SEASONAL VARIATIONS IN VERTICAL REDOX STRATIFICATION AND POTENTIAL INFLUENCE ON TRACE METAL SPECIATION IN MINEROTROPHIC PEAT SEDIMENTS

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Abstract. Seasonal variations in pore water and solid phase geochemistry were investigated in urbanized minerotrophic peat sediments located in southwestern Michigan, USA. Sediment pore waters were collected anaerobically, using pore water equilibrators with dialysis membranes ("peepers") and analyzed for pH, alkalinity, dissolved ΣPO_4^{-3}, ΣNH_4^+, ΣS^{-2}, SO_4^{-2}, Fe^{+3}, Fe^{+2}, and Mn^{+2} at 1–2 cm intervals to a depth of 50 cm. Cores collected adjacent to the peepers during all four seasons were analyzed for reactive solid phase Fe according to extraction methods proposed by Kostka and Luther (1994). The association of Fe and trace metals (Mn, Pb, Zn, Cu, Cr, Co, Cd, U) with operationally defined solid phase fractions (carbonates, iron and manganese oxides, sulfides/organics and residual) was assessed for cores extracted during winter and spring using extraction methods proposed by Tessier *et al.* (1979, 1982). Pore water Fe and S data demonstrate a clear seasonal variation in redox stratification of these sediments. The redox stratification becomes more compressed in spring and summer, with relatively more reducing conditions closer to the sediment water interface (SWI), and less reducing conditions near the SWI in fall and winter. In the upper 10–15 cm of sediment, the pool of ascorbate extractable Fe, thought to be indicative of reactive Fe(III) oxides, diminishes during spring and summer, in agreement with seasonal changes in redox stratification indicated by the pore water data. Tessier extractions indicate that the total extractable quantity of all metals analyzed in this study decrease with depth, and that the majority of the non-residual Fe, Pb, Zn, Cu, Cr, Co, Cd, and U is typically associated with the sulfide/organic fraction of the sediments at all depths. Non-residual Mn, in contrast, is significantly associated with carbonates in the upper 15–25 cm of the sediment, and predominantly associated with the sulfide/organic fraction only in deeper sediments.

1. Introduction

Freshwater wetlands comprise an estimated 5–6% of the Earth's surface and play an important role in the biogeochemical cycling of C, both as reservoirs of sedimentary organic matter and as foci for microbial processing and mineralization of organic carbon residue (Mitsch and Gosselink, 2000; Haslam, 2003). Natural wetlands are estimated to be the single largest source of methane to the atmosphere, emitting an estimated 92–237 Tg CH_4/yr (Houghton *et al.*, 2001). Recent work demonstrates that wetlands can play an important role in the biogeochemical sulfur (S)

cycle as well, particularly in areas impacted by acid rain with high concentrations of sulfate (e.g. Brown, 1985; Urban *et al.*, 1989; Marnette *et al.*, 1992; Lazerte, 1993; Smolders and Roelofs, 1993; Morgan, 1995; Morgan and Mandernack, 1996; Lamars *et al.*, 1998, 2001; Branfireun *et al.*, 1999; Devito *et al.*, 1999; Moore *et al.*, 2004).

Most of the S (65 – 80%) occurring in ombrotrophic (primarily precipitation fed) and minerotrophic (primarily groundwater fed) peatlands is present in the form of carbon-bonded sulfur. Of the remaining S in natural peatlands, 10–25% is present as ester sulfates, <10% is present as inorganic iron sulfides, including pyrite and acid volatile sulfides (AVS), and typically <2% occurs as dissolved inorganic sulfide or sulfate (Brown, 1985; Wieder and Lang, 1988; Urban *et al.*, 1989; Morgan, 1995; Chapman, 2001; Chapman and Davison, 2001; Gauci *et al.*, 2004; Novak *et al.*, 2005). Although sulfate-S is a minor component of the freshwater peatland S budget, rapid microbial and chemical processing of S via, for example, sulfate reduction and sulfide oxidation, magnify the importance of sulfate-S as an instrument of biogeochemical transformation. Sulfate reduction rates (SRR) measured in freshwater wetlands using radiotracer techniques can be an order of magnitude faster than those observed using similar techniques in coastal marine saltmarshes (Wieder and Lang, 1988; Wieder *et al.*, 1990; Marnette *et al.*, 1992; DeLaune *et al.*, 2002). Sulfate reduction in peatlands is likely limited by low transient concentrations of labile sulfate. However, locally high sulfate concentrations resulting from reoxidation of sulfide, coupled to reduction of O_2, Mn(IV) or Fe(III), can fuel sustained microbial sulfate reduction and lead to extremely rapid inorganic S turnover. A net effect of this coupled process is a high gross rate of both S oxidation and reduction (Wieder and Lang, 1988; Urban *et al.*, 1989; Wieder *et al.*, 1990; Marnette *et al.*, 1992; Urban and Brezonik, 1993; Morgan and Mandernack, 1996; Chapman, 2001; Mandernack *et al.*, 2000; Chapman and Davison, 2001).

Many studies of S cycling in freshwater wetlands have focused on the impact of sulfate-laden acid rain (e.g. Gorham *et al.*, 1984; Von Dam, 1988; Urban *et al.*, 1989; Lazerte, 1993; Smolders and Roelofs, 1993; Morgan, 1995; Morgan and Mandernack, 1996; Lamars *et al.*, 1998a,b, 2001; Devito *et al.*, 1999; Moore *et al.*, 2004). Sulfate addition to wetlands from acid precipitation, groundwater or run-off containing high S levels results in S accumulation in wetland sediments, primarily in the form of sulfides produced via microbial sulfate reduction. However, during dry periods, water table drawdown and penetration of O_2 into the upper marsh sediments can reoxidize the accumulated reduced sulfur. Subsequent flooding can lead to pulses of acidic, sulfate-laden runoff from the marsh sediments (Wieder, 1985; Bayley *et al.*, 1986; Devito and Hill, 1997; Devito *et al.*, 1999; Lazerte, 1993; Devito and Hill, 1999; Mandernack *et al.*, 2000; Lamars *et al.*, 2001; Blodau *et al.*, 2002; Eimers *et al.*, 2003).

Anthropogenic additions of sulfate to wetland budgets may also affect the net rate of C turnover in these systems. Sulfate addition fuels microbial sulfate reduction and suppresses methanogenesis, which could have long term consequences for wetland

microbial ecology. Suppression of methanogenesis in freshwater wetlands could lead to increased CO_2 and decreased CH_4 fluxes, potentially affecting atmospheric radiative forcing. The net effect of sulfate-induced methanogenesis inhibition on C storage remains unclear (Yavitt *et al.*, 1987; Wieder *et al.*, 1990; Nedwell and Watson, 1995; Watson and Nedwell, 1998; Dise and Verry, 2001; Blodau and Moore, 2003; Gauci *et al.*, 2004).

Studies have also focused on the connection between sulfate addition to freshwater wetlands and cultural eutrophication. Sulfate addition leads to microbial production of sulfide, which binds available Fe into Fe-sulfide minerals. Most sulfate-reducing bacteria can also facultatively reduce Fe(III). Both of these process combine to diminish the pool of sedimentary Fe(III) (hydr)oxides (e.g. Roden and Wetzel, 2002). Because phosphate has a strong affinity for adsorption onto Fe(III) (hydr)oxides, their removal releases labile phosphate, leading to eutrophication (e.g. Smolders and Roelofs, 1993; Lamars *et al.*, 1998a,b; Lamars *et al.*, 2001, 2002).

Studies of peatlands have also considered whether peat, especially in ombrogenic wetlands, can provide an historical record of atmospheric trace metal deposition (Wieder and Lang, 1986; Norton *et al.*, 1987; Shoytk *et al.*, 1992; Novak and Wieder, 1992; Shoytk, 1996; Chague-Goff *et al.*, 1996; Farmer *et al.*, 1997; Steinnes, 1997; Espie *et al.*, 1997; Martinez-Cortizas *et al.*, 1997; Shoytk *et al.*, 1997; West *et al.*, 1997; Gorres and Frenzel, 1997; Holynska *et al.*, 1999; Perkins *et al.*, 2000; Gorhams and Janssens, 2005). However, the correlation between atmospheric deposition of metals and vertical concentration profiles in peat is often unclear, in part because of post-depositional diagenetic processes that can solubilize, mobilize, or transpeciate trace elements. For example, S enrichment that results in microbial sulfate reduction, which can promote the reductive dissolution of Fe(III) (hydr)oxides and liberation of phosphate as discussed above, can also release adsorbed or co-precipitated metals from Fe(III) phases (e.g. Dzombak and Morel, 1990). Alternatively, enhanced sulfide production could promote the sequestration of chalcophile elements, such as Pb, Zn, Cu, As, or Se, by co-precipitation with Fe(II) sulfide phases. Enhanced sulfate reduction can also enhance the sequestration of uranium, by promoting the reduction of U(VI) to insoluble U(IV) hydr(oxide) via microbial catalysis (e.g. Klinkhammer and Palmer, 1991; Lovley *et al.*, 1991). Significantly, in freshwater peatland systems where sulfate reduction is negligible, microbial U(VI) reduction also appears to be negligible (e.g. Zielinski and Meier, 1988). Clearly, sulfate addition to peatland systems can affect the geochemistry of trace constituents in numerous ways beyond the direct outcomes of acid deposition.

In this paper, the geochemistry of porewaters and sediments of an urbanized minerotrophic peatland (Kleinstuck Marsh) is assessed during fall, winter, spring and summer. This study presents geochemical data at spatial resolution of $2-5$ cm to a depth of 50 cm for peatland pore waters from a minerotrophic site in southwestern Michigan, including analyses of dissolved ΣPO_4^{-3}, ΣNH_4^+, ΣS^{-2}, SO_4^{-2}, Fe^{+3}, Fe^{+2}, and Mn^{+2}. Information is also presented assessing Fe solid phase mineralogy

and trace metal speciation associated with sequential sediment extraction fractions. The body of data presented in this paper represents a particularly comprehensive dataset assessing minerotrophic freshwater peatland pore water and solid phase geochemistry. We have used these data to explore how seasonal variations in pore water and solid phase redox stratification may affect trace metal distribution and speciation among operationally-defined sediment fractions of the minerotrophic peat depth profiles.

2. Field Site

Kleinstuck Marsh is a minerotrophic fen located in an urbanized setting of south-western Michigan (Kalamazoo County) within the ∼50-acre Kleinstuck Nature Reserve, owned by the Michigan State Board of Education and managed by Western Michigan University (Buechler, 1996). The marsh is located in a glacial kettle where local sediments are glaciofluvial sand and gravel. Although the fen area was likely a bog in the 19th century, extensive logging and peat mining, together with urbanization and erosion have transformed it into a minerotrophic fen (Buechler, 1996). Recharge of the marsh occurs primarily via groundwater, although some precipitation and runoff recharge does occur seasonally. The hydrology of the area is greatly effected by drawdown of groundwater at a municipal water pumping station located at ∼725 m to the NE of the marsh (see Buechler, 1996 for details).

Cores of the upper 50 cm of waterlogged peat were collected for sediment analysis, and pore water samples were collecting using peepers (see Koretsky *et al.*, 2003 for peeper construction details), during November 2001, March 2002, June 2002 and September 2002. All samples were taken from an area within 2 m of a location benchmark near the center of the bog, placed at the beginning of the study. Air temperatures, monthly precipitation data and surface conditions associated with each sample are shown in Table I. This region has a significant history of sulfate-rich acid rain precipitation. The National Atmospheric Deposition Program maintains a sampling station in SW Michigan, approximately 25 miles from the study site. Over the past ten years, precipitation at this site has had an average pH of 4.49 and sulfate concentration of 1.58 $g \cdot m^{-2} \cdot a^{-1}$ (National Atmospheric Deposition Program, 2005).

3. Materials and Methods

3.1. PORE WATER SAMPLING AND ANALYSIS

Pore waters were collected anaerobically at 1–2 cm intervals from the sediment-water interface (SWI) to a depth of 50 cm using pore water diffusion equilibrators ("peepers"). Prior to deployment in the field, peepers were washed with dilute

TABLE I

Detailed descriptions of sample sites. Sampling date is date of peeper and core extraction (3–4 weeks after emplacement of peepers). Monthly air temperature and precipitation averages are from unedited local climatological data provided by NOAA (2005), National Climatic Data Center for the Kalamazoo/Battle Creek International Airport (42°14′N Lat; 85°33′W Lon.; 892 ft elevation)

Sampling date(s)	Monthly average air temperature	Monthly precipitation	Site description
11/27/01 11/28/01	7.8 °C	6.7 cm in 11/01	Replicate samples separated by ~1 m; Peeper 1 in small unvegetated drainage area, P2 in vegetated area; no standing water at sediment surface
3/24/02	0.11 °C	5.5 cm in 3/02	Replicate samples separated by ~1.5 m; Peeper 1 in small unvegetated drainage area, P2 in sparse vegetation; under thin layer of ice
6/2/02	11.1 °C	9.1 cm in 5/02	Peeper 1 in sparsely vegetated area; P2 in vegetation; ~30 cm standing water at sediment surface
9/5/02	22.2 °C	11.0 cm in 8/02	Peeper 1 in unvegetated area surrounded by vegetation; P2 in dense vegetation (up 0.5 m tall); no standing water at sediment surface

HCl or HNO_3 and then kept in a Plexiglas box filled with deionized (DI) water and degassed using N_2 for 3 to 4 days. The peepers were then placed in vinyl bags filled with N_2 and transported to the field, where they were inserted into the sediments and left to equilibrate with the surrounding sediment pore waters for 3–4 weeks. Peepers were emplaced during November 2001, February 2002, May 2002 and August 2002. Upon retrieval (in December 2001, March 2002, June 2002 and August 2002) peepers were placed into fresh vinyl bags continuously flushed with N_2, and were immediately returned to the lab. Pore waters were extracted from each bag using precleaned polypropylene syringes attached to stainless steel needles. Each pore water sample was subsequently filtered through a 0.2 μm pore size syringe filter. Throughout the fluid extraction, N_2 was periodically flushed into the inflated vinyl bag to maintain positive internal pressure and avoid leakage of atmospheric O_2 into the peeper surroundings.

All reagents were ACS reagent grade or purer, and all glassware or plasticware was precleaned with trace metal grade nitric acid. Solution pH was measured for each filtered sample, which was then divided into portions for analysis of redox-sensitive species (alkalinity, dissolved Fe^{+2}/Fe^{+3}, ΣNH_4^+, ΣPO_4^{-3}, ΣS^{-2}, SO_4^{-2}, and Mn^{+2}). Analyses for ferrous and ferric iron, alkalinity, ammonium, sulfide and phosphate analysis were immediately conducted via UV/Vis spectrophotometry. Samples to be analyzed for sulfate and manganese were preserved by acidification using concentrated nitric acid and concentrated sulfuric acid, respectively (see

Koretsky *et al.*, 2003 for colorimetric methods). Trace metal concentrations were analyzed using a ThermoElectron PQ ExCell inductively coupled plasma mass spectrometer (ICP-MS).

3.2. SEDIMENT SOLID PHASE SAMPLING AND ANALYSIS

Peat cores were collected from within 1 m of peeper insertion points, within 1–2 days of peeper extraction, using a Russian peat borer (Aquatic Research Instruments Inc.). Core samples were taken in hemispheric sections 0.5 m in length, and were divided on site into subsections stored in sealed plastic bags and freeze-dried in a LabConco sediment freeze dryer. Freeze-dried sediments were combusted at 550 °C for 2 hours for determination of loss on ignition.

Sequential sediment extractions were carried out on freeze-dried peat samples using two different methods (Kostka and Luther, 1994; Tessier *et al.*, 1979, 1982). The 2-step Kostka and Luther extraction scheme is intended to quantify the proportions of amorphous Fe (hydr)oxide phases and iron-containing monosulfides, respectively. Briefly, 10 mL of ascorbic acid reagent (10 g sodium citrate or bicarbonate in 200 mL N_2-sparged >17.4 MΩ water with 4 g ascorbic acid added to give final pH of 8) is added to approximately 1 g of freeze-dried, homogenized sediment from each depth interval. This is mixed on a rotating wheel in a Coy anaerobic chamber ($\sim5\%$ H_2, 10% CO_2, 85% N_2) at 25 rpm for 24 h, removed from the chamber and centrifuged at 6500 rpm for 30 min. The supernatant is filtered through an 0.2 μm syringe filter and analyzed colorimetrically for dissolved total Fe. This step is used to release readily reducible, mostly amorphous, Fe(III) (hydr)oxides. The remaining sediment is thoroughly washed using >17.4 MΩ water, and is then extracted for 1 h using 0.5 M HCl to liberate remaining amorphous Fe(III) (hydr)oxides and acid volatile sulfides (AVS) (Kostka and Luther, 1994). Filtered supernatants are analyzed immediately using UV/Vis spectrophotometry for dissolved Fe^{+3} and Fe^{+2}.

The five-step Tessier method is intended to assess trace metal partitioning among the following operationally-defined sediment fractions: readily exchangeable, carbonates, iron and manganese oxyhydroxides (FMOs), oxidizable (organics and sulfides) and residuals (primarily silicates). Approximately 0.2 g of freeze-dried, homogenized sediment from each depth interval are sequentially extracted using reagents shown in Table II. After each extraction step, mixtures are centrifuged at 6500 rpm for 30 min and supernatants filtered through 0.2 μm syringe filters. As above, dissolved Fe is analyzed colorimetrically. Concentrated trace metal grade HNO_3 is added to preserve a second portion of each sample for trace metal analyses using ICP-MS. Between steps, sediment residues are washed repeatedly using >17.4 MΩ DI water which is carefully drained before addition of the next reagent. Step 5 of the original Tessier method calls for dissolution of the sample using HF. In this study, this step is instead completed using a microwave digestion method modified from the "EPA 3051" method used for total soil digestion (EPA, 2005).

TABLE II

Procedure used for 5-step Tessier sediment extractions

Targeted fraction	Method
1. Exchangeables	8 mL 1.0 M $MgCl_2$ adjusted to pH = 5–7 1 h at room temperature
2. Carbonates	8 mL 1.0 M sodium acetate adjusted to pH = 5 with acetic acid 5 h at room temperature
3. Fe and Mn oxides	10 mL 0.04 M Hydroxylamine HCl in 25% (v/v) acetic acid 6 h at 96 °C
4. Organics/Sulfides	3 mL 30% H_2O_2 adjusted to pH 2 with HNO_3 3 h at 85 °C at room temperature add 3.2 N ammonium acetate in 20% (v/v) HNO_3, dilute to 20 mL and agitate an additional 30 minutes
5. Residual	Microwave digestion (see text)

In PFA-Teflon vessels, 25 mL of 50% HNO_3 (trace metal grade) was added to the sediment residue remaining after step 4 and heated under controlled pressure and temperature in a MARS5-DS 9015 Microwave Digester.

4. Results

4.1. PORE WATERS

Sediment pore waters collected using two sets of peepers during four seasons (eight peeper data sets, total) were analyzed for pH, alkalinity, redox-sensitive dissolved species (dissolved Fe^{+2}, Fe^{+3}, Mn^{+2}, ΣS^{-2}, SO_4^{-2}), and dissolved nutrients (ΣNH_4^+, ΣPO_4^{-3}). Peepers were emplaced in areas separated by not more than $\sim$1.5 m (see Table I). However, to assess sediment heterogeneity, one of each pair of peepers was placed into an area of maximum vegetation density ("vegetated" peepers) and one into a site of relatively sparser vegetation ("unvegetated" peepers).

Peeper pH data generally shows circumneutral values at the peat SWI, with slightly decreasing values below the sediment surface. Pore water pH was not measured during Nov/Dec 2001. In all other seasons, pH is similar in samples from both peepers with a constant value of $\sim$6.5–6.8 from 5–10 cm below the sediment surface to 50 cm depth (Figure 1A-C). In Aug/Sept, pH is considerably higher ($\sim$8) near the sediment surface, but decreases to $\sim$6.5–6.8 by 4–8 cm depth. In Feb/Mar, pH is $\sim$7 above the sediment surface, decreasing to $\sim$6.5–6.6 by 1 cm depth. Alkalinity profiles in the two sets of peepers are generally quite similar, although the more densely vegetated site registered slightly higher alkalinity values in fall, winter and summer compared to the more sparsely vegetated site (Figure 1D-G). Alkalinity typically increases gradually from ≤5 mM near the sediment surface to between 5 and 11 mM at 50 cm depth. The largest alkalinity increases are observed during Nov/Dec and May/Jun.
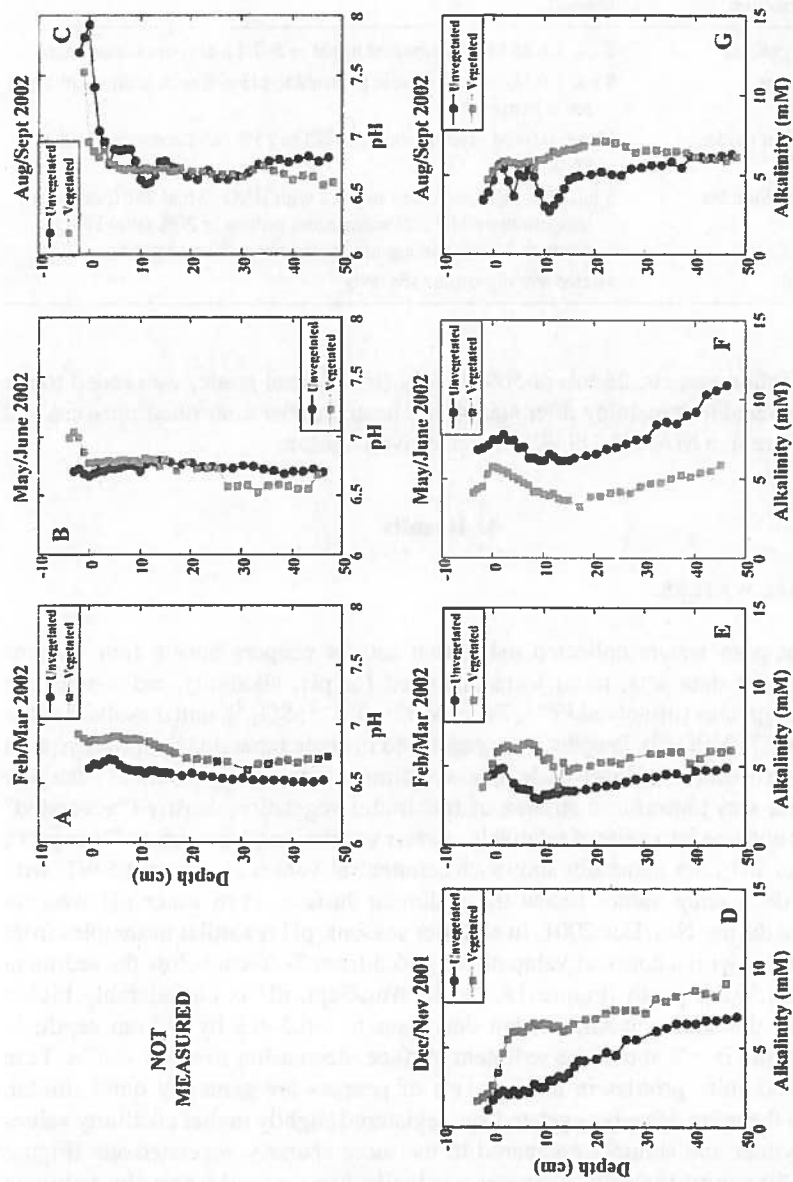
Figure 1. Pore water constituents as a function of depth measured at a densely vegetated site (circles) and nearby sparsely vegetated site (squares) in NovDec 2001, Feb/Mar 2002, May/June 2002 and Aug/Sept 2002. *(Continued on next page)*
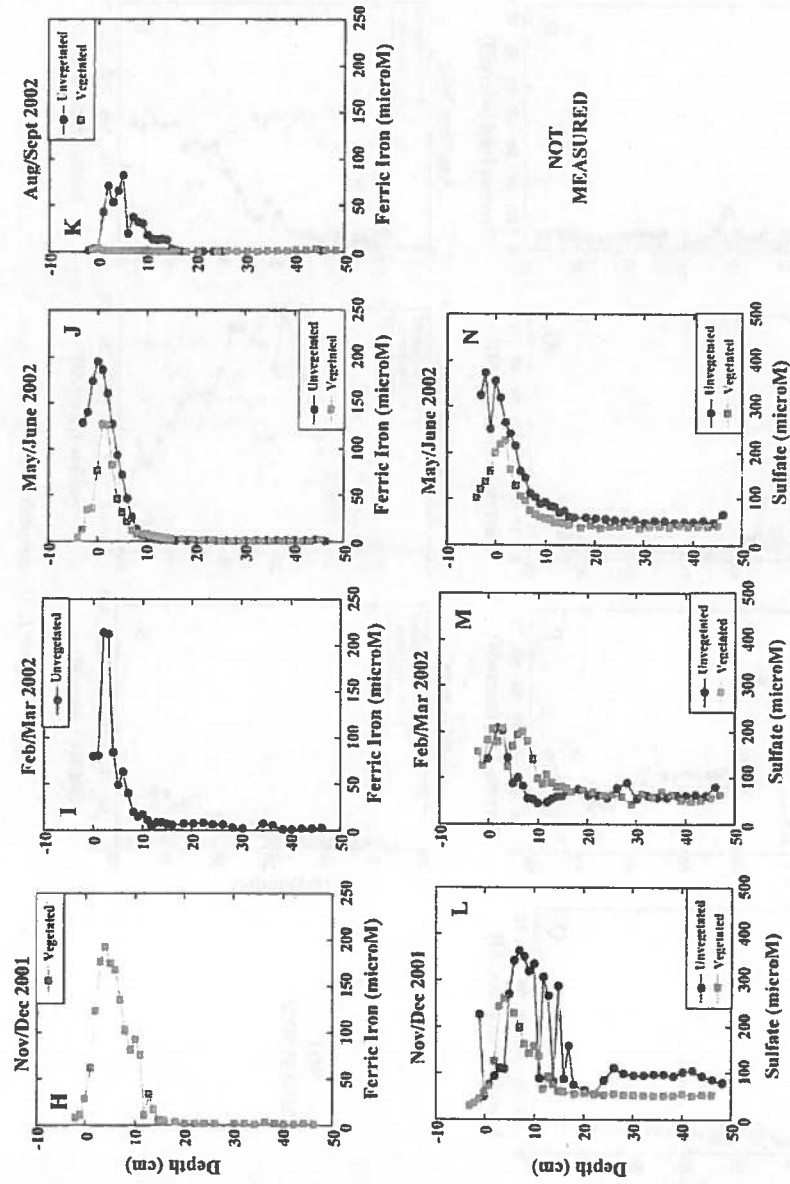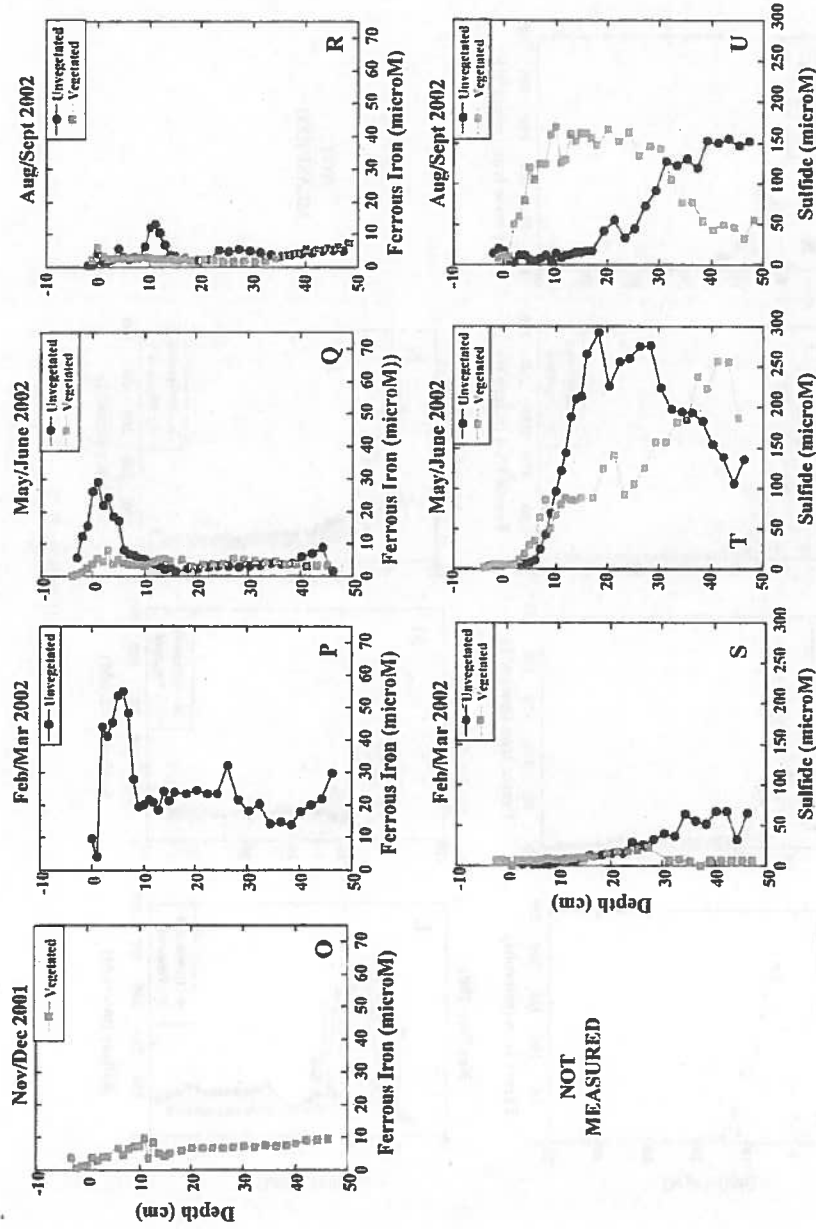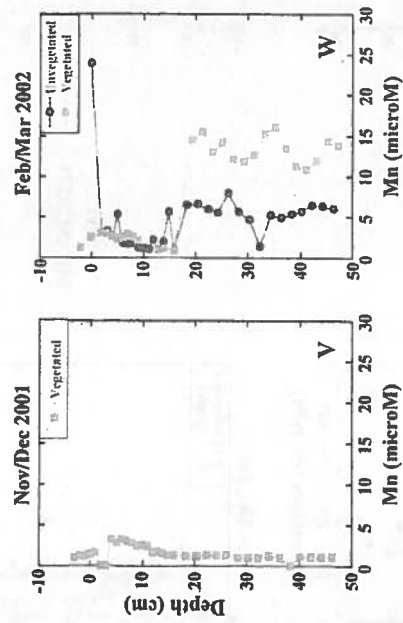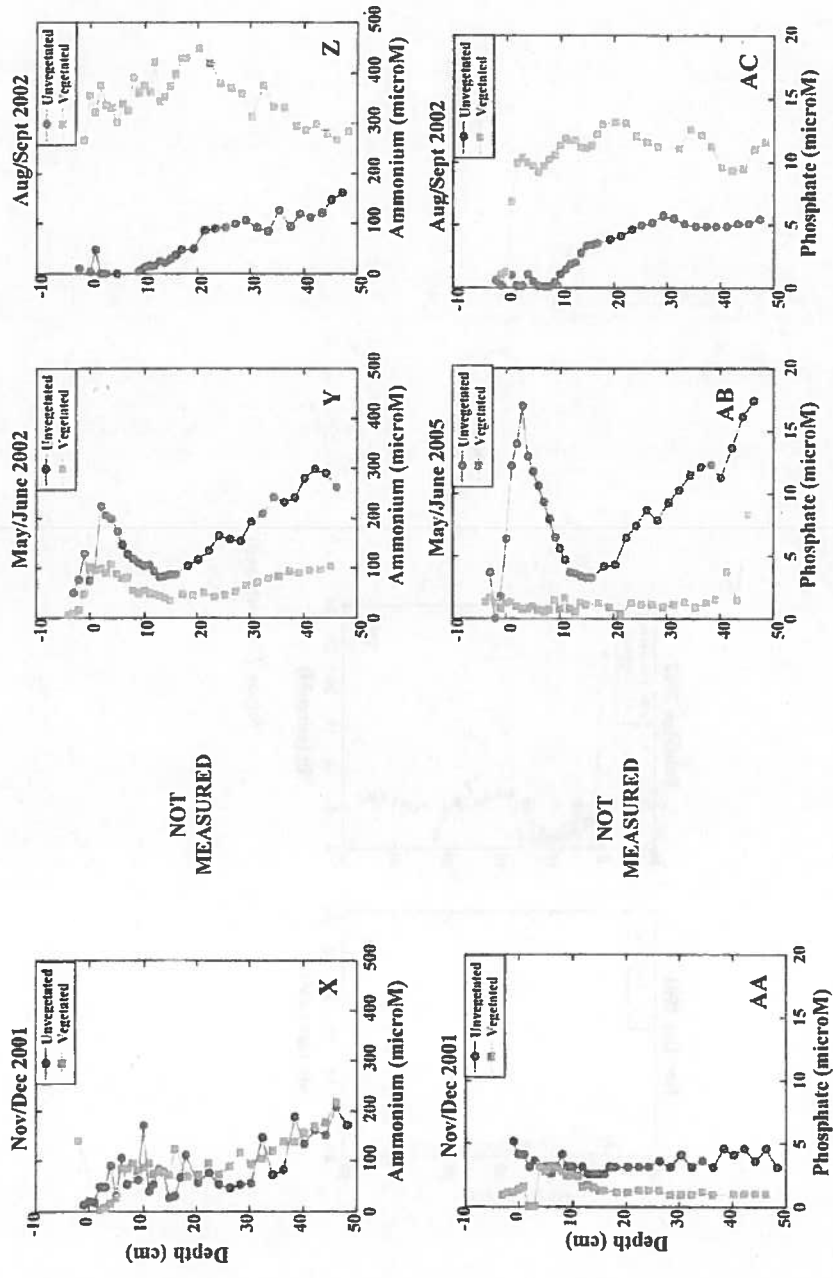
Figure 1. (Continued)

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Dissolved Fe(III) is significantly above detection limits ($\sim$1 μM) only in the upper $\sim$15 cm in all depth profiles, and generally shows a subsurface maximum below which concentrations decline sharply (Figure 1H-K). Except in summer (Aug/Sept), dissolved Fe(III) concentrations increase sharply from low concentrations at or just above the sediment surface to a subsurface maximum of $\sim$200 μM by 1–5 cm depth. In summer no peak in Fe(III) concentrations is apparent in the more densely vegetated site and the Fe(III) concentrations only reach $\sim$100 μM at 5 cm depth at the less densely vegetated site.

Below a depth of 10 cm, dissolved Fe(II) concentrations are typically quite low ($<$10 μM), except in winter (Feb/Mar) at the less vegetated site when concentrations of 25–30 μM persist to 50 cm depth (Figure 1O-R). Fe(II) was not measured at the less vegetated site during fall (Nov/Dec) or at the more densely vegetated site in winter (Feb/Mar). Large subsurface maxima (up to 55 μM) in dissolved Fe(II), centered at $\sim$5 cm in winter (Feb/Mar) and $\sim$2 cm in spring (May/Jun) occur at the less vegetated site.

Dissolved sulfate concentrations in both sets of peepers show similar seasonal variations (Figure 1L-N). During all seasons, dissolved sulfate concentrations below 15 cm are between 40 and 100 μM. In most of the sulfate profiles, there is a single distinct subsurface maximum in sulfate, ranging from $\sim$200–400 μM. In winter (Feb/Mar), at the more densely vegetated site, there appears to be a double subsurface maximum, and during fall (Nov/Dec), at the less vegetated site, the subsurface maximum is much broader than during other seasons. Sulfate was not measured in summer.

Except in summer (Aug/Sept) at the more vegetated site, dissolved sulfide concentrations are typically below detection limit at the sediment surface (Figure 1S-U), but increase with depth. Sulfide concentrations were not measured in fall (Nov/Dec). In winter (Feb/Mar), sulfide concentrations are lowest, reaching at most $\sim$50 μM in the less vegetated site at 50 cm depth, with sulfide concentrations near detection limits to a depth of $\sim$15 cm at both sites. The highest dissolved sulfide concentrations occur in spring (May/Jun), with more dissolved sulfide accumulation at shallower depths in the less vegetated site. At both sites, sulfide begins to accumulate in the pore waters at just 2–3 cm below the sediment surface. At the less vegetated site, sulfide concentrations decline between $\sim$25 and 50 cm depth. In summer (Aug/Sept), a broad peak in dissolved sulfide concentration occurs, with rapid accumulation just below the sediment surface increasing to $\sim$150 μM by 10 cm depth is apparent at the more vegetated site. Sulfide also increases to $\sim$150 μM in the less vegetated site, but concentrations are considerably lower near the sediment surface, with significant accumulation only below $\sim$10 cm depth.

Dissolved manganese levels measured in fall (Nov/Dec) at the vegetated site are very low ($<$5 mM) at all depths (Figure 1V). In winter (Feb/Mar), dissolved Mn concentrations are near detection limits in both peepers to a depth of $\sim$15 cm (Figure 1W). Below 15 cm, there is a sharp increase in Mn concentrations in both peepers to $\sim$5 μM in the less vegetated area and $\sim$10–15 μM in the more vegetated area.

Phosphate depth profiles differ with season and as a function of vegetation cover (Figure 1AA-AC). In general, vegetated site data show lower phosphate concentrations throughout the examined depth interval in fall and spring, however, in summer this trend is reversed, with higher phosphate concentrations at the vegetated site. In fall and spring, vegetated site phosphate concentrations hover at $\sim 2\,\mu$M throughout the measured depth interval, while unvegetated phosphate data varies from slightly higher (up to $\sim 5\,\mu$M) throughout the depth interval in fall, to significantly higher (up to $\sim 18\,\mu$M) in spring. Spring values for the unvegetated site show a subsurface maximum of $\sim 18\,\mu$M at ~ 5 cm depth, followed by a gradual decline to about $4\,\mu$M at ~ 10–20 cm depth, followed by a gradual return to $\sim 18\,\mu$M at 50 cm depth. In summer, both profiles show minimal phosphate concentrations at the SWI, with broadly increasing concentrations with depth, however in contrast to fall and spring, vegetated site values are much higher (up to $\sim 12\,\mu$M) than unvegetated values (up to $\sim 5\,\mu$M). Nutrients (phosphate, ammonium) were not analyzed in winter (Feb/Mar).

Ammonium trends are broadly similar to phosphate trends, with respect to seasonality, site, and depth profile shape (Figure 1X-Z). In fall, depth profiles for ammonium monotonically increase from a SWI minimum near the detection limit to a maximum of $200\,\mu$M at 50 cm, with vegetated and unvegetated data being virtually indistinguishable. In spring, ammonium values show a minimum at the SWI, increasing to a local maximum at about 2 cm depth, then increasing gradually to about half the maximum value at about 10 cm, and increasing again to a maximum near 50 cm depth. Spring data show maxima of $\sim 300\,\mu$M and $100\,\mu$M at the unvegetated and vegetated sites, respectively. In summer, ammonium values at the vegetated site are significantly higher than at the unvegetated site throughout the entire depth range. Values at the unvegetated site are essentially the same as those observed in fall. In contrast, the vegetated site pore waters contain about $300\,\mu$M ammonium at the SWI, increasing gradually to $\sim 400\,\mu$M at ~ 20 cm depth, and then decreasing to $\sim 300\,\mu$M at 50 cm.

4.2. SOLID PHASE

4.2.1. *Loss on Ignition (LOI)*

These marsh sediments are extremely organic rich, with loss on ignition measurements indicating that most of the sediment is composed of readily combustable material (Figure 2). LOI increases with depth to nearly 100% at 30 cm and shows little variation between December and June 2002.

4.2.2. *Ascorbate and HCl Extractions*

An extraction scheme developed by Kostka and Luther (1994) to measure the solid phase speciation of reactive Fe in marine sediments was used to assess Fe speciation in cores from December 2001, March 2002, June 2002 and September 2002. Cores were extracted sequentially first using ascorbic acid, which targets
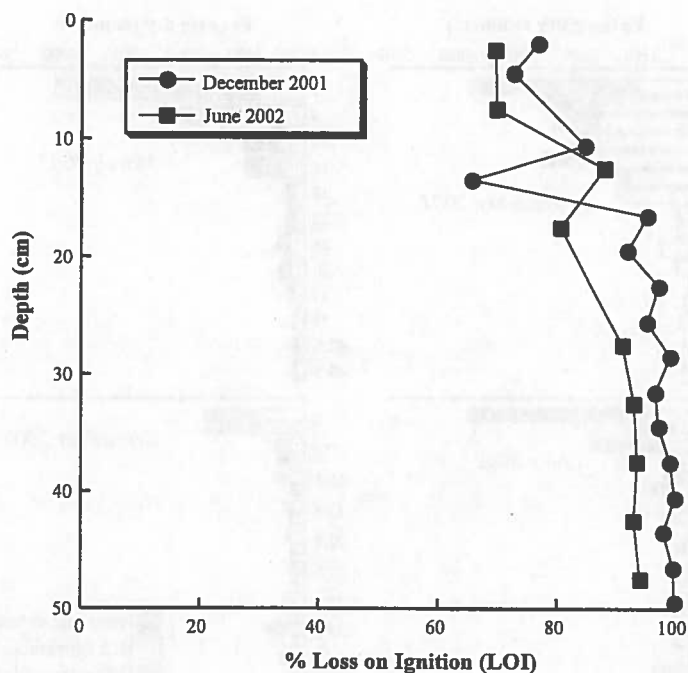
Figure 2. Loss on ignition as a function of depth for cores collected in December 2001 (circles) and June 2002 (squares).

primarily amorphous Fe(III) minerals and then using 0.5M HCl, which targets remaining amorphous Fe(III) minerals and acid volatile sulfides (AVS). Extractions were completed on replicate cores in June and September and on single cores in December and March (Figure 3).

During all four seasons, total concentrations of ascorbate extractable Fe (AEF) and HCl extractable Fe (HEF) are greatest at the top of the core (reaching a maximum of ~4000 μg total Fe/g dry sediment) and decrease asymptotically with depth. In the upper 5–15 cm of the cores, most of the iron is AEF, with the relative contribution of HEF increasing with depth. HEF in cores collected in March, June and September 2002 was analyzed for Fe(II) and Fe(III). In all five cores, the HEF is almost entirely comprised of Fe(II).

AEF concentrations are more seasonally variable than HEF concentrations. The highest levels of AEF are measured during December and March, with considerably lower concentrations in both September cores. AEF concentrations in one of the June cores, and in all but the uppermost 5 cm of the other June core, are also much lower than in December and March. HEF is <1000 μg Fe/g dry sediment in all seasons, except in the upper half of the December core, which contains up to ~2000
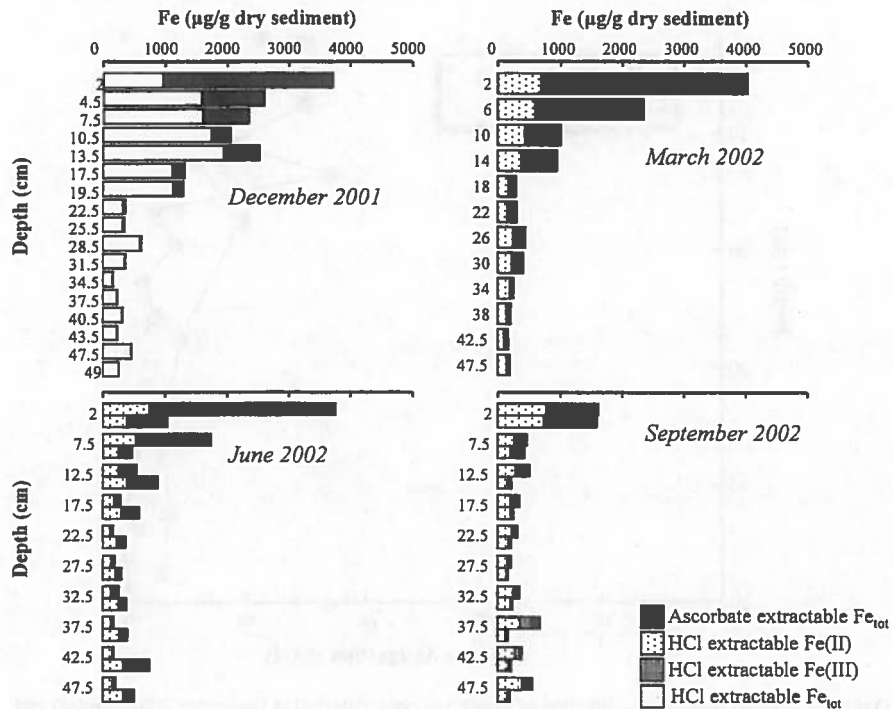
Figure 3. Fe concentrations associated with Kostka and Luther (1994) extractions completed on cores collected in (A) December 2001, (B) March 2002, (C) June 2002 and (D) September 2002. Only total Fe was measured in HCl extractions completed on December cores. Two cores were collected and analyzed in June and September 2002.

μg HCl extractable Fe/g dry sediment.

4.2.3. *Tessier Sequential Extractions: Trace Metals*

Tessier extractions (Tessier *et al.*, 1979, 1982) were used to determine the association of Cr, Mn, Fe, Co, Cu, Zn, Cd, Pb, and U with four operationally defined sediment fractions: carbonates, FMO, organics/sulfides, and residual (primarily silicates) on one core extracted in March 2002 (winter) and one core extracted in June 2002 (spring). Arsenic, Cr, Cd, U and Co are near detection limits in most of the samples. Arsenic data is not shown. A fifth fraction, readily exchangeables, was extracted, but due to the high ionic strength of the extracting solution and low concentration of the extracted metals could not be analyzed using ICP-MS. This fraction was analyzed via UV/Vis spectrophotometry for Fe, which was found to be negligible (<1% of total Fe at all depths). The residual fraction was analyzed and found to dominate Cr, Mn, and Cd at all depths. In contrast, the residual fraction typically

accounted for less than half of Fe, Cu, Zn, Co, U and Pb. Only the distribution of metals in the carbonates, FMO and organics/sulfides fractions are shown here.

Total iron concentrations are typically less than 5000 μg Fe/g dry sediment (Figure 4). In the March 2002 core, total Fe concentrations in the sediments are relatively constant as a function of depth, while in the June 2002 core, total Fe concentrations are higher in the upper 15 cm of sediment than deeper in the sediment. In both cores, the majority of Fe at all depths is extracted in the organics/sulfides fraction. Up to ~25% of the Fe is extracted in the FMO fraction, with most Fe associated with FMO occurring in the upper 15 cm of the sediments. Below ~18 cm depth, well into the sulfidic zone according to both the winter and spring pore water data, negligible iron is found in any fraction other than organics/sulfides.

Total extractable Co (i.e. non-residual) concentrations are near the instrumental detection limit, and never exceed ~0.8 μg/g dry sediment (Figure 4). In both March and June approximately two-thirds of Co typically comes from the organics/sulfides fraction with ~10 and 20–30% each coming from the FMO and carbonate fractions, respectively. The proportion of Co coming from the different fractions does not systematically change with depth.

Unlike many of the other trace elements, significant extractable Zn was obtained from all three measured fractions. Zinc concentrations are maximal in the upper
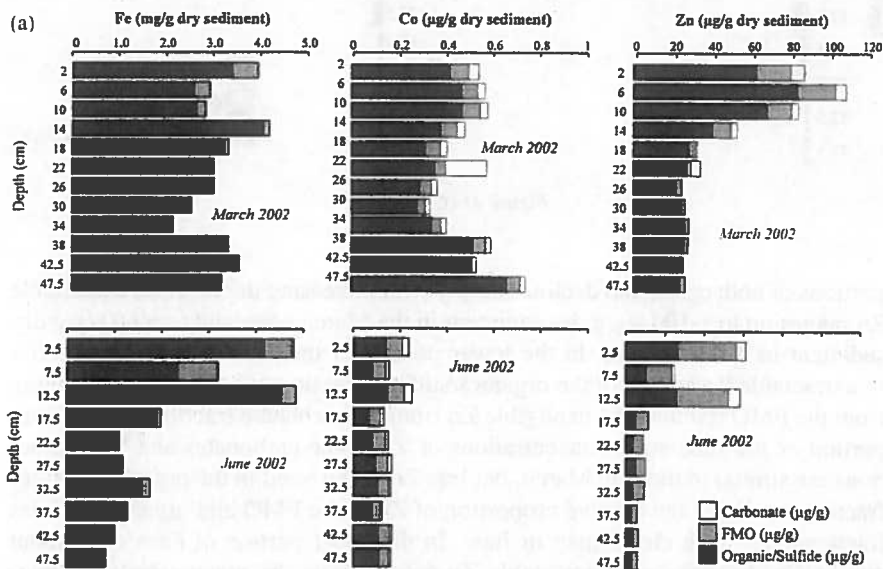

Figure 4. Fe, Co, Cd, Zn and Pb associated with operationally-defined carbonate, FMO, and organics/sulfides fractions (Tessier *et al.*, 1979, 1982) for cores collected in March and June 2002.
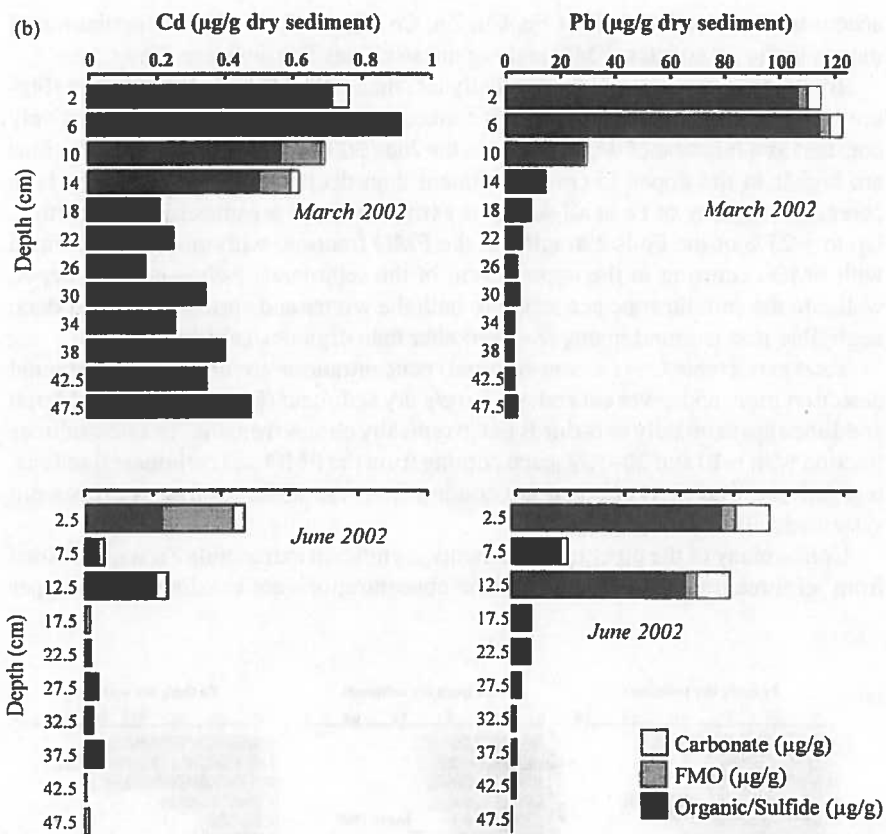
(*Continued on next page*)

Figure 4. (Continued)

portions of both cores, and decline sharply with increasing depth. Total extractable Zn ranges up to ~100 μg/g dry sediment in the March core, and to ~60 μg/g dry sediment in the June core. In the lower portion of the March core the majority of extractable Zn occurs in the organics/sulfides fraction, with minor Zn deriving from the FMO fraction and negligible Zn from the carbonate fraction. In the lower portion of the June core, concentrations of Zn in the carbonates and FMO fractions are similar to those in March, but less Zn is extracted in the organics/sulfides fraction, such that the relative proportion of Zn in the FMO and organics/sulfides fractions are much closer than in June. In the upper portion of each core about one half to two thirds of extractable Zn derives from the organics/sulfides fraction, about 5–10% from the carbonate fraction, and roughly 25–50% from the FMO fraction. A similar fractional distribution and depth-concentration profile is found for Cd in both cores, except that total concentrations (up to ~1 μg/g dry
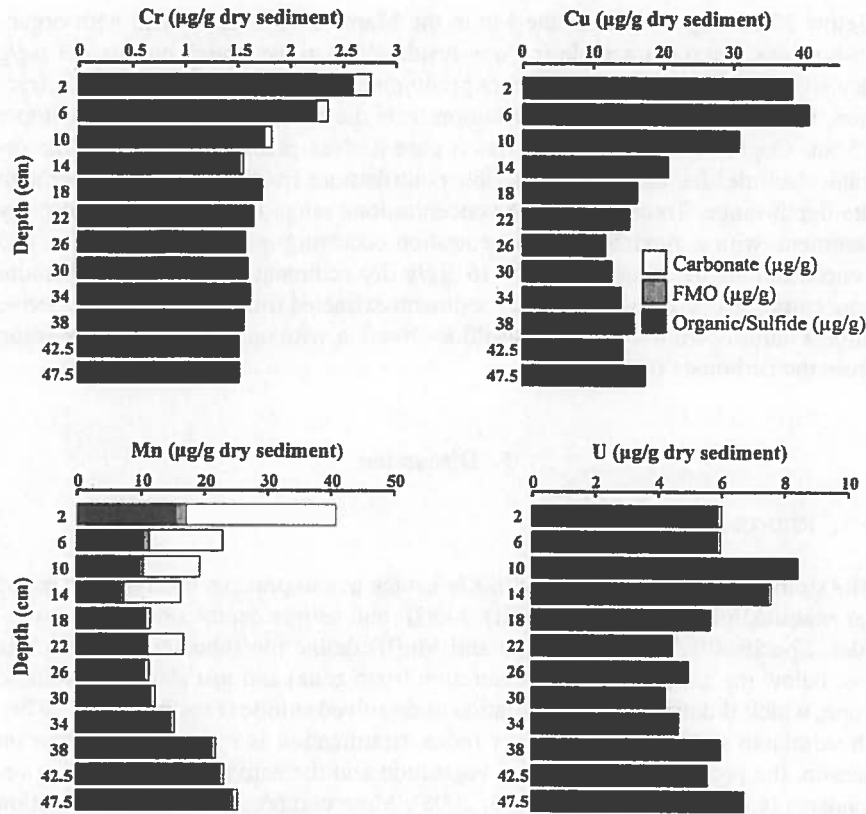
Figure 5. Mn, Cr, Cu and U associated with operationally-defined carbonate, FMO, and organics/sulfides fractions (Tessier *et al.*, 1979, 1982) for cores collected March 2002.

sediment) are much lower than for Zn, and are quite close to the instrument detection limits.

Extractable Pb concentrations are strongly depth dependent, with the highest concentrations (nearly 120 μg/g dry sediment) in the upper 15 cm of both March and June cores. Most extractable Pb occurs in the organics/sulfides fraction, with no more than 15% and 7% of extractable Pb present in the carbonate and FMO fractions, respectively, of the uppermost portion of the core.

Mn, Cr, Cu and U data are only shown for the March core, because of large uncertainties associated with data for these elements in the June core (Figure 5). Non-residual Mn concentrations are ~40 μg/g dry sediment in the upper 5 cm, decreasing to ~25 μg/g dry sediment in the lower portion of the core. Manganese deriving from the carbonate fraction dominates the upper 25cm of the sediment.

Below 25 cm depth, most of the Mn in the March core is associated with organics/sulfides. Total extractable (i.e non-residual) Cr in the March core is <3 $\mu g/g$ dry sediment. Extractable Cr occurs predominantly in the organics/sulfides fraction, with a relatively minor contribution from the carbonate fraction in the upper 15 cm. Copper extracted in the March core derives predominantly from the organics/sulfides fraction, with negligible contributions from other fractions through the depth range. Total extractable concentrations range up to about 40 $\mu g/g$ dry sediment, with a maximum in concentration occurring in the upper 5–10 cm and concentrations trending down to $\sim$15 $\mu g/g$ dry sediment below 10 cm. Uranium concentrations of up to $\sim$8 $\mu g/g$ dry sediment extracted from the March core derive almost entirely from the organics/sulfides fraction with only a minor contribution from the carbonate fraction.

5. Discussion

5.1. REDOX STRATIFICATION

The stratification of redox zoning in Kleinstuck marsh peat can be discerned based on examination of pore water Fe(II), Mn(II) and sulfide depth-concentration profiles. Specifically, dissolved Fe(II) and Mn(II) define the suboxic zone which is just below the zone of oxygen penetration (oxic zone) and just above the sulfidic zone, which is defined by accumulation of dissolved sulfide (Froelich *et al.*, 1979). In saltmarsh sediments, pore water redox stratification is strongly dependent on season, the presence or absence of vegetation and the activity of bioturbating organisms (e.g., Koretsky *et al.*, 2003; 2005). More compressed redox stratification (thinner zones, with the onset of the sulfidic zone nearer to the sediment surface) is favored by warmer temperatures, more dense vegetation and less bioturbation activity.

Pore water profiles in this study also point to distinct redox stratification of these freshwater sediments. Large subsurface maxima in dissolved Fe(III) and sulfate occur in the pore waters of these sites during nearly all seasons. The Fe(III) and sulfate peaks are not spatially separated, but occur at the same depth, at least within the spatial resolution of our measurements. These subsurface maxima likely result from upward diffusion of Fe(II) and sulfide, which react with oxidants, such as oxygen, diffusing downward from the oxic or suboxic zones, respectively (e.g. Bayley *et al.*, 1986; Urban *et al.*, 1989; Wieder and Lang, 1988; Wieder *et al.*, 1990; Marnette *et al.*, 1992; Luther *et al.*, 1992; Chapman, 2001). The depth of the subsurface sulfate and Fe(III) maxima varies seasonally, from $\sim$4 cm depth in fall to $\sim$2.5 cm depth in winter, and up to the SWI in spring. Sulfate was not measured during summer, and very little dissolved Fe(III) accumulation is observed in summer compared to other seasons. These observations suggest that the oxic zone penetrates deepest in fall and that redox stratification becomes more compressed

(i.e., zones thin and move closer to the sediment surface) from fall through winter, spring and summer.

The pore water Fe and S data demonstrate a clear seasonal variation in redox stratification of these sediments. The seasonal variation in redox stratification suggested by the Fe(III) and sulfate pore water data is further substantiated by the Fe(II) and sulfide pore water profiles. During fall, winter and spring, a subsurface maximum in Fe(II) occurs just below the peak in sulfate and Fe(III). In summer, this subsurface maximum is apparent in the pore waters collected at the more sparsely vegetated site, but not at the more densely vegetated site, which also lacks a sulfate subsurface maximum. Pore water Fe(II) concentrations are low year-round, with concentrations generally $\sim$10–30 μM, except for a winter peak of $\sim$60 μM at the unvegetated site. Ferrous iron concentrations in these porewaters are likely kept at low levels due to the generation of sulfide via microbial sulfate reduction, with subsequent precipitation of iron sulfide minerals (e.g., Urban *et al.*, 1989; Luther *et al.*, 1992; Lamars *et al.*, 1998a,b; Novak *et al.*, 2005). Sulfide accumulation in the pore waters begins at or near the depth of Fe(II) peak concentrations and increases with depth. There is considerably more accumulation of sulfide during spring and summer than during winter. Sulfide accumulation begins immediately at the SWI at the more densely vegetated site in summer, which explains the lack of subsurface peaks of Fe(II), Fe(III) or sulfate. Pore water redox stratification is much more compressed in spring and summer than in fall and winter. There is considerable heterogeneity within the sediments, however, such that the redox stratification at the more sparsely vegetated site in summer is somewhat less compressed than at either site in spring.

Seasonal changes in redox stratification inferred from the pore water profiles are also in agreement with solid phase Fe data. Kostka and Luther (1994) attribute ascorbate extractable Fe (AEF) primarily to reactive Fe(III) oxyhydroxide phases. Figure 3 demonstrates that AEF decreases sharply with depth, presumably reflecting either microbially- or chemically – mediated, reductive dissolution of the Fe(III) oxyhydroxides (e.g. Luther *et al.*, 1992; Kostka *et al.*, 2002a,b; Roden and Wetzel, 2002; Koretsky *et al.*, 2003). The concentration of AEF in the upper portion of the sediment column varies seasonally, as expected from the seasonal variation in pore water redox stratification: there is more AEF present in the upper portion of the sediment column in fall and winter and less present during spring and summer (Figure 3).

Depth-pH profiles have been used as a proxy for O_2 penetrations depths in marine saltmarsh sediments and have been suggested as indicators of water table fluctuations in freshwater marsh sediments (Shotyk, 1988; Koretsky *et al.*, 2005) because oxidation of reduced manganese, iron or sulfide with oxygen produces protons, whereas reactions such as dissimilatory iron or sulfate reduction consume protons. During winter and spring, the Kleinstuck sediment surface is covered by ice and standing water, respectively. Depth profiles of pH measured during these seasons suggest that the oxic zone is above the sediment surface, with little or no

penetration of oxygen into the sediments. In contrast, during summer, decreasing pH is evident to a depth of ~5cm is apparent. Although this might be interpreted as a reflection of O_2 penetration depth, this is not in agreement with dissolved Fe(II), Fe(III), and sulfide profiles measured at this site, which suggest that oxygen is depleted at or near the SWI. The decreasing pH may reflect other reactions occurring in the shallow sediments, e.g. carbonate precipitation, but this cannot be confirmed without further data.

5.2. SOLID PHASE IRON

The HCl extractable Fe (HEF) fraction is dominated by Fe(II) (Figure 3), very likely from iron monosulfides (Kostka and Luther, 1994). This is in agreement with previous freshwater work demonstrating that the majority of the inorganic solid phase sulfur in freshwater wetlands is present as acid volatile or chromium reducible sulfides (Wieder and Lang, 1988; Urban et al., 1989; Chapman 2001; Gauci et al., 2004). Tessier extractions completed on winter and spring sediments also show that the majority of the Fe in these sediments, along with a majority of the extractable trace metal budget, is associated with an organic or sulfide solid phase (Figure 4). The Tessier extractions suggest that an Fe oxyhydroxide fraction (FMO) is found primarily in the upper 20 cm of the sediments, but that the contribution of this fraction decreases with depth. This observation is consistent with AEF measurements, however AEF measurements using the extraction method of Kostka and Luther (1994) predict much more FMO than is inferred from the Tessier extraction data. For example, Tessier and Kostka & Luther data both show ~4000 μg extractable Fe/g dry sediment near the top of both March and June cores. However, AEF data (Kostka & Luther method) predict the majority of this extractable Fe to have been Fe(III) oxyhydroxides, whereas the Tessier data predict most to have been in the form of organics/sulfides. This disagreement is likely an artifact of the chosen operationally-defined sequential extraction schemes, the results of which can be difficult to interpret due to incomplete dissolution of phases, dissolution of phases during steps prior to their "target" step and readsorption of released metals on to remaining solids (e.g. Tipping et al., 1985; Kehobian and Bauer, 1987; Gomez-Ariza et al., 1999; Peltier et al., 2005). The Tessier sequential method extracts FMO prior to organics/sulfides, and does so by ostensibly reductively dissolving Fe(III) and Mn(IV) (hydr)oxide phases. However, in organic-rich sediments such as these, reductively dissolved Fe(II) and Mn(II) may adsorb onto or chelate with available organic functionalities in the sediment, resulting in underprediction of the concentration of original FMO (e.g. Kheboian and Bauer, 1987). In the subsequent organics/sulfides extraction, Fe(II) and other elements liberated from FMO but then adsorbed onto organic functionalities would be removed along with any materials originally bound up with organics or sulfides. Thus, the Tessier method can substantially overpredict the concentrations of elements associated with organics/sulfides, by displacement from the original FMO. Furthermore, Rapin et al.

(1986) have demonstrated that preservation of sediments via freeze-drying, as in this study, can increase the quantity of Fe extracted with organics/sulfides and decrease Fe extracted in the exchangeable or carbonates fractions relative to samples extracted immediately after collection.

Data obtained in this study from Tessier extractions also shows much larger extractable Fe concentrations from lower in the cores, relative to that obtained from Kostka & Luther methods. This is also likely to be an artifact of the two operationally-defined methods. Neither ascorbate nor HCl extractions (Kostka & Luther method) are likely to extract significant quantities of chromium reducible sulfides (e.g. pyrite), however the Tessier organics/sulfides step can remove pyrite along with monosulfides (e.g. Dollar *et al.*, 2001). A likely interpretation of the discrepancy between our Tessier and Kostka & Luther data with respect to extractable Fe at depth is that a significant fraction of the sulfides present in the lower sections of the cores occurs in the form of pyrite (and associated disulfide phases), while more of the sulfides present in the younger sediments near the tops of cores occur as monosulfides (e.g. greigite, mackinawite, pyrrhotite). Progressive aging of Fe(II) monosulfides to disulfides occurs under environmental conditions on a timescale of months to years (e.g. Schoonen and Barnes, 1991), and the trend of monosulfide to disulfide conversion with increasing depth as inferred from comparison of Tessier and Kostka & Luther data from Kleinstuck sediments is consistent with this expectation.

5.3. DISSOLVED NUTRIENTS

Phosphate concentrations are fairly low in Kleinstuck pore waters, typically below $\sim 15\ \mu M$, although there is considerable spatial and temporal variability. In summer, and at the more sparsely vegetated site in spring, there is accumulation of dissolved phosphate with depth. In contrast, phosphate levels are low and nearly constant with depth during winter and at the more densely vegetated site in spring. Although phosphate concentrations are generally higher in spring and summer compared to fall, the variability between the peepers is as great as the seasonal variability. Phosphate accumulation in peatland pore waters can reflect a number of processes, including production from mineralization of organic matter, uptake by vegetation and release from reductive dissolution of Fe(III) oxides with subsequent precipitation of Fe(II) sulfides (Sperber, 1958; Lamars *et al.*, 1998a,b, 2001, 2002; Smolders and Roelofs, 1993; Mitch and Gosselink, 2000). During summer and at the more sparsely vegetated site in spring, accumulation of pore water phosphate begins just below peak Fe(II) levels, as sulfide accumulation in the pore waters begins. The largest concentrations of phosphate are observed during summer and in spring at the sparsely vegetated sites, corresponding to periods when the largest accumulations of pore water sulfide occur and ascorbate extractable Fe concentrations in the upper sediments diminish. This suggests that release of phosphate from reductive dissolution of Fe(III) oxides may play an important role in these sediments.

Ammonium concentrations are much greater (up to ~500 μM) than phosphate concentrations and increase with depth during all seasons. Increasing ammonium concentrations with depth have been observed in other peatlands (e.g. Vitt *et al.*, 1995). The variability in ammonium concentration between peepers is nearly as large as the seasonal variability, however the data suggest that, in general, there is more ammonium present in the pore waters during spring and summer compared to winter. Like phosphate, dissolved ammonium concentrations are influenced both by production via mineralization of organic matter (ammonification) and by uptake by vegetation (e.g., Mitsch and Gosselink, 2000). Thus, increased ammonium concentrations in spring and summer may be due to increased anaerobic processing of organic matter at shallower depths during those seasons.

5.4. TRACE METAL DISTRIBUTION

The pore water and iron solid phase data measured here demonstrate that these peatland sediments are redox stratified and furthermore that redox zonation depends strongly on season. In the upper portion of the sediment column, Fe and S undergo seasonal cycles of reduction and oxidation. Previous studies have suggested that inorganic S, in particular, is very rapidly turned over in peatland sediments (Wieder and Lang, 1988; Urban *et al.*, 1989; Wieder *et al.*, 1990; Marnette *et al.*, 1992; Urban and Brezonik, 1993; Morgan and Mandernack, 1996; Chapman, 2001; Mandernack *et al.*, 2000; Chapman and Davison, 2001). This study confirms that reactive solid phase Fe is subjected to a seasonal cycle of reductive dissolution followed by periods of oxidative precipitation. Because many trace metals bind strongly to Fe and Mn oxyhydroxide mineral surfaces, and in the case of chalcophile elements, also precipitate readily with sulfide, this seasonal redox cycle should have important consequences for trace metal speciation, transport and bioavailability in freshwater sediments. Trace metal transpeciation among sulfide or oxide minerals that are rapidly cycled may also obscure historic patterns of atmospheric trace metal deposition (e.g. Shotyk, 1996).

Tessier extraction data for trace metals (Cr, Mn, Co, Cu, Zn, Cd, Pb, U) demonstrate that (1) metal concentration profiles typically decline with depth from maximum concentrations near the SWI, and (2) the majority of trace metals are associated with the operationally-defined organics/sulfides fraction. Chromium, Mn, Cu, Zn, Cd and Pb show clear trends of increasing solid-phase concentration with decreasing sediment depth, and presumably decreasing sediment age. Chromium displays a weaker depth-concentration trend than most of the other analyzed metals, while Co and U display essentially uniform concentrations throughout the cores.

The field site is in an urbanized setting impacted by regional long-term atmospheric deposition of S and trace metals from coal combustion, historic use of Pb-amended fuel, and fertilizer runoff from adjoining lawns and fields. Because the field site is minerotrophic, it is expected that groundwater recharge plays an important role in the supply and throughput of solutes, together with continuous wet

and dry atmospheric deposition onto the site surface. The combination of both these primary mass sources (atmospheric fallout, groundwater flow) is likely to produce a complex result with respect to trace element distribution and speciation in the peat profiles. Atmospheric fallout will tend to deposit elements continuously through time, with each annual layer of accumulated peat recording contemporaneous element deposition. Simultaneously, groundwater flow provides a significant advective drive through the peat, which could result in transport of labile species. This latter process would tend to obfuscate primary imprints of trace element concentration as a function of depth (i.e. time), especially where cyclic microbial activity affects significant transpeciation of trace elements amongst oxide and sulfide phases, as is the case in this field site. Without further data constraining advective transport patterns through the peat as a function of season, rainfall, and bioturbative influences, rigorous deconvolution of the trace element depth profiles is not possible. However, an examination of the qualitative trends in trace element distribution can provide important insights regarding inter-element covariability and operationally-defined fractional association.

Many of the analyzed trace metals are associated with industrial fallout from wind-borne ash and particulate matter from coal combustion. Coal burning provides a substantial source of atmospherically delivered chalcophile elements, such as Co, Cu, Zn, Cd and Pb. Uranium fallout is also associated with coal combustion, due to the presence of organically complexed U(VI) in coal. In contrast, Cr and Mn are primarily lithophile elements and are not disseminated in equivalently high concentrations from coal combustion. Based on their geochemical affinities, it would be expected that chalcophile elements deposited into these sediments would strongly partition into sulfides formed as a result of microbial sulfate reduction. Tessier extraction data support this expectation: most of the Co, Cu, Zn, Cd, Pb and U derive from the organics/sulfides step. Uranium is not chalcophile, but does strongly complex with organic matter, and its association with the organics/sulfides fraction would be expected on that basis. In their study of inundated peaty sediments using Tessier extractions, Dollar *et al.* (2001) also found that the organic/sulfide reservoir was predominant for Cu, Zn, Cd and Pb. They observed, in agreement with this study, a significant fraction of Zn and Cd in the FMO and carbonates pool. In contrast to this study, Dollar *et al.* (2001) found a significant proportion of Pb in the FMO fraction (~30% in the upper 50 cm) with much less (<5%) in the carbonates fraction.

Unlike the other analyzed trace elements, the majority of Mn in the upper 15 cm of the sediment is associated with the carbonate fraction, with ~35–45% associated with organics/sulfides and <5% with FMO. Dollar *et al.* (2001) also reported significant association of Mn with the carbonates fraction, although the organics/sulfides fraction did account for the majority of Mn throughout the upper 50 cm of their sediment, rather than only accounting for the majority below 15 cm depth, as observed here. The results of this study suggest that a significant quantity of Mn may be stored in the upper portion of the sediments via carbonate precipitation, rather

than FMO production. This appears to be the case in spite of the fact that in the upper portion of the cores Mn(II) oxidation to Mn(IV) would be expected based on pore water data, and where a simple speciation calculation (pH $= 7$, bicarbonate $=$ 5mM, Mn(II) $= 5 \mu$M) with the software JCHESS (van der Lee, 1993) indicates that rhodochrosite is near saturation (SI $= -0.6$). It is also possible that the sequential extraction scheme overestimates the proportion of Mn in the carbonates fraction via dissolution of Mn in amorphous monosulfides during the carbonate extraction step, as reported for Pb and Zn in anoxic sediments by Peltier *et al.* (2005). However, it is not clear why this process would have influenced primarily Mn and not the other trace elements analyzed in this study.

Trace metal associations for Fe, Co, Zn, Cd and Pb were analyzed in cores extracted in March 2002 and June 2002. The general patterns of metal speciation between the three extractable fractions are similar in March and June. However, we do not have sufficient data to make a definitive statement regarding temporal heterogeneity, nor can we separate temporal from spatial heterogeneity.

6. Conclusions

This study clearly indicates a distinct seasonal variation in the depth profiles of redox sensitive pore water constituents including sulfide, sulfate, Fe(III), Fe(II) and pH in these minerotrophic peatland sediments. Specifically, redox stratification is more compressed, with accumulation of higher concentrations of more reduced species (e.g. Fe(II) and sulfide) at shallower depth, during spring and summer compared to fall and winter. The seasonally-variable redox stratification indicated by the pore water constituents is also reflected in the solid phase Fe pools. Concentrations of ascorbate extractable Fe, likely indicative primarily of Fe(III) oxides, in the upper portion of the sediments are greater during winter and fall, when redox stratification is less compressed, then in spring and summer.

Two extraction schemes were used to examine seasonal variations in solid phase Fe profiles. It appears that neither scheme, considered alone, gives a complete picture of the solid phase Fe speciation in these sediments. Taken together, however, the results present a coherent picture, suggesting that the upper portion of the sediments is dominated by Fe(III) oxides. These oxides undergo a seasonal cycle of reductive dissolution, producing Fe(II) that can precipitate to form monosulfides. Over time, these monosulfides age to form disulfides, such as pyrite, which appear to be more abundant in the lower portion of the sediment column.

Extraction of four operationally-defined sediment fractions suggests that the majority of Fe, Mn, Pb, Zn, Cu, Cr, Co, Cd, and U is associated with organics/sulfides. With trace metal data for only two cores (one each in March and June) it is not possible to distinguish temporal and spatial heterogeneity, and it is unclear if significant seasonal changes in trace metal speciation, particularly in the upper 10–20 cm of the sediment occur. However, the dynamic nature of the pore

water and Fe solid phase geochemistry suggests that trace metals in these sediments may also undergo significant seasonal variations in speciation. This could have important ramifications for metal bioavailability/toxicity and mobility in these shallow, organic-rich sediments. In spite of potential problems with interpretation of operationally-defined sequential extractions due to incomplete dissolution of target phases, partial dissolution of non-target phases and redistribution of extracted metals, we suggest that these methods may yet yield important insights regarding the potential for seasonal changes in metal speciation in peatland sediments. Future research, using larger suites of cores than in this study, should be completed to assess the significance of spatial and temporal changes in trace metal speciation in peatland sediments.

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