon (C) content. *Numbers* indicate position along the hydrologic gradient with one furthest up-gradient and nearest the upland–wetland interface. Sites include East Malloryville rich fen (EM), Pumpkin Hollow rich shrub fen (PH), Junius Pond marl fen (JP), and Rainbow Shores poor fen (RS)

groundwater delivery of terminal electron acceptors, including NO_3^- and especially SO_4^{2-}, can induce distinct hydrochemical gradients extending across a wetland complex, on a scale of tens of meters (Boomer and Bedford 2008; Christensen et al. 2000). In intensely managed wetlands throughout Europe, where the water budget has been altered significantly, such external supply of terminal electron acceptors has induced eutrophication (Smolders et al. 2006) and altered plant species composition (Lucassen et al. 2006). Results from our study suggest similar mechanisms could play a significant role in regulating P-availability and soil composition, perhaps contributing to the unique diversity of plant species often observed in these relatively pristine wetlands (Bedford and Godwin 2003; Gusewell et al. 2005).

Higher decomposition rates, as evidenced by reduced organic matter content and higher bulk densities, were observed in the peat soils where the water table remained at the land surface. The lack of surface water overflow limited the potential for erosion of organic material. Results were consistent with earlier comparisons of decomposition rates based on loss of tensile strength in cotton strips (K.B. Boomer and B.L. Bedford , unpublished data) and corroborated by others who have shown the importance of water quality to regulating decomposition processes (e.g., Brinson et al. 1981; Moore et al. 2007). Although increased decomposition and mineralization rates are often linked with fluctuating water table elevations (Devito and Dillon 1993; Haraguchi et al. 2003), groundwater supply of terminal electron acceptors under saturated conditions can sustain heterotrophic respiration and also enhance decomposition in carbon-rich environments (D'Angelo and Reddy 1999), effectively concentrating recalcitrant organic matter, minerals, and metals (Lucassen et al. 2004a; Todorova et al. 2005). Our results further suggested the importance of sub-oxic conditions, maintained by groundwater delivery of sulfate, to

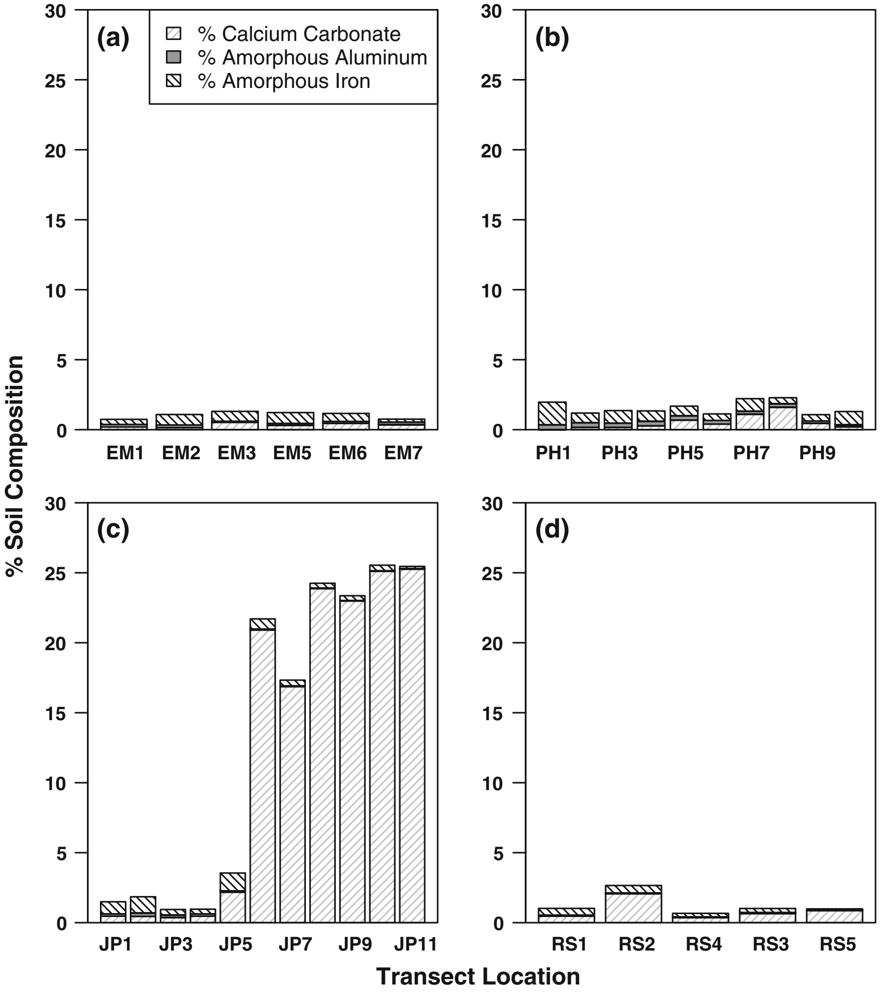


Fig. 4 Calcium carbonate ($CaCO_3$) and non-crystalline iron (Fe_{ox}) and aluminum (Al_{ox}) contents in shallow (5–20 cm depth) soils along hydrologic gradients in four New York fens. Transect location refers to position along groundwater flowpath. Sites include **a** East Malloryville rich fen (EM), **b** Pumpkin Hollow shrub fen (PH), **c** Junius Pond marl fen (JP), and **d** Rainbow Shores poor fen (RS)

regulating intra- and inter-site variation in decomposition rates and organic matter accumulation.

Counter to expectations, we did not find strong evidence to suggest that Ca–P dynamics control P availability across the rich fens (Bedford and Godwin 2003; Boyer and Wheeler 1989). With the exception of the marl fen, calcium carbonate did not contribute substantially to soil composition in any of the sites; estimates from the rich fen soils were comparably low to those from the poor fen. These results reinforced previous geochemical analyses of the shallow porewater, which indicated net dissolution of Ca-carbonate minerals due to elevated CO_2 concentrations (Boomer and Bedford 2008). Further, HCl_{ext}-P decreased with Ca-mineral content, rather than increased as expected. A slight increase in HCl_{ext}-P occurred only in the marl fen where $CaCO_3$ content exceeded 20%; however, the soil P_{total} content in the marl fen was extremely low, indicating no long-term storage in the soil matrix. Although some studies have suggested the importance of Ca–P reactions to regulating nutrient availability (Boyer and Wheeler 1989; Futyma and Miller 2001; Komor 1994) and plant species distributions in fens (Bedford and Godwin 2003), our results are consistent with other studies suggesting alternative mechanisms play a more critical role in regulating P dynamics under conditions of circumneutral pH and low P-availability. Specific processes include plant and microbial uptake, sorption to iron oxides, clays and organic matter, and precipitation with more reactive minerals (House 2003). Plant production of tannic acids and polyphenols also inhibits calcite growth (Hoch et al. 2000) while biological production of CO_2 accelerates

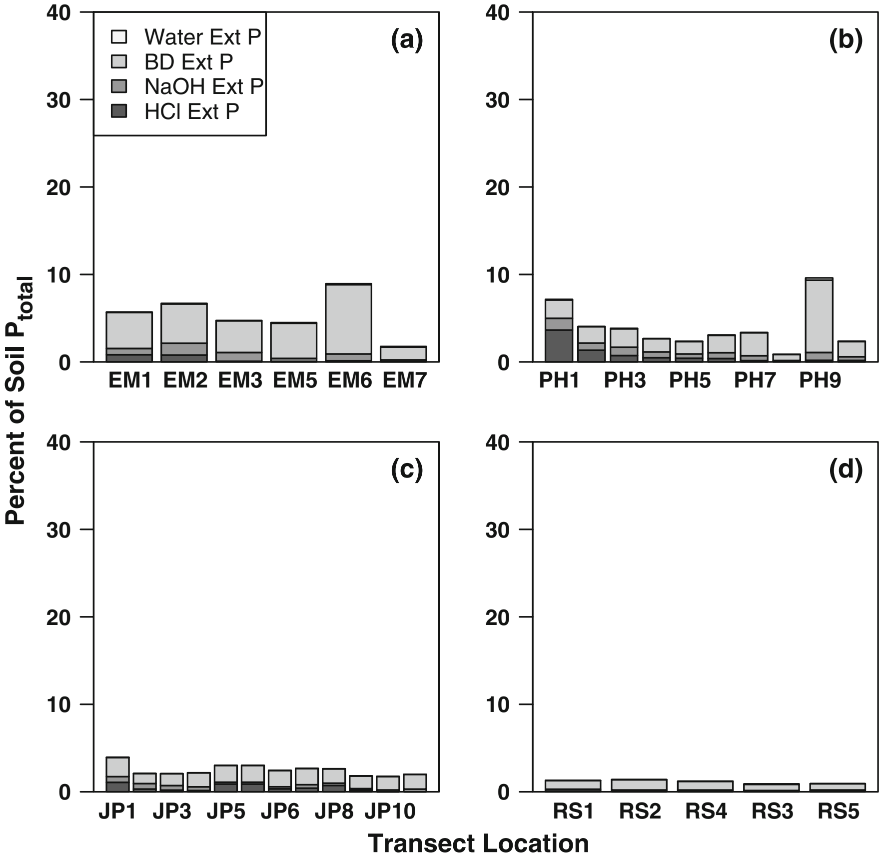


Fig. 5 Variation in shallow (5–20 cm depth) soil inorganic phosphorus pools along hydrologic gradients in four New York fens. Transect location refers to position along groundwater flowpath. Sites include **a** East Malloryville rich fen (EM), **b** Pumpkin Hollow rich shrub fen (PH), **c** Junius Pond marl fen (JP), and **d** Rainbow Shores poor fen (RS)

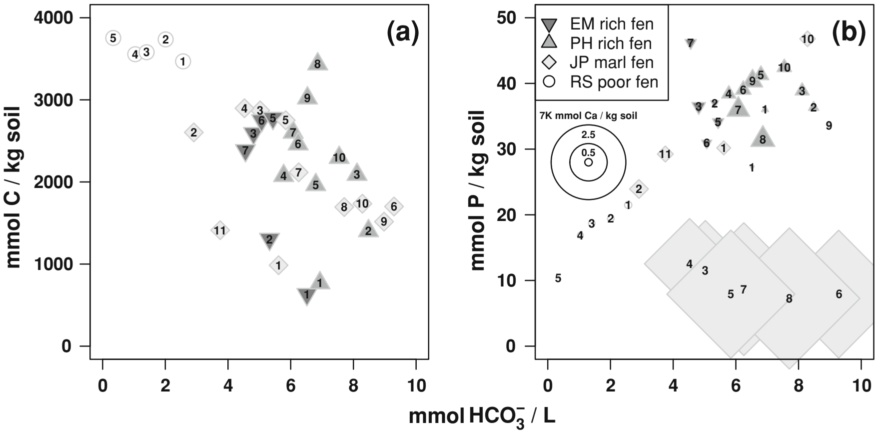


Fig. 6 **a** Soil carbon content and **b** soil phosphorus and calcium content in relation to pore water alkalinity from samples collected at 5–20 cm depth. Calcium concentration is indicated by *symbol size*. *Numbers* indicate position along the hydrologic gradient with one furthest up-gradient and nearest the upland–wetland interface. Sites include East Malloryville rich fen (EM), Pumpkin Hollow rich shrub fen (PH), Junius Pond marl fen (JP), and Rainbow Shores poor fen (RS)

$CaCO_3$ dissolution (DePinto et al. 1989). Because these processes are thermodynamically more favorable than formation of calcium carbonate precipitates, these processes will predominate even when pore water is supersaturated with respect to calcite minerals (Golterman 1988; Wilson and Fitter 1984).

Consistent with previous studies of organic-rich riparian wetland soils (Carlyle and Hill 2001), we found that redox conditions and the associated Fe–S reactions most strongly influenced internal P dynamics. Phosphorus availability increased with total soil S, Fe, and P at sampling locations under sub-oxic conditions. The exact mechanism to explain these patterns, however, remains less certain. It is widely known that SO_4^{2-} reduction enhances iron mineral dissolution and consequently releases P (Caraco et al. 1989; Roden and Edmonds 1997; Smolders and Roelofs 1993), but other processes secondary to iron and sulfur redox reactions also can increase P mobilization (Gachter and Muller 2003). In particular, alkalinity generation enhances internal eutrophication by neutralizing acidity generated by microbial respiration (Lamers et al. 1998a; Smolders et al. 2003) and facilitating microbial mineralization (Lamers et al. 2001; Lucassen et al. 2004a; Roelofs 1991; Smolders et al. 1995), as well as by inhibiting P sorption onto iron oxides in sediments (Hawke et al. 1989). Reduced conditions also can increase available P due to microbial release of polyphosphates (Khoshmanesh et al. 1999). These biogeochemical processes likely occur simultaneously and together explain the elevated P-availability observed under sub-oxic conditions.

Despite that hydrology is recognized as a primary control of wetland function, it has been difficult to associate P-availability with hydrologic or pH gradients (Kellogg and Bridgham 2003). Water-table drawdown and subsequent iron oxidation clearly promote P sequestration (Mitsch and Gosselink 2000; Van Duren and Pegtel 2000), but identifying controls on horizontal gradients and spatial heterogeneity of P pools, more pertinent to characterizing wetland function, has remained difficult (e.g., Axt and Walbridge 1999). We found that P dynamics depend on the composition of incoming water sources and resulting hydrochemical gradients, which are not captured when comparing soil processes along a water-table gradient (i.e., in one dimension). Patterns in soil chemistry were identifiable only by relating soil properties to horizontal and vertical groundwater flow patterns. Our results explain why soil redox status, base status, and total P content relate strongly to P mineralization (Verhoeven et al. 1996) and are consistent with observations in highly managed wetlands, where eutrophication status changed in response to alterations of the groundwater-regime (e.g., Lucassen et al. 2004a, b).

We focused our work in fens partially because the constant hydroperiod minimized confounding effects on soil mineralization and P-cycling by water table fluctuations (Corstanje and Reddy 2004). The impacts of hydrochemical gradients on biogeochemical processes and soil development that we observed, however, are likely true to some extent in all wetland systems. Distinct horizontal gradients in pore-water chemistry with distance from a water source or in relation to multi-source mixing zones have been observed in riparian buffers (Duval and Hill 2007; Hill et al. 2000; Vidon and Hill 2004), coastal wetlands (Bailey and Bedford 2003; Williams et al. 2008), and expansive northern peatlands (Bubier 1995; Glaser et al. 1997). Results from all of these studies emphasize the importance of explicitly relating plot-scaled biogeochemistry studies to local hydrologic settings.

Groundwater-induced redox gradients could play a key role in driving the exceptional species diversity observed in plant-nutrient limited, base-rich fens (Bedford et al. 1999) by enhancing P-availability (Gusewell et al. 2005) and creating spatial heterogeneity of the plant environment (Boeye et al. 1994). In addition, redox generated alkalinity could promote species diversity by buffering pH changes (Lamers et al. 1998b; Smolders et al. 2003) or by inhibiting P-sorption onto iron oxides (Hawke et al. 1989; Moore and Reddy 1994). In fact, we have observed that species richness increased with alkalinity in NY fens (B.L. Bedford and K.M. Bailey, unpublished data) and that sites with the highest species diversity occurred at sites with HCO_3^- concentrations exceeding background concentrations observed in deep (sub-peat) observation wells, suggesting additional alkalinization from redox processes (Lamers et al. 1998a; Lucassen et al. 2004a). Our results provided additional evidence of the importance of redox processes in regulating the plant environment (Lucassen et al. 2000, 2006; Smolders et al. 2003, 2006). Alterations to the water budget, due to climate change or watershed development could significantly impact headwater wetlands by affecting local versus regional groundwater supplies and subsequently altering biogeochemical processes, nutrient availability, and plant species composition.

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References

Almendinger JE, Leete JH (1998a) Peat characteristics and groundwater geochemistry of calcareous fens in the Minnesota River Basin, USA. Biogeochemistry 43:17–41. doi:10.1023/A:1005905431071

Almendinger JE, Leete JH (1998b) Regional and local hydrogeology of calcareous fens in the Minnesota River Basin, USA. Wetlands 18:184–202

American Water Works Association (AWWA) (1998) Standard methods for the examination of water and wastewater. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC

Amon JP, Thompson CA, Carpenter QJ, Miner J (2002) Temperate zone fens of the glaciated midwestern USA. Wetlands 22:301–317. doi:10.1672/0277-5212(2002)022[0301:TZFOTG]2.0.CO;2

Axt JR, Walbridge MR (1999) Phosphate removal capacity of palustrine forested wetlands and adjacent uplands in Virginia. Soil Sci Soc Am J 63:1019–1031

Bailey K (2006) Effects of ground-water flow on soil chemistry, nutrient availability and plant species distributions in four New York State fens. Ph.D. Dissertation. Cornell University, Ithaca

Bailey KM, Bedford BL (2003) Transient geomorphic control of water table and hydraulic head reversals in a coastal freshwater peatland. Wetlands 23:969–978. doi:10.1672/0277-5212(2003)023[0969:TGCOWT]2.0.CO;2

Bedford BL (1999) Cumulative effects on wetland landscapes: links to wetland restoration in the United States and Southern Canada. Wetlands 19:775–788

Bedford BL, Godwin KS (2003) Fens of the United States: distribution, characteristics, and scientific connection versus legal isolation. Wetlands 23:608–629. doi:10.1672/0277-5212(2003)023[0608:FOTUSD]2.0.CO;2

Bedford BL, Walbridge MR, Aldous A (1999) Patterns in nutrient availability and plant diversity of temperate North American wetlands. Ecology 80:2151–2169

Bisutti I, Hilke I, Raessler M (2004) Determination of total organic carbon—an overview of current methods. Trends Analyt Chem 23:716–726. doi:10.1016/j.trac.2004.09.003

Boeye D, Clement L, Verheyen RF (1994) Hydrochemical variation in a ground-water discharge fen. Wetlands 14:122–133

Boomer KB, Bedford BL (2008) Influence of nested groundwater systems on reduction–oxidation and alkalinity gradients with implications for plant nutrient availability in four New York fens. J Hydrol (Amsterdam) 351:107–125. doi:10.1016/j.jhydrol.2007.12.003

Boyer MLH, Wheeler BD (1989) Vegetation patterns in spring-fed calcareous fens: calcite precipitation and constraints on fertility. J Ecol 77:597–609. doi:10.2307/2260772

Brinson MM, Lugo AE, Brown S (1981) Primary productivity, decomposition and consumer activity in fresh-water wetlands. Annu Rev Ecol Syst 12:123–161. doi:10.1146/annurev.es.12.110181.001011

Brouwer E, Soontiens J, Bobbink R, Roelofs JGM (1999) Sulphate and bicarbonate as key factors in sediment degradation and restoration of Lake Banen. Aquat Conserv: Mar Freshwat Ecosyst 9:121–132. doi:10.1002/(SICI)1099-0755(199901/02)9:1<121::AID-AQC322>3.0.CO;2-W

Bubier JL (1995) The relationship of vegetation to methane emission and hydrochemical gradients in northern peatlands. J Ecol 83:403–420. doi:10.2307/2261594

Caraco NF, Cole JJ, Likens GE (1989) Evidence for sulphate-controlled phosphorus release from sediments of aquatic systems. Nature 341:316–318. doi:10.1038/341316a0

Carlyle GC, Hill AR (2001) Groundwater phosphate dynamics in a river riparian zone: effects of hydrologic flowpaths, lithology and redox chemistry. J Hydrol (Amsterdam) 247:151–168. doi:10.1016/S0022-1694(01)00375-4

Carter MR (1993) Soil sampling and methods of analysis. Lewis, Boca Raton

Christensen TH, Bjerg PL, Banwart SA, Jakobsen R, Heron G, Albrechtsen H-J (2000) Characterization of redox conditions in groundwater contaminant plumes. J Contam Hydrol 45:165–241. doi:10.1016/S0169-7722(00)00109-1

Corstanje R, Reddy KR (2004) Response of biogeochemical indicators to a drawdown and subsequent reflood. J Environ Qual 33:2357–2366

Curtis PJ (1989) Effects of hydrogen-ion and sulfate on the phosphorus cycle of a Precambrian shield lake. Nature 337:156–158. doi:10.1038/337156a0

D'Angelo EM, Reddy KR (1999) Regulators of heterotrophic microbial potentials in wetland soils. Soil Biol Biochem 31:815–830. doi:10.1016/S0038-0717(98)00181-3

Darke AK, Walbridge MR (2000) Al and Fe biogeochemistry in a floodplain forest: implications for P retention. Biogeochemistry 51:1–32. doi:10.1023/A:1006302600347

DePinto JV, Scheffe RD, Booty WG, Young TC (1989) Predicting reacidification of calcite treated acid lakes. Can J Fish Aquat Sci 50:2222–2234. doi:10.1139/f89-043

Devito K, Dillon PJ (1993) The influence of hydrologic conditions and peat oxia on the phosphorus and nitrogen dynamics of a conifer swamp. Water Resour Res 29:2675–2685. doi:10.1029/93WR00622

Drever JI (1988) The geochemistry of natural waters. Prentice Hall, Englewood Cliffs

Drexler JZ, Bedford BL (2002) Pathways of nutrient loading and impacts on plant diversity in a New York peatland. Wetlands 22:263–281. doi:10.1672/0277-5212(2002)022[0263:PONLAI]2.0.CO;2

Drexler JZ, Bedford BL, DeGaetano A, Siegel DI (1999) Quantification of the water budget and nutrient loading in a small peatland. J Am Water Resour Assoc 35:753–769. doi:10.1111/j.1752-1688.1999.tb04172.x

Duval TP, Hill AR (2007) Influence of base flow stream bank seepage on riparian zone nitrogen biogeochemistry. Biogeochemistry 85:185–199. doi:10.1007/s10533-007-9128-9

Elliott ET, Heil JW, Kelly EF, Monger HC (1999) Soil structural and other physical properties. Oxford University Press, New York

Futyma RP, Miller NG (2001) Postglacial history of a marl fen: vegetational stability at Byron-Bergen Swamp, New York. Can J Bot 79:1425–1438. doi:10.1139/cjb-79-12-1425

Gachter R, Muller B (2003) Why the phosphorus retention of lakes does not necessarily depend on the oxygen supply to their sediment surface. Limnol Oceanogr 48:929–933

Giesler R, Hogberg M, Hogberg P (1998) Soil chemistry and plants in Fennoscandian boreal forest as exemplified by a local gradient. Ecology 79:119–137

Glaser PH, Siegel DI, Romanowicz EA, Shen YP (1997) Regional linkages between raised bogs and the climate, groundwater, and landscape of north-western Minnesota. J Ecol 8:3–16. doi:10.2307/2960623

Golterman HL (1988) The calcium- and iron bound phosphate phase diagram. Hydrobiologia 159:149–151. doi:10.1007/BF00014722

Gusewell S, Bailey K, Roem WJ, Bedford BL (2005) Nutrient limitation and botanical diversity in wetlands: can fertilisation raise species richness? Oikos 109:71–80. doi:10.1111/j.0030-1299.2005.13587.x

Haraguchi A, Hasegawa C, Hirayama A, Kojima H (2003) Decomposition activity of peat soils in geogenous mires in Sasakami, central Japan. Eur J Soil Biol 39:191–196. doi:10.1016/j.ejsobi.2003.05.001

Hawke D, Carpenter PD, Hunter KA (1989) Competitive adsorption of phosphate on goethite in marine electrolytes. Environ Sci Technol 23:187–191. doi:10.1021/es00179a008

Hill AR, Devito KJ, Campagnolo S, Sanmugadas K (2000) Subsurface denitrification in a forest riparian zone: interactions between hydrology and supplies of nitrate and organic carbon. Biogeochemistry 51:193–223. doi:10.1023/A:1006476514038

Hoch AR, Reddy MM, Aiken GR (2000) Calcite crystal growth inhibition by humic substances with emphasis on hydrophobic acids from the Florida Everglades. Geochim Cosmochim Acta 64:61–72. doi:10.1016/s0016-7037(99)00179-9

House WA (2003) Geochemical cycling of phosphorus in rivers. Appl Geochem 18:739–748. doi:10.1016/S0883-2927(02)00158-0

Johnson AM, Leopold DJ (1994) Vascular plant species richness and rarity across a minerotrophic gradient in wetlands of St. Lawrence County, New York, USA. Biodivers Conserv 3:606–627. doi:10.1007/BF00114204

Kellogg LE, Bridgham SD (2003) Phosphorus retention and movement across an ombrotrophic-minerotrophic peatland gradient. Biogeochemistry 63:299–315. doi:10.1023/A:1023387019765

Khoshmanesh A, Hart BT, Duncan A, Beckett R (1999) Biotic uptake and release of phosphorus by a wetland sediment. Environ Technol 20:85–91. doi:10.1080/09593332008616796

Komor SC (1994) Geochemistry and hydrology of a calcareous fen within the Savage Fen wetlands complex, Minnesota, USA. Geochim Cosmochim Acta 58:3353–3367. doi:10.1016/0016-7037(94)90091-4

Lajtha K (1988) The use of ion-exchange resin bags for measuring nutrient availability in an arid ecosystem. Plant Soil 105:105–111. doi:10.1007/BF02371147

Lamers LPM, Tomassen HBM, Roelofs JGM (1998a) Sulfate-induced eutrophication and phytotoxicity in freshwater wetlands. Environ Sci Technol 32:199–205. doi:10.1021/es970362f

Lamers LPM, van Roozendaal SME, Roelofs JGM (1998b) Acidification of freshwater wetlands: combined effects of non-airborne sulfur pollution and desiccation. Water Air Soil Pollut 105:95–106. doi:10.1023/A:1005083526455

Lamers LPM, Dolle GET, Berg STGVd, Delft SPJV, Roelofs JGM (2001) Differential responses of freshwater wetland soils to sulphate pollution. Biogeochemistry 55:87–102. doi:10.1023/A:1010629319168

Lamers LPM, Falla SJ, Samborska EM, van Dulken LAR, van Hengstum G, Roelofs JGM (2002) Factors controlling the extent of eutrophication and toxicity in sulfate-polluted freshwater wetlands. Limnol Oceanogr 47:585–593

Li YL, Vali H, Yang J, Phelps TJ, Zhang CL (2006) Reduction of iron oxides enhanced by a sulfate-reducing bacterium and biogenic H_2S. Geomicrobiol J 23:103–117. doi:10.1080/01490450500533965

Loeppert RH, Suarez DL (1996) Carbonate and gypsum. In: Bartels JM (ed) Methods of soil analysis: part 3 chemical methods. ASA and SSSA, Madison, pp 437–474

Lucassen ECHET, Smolders AJP, Roelofs JGM (2000) Increased groundwater levels cause iron toxicity in *Glyceria fluitans* (L.). Aquat Bot 66:321–327. doi:10.1016/S0304-3770(99)00083-2

Lucassen ECHET, Smolders AJP, van de Crommenacker J, Roelofs JGM (2004a) Effects of stagnating sulphate-rich groundwater on the mobility of phosphate in freshwater wetlands: a field experiment. Arch Hydrobiol 160:117–131. doi:10.1127/0003-9136/2004/0160-0117

Lucassen ECHET, Smolders AJP, van de Salm AL, Roelofs JGM (2004b) High groundwater nitrate concentrations inhibit eutrophication of sulphate-rich freshwater wetlands. Biogeochemistry 67:249–267. doi:10.1023/B:BIOG.0000015342.40992.cb

Lucassen ECHET, Smolders AJP, Roelofs JGM (2005) Effects of temporary desiccation on the mobility of phosphorus and metals in sulphur-rich fens: differential responses of sediments and consequences for water table management. Wetlands Ecol Manage 13:135–148. doi:10.1007/s11273-004-0314-4

Lucassen ECHET, Smolders AJP, Boedeltje G, van den Munckhof PJJ, Roelofs JGM (2006) Groundwater input affecting plant distribution by controlling ammonium and iron availability. J Veg Sci 17:425–434. doi:10.1658/1100-9233(2006)17[425:GIAPDB]2.0.CO;2

McNamara JP, Siegel DI, Glaser PH, Beck RM (1992) Hydrogeologic controls on peatland development in the Malloryville wetland, New York (USA). J Hydrol (Amsterdam) 140:279–296. doi:10.1016/0022-1694(92)90244-P

Mitsch WJ, Gosselink JG (2000) Wetlands. Van Nostrand Reinhold, New York

Moore PA, Reddy KR (1994) Role of Eh and pH on phosphorus geochemistry in sediments of Lake Okeechobee, Florida. J Environ Qual 23:955–964

Moore TR, Bubier JL, Bledzki L (2007) Litter decomposition in temperate peatland ecosystems: the effect of substrate and site. Ecosystems 10:949–963. doi:10.1007/s10021-007-9064-5 NY, Print

Murphy J, Riley J (1962) A modified single solution for the determination of phosphate in natural waters. Anal Chim Acta 27:31–36. doi:10.1016/S0003-2670(00)88444-5

Murray JW, Jannasch HW, Honjo S, Anderson RF, Reeburgh WS, Top Z et al (1989) Unexpected changes in the oxic anoxic interface in the Black Sea. Nature 338:411–413. doi:10.1038/338411a0

Olivero AM (2001) Classification and mapping of New York's calcareous fen communities. New York Natural Heritage Program. Albany, NY

Paludan C, Jensen HS (1995) Sequential extraction of phosphorus in freshwater wetland and lake sediments: significance of humic acids. Wetlands 15:365–373

Reddy KR, Kadlec RH, Flaig E, Gale PM (1999) Phosphorus retention in streams and wetlands: a review. Crit Rev Environ Sci Technol 29:83–146. doi:10.1080/10643389991259182

Reschke CA (1990) Ecological communities of New York State. New York Natural Heritage Program, New York State Department of Environmental Conservation, Latham

Richardson CJ (1985) Mechanisms controlling phosphorus retention capacity in freshwater wetlands. Science 228:1424–1427. doi:10.1126/science.228.4706.1424

Richardson CJ, Marshall PE (1986) Processes controlling movement, storage, and export of phosphorus in a fen peatland. Ecol Monogr 56:279–302. doi:10.2307/1942548

Roden EE, Edmonds JW (1997) Phosphate mobilization in iron-rich anaerobic sediments: microbial Fe(III) oxide reduction versus iron–sulfide formation. Arch Hydrobiol 139:347–378

Roelofs JGM (1991) Inlet of alkaline river water into peaty lowlands: effects on water quality and *Stratiotes aloides* L. stands. Aquat Bot 39:267–293. doi:10.1016/0304-3770(91)90004-O

Sharpley AN (1995) Soil phosphorus dynamics: agronomic and environmental impacts. Ecol Eng 5:261–279. doi:10.1016/0925-8574(95)00027-5

Smolders AJP, Roelofs JGM (1993) Sulfate-mediated iron limitation and eutrophication in aquatic ecosystems. Aquat Bot 46:247–253. doi:10.1016/0304-3770(93)90005-H

Smolders AJP, Roelofs JGM, Den Haratog C (1995) Internal eutrophication of aquatic ecosystems: mechanisms and possible remedies. Acta Bot Gallica 142:707–717

Smolders AJP, Lamers LPM, den Hartog C, Roelofs JGM (2003) Mechanisms involved in the decline of *Stratiotes aloides* L. in The Netherlands: sulphate as a key variable. Hydrobiologia 506:603–610. doi:10.1023/B:HYDR.0000008551.56661.8e

Smolders AJP, Lamers LPM, Lucassen ECHET, Van der Velde G, Roelofs JGM (2006) Internal eutrophication: how it works and what to do about it—a review. Chem Ecol 22:93–111. doi:10.1080/02757540600579730

Todorova SG, Siegel DI, Costello AM (2005) Microbial Fe(III) reduction in a minerotrophic wetland—geochemical controls and involvement in organic matter decomposition. Appl Geochem 20:1120–1130. doi:10.1016/j.apgeochem.2005.02.005

U.S. Department of Agriculture NRCS (1998) Soil survey geographic (SSURGO) database for Cortland, Onondaga, Oswego, and Tompkins counties, New York

U.S. Environmental Protection Agency (1996). Standard methods SW-846:3052. Microwave assisted acid digestion of siliceous and organically based matrices. Washington, DC

U.S. Environmental Protection Agency (1998). Standard methods SW-846:3020A. Acid digestion of aqueous samples and extracts for total metal analysis by GFAA spectroscopy. Washington, DC

Van Duren IC, Pegtel DM (2000) Nutrient limitations in wet, drained and rewetted fen meadows: evaluation of methods and results. Plant Soil 220:35–47. doi:10.1023/A:1004735618905

Verhoeven JTA, Keuter A, Logtestijn RV, Kerkhoven MBV, Wassen M (1996) Control of local nutrient dynamics in mires by regional and climatic factors: a comparison of Dutch and Polish sites. J Ecol 84:647–656. doi:10.2307/2261328

Vidon P, Hill AR (2004) Denitrification and patterns of electron donors and acceptors in eight riparian zones with contrasting hydrogeology. Biogeochemistry 71:259–283. doi:10.1007/s10533-004-9684-1

Vitt DH (1994) An overview of factors that influence the development of Canadian peatlands. Mem Entomol Soc Can 169:7–20

Williams CJ, Boyer JN, Jochem FJ (2008) Indirect hurricane effects on resource availability and microbial communities in a subtropical wetland–estuary transition zone. Estuaries Coasts 31:204–214. doi:10.1007/s12237-007-9007-6

Wilson KA, Fitter AH (1984) The role of phosphorus in vegetational differentiation in a small valley mire. J Ecol 72:463–473. doi:10.2307/2260059