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Metal-bound carbon and nutrients across hydrologically diverse boreal peatlands

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Abstract Boreal peatlands store abundant carbon (C) belowground because of saturated conditions and cold temperatures, which inhibit the enzymatic release of dissolved organic carbon (DOC) from organic matter. However, metals may also bind DOC, as well as nitrogen (N) and phosphorus (P), and their impact may vary among peatlands with differing hydrology. To assess variation of metal-C-nutrient interactions within and among peatlands and with depth, we sampled cores from seven peatlands in the Marcell Experimental Forest, Minnesota, including bogs, poor fens, and a rich fen. We extracted peat with sodium sulfate to release elements bound with exchangeable metals such as calcium (Ca) or aluminum (Al), and with sodium dithionite to release elements bound with the redox-active metals iron (Fe) and manganese (Mn). We compared extracted elements to long-term peat porewater measurements. Mean DOC extracted by sulfate or dithionite in the bogs and poor fens was 5 or 8 times greater, respectively, than porewater DOC, and in the rich fen it was 8 or 38 times greater. Similarly, N and P extracted by sulfate and dithionite were 10–24 times higher than porewater in the bogs and poor fens and 7–55 times higher in the rich fen. The ratio and absolute values of redox-sensitive and ion-exchangeable elements varied by element among peatland types and with peat depth and values were not always greater in fens than bogs. We conclude that both redox-active (Fe) and non-redox-active (Ca and Al) metals bind important pools of peatland C and nutrients regardless of peatland hydrologic type and despite the very low total mineral content of these boreal peats.

Keywords Bog · Calcium · Dissolved organic carbon · Fen · Iron · Peatland · Redox

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Introduction

Northern peatlands influence the global carbon (C) cycle because they store 415 ± 150 Pg of C belowground as peat (Hugelius et al. 2020), which may become a C source to the atmosphere as decomposition increases with temperature (Hanson et al. 2020). Peatland plants and microbes can be nitrogen

(N) and phosphorus (P) limited (Bridgham et al. 1996; Wang and Moore 2014; Hill et al. 2014), and the availability of these nutrients may also influence peatland C dynamics following warming. Organic matter has accumulated in peatlands due to the predominance of saturated and anoxic conditions, low pH, and cold temperatures, which reduce organic matter solubilization and decomposition via multiple mechanisms, including suppression of extracellular enzymes (Bergman et al. 1999; Freeman et al. 2001; Limpens et al. 2008; Hanson et al. 2020; Wilson et al. 2021). Extracellular enzymes solubilize organic matter by breaking down complex particulate matter into smaller compounds, some of which can be directly assimilated by microbes (Schimel and Weintraub 2003). Organic matter solubilization also regulates the leaching of dissolved organic carbon (DOC) to downstream waters, which is a major C flux in peatlands. For example, DOC leaching was 37% of net ecosystem production in a bog at the Marcell Experimental Forest, Minnesota (Griffiths et al. 2017) and 24% of net ecosystem exchange from a bog in Edinburgh, Scotland (Dinsmore et al. 2010). However, other biogeochemical mechanisms aside from extracellular enzymes can also influence the binding and solubilization of DOC and nutrients in peatlands. Recent studies have demonstrated the importance of metals in binding C across diverse peatland types, especially in Chinese peatlands with substantial silicate mineral content (Huang et al. 2021; Zhao et al. 2023; Liu et al. 2024). Nevertheless, the role of landscape-scale hydrologic variation in mediating metal-C-nutrient interactions within and among peatlands remains poorly understood, especially for boreal peats that are comprised almost entirely of organic matter and are largely devoid of silicate minerals.

Metals can directly and indirectly bind organic matter and other nutrients in upland soils but have received less attention in peatlands (Wang et al. 2017), particularly in sites with very low mineral content (Herndon et al. 2019; Curtinrich et al. 2022). Iron (Fe) may protect organic C from decomposition by sorption and coprecipitation (Wagai and Mayer 2007; Kleber et al. 2015; Wang et al. 2021), and Fe-bound C may be released when Fe(III) is chemically reduced to Fe(II) under anoxic conditions (Chen et al. 2020). Similarly, Fe(III) may also bind P and release it following reduction to Fe(II) (Chacon et al. 2006), thereby influencing peatland P availability (Herndon et al. 2019). Apart from Fe, calcium (Ca), aluminum (Al), manganese (Mn), and to a much lesser extent, magnesium (Mg), can bind organic matter to soil through cation bridging and/or co-precipitation with DOC (Kalinichev and Kirkpatrick 2007; Schaumann et al. 2013; Rowley et al. 2018; Cheng et al. 2020; Li et al. 2021).

Because bogs have abundant organic matter and limited nutrients, metal-C-nutrient associations could be important even in sites with low metal concentrations. Our prior work showed that the reduction of Fe(III) to Fe(II) in peat samples from two bogs in Minnesota, USA, led to the release of C as DOC, and that Fe(II) and DOC were positively correlated in bog surface water samples (Curtinrich et al. 2022). Similarly, surface peat in 10 bogs and fens in China had substantial Fe-bound C (Huang et al. 2021). However, the role of redox-active vs. non-redox active metals in binding peatland C and nutrients remains poorly understood, and it is unclear how the contributions of redox-sensitive and non-redox sensitive metals vary among and within different peatland types.

Peatland classification, which is based partly on hydrology, might be useful in the prediction of the importance of metals for C and nutrient cycling within and among peatlands. Bogs only receive water and nutrients from atmospheric deposition, while fens also receive water and nutrients from surface water or groundwater (Bay 1967; Vitt 2006; Verry et al. 2011). Fens may be further subdivided into poor fens and rich fens based on vegetation, nutrient concentration, or pH. Poor fens are *Sphagnum* moss-dominated with surface water pH < 5.5, while rich fens typically have more plant species, less *Sphagnum* moss, and pH > 5.5 (Vitt 2006). Since fens receive groundwater inputs and bogs do not, fens often have higher concentrations of metals derived from mineral weathering (Urban et al. 2011; Griffiths et al. 2019). Higher Fe concentrations may increase the content of metal-bound C and nutrients in fens vs. bogs (Huang et al. 2021), with intermediate values in poor fens, which can receive some groundwater input (Vitt et al. 1995).

Nevertheless, Fe content is not necessarily the primary driver of Fe-bound C due to differences in C to Fe ratios (Zhao et al. 2016), which may vary with pH and Fe speciation (Ye et al. 2022). For instance, the concentration of Fe-bound C in two Minnesota bogs was similar to some upland soils with much greater reactive Fe content (Curtinrich et al. 2022). Even

when comparing bogs within the same landscape, differences in vegetation composition, extent of peat formation, water table variation, or water flow paths might influence redox potential and/or pH among sites, thereby influencing the capacity of Fe to bind C and nutrients. Depth within the peat profile is another likely control on metal-bound C and nutrients, since oxygen availability declines with depth in peat. The acrotelm is the variably oxic layer near the peat surface, where Fe(III) and Fe-bound elements are likely to be greatest, whereas the catotelm is the consistently anoxic layer where Fe(II) rather than Fe(III) is more likely to predominate. The precise depths of the acrotelm and catotelm vary among peatlands and over time, and our previous measurements from Marcell Experimental Forest bogs indicate a shift in Fe speciation and abundance at approximately 30 to 50 cm depth (Curtinrich et al. 2022). For this study, we have adopted an operational definition of the catotelm as 0–30 cm depth, acknowledging that the depth distribution of metals within and among peatlands remains poorly understood (Griffiths and Sebestyen 2016; Griffiths et al. 2019).

To quantify the potential roles of extractable metals and metal-bound elements in peat, we compared these pools with element concentrations in porewater. Several studies examined salt- or acid-extractable elements in peat along with porewater samples (Blodau et al. 2002; Koretsky et al. 2007; Küsel et al. 2008; McLaughlin and Webster 2010; Mettrop et al. 2018), but these values were not typically expressed in units that allowed direct comparison of these nutrient stocks. Here, we express extractable and porewater nutrients as mass per porewater volume, a measure of the maximum potential contribution of extractable elements to porewater that could occur given a shift in biogeochemical factors that control partitioning of metals between solid and solution phases, such as redox potential, pH, or ionic strength. We used sodium dithionite, a strong reductant, to extract redox-sensitive metals (Fe and Mn) and associated elements, and sodium sulfate to extract non-redox sensitive elements (e.g. Ca and Al) through ion exchange, along with any associated elements (Reemtsma et al. 1999; Wagai and Mayer 2007; Ye et al. 2018). We quantified extractable elements from seven peatlands of different types (four bogs, two poor fens, and one rich fen) and used linear mixed models to compare how concentrations of elements and mechanisms controlling their solubility (chemical reduction or ion exchange) varied across sites and depth.

We first hypothesized that dithionite- and sulfate-extractable element concentrations would be consistently greater than porewater values across all sites, indicating direct and indirect binding of elements with peat. This hypothesis is relevant because while other studies have quantified metal-bound C in temperate peatland soils with relatively high silicate mineral content and lower organic C (e.g., mean of 29% C in the *Sphagnum* peatlands of Zhao et al. 2023), much less is known about metal-C interactions in boreal peatlands, which are often nearly devoid of silicate minerals and often have C content > 50% by mass (Iversen et al. 2014). Furthermore, we are unaware of any peatland study that quantified C released in a sodium sulfate extraction, thereby providing insight into the role of non-redox-active minerals. Second, we hypothesized that element concentrations in the dithionite extraction would be greater than the sulfate extraction, consistent with the importance of redox-active metals Fe(III) and Mn(IV) in directly and indirectly binding other elements with peat, even in peatlands with low metal abundance. Third, we hypothesized that extractable element concentrations would vary among peatland types, with greater values in the rich fen, intermediate values in the poor fen, and lowest values in the bogs (Fig. 1).

Methods

Site description

Peat cores were sampled from seven peatlands at the Marcell Experimental Forest, Minnesota (Fig. 1) on June 24–27, 2018. Sampling sites S1, S2, S4, and S6 are bogs, Bog Lake Peatland and Junction Fen are poor fens, and S3 is a rich fen (Table 1), as classified based on their chemistry, vegetation, and hydrology (Sebestyen et al. 2011a). The fens receive groundwater with mineral-dissolved solutes from the surrounding aquifer, while the bogs are perched above the aquifer and only receive water from precipitation (Sebestyen et al. 2011a; Urban et al. 2011). The S1, S2, S4, and S6 bogs each have an intermittent outlet stream (or streams) while the S3 fen has a perennial outlet stream, and Bog Lake and Junction Fen do not

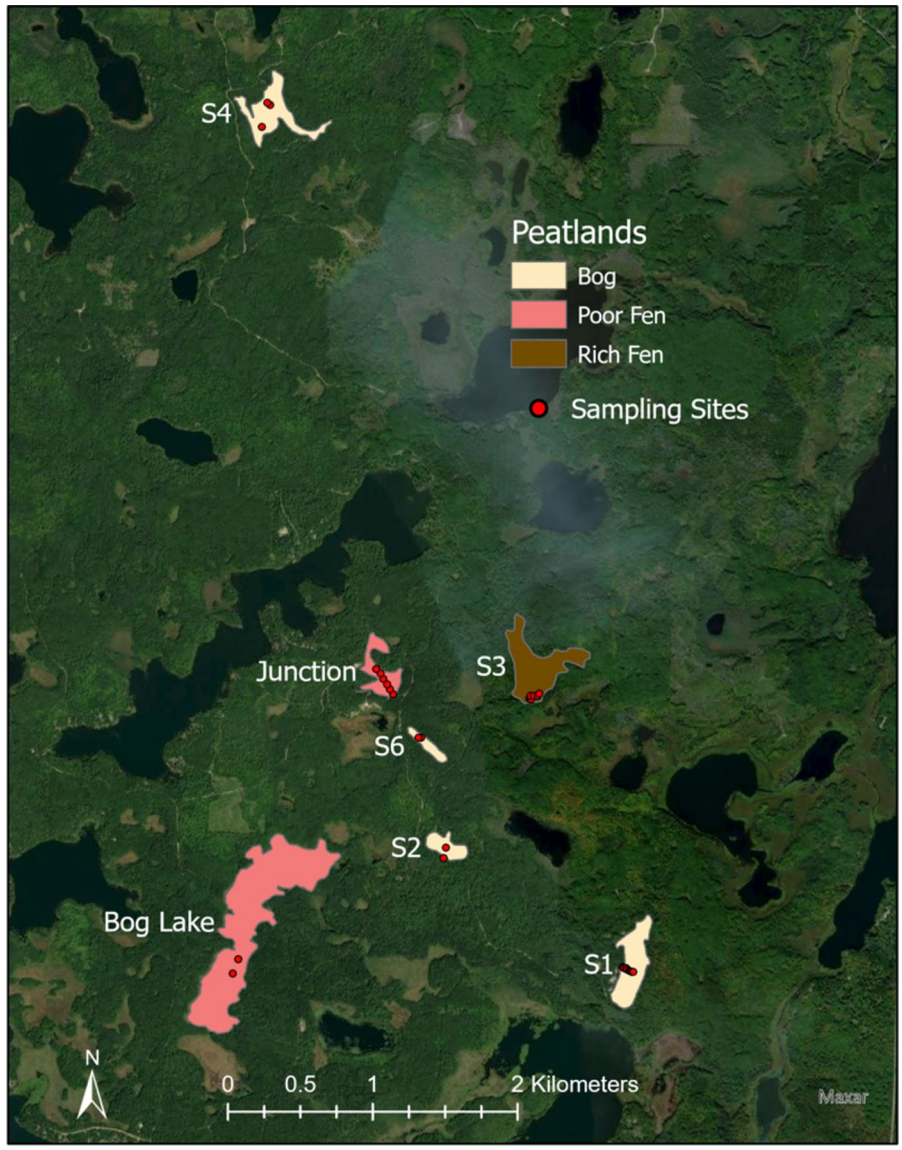

Fig. 1 Map of sampling sites. Peatlands S1, S2, S4, and S6 are bogs, Bog Lake and Junction are poor fens, and S3 is a rich fen. Background imagery is from Maxar

have outlet streams (Sebestyen et al. 2011a). Water levels fluctuate more in the bogs than in the fens and the S1 bog had the most variability, although no water level data was available for Junction Fen (Sebestyen et al. 2021e).

Some of these sites have been used for past and present experiments. Trees were harvested in the S1 bog in 1969 and 1974 with no resulting impact on the bog water table or outlet stream water yield (Sebestyen et al. 2011b). Since 2015, a portion of the S1 bog has used for SPRUCE (Spruce and Peatland Responses Under Changing Environments), an experiment to study ecosystem effects of climate change on peatlands through application of aboveground and belowground warming, and atmospheric carbon dioxide (CO_2) treatments to open-top enclosures (Hanson et al. 2020). For this manuscript, cores were collected > 50 m away from the nearest SPRUCE enclosure. The S2 bog has been used as a reference for experiments on other Marcell peatlands (Sebestyen et al. 2011a). Similar to S1, the S3 fen was experimentally clearcut in 1972–1973 with little effect on stream water yield (Sebestyen and Verry 2011). Sulfate was added from 2001 to 2008 to the downstream half of S6 to study effects on methylmercury (Coleman Wasik et al. 2015), but samples for

Table 1 Characteristics of sampled peatlands in the marcell experimental forest (Dise et al. 2011; Sebestyen et al. 2011a; Griffiths et al. 2019)

Site	Peatland type	Area (ha)	Vegetation
S1	bog	8.1	Black spruce (*Picea mariana*), eastern tamarack (*Larix laricina*), *Sphagnum* moss, ericaceous shrubs*, and blueberry (*Vaccinium angustifolium*)
S2	bog	3.2	Black spruce, some eastern tamarack, *Sphagnum* moss, ericaceous shrubs, blueberry, pitcher plant (*Sarracenia purpurea*), and bog cranberry (*Vaccinium oxycoccos*)
S3	rich fen	18.6	Eastern tamarack, black spruce, alder (*Alnus* spp.), willow (*Salix* spp.), sedges (*Carex* spp.), rushes (*Juncus* spp.), *Sphagnum* moss, ericaceous shrubs, ferns, and herbs
S4	bog	8.1	Eastern tamarack, black spruce, *Sphagnum* moss, ericaceous shrubs, sedges, buckbean (*Menyanthes trifoliata*), and pitcher plant
S6	bog	2	Black spruce, eastern tamarack, *Sphagnum* moss, and ericaceous shrubs
Junction Fen	poor fen	6	Sedges, rushes, *Sphagnum* and hair cap (Polytrichum spp.) moss, leatherleaf (*Chamaedaphne calyculata),* bog cranberry, and arrowgrass (*Scheuchzeria palustris*)
Bog Lake	poor fen	20	Sparse, stunted eastern tamarack, sedges, pitcher plants, *Sphagnum* moss, leather leaf, bog cranberry, bog rosemary (*Andromeda glaucophylla*)

*Ericaceous shrubs include Labrador tea (*Rhododendron greonlandicum*) and leatherleaf (*Chamaedaphne calyculata*)

this manuscript were collected > 50 m upslope of that experimental area to minimize potential effects of that study. In the uplands surrounding the S4 and S6 peatlands, the forests were harvested during 1970–1972 and 1980, respectively (Sebestyen et al. 2011a), and bog water levels somewhat increased for several years after harvest but returned to pre-harvest levels within no more than ten years (Sebestyen et al. 2011b).

Peat core sampling

Peat cores were sampled on June 24–27, 2018 with a stainless-steel Russian corer (5 cm diameter; Eijelkamp Agrisearch Equipment, Giesbeek, The Netherlands). Eight cores were sampled from S1, two from S2, six from S3, three from S4, two from S6, two from Bog Lake, and six from Junction Fen (Fig. 1 and Table 1); sampling intensity differed among peatlands due to differences in area, accessibility constraints, and analytical limitations. Cores were sampled from the surfaces of hollows to the bottom of the peat (as shallow as 75 cm) or to 250 cm, whichever came first. Some cores are missing segments near the surface because of air voids or plant matter that was not decomposed enough to sample. Two core segments out of 242 total segments are missing due to sampling error. Peat core analyses are similar to those in Curtinrich et al. (2022), with data reported in Curtinrich et al. (2021). Cores were split into segments of 10 cm for the top 50 cm and 25 cm thereafter. Partial segments were treated as whole segments for plotting purposes, for example 46–50 cm was treated as 40–50 cm; measurements were unaffected by this convention because they were expressed per unit mass of peat or solution that was analyzed. Five samples were removed because they showed visible signs that they were in the mineral layer below the peat. Samples were stored at -20 °C and then thawed at 22 °C, homogenized inside their storage bags, and subsampled for chemical extractions and measurement of moisture and pH. To express element concentrations on a peat dry mass basis, gravimetric moisture content was measured by drying ~ 10 g at 100 °C for > 48 h, and pH was measured on ~ 5 g field-moist subsamples with an electrode. We did not measure pH on 8 samples due to limited mass for these samples.

Chemical analyses

Field-moist subsamples were extracted separately with 0.05 mol L^{-1} sodium dithionite and 0.05 mol L^{-1} sodium sulfate with a ratio of 1:180 dry mass equivalent to solution, as described in Curtinrich et al (2022). Briefly, dithionite reduces Fe(III) to Fe(II), releasing any C that was directly or indirectly associated with Fe(III). A separate extraction with sodium sulfate, the oxidation product of sodium dithionite, acts as a control that accounts for organic C extracted via sodium or sulfate (Reemtsma et al. 1999; Wagai and Mayer 2007; Ye et al. 2018; Table S1). Samples and extractant solutions were vortexed for 1 min, shaken for 16 h, and centrifuged for

10 min at 20,000 g. Part of the supernatant (20 ml) was removed by pipet and acidified with hydrochloric acid (HCl) to pH < 2 before storage in the dark at 4 °C. The remaining peat suspension from the samples extracted by dithionite and sulfate was further extracted with 0.1 mol L^{-1} HCl to release additional ions that may have precipitated during the dithionite extraction (Wagai and Mayer 2007). We refer to these secondary extractions as dithionite + HCl and sulfate + HCl, respectively. The HCl extraction was done by adding 20 ml of 0.1 mol L^{-1} HCl to the remaining peat suspension, shaking for 1 h, and centrifuging for 10 min at 20,000 g. The supernatant was removed and stored in the dark at 4 °C. The dithionite extraction alone (without HCl) had a slightly lower pH than the sulfate extraction, measuring 3.2–4.3 vs. 3.6–5.8 on a subset of 7 samples. The dithionite + HCl and sulfate + HCl extractions had similar pH values (1.7–1.8 and 1.6–1.7, respectively).

The difference in element concentrations measured between the dithionite and sulfate extractions represents elements released during the reduction of Fe(III) to Fe(II) and any influence of pH differences between the extractions, whereas the difference between the dithionite + HCl and the sulfate + HCl extractions would also include any additional elements extracted by dithionite via Fe(III) reduction that were subsequently complexed in the peat or co-precipitated, but were soluble in the secondary HCl extraction. By calculating the difference between element concentrations in dithionite and sulfate extractions, and comparing with the difference between dithionite + HCl and sulfate + HCl, we can estimate elements extracted by Fe(III) reduction vs. elements extracted by HCl. If dithionite minus sulfate is approximately equivalent to dithionite + HCl minus sulfate + HCl then we can attribute the difference in dithionite minus sulfate to largely reflect Fe-associated elements (Table S2), rather than a result of the difference in pH between extractions. Given that these values were equivalent for many elements (Figure S1), we narrowed our subsequent focus to comparison of the dithionite and sulfate extractions.

Iron, Al, Mg, Mn, Ca, potassium (K), and P in the extractions were measured with inductively coupled plasma optical emission spectrometry (ICP-OES; Perkin Elmer Optima 5300 DV, Waltham, Massachusetts, USA). Using Fe as an example, the dithionite, sulfate, dithionite + HCl, and sulfate + HCl extractions were denoted as Fe_d, Fe_s, Fe_{d+HCl}, and Fe_{s+HCl}, respectively. A subset of the dithionite + HCl and sulfate + HCl extractions (146 out of 242 total samples) was also analyzed by ICP-OES to test for additional ions bound or complexed with organic matter or precipitated in the dithionite extraction, as described above. We also measured silicon (Si) concentrations in a subset of the dithionite and sulfate extractions (57 samples) to test for the presence of silicate phases dissolved by the extractions. Element concentrations in the dithionite + HCl extractions were calculated as the sum measured in the dithionite and in the following HCl extraction after accounting for the residual remaining from the previous extraction. Elements in the sulfate + HCl extractions were calculated in a similar way. Dissolved organic carbon (DOC) and total nitrogen (N) in the dithionite, sulfate, dithionite + HCl, and sulfate + HCl extractions were measured on a Shimadzu TOC-L (Columbia, Maryland, USA). Samples were filtered through pre-combusted glass fiber filters (Whatman GF/F, nominal pore size 0.7 µm) prior to measurement. A subset (48 samples) of the dithionite + HCl and sulfate + HCl extractions was measured for DOC and N to assess precipitation or complexation during the dithionite extraction as described above.

Concentrations of DOC, N, Fe, Al, Mg, Mn, Ca, K, P, and Si in the extractions (Table S1) were compared to concentrations in monthly porewater samples measured at multiple depths over at least six years at four of the sites where peat was sampled (see the Supplementary Information for further details; Griffiths et al. 2016; Sebestyen et al. 2021b, c, d). Briefly, porewater was sampled at 0, 30, 50, 100, and a depth between 150 and 200 cm depending on peat depth or physical properties of each sampling site. Porewater sampling depths do not precisely correspond with the depths of peat sampling and are presented to illustrate trends in element concentration with depth, and to compare their relative magnitude with values from peat extractions. Porewater data were not available for the sites S4, S6, and Junction. Solution C was measured as total organic carbon (TOC) in the porewater samples, as TOC is equivalent to DOC in these peatlands (Sebestyen et al. 2021a) and will hereafter be referred to as DOC. Total N and total P were also measured in the porewater.

To compare elements released in the peat extractions with the porewater values, we expressed

extracted element concentrations on a porewater concentration basis by dividing the extracted element mass by the moisture volume of each sample (Figs. 2, 3, and S2). We compared the peat samples to the porewater in this way because the elements in the extractions appear to represent dynamic pools (Curtinrich et al. 2022) that have the potential to be released to or sorbed from the porewater. We estimated the concentration of C bound with the non-redox-active metals Ca and Al as DOC_s minus the average DOC_{pore} in the bogs and poor fens or in the rich fen. Bulk density data were available for five of the seven sites and showed similar values and trends with depth among sites (Figure S3), such that patterns in element concentrations among sites could likely be extrapolated to element stocks. We did not conduct a formal statistical comparison between the porewater and extraction datasets given the differences in how they were collected, and for clarity, we reported the median values for each element by samples binned from 0–30 cm depth (i.e., the variably saturated acrotelm) and > 30 cm depth (i.e., the persistently saturated catotelm; Table 2).

Statistical analyses

Cluster analysis based on Fe, Ca, Mg, and Al concentrations in the dithionite extraction was used to determine whether the chemical composition of different peat samples segregated consistently among peatland types. Clustering was done with the functions "hclust" and "as.dendrogram" using the R 'stats' package (R Development Core Team 2023) using a Euclidian distance matrix of Fe, Ca, Mg, and Al in mmol L^{-1} and UPGMA (Unweighted Pair-Group Method using Arithmetic mean), where samples are added to a cluster based on the average distance to the points in the cluster. Bog and poor fen samples were similar (Figure S4) and thus were grouped together in subsequent figures (Figs. 2, 3, S1, and S2) and in calculations of averages medians, and ranges. Most rich fen samples distinctly separated from bog and poor fen samples (Figure S4) and were therefore plotted separately.

To compare the effects of the dithionite and sulfate extractions on element concentrations released from peat among sites and depths, we fit a linear mixed model for each element with the natural log of the ratio of the concentration in the dithionite extraction to the concentration in the sulfate extraction as the response variable, known as the log response ratio (Hedges et al. 1999). We also fit a second set of models using the natural log of the element concentration in each extraction as the response variable. We used the package "lme4" (Bates et al. 2015) to fit the models and "lmertest" (Kuznetsova et al. 2017) to obtain an analysis of variance (ANOVA) table with p values. We included the following candidate variables in the model for each element: a random intercept for each core, a random slope for sampling depth within each core, linear and quadratic terms for depth, a site category (discussed below) and interactions between linear depth and a site category. Models were first evaluated to determine the optimum variable to account for the spatial structure of the data, using either the individual sites defined in Table 1, peatland type (bog, poor fen, rich fen), or a simpler peatland type variable based on our cluster analysis and porewater data, where bog and poor fen sites were grouped and contrasted with the rich fen. Porewater from the S1 and S2 bogs were similar to the poor fen Bog Lake and distinct from the rich fen S3 (Griffiths et al. 2019). For models including separate values for each extraction (as opposed to their log ratio), we also tested candidate fixed effects for extraction, extraction by depth, extraction by spatial structure, and three-way interactions. We used Akaike's Information Criterion (AIC) values of models fit using restricted maximum

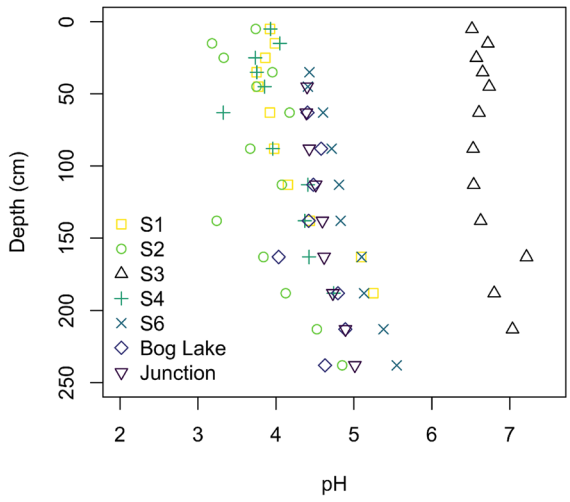

Fig. 2 Mean peat pH values for each site plotted by the midpoint of each sampled depth increment

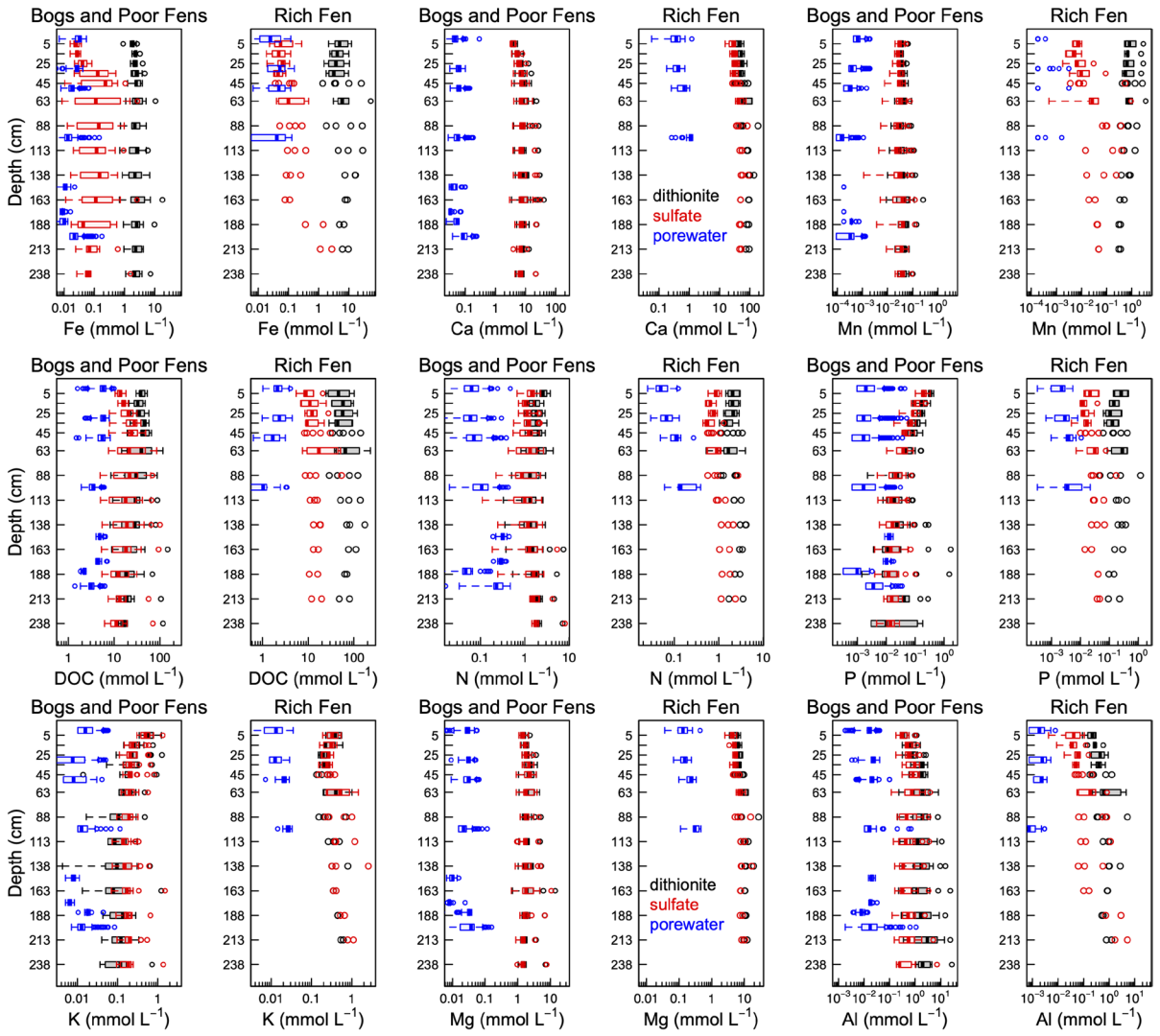

Fig. 3 Element concentrations in the dithionite and sulfate extractions, expressed on a porewater concentration basis, compared with porewater data available from a subset of sites. The color scheme is defined in the panel showing the Ca data for the rich fen. Sites are grouped into bogs and poor fens vs. the rich fen. Depths with fewer than 6 samples are shown as dots only instead of boxplots, and porewater samples with values less than the axis limit are not shown

likelihood to determine the optimal random effects structure and to select the optimum spatial structure variable (site, peatland type, or bog or poor fen vs. rich fen). We then used p values of fixed effects and stepwise backward elimination for models fit using maximum likelihood to select the other fixed effects. Final F values and p values for the models were calculated using restricted maximum likelihood. We used a conservative α of 0.001 for fixed effects to select models that were simpler to interpret, and because many models and parameters were tested. Fixed effect terms were included if an interaction term including the effect was significant. R version 4.0.3 was used for analyses.

Results

Peat from bogs and poor fens was highly acidic and pH generally increased with depth, although mean values from some sites (e.g., S2) varied idiosyncratically with depth. Measurements of pH

Table 2 The median concentration of each element (all values reported in mmol L^{-1}) grouped by peatland type and sampling depth, where 0–30 cm represents the variably saturated acrotelm and > 30 cm is the consistently saturated catotelm

Peatland type	Depth (cm)	Fe			Ca			P		
		Dithionite	Sulfate	Porewater	Dithionite	Sulfate	Porewater	Dithionite	Sulfate	Porewater
Bog/poor fen	0–30	2.07	0.03	0.03	5.01	4.83	0.05	0.19	0.11	0.002
	> 30	2.34	0.1	0.02	8.13	7.21	0.07	0.03	0.03	0.002
Rich fen	0–30	4.15	0.05	0.04	48.41	29.14	0.4	0.16	0.01	0.002
	> 30	7.06	0.11	0.05	67.68	42.88	0.84	0.2	0.03	0.004
Peatland type	Depth (cm)	Mg			Mn			K		
		Dithionite	Sulfate	Porewater	Dithionite	Sulfate	Porewater	Dithionite	Sulfate	Porewater
Bog/poor fen	0–30	1.72	1.64	0.03	0.04	0.03	0.0005	0.33	0.29	0.01
	> 30	1.9	1.72	0.03	0.04	0.03	0.0002	0.13	0.18	0.01
Rich fen	0–30	6.4	4.84	0.14	0.69	0.01	0	0.23	0.28	0.01
	> 30	8.96	7.27	0.26	0.6	0.03	0	0.29	0.37	0.02
Peatland type	Depth (cm)	Al			N			DOC		
		Dithionite	Sulfate	Porewater	Dithionite	Sulfate	Porewater	Dithionite	Sulfate	Porewater
Bog/poor fen	0–30	0.65	0.5	0.02	2.02	1.17	0.06	36.77	14.95	5.76
	> 30	1.83	0.54	0.02	1.67	1.27	0.17	29.48	18.77	3.56
Rich fen	0–30	0.28	0.05	0.002	2.04	0.75	0.06	54.49	10.88	2.27
	> 30	0.65	0.1	0.001	2.22	0.94	0.12	70.19	13.14	1.22

across individual samples from each site varied as follows: S1 = 3.6–5.7, S2 = 2.7–4.9, S4 = 2.9–4.7, S6 = 4.3–5.6, Bog Lake = 3.2–4.9, and Junction = 4.3–5 (note that site mean values are shown in Fig. 2). The S3 rich fen peat was weakly acidic to neutral (5.8–7.4). For many elements, the difference in concentration between the dithionite and sulfate extraction was similar to the difference between the dithionite + HCl extraction and sulfate + HCl extraction (Figure S1). For example, in the bogs and poor fens, DOC_d—DOC_s (median: 98.6 umol g^{-1}; range: -30.5–572.0 umol g^{-1}) was similar to DOC_{d+HCl}—DOC_{s+HCl} (median: 107.4 umol g^{-1}; range: -134.4–596.9 umol g^{-1}), and similar trends were observed for N, P, Mn, and K (Supplementary Results). There were some elements where differences between the dithionite and sulfate extractions tended to diverge from the differences between the dithionite + HCl and sulfate + HCl extractions, and the S3 fen tended to have larger differences than the bogs and fens, especially for Fe, Al, Mg, and Ca (Figure S1). With these caveats, we subsequently focused on the dithionite and sulfate extractions for clarity of interpretation.

Element concentrations in dithionite and sulfate extractions tended to be much greater than porewater (by as much as two orders of magnitude) regardless of depth, with few exceptions (Fig. 3). Concentrations of Si_d, Si_s, and Si_{pore} were similar, indicating that the salt extractions did not dissolve silicate minerals (Figure S2). Concentrations of Fe_d were several-fold greater than Fe_{pore} for all depths, but Fe_s was similar in magnitude to Fe_{pore}. For almost all other measured elements, element concentrations in the sulfate extractions were greater than porewater values (Fig. 3, Table 2).

The linear mixed models of the log ratio of the dithionite and sulfate extractions showed that extraction and either site, peatland type, or bog or poor fen vs. rich fen were important predictors for most elements, and depth and interactions were important for some elements (Fig. 4). Each optimum model (Table S3) included random intercepts for individual peat cores and the optimum models for DOC, P, and K also included random slopes for depth within core. Site was the optimal spatial predictor for Fe, Ca, and Al, peatland type (bog vs. poor fen vs. rich fen) was the optimal spatial predictor for P and N, and bog or

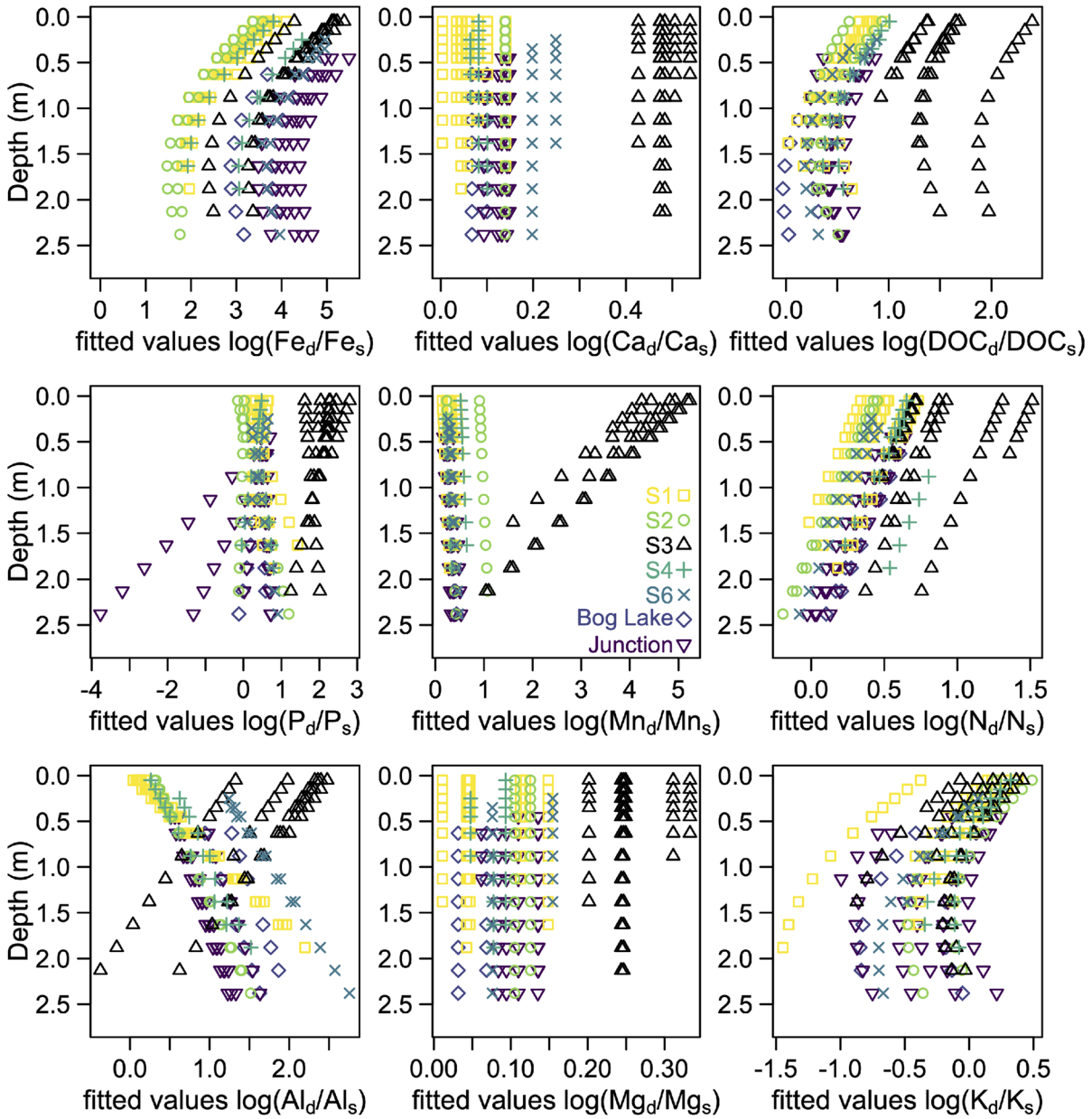

Fig. 4 The predicted values of linear mixed models of the log ratio of element concentrations in the dithionite and sulfate extractions, plotted by sampling depth, site, and peat core

poor fen vs. rich fen was the optimal spatial predictor for DOC, Mn, and Mg. Depth was a significant linear predictor for Fe, DOC, Mn, N, Al, and K ($p < 0.001$) and there was a significant quadratic trend with depth for Fe, DOC, and K ($p < 0.001$, Table S3).

For the models of the log ratio of the element extraction data, predicted values > 0 indicated that concentrations in the dithionite extractions were higher than in the sulfate extractions. Predicted values were generally positive for each element except K (Fig. 4), indicating that dithionite extracted more of each element (except K) than sulfate did. The redox-active elements Fe and Mn had the highest predicted values and the S3 fen generally had higher values than

the other sites for Ca, DOC, P, Mn, N, and Mg, but not for Fe. There was a significant interaction between depth and site for Al and between depth and bog or poor fen vs. rich fen for Mn ($p < 0.001$, Table S3), illustrated by the contrasting patterns of fitted values with depth among sites (Fig. 4). At all sites, predicted values for Fe, DOC, and K varied quadratically with depth, starting high at the surface and decreasing to about 175 cm. The predicted values for several other elements (Mn, N, and Al) varied linearly with depth: N decreased with depth, Al increased with depth in the bog and poor fen samples but decreased in the S3 fen, and Mn slightly increased with depth in the bog and poor fen samples but decreased in the S3 fen (Fig. 4).

The linear mixed models using the log of the element concentration as the response variable allowed us to compare the absolute (rather than relative) concentrations in each extraction, but these models were more complex due to differing trends between extractions and depth among sites (Fig. 5). The optimal log element concentration models (Table S4) showed that extraction was a significant predictor for each element ($p < 0.001$) except K. Site was the optimal spatial predictor for Fe, Ca, DOC, P, N, Al, and Mg, and it was significant in the models for Ca, Al, and Mg ($p < 0.001$). Site was not significant but was retained in the models for Fe, DOC, P, and N due to significant interactions with depth. Bog or poor fen vs. rich fen was the optimal spatial predictor and it was significant and retained in the model for Mn ($p < 0.001$, Table S4). Peatland type was the optimal spatial predictor for K (indicated by AIC) and was retained in the model due to a significant interaction with depth. Each optimum model (Fig. 5, Table S4) had a random slope of depth within core and a random intercept for each core. Depth was a significant predictor for Fe, Ca, P, Mn, and K ($p < 0.001$) and a quadratic depth term was significant for Fe, Ca, P, N, and K ($p < 0.001$). There were significant interactions of extraction by depth for Fe, DOC, Mn, N, Al, and K ($p < 0.001$), extraction by bog or poor fen vs. rich fen for Mn ($p < 0.001$), site by extraction for Fe, Ca, DOC, P, N, and Al ($p < 0.001$), depth by bog or poor fen vs. rich fen for Mn ($p < 0.001$), peatland type by depth for K ($p < 0.001$), site by depth for P ($p < 0.001$), extraction by depth and bog/poor fen vs. rich fen for Mn ($p < 0.001$), and site by extraction and depth for Al ($p < 0.001$).

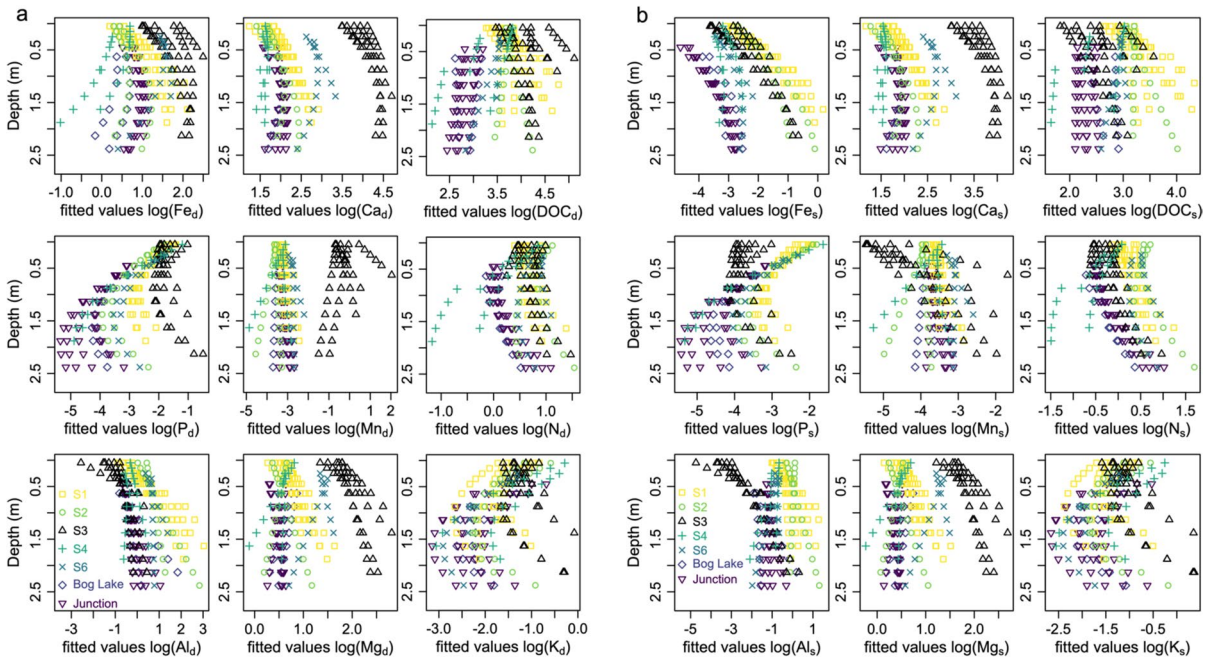

Fig. 5 The predicted values of linear mixed models of the element concentrations in the dithionite extraction **a** and sulfate extraction **b** plotted by sampling depth, site, and individual peat core

The linear models of log element concentration showed that across all depths, the S3 rich fen consistently had the highest predicted values of dithionite-extractable Ca, Mg, and Mn and sulfate-extractable Ca and Mg, but this pattern was not always observed for the other elements, consistent with the differences in spatial predictors among models described above (Fig. 5). Individual cores from the S3 rich fen had the highest predicted values for dithionite-extractable P, Fe, and DOC, but values were highly variable among cores and depths from that site, such that there was no significant spatial predictor of Fe, P, or DOC in the models; S3 had similar predicted values for dithionite-extractable N as the other sites (Fig. 5 and Table S4). The S1 and S6 bogs, rather than the poor fens (bog lake and junction), generally had the next highest predicted values (after S3) of dithionite-extractable Fe, Ca, and Mg, and sulfate-extractable Ca and Mg.

Discussion

Metals are important for C and nutrient stabilization in upland soils (Chacon et al. 2006; Wagai and Mayer 2007; Kleber et al. 2015; Wang et al. 2021), but they have received little attention as possible drivers of C and nutrient cycling in mineral-poor peatlands. Researchers have examined metal-C interactions in peatlands (e.g., Riedel et al. 2013; Kügler et al. 2019; Herndon et al. 2019; Curtinrich et al. 2022; Zhao et al. 2023; Liu et al. 2024), but few have assessed variation of metal-C relationships within or among peatland hydrologic types (Huang et al. 2021), especially as a function of depth. Consistent with our first hypothesis, we found that element concentrations in the dithionite and sulfate extractions were almost always greater than long-term porewater values, implying that substantial pools of metals and associated organic compounds were bound with the peat. Consistent with our second hypothesis, element concentrations were almost always greater in the dithionite extraction than in the sulfate extraction and the difference between the extractions (expressed as a log ratio) often but not always decreased with depth, indicating the importance of redox-active metals in binding elements with peat, particularly in the variably oxic surface peat. Partially refuting our third hypothesis, the statistical models showed that spatial variation in most extracted elements was more strongly associated with individual peatland sites than peatland types (i.e., bog, poor fen, rich fen). Element concentrations were not consistently greatest in the S3 rich fen for all elements and depths, and values from the bogs and poor fens varied idiosyncratically and often differed among sites. This finding implies that biogeochemical factors other than the presence or absence of groundwater inputs impacted the amount and composition of salt-extractable elements, even in the case of the bogs, where contemporary metal inputs originate entirely from atmospheric deposition (Curtinrich et al. 2022).

Roles of redox-active metals in binding organic matter and nutrients

As expected, concentrations in the dithionite extractions were greater than in the sulfate extractions for almost all elements (except K; Figs. 4 and 5). Dithionite is a strong reductant and was used to reduce Fe(III) to Fe(II), while sodium sulfate, the oxidation product of sodium sulfate, was used as a control to extract ion-exchangeable elements (Reemtsma et al. 1999; Wagai and Mayer 2007). When Fe(III) is reduced to Fe(II), elements that were bound to Fe, such as C and P, may be released (Chacon et al. 2006; Chen et al. 2020), along with any elements that were directly or indirectly bound with the organic matter, such as organic N, or the occluded cations Ca, Mg, or K (Hall and Huang 2017). Therefore, the differences in element concentration between the dithionite and sulfate extractions largely represent elements that were extracted by chemical reduction (principally Fe) or elements that were associated with those reduced elements. The difference between the dithionite and sulfate extractions could also be influenced by the slightly lower pH of the dithionite extraction, although additional measurements showed that effects of the lower pH of the dithionite extraction were largest in the S3 fen (Figure S1).

The median ratio of Fe-associated C to Fe-associated N was 26 (Table S2), suggesting that Fe-bound organic matter could be derived from partially decomposed plant biomass, with possible contributions from microbial residues. Microbial residues have an average C/N of 8.5 (Cleveland and Liptzin 2007) while plant foliage in the S1 bog had a C/N of 15–76, *Sphagnum* had a C/N of 28–63, and twigs had

a C/N of 52–126 (Phillips et al. 2017). The plant foliage in the Mer Bleue ombrotrophic bog in Ontario had an average C/N of 46 (Wang et al. 2014).

Our dithionite-extracted Fe concentrations were generally lower than values from other bogs and fens reported in the literature. In 10 peatlands (bogs and fens) in China, reactive Fe (0–20 cm) measured 3.5 ± 0.2 g Fe kg^{-1} to 6.3 ± 0.2 g Fe kg^{-1} (mean ± standard error) in three bogs and 6.7 ± 0.5 g Fe kg^{-1} to 12.0 ± 0.2 g Fe kg^{-1} in 7 fens (Huang et al. 2021); no data were collected below 20 cm. In another study of Chinese peatlands, 0–20 cm dithionite-extractable Fe was even higher, averaging 13.7 and 11.3 g Fe kg^{-1}, respectively, for *Sphagnum*- and non-*Sphagnum*-dominated sites (Zhao et al. 2023). For comparison, dithionite-extracted Fe (0–20 cm) at our sites in the Marcell Experimental Forest measured 1.5 ± 0.2 g Fe kg^{-1} (mean ± standard deviation) in the bogs and 2.9 ± 1.4 g Fe kg^{-1} in the rich fen (Table S1). The Chinese peatlands described above generally had several-fold higher Fe-bound C than our bog and fen samples (Huang et al. 2021; Zhao et al. 2023; Table S2), although our Fe-bound C values were often still higher than reported for mineral soils, which vary widely among ecosystems (Ye et al. 2022; Curtinrich et al. 2022). Compared to peatlands in Northeastern Bavaria, Germany (Küsel et al. 2008), we found slightly higher dithionite-extracted Fe in our bogs (0–10 cm: 1.5 g Fe kg^{-1}; 10–20 cm: 1.6 g Fe kg^{-1}; 20–30 cm: 1.3 g Fe kg^{-1}) than in their "acidic upland fen" (0–10 cm: 0.5 g Fe kg^{-1}; 10–20 cm: 0.4 g Fe kg^{-1}; 20–30 cm: 0.3 g Fe kg^{-1}), but our rich fen values (0–10 cm: 3.4 g Fe kg^{-1}; 10–20 cm: 2.5 g Fe kg^{-1}; 20–30 cm: 2.1 g Fe kg^{-1}) were lower than in their "acidic lowland fen" (0 – 10 cm: 18.9 g Fe kg^{-1}; 10 – 20 cm: 9.8 g Fe kg^{-1}; 20 – 30 cm: 3.4 g Fe kg^{-1}). The dithionite-extracted Fe in our rich fen was relatively similar to the reducible Fe measured in a Michigan fen, while Mn was about an order of magnitude higher in our rich fen (Koretsky et al. 2007).

In our study, we found that individual peatlands not only differed in their log ratios of dithionite- and sulfate-extractable Fe and DOC, but that the peatlands with higher Fe log ratios did not always have higher DOC log ratios. This finding implies that the pool of reduceable Fe was not directly related to Fe-bound C (Fig. 4), counter to findings from a study of peatlands with greater mineral content than our sites (Liu et al. 2024), but similar to the conclusion of a synthesis that examined predictors of Fe-bound C and nutrients among diverse ecosystems (Ye et al. 2022). The much lower pH values in the bogs than in the rich fen (Fig. 2) imply greater Fe solubility and a likely difference in Fe speciation among these sites. Under increasingly acidic conditions, a greater fraction of Fe is likely bound with organic matter rather than with oxygen in Fe oxyhydroxide mineral phases (Herndon et al. 2019), thereby increasing the capacity of a given Fe atom to bind with C and N. Consequently, low-pH soils tend to have greater Fe-bound organic C (Ye et al. 2022), partially counteracting differences that would be expected if Fe content alone were controlling the amount of Fe-bound C. These pH effects on Fe speciation are one mechanism that might explain the decoupling between reducible Fe content and Fe-associated C observed in our study.

Roles of non-redox-active metals in binding organic matter and nutrients

In addition to the redox-sensitive metals (principally Fe, given generally low Mn content), non-redox-active metals such as Ca and Al likely contributed to binding organic matter in these peatlands. In upland soils, Ca often binds significant C by bridging between negatively charged surfaces in clays and/or between organic molecules (Kalinichev and Kirkpatrick 2007; Rowley et al. 2018; Wang et al. 2021). In acidic peatland soils, Al is much more soluble than in upland mineral soils with circumneutral pH, and Al may also bind organic matter through cation bridging and co-precipitation (Schaumann et al. 2013). The DOC solubilized after extraction of soil with sodium sulfate is often interpreted as Ca-bound C in mineral soils because high concentrations of Na will disrupt cation bridges, which are largely thought to be mediated by Ca in soils with circumneutral pH (Ye et al. 2018). In acidic peatland samples, this DOC may also include a portion of C formerly bound with Al that was released during the extraction. Indeed, median Al in the sulfate extraction was ~ 25-fold greater than in porewater, implying that substantial Al had been solubilized by cation exchange with Na. Nevertheless, median Al was at least tenfold lower than Ca on a molar basis in the sulfate extraction, implying that Ca was likely important in binding DOC through cation bridging in these samples.

Assuming that the DOC released in the sulfate extraction mainly reflected Ca-bound C, values from these mineral-poor peatlands (estimated as TOC_s—TOC_{pore}) were slightly greater than Ca-bound C in some other upland soils even though the sulfate-extracted Ca in the peatlands was generally lower (with the exception of the rich fen). The concentration of Ca-bound C (0–10 cm), extracted in a similar way to our samples, measured 0.78 ± 0.75 mg g^{-1} (mean ± standard deviation) across 22 Chinese grasslands, and Ca was 3.08 ± 1.65 mg g^{-1} (Wang et al. 2021). In our samples, putatively Ca-bound C (0–10 cm) measured 1.66 ± 0.58 mg g^{-1} in the bogs and poor fens and 1.09 ± 0.53 mg g^{-1} in the rich fen, and Ca_s was 2.30 ± 0.48 mg g^{-1} in the bogs and poor fen and 10.82 ± 0.90 mg g^{-1} in the rich fen. These results highlight that substantial exchangeable Ca stocks and associated C can be present in peat soils despite their overall acidic pH values, likely due to the high overall cation exchange capacity characteristic of many peat samples (Schaumann et al. 2013).

Implications for global change

The higher element concentrations in the sulfate and dithionite extractions compared to the porewater across the peat profile suggests that these elements could be released into the porewater with environmental change. Warmer temperatures may promote Fe(III) reduction and the release of Fe-associated elements, provided that the peat remains saturated with water (Curtinrich et al. 2022). However, expected increases in evapotranspiration with warming (Helbig et al. 2020) may lead to lower water tables and greater aeration of peat during the summer (Roulet et al. 1992; Hanson et al. 2020). This could increase Fe oxidation and potential for binding C and nutrients. Conversely, higher water levels and saturation from increased precipitation or snowmelt (Dasgupta et al. 2010) could promote Fe(III) reduction to Fe(II) and release of associated elements (Curtinrich et al. 2022). Changes in water table could also vary by site due to local influences. The water table of some Marcell bogs has increased from 1961 to 2019 while it has decreased in others (Stockstad et al. 2021). Some of our study peatlands (e.g., S4 and S6) experienced historical disturbances such as deforestation of the surrounding watershed and transient water level increases that conceivably might have influenced extractable elements, but values measured at these sites did not consistently differ from the other peatlands. Changes in ionic strength and pH from shifts in hydrology, extreme precipitation, or vegetation could also affect elements released from the peat by ion exchange and lead to a higher or lower concentration of these in the porewater. For example, the pH of stream water draining the S2 bog has decreased in recent decades (Urban et al. 2011; Sebestyen et al. 2022). Alternatively, *Sphagnum* moss may decrease in bogs with increasing temperatures (Norby et al. 2019), which could also lead to increased pH since *Sphagnum* contributes to the low pH of bogs (van Breemen 1995). Dynamics of metal-mediated sorption and release of C and nutrients from peat could potentially contribute to long-term variation in DOC export from peatland catchments, a topic for future research given the importance of DOC fluxes in peatland C budgets (Dinsmore et al. 2010; Griffiths et al. 2017).

Conclusions

Anaerobic suppression of enzyme activity, acidic conditions, and cold temperatures are typically thought to regulate production of DOC and release of nutrients from decomposing organic matter in peatlands (Bergman et al. 1999; Freeman et al. 2001; Hanson et al. 2020). Here, we show that in addition to those factors, metals impact DOC and nutrient availability across diverse peatland types (bogs, poor fens, and a rich fen) within the same landscape. Extractions showed that substantial element stocks were bound directly or indirectly with the peat, and these peat-bound elements could be sensitive to redox or geochemical changes expected with climate change. On average, the concentrations of these elements extracted from the peat were much greater than the concentrations already present in the porewater, suggesting release from peat to the porewater could be ecologically relevant, especially given that these ecosystems are typically N and P limited (Bridgham et al. 1996; Wang and Moore 2014; Hill et al. 2014). The mechanisms regulating the accessibility of elements (redox and non-redox sensitive mechanisms) varied within and among peatland types, and the rich fen did not have

consistently greater values for many extracted elements despite its groundwater input. Notably, the average Fe-bound C concentration at the surface of the bogs was only slightly lower than the rich fen despite lower metal content, and dithionite-extractable elements (e.g. Fe and DOC) tended to peak toward the middle of the peat profile, rather than the surface. Both of these findings are consistent with previously observed differences in Fe speciation among sites and depths (Herndon et al. 2019) and increased complex formation between organic molecules and individual Fe atoms under acidic conditions, leading to greater binding of C and nutrients per unit Fe (Ye et al. 2022). Given our findings, previous conclusions based on shallow peat sampling depths and extrapolation of data from terrestrial soils to peatlands would underestimate the potential biogeochemical importance of redox-dynamic elements in peatlands and their potential to mediate C and nutrient availability in a changing climate.

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Author contributions All authors contributed to study design. Peat core data were collected and analyzed by HJC, all additional data were synthesized by SDS, and the manuscript was written by HJC and SJH with input from SDS.

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Data availability Datasets used in this study are publicly available from the Environmental Data Initiative repositories cited in the References section and in the Supplementary Material.

Declarations

Competing Interests The authors declare no competing interests.

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