

The Biogeochemistry of Metal-Contaminated Peatlands in Sudbury, Ontario, Canada

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Received: 1 June 2015 / Accepted: 31 July 2015 / Published online: 4 September 2015
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Abstract Understanding the biogeochemistry of metal-contaminated peatlands is important for predicting the impact of mining and industrial activities on peatlands and downstream surface waters and for predicting recovery of previously impacted sites. The objective of this work was to characterize the factors controlling spatial and temporal variability in surface peat (0–15 cm) and pore water chemistry of 18 regionally representative peatlands in Sudbury, Ontario, Canada. The pollution gradient is clearly evident as Cu and Ni concentrations in surface peat are elevated close to the main Copper Cliff smelter. Surface peat also differs greatly in acidity (pH) and organic matter content among sites, and dissolved organic carbon (DOC) concentrations in pore water are positively correlated with peat carbon content. In addition, sites having surface peat that is more decomposed also have pore water DOC that is more humified. Pore water chemistry varies seasonally; samples taken in late summer and fall were characterized by higher SO_4 , and lower pH and higher concentrations of base cations and metals such as Ni, Co, and Mn compared with those in late spring that had higher DOC, higher pH, and higher concentrations of metals such as Cu and Fe. Despite the large spatial and temporal variability in pore water chemistry, soil-solution partitioning (K_d) of some metals (Ni, Co, and Mn) can be explained by pH alone. Modeling soil-solution partitioning for these metals and Cu, Al, and Fe is significantly

improved with the addition of SO_4 ; dissolved organic matter quality and quantity and/or the $\delta^{18}\text{O}$ signature of the pore water in regression models indicating several factors other than acidity has an influence on pore water chemistry.

Keywords Wetlands · Metals · Sudbury · Dissolved organic carbon · Acidity · Peat · Climate

1 Introduction

Sudbury, Ontario, is perhaps the most widely studied region in the world with respect to the impact of metal and acid deposition on the surrounding ecosystem (Hutchinson and Whitby 1977; Keller et al. 2007). Previous work has clearly shown that metal deposition decreases in a logarithmic fashion from the main smelters (dominated by the Copper Cliff smelter) and that metal levels in soils and surface waters follow a similar pattern (Dudka et al. 1995; Gignac and Beckett 1986; Hazlett et al. 1984). During the early development in Sudbury (circa 1900), roast beds were used to process the metal ore, which required large volumes of timber that was supplied from the surrounding forest (Gunn et al. 1995). The combination of widespread deforestation and high metal levels in soil along with high atmospheric SO_2 levels led to the creation of large swaths of barren lands (Gunn et al. 1995; Winterhalder 1996). These industrial processes eventually led to isolated pockets of usually metal-tolerant flora and high levels of soil erosion (Gunn et al. 1995; Winterhalder 1996). Lakes in the Sudbury

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region were equally affected, with many lakes acidifying, which when combined with high levels of copper (Cu) and nickel (Ni) resulted in the loss of fish species and other aquatic biota (Keller et al. 2007). In response to concerns over the devastating ecological impacts, the emissions of metals and sulphur (S) have decreased dramatically (>95 %) since the 1970s resulting in the chemical recovery (increase in pH) of many lakes (Keller et al. 2007). Due to large reclamation efforts (liming and tree planting), the forests are slowly recovering (Winterhalder 1996), although it has been estimated that the chemical recovery of soils may take centuries even with the elimination of metal emissions from the smelters (Meadows and Watmough 2012).

In contrast to aquatic and upland ecosystems, wetlands in the Sudbury region have been relatively less studied, yet they are prevalent in the Sudbury area (Monet 2013). Studies conducted almost 40 years ago showed that peatlands close to the smelters were heavily enriched with Cu and Ni. In addition, vegetation, and *Sphagnum* in particular, in wetlands within 10 km of the main Copper Cliff smelter were heavily impacted with sensitive species missing entirely (Gignac and Beckett 1986). Much less is known about the biogeochemistry of peatlands in the area and factors that control metal release to pore water. Previous studies have shown that dissolved organic carbon (DOC) and pH (H^+) are the two most important variables that control metal release to soil solution, although the relative importance of these two factors varies by metal and soil type (Tipping et al. 2003). Studies have also shown that biogeochemical process occurring in wetlands can result in large changes in pH and DOC concentration in pore water. For example, following summer droughts, SO_4 concentrations in water-draining peatlands increase dramatically due to the oxidation of S stored in peat and subsequent rewetting events that generate sulphuric acid leading to a decrease in pore water pH (Eimers et al. 2007). The increase in acidity has been shown to result in elevated metal export from wetlands (Juckers and Watmough 2014; Szkokan-Emilson et al. 2013). Wetlands are also major sources of DOC to aquatic ecosystems, and in the Sudbury region, terrestrial DOC production has recently been linked with increased aquatic productivity in the area (Tanentzap et al. 2014). Several metals (e.g., Cu) are known to have strong affinities for DOC, and because DOC concentrations in surface waters can vary seasonally and

spatially (Dillon and Molot 1997), differences in metal mobility among sites and by season may be expected. Additionally, DOC is a heterogeneous mixture of organic molecules with differing aromaticity, molecular weight, and functional groups that may modify metal toxicity to aquatic organisms (Guéguen et al. 2012). Changes in DOC concentration seasonally may reflect changes in the source of DOC, which may be reflected in altered DOC composition. For example, allochthonous dissolved organic matter (DOM), derived from terrestrial plant material outside of the lake, is more aromatic and has a higher molecular weight than autochthonous material that originates from biological processes within the lake (McKnight et al. 2001). Richards et al. (2001) found that high molecular weight allochthonous material tends to have more carboxylic and phenolic functional groups that act as sites of reactivity and metal binding. While it is recognized that several processes occur in wetlands that may influence metal release to solution, no attempt has been made to evaluate whether metal concentrations in pore water are predictable in wetlands that vary widely in metal contamination as well as pH and organic matter content.

As peatlands often operate at the interface between terrestrial and aquatic ecosystems and can greatly modify the chemistry of water entering lakes (Szkokan-Emilson et al. 2014), gaining a greater understanding of wetland biogeochemistry of a metal-contaminated peatland is critical to understanding and predicting the recovery process and the need for further emission reductions. Specifically, in this study, we sought to investigate how peat and pore water chemistry varies spatially and seasonally among 18 regionally representative peatlands in Sudbury that vary in a range of physical and chemical characteristics and in their exposure to past and present metal and acid deposition. Sudbury was chosen because of the range in peatland characteristics as well as the expected variability in metal contamination, and we expect that results from this work would be broadly applicable to other northern peatlands. We hypothesized that metal concentrations in pore water could be predicted using parameters that reflect the degree of past and present metal contamination, peatland acidity, organic matter content, and

hydrology. We also expected that pore water chemistry would vary seasonally, reflecting the influence of drought (changing water table height) and organic matter mineralization.

2 Methods

The Sudbury area (46° 30' N, 81° 00' W) is located on the southern province of the Canadian Shield in central Ontario, Canada, and has a mean elevation of 300 m above sea level. The Sudbury area experiences a continental climate. The long-term average daily temperature in January is −13.6 °C, increasing to 19 °C in July. The total annual precipitation averages 657 mm of rainfall

and 243 mm of snowfall (water equivalent) and is distributed relatively uniformly throughout the year.

3 Study Sites

The 18 study sites were located between 6 and 43 km from the main (Copper Cliff) smelter extending primarily in a northwest direction, starting just west-southwest of the city of Sudbury (Fig. 1). The 18 sites are considered to be regionally representative based on a larger survey of >50 wetlands in the area and are dominated by shrubs (primarily *Chamaedaphne calyculata*) and sedges and range in size from 0.20 to 5.86 ha with an average wetland size of 1.3 ha (Table 1). Peatlands

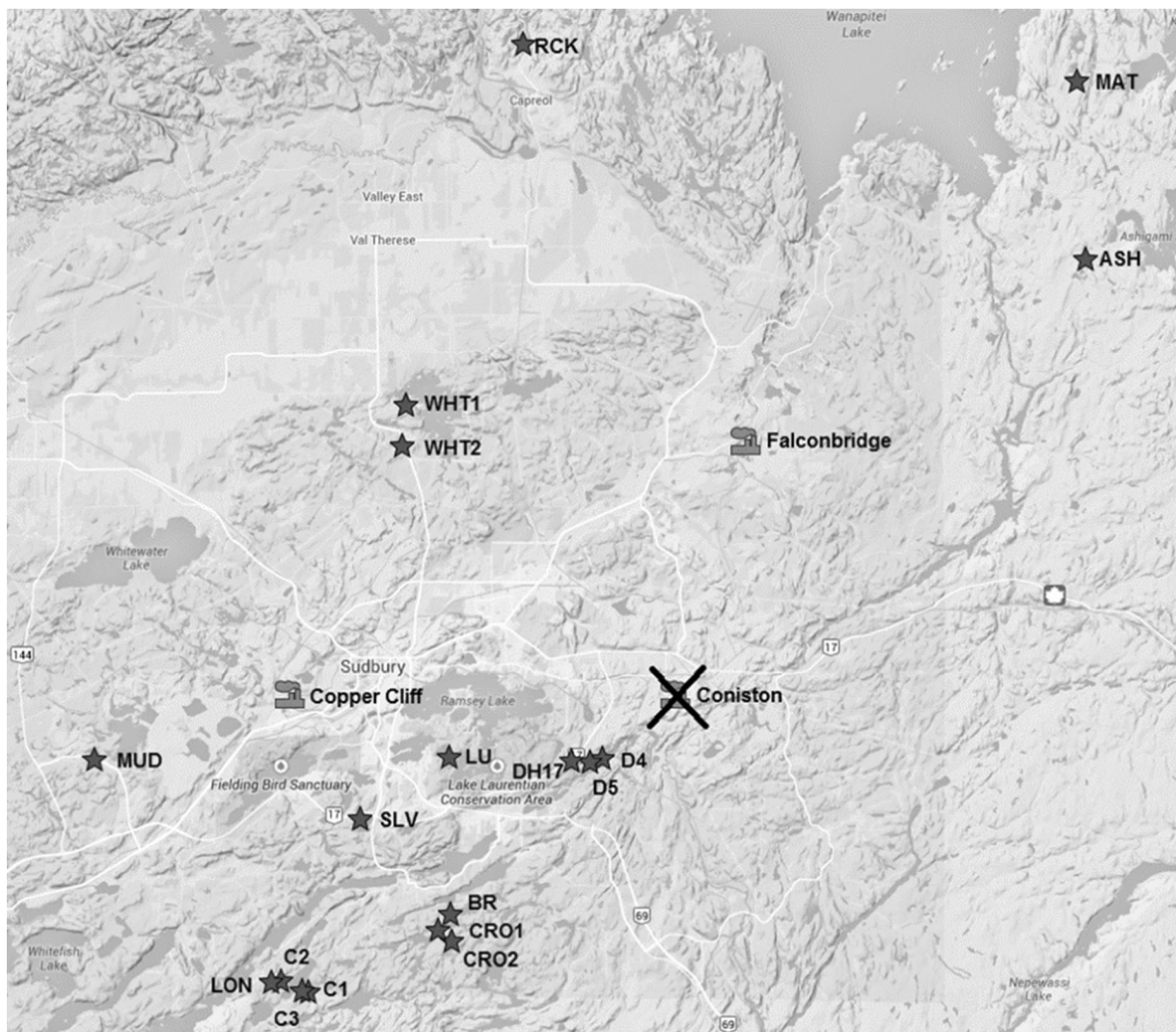


Fig. 1 Location of the study sites and the three primary smelters (Copper Cliff, Coniston, and Falconbridge) in Sudbury, Ontario

draining into the same lake are located in different sub-catchments and are hydrologically unconnected.

4 Field Sampling

Surface (0–15 cm) peat was sampled at three locations in the central portion of each wetland. The distance from the edges of a wetland and the level of interaction with the surrounding catchment can affect the quality and quantity of DOC and nutrients within a wetland (Gignac and Beckett 1986), and so the edges of the wetlands were purposely avoided. Surface peat was sampled on two occasions—during October 2011 and in August 2012. Peat samples were collected by hand and stored in Ziploc bags at 4 °C until processing. Peat pore water was sampled on three occasions to capture potential seasonal variability in chemistry. In October 2011, three shallow (0–30 cm) wells were inserted near the center of each wetland and were approximately 2–3 m away from each of the peat collection sites. Wells were constructed by cutting polyvinyl chloride tubing (ID of 2 cm) into 60-cm-long pieces. Polyvinyl chloride stoppers were

inserted into the bottom end of the tubes to stop debris and peat from entering when inserted into the peat. From approximately 2 cm from the bottom of the wells up to 30 cm, 1-mm slits were cut halfway into the tubing alternating up from side to side, in 1-cm intervals, to allow pore water to flow inside. A fine mesh was slid over the slits as a primary filter, and tin foil with an elastic was used on the top of well to prevent debris from entering in between sampling campaigns. Pore water was sampled from each well using a syringe pump and a 5-mm-diameter plastic hose in October 2011, May 2012, and August 2012. Wells were first emptied with the sample being discarded so that stagnant water in the well was not sampled. The wells were then allowed to refill where a 200-mL sample was obtained. Samples were then filtered through an 80- μ m mesh in the field and stored in 500-mL (acid-washed) Nalgene bottles at 4 °C until processing. At 6 of the 18 sites (C1, C2, BR LU, D4, and D5), water table height was recorded at 15-min intervals using TruTrack™ WT-HR 1000 Water Level Loggers installed in a well in each wetland from 0.70 m belowground to 0.30 m aboveground.

Table 1 Location and characteristics of the 18 wetlands

Site code	Drainage water body	Latitude	Longitude	Distance from Copper Cliff (km)	Area (ha)	Dominant vegetation
ASH	Ashigami Lake	46° 38' 45" N	80° 36' 52" W	42.99	0.41	<i>C. magellanica</i>
BR	Broder Lake	46° 23' 44" N	80° 58' 02" W	11.46	0.92	<i>J. canadensis</i>
C1	Clearwater Lake	46° 21' 56" N	81° 02' 46" W	12.65	5.86	<i>S. atrovirens</i>
C2	Clearwater Lake	46° 22' 10" N	81° 03' 41" W	12.13	2.09	<i>C. calyculata</i>
C3	Clearwater Lake	46° 21' 58" N	81° 02' 59" W	12.17	0.42	<i>C. calyculata</i>
CRO1	Crowley Lake	46° 23' 5" N	80° 57' 58" W	11.69	0.86	<i>K. angustifolia</i>
CRO2	Crowley Lake	46° 23' 5" N	80° 57' 58" W	12.45	1.03	<i>R. alba</i>
D4	Daisy Lake	46° 27' 18" N	80° 52' 57" W	13.93	1.05	<i>M. uniflora</i>
D5	Daisy Lake	46° 27' 13" N	80° 53' 21" W	13.44	2.05	<i>S. purpurascens</i>
H17	Daisy Lake	46° 27' 15" N	80° 53' 60" W	12.62	0.29	<i>C. calyculata</i>
LON	Long Lake	46° 22' 10" N	81° 03' 60" W	11.78	0.22	<i>C. calyculata</i>
LU	Lake Laurentian	46° 27' 18" N	80° 58' 04" W	7.53	3.08	<i>C. calyculata</i>
MAT	Matagamasi Lake	46° 42' 48" N	80° 55' 36" W	39.15	0.47	<i>C. calyculata</i>
MUD	Mud Lake	46° 27' 16" N	81° 09' 55" W	8.30	0.20	<i>C. calyculata</i>
SLV	Silver Lake	46° 25' 54" N	81° 01' 01" W	6.00	1.07	<i>R. alba</i>
RCK	Rockcut Lake	46° 43' 39" N	80° 55' 36" W	29.86	0.46	<i>M. gale</i>
WHT1	Whitson Lake	46° 35' 24" N	80° 59' 30" W	13.88	1.56	<i>D. arundinaceum</i>
WHT2	Whitson Lake	46° 34' 28" N	80° 59' 38" W	12.18	1.09	<i>C. calyculata</i>

Additional samples were taken for measurements of DOM, humification index (HIX), and spectral slope (Sr) in the field and were stored at 4 °C until processing. These measures were taken to evaluate whether the optical properties of DOM varied seasonally or spatially and whether differences in quality influenced metal release to pore water. These extra samples were also filtered through an 80- μm mesh in the field and stored in 25-mL colored glass vials that were previously washed in an acid bath for 24 h and combusted at 500 °C for 4 h to remove all organic material.

5 Chemical Analysis

5.1 Peat Chemistry

Peat samples were air-dried for 3 weeks and then oven-dried at 60 °C for 48 h. Oven-dried samples were milled and pulverized prior to analysis. The pH (H^+ used interchangeably in this study) was measured by adding 25 mL deionized water to 0.2 g sub-samples and reading the solution after 20 min. Sub-samples (0.2 g of dry peat sample) were cold-digested in 2.5 mL of concentrated nitric acid (trace-grade assay 67–70 % HNO_3) for 24 h, followed by hot digestion for 8 h at 100 °C prior to the analysis of aluminum (Al), iron (Fe), manganese (Mn), Ni, Cu, zinc (Zn), cobalt (Co), sodium (Na), potassium (K), calcium (Ca), and magnesium (Mg) by inductively coupled plasma–optical emission spectrometry (ICP-OES). To analyze peat samples for carbon (C), nitrogen (N), and sulphur (S), approximately 0.50–0.70 mg of oven-dried sample was weighed out to a 1:2 plant matter/tungsten oxide ratio and measured for concentrations using an Elementar Vario MACRO CNS analyzer. Trace-grade apple leaves (NIST SRM 1515) were also analyzed with each batch sample, and recovery values were typically between 85 and 95 %.

5.2 Pore-Water Chemistry

The pH of pore water was determined immediately on return from the field. In the laboratory, water samples were vacuum-filtered through 0.45- μm filters, and a sub-sample of approximately 10 mL of sample was mixed with 0.05 mL solution of 1–1 B-Pure water and nitric acid (trace-grade assay 67–70 % HNO_3) prior to analysis by ICP-OES for Ni, Cu, Co, Zn, Al, Fe, Mn, Na, Ca, Mg, and K. Total organic carbon (TOC; of the

dissolved phase only=DOC) in the filtered samples was determined on the TOC-V CPH analyzer by Shimadzu while SO_4 , Cl, and NO_3 were measured using ion chromatography (IC; DIONEX 1100).

5.3 Oxygen Isotopic Analysis

To evaluate whether potential differences in hydrology (e.g., groundwater inputs and amount of evaporation) occurred among the sites that may influence metal concentrations in pore water, we also measured oxygen isotopes in water samples. Oxygen isotopic analysis (ratio of $^{18}\text{O}/^{16}\text{O}$ was measured in the headspace gas of a water sample) was carried out by the CO_2 equilibration method at the Water Quality Centre at Trent University. A 2.5-mL sub-sample of pore water was filtered through a 0.45- μm filter and stored at the Water Quality Centre at 4 °C until analysis. A 300- μL sample of the pore water was then sealed in a septum-capped vial; the headspace was flushed with 5 % CO_2 gas for 5 min followed by 4.5-h equilibration. The resulting headspace CO_2 was then sampled and injected into the Micromass IsoPrime Continuous Flow Isotope Ratio Mass Spectrometer. The $^{18}\text{O}/^{16}\text{O}$ ratio was measured using calibrated standards resulting in $\delta^{18}\text{O}$ values that are relative to the Vienna Standard Mean Ocean Water (VSMOW) on a per mil (‰) basis.

5.4 Spectral Properties of DOM

The spectral slope was determined following the method described by Helms et al. (2008). Samples were filtered through a previously combusted 0.70- μm carbon glass filter and then pipetted into a 1-cm glass cuvette to determine absorbance values (Shimadzu's UV 2550 Spectrophotometer). Absorbance values from the 275–295-nm and 350–400-nm ranges were targeted and converted to the Napierian absorption coefficient (m^{-1}). The humification index (HIX) of DOM in pore water samples was determined by the method described by Zsolnay et al. (1999). Absorbance values obtained from the spectral slope determination were used in order to dilute each sample to below 0.05 AU. This dilution was required to correct for the inner filtering effect of the spectrophotometer. The diluted samples were placed in a 1-cm cuvette and analyzed to record fluorescence at an excitation wavelength of 254 nm (HORIBA Jobin Yvon Spectrophotometer). Emission wavelengths between 300 and 345 nm and 435 and 480 nm were then recorded for HIX calculations. The fluorescence values within each range were plotted,

and the area under each curve was calculated to provide for the unitless HIX value for each of the ranges (300–345 and 435–480 nm).

5.5 Statistical Analysis

There was no significant difference ($p < 0.05$) in peat chemistry collected during the two campaigns; therefore, average values were calculated using the six surface samples from each peatland. Relationships between chemical variables in surface peat were assessed using principal component analysis (PCA). The first two factors of the PCA were used to help identify drivers, relationships, and differences among the variables and the sites under study. Relationships between distance from the Copper Cliff smelter and metal concentrations in surface peat were then assessed for significance using non-linear regression analysis.

Pore water chemistry was first assessed by determining mean, standard deviation, maximum, minimum, and coefficient of variation during all three campaigns. Kruskal-Wallis one-way ANOVA on ranks was run for each variable followed by the post hoc Dunn's test for differences between each sample time. Similar to surface peat chemistry, relationships between metal and SO_4 concentrations in pore water and distance to Copper

Cliff were assessed separately for each sampling campaign.

5.6 Partitioning Coefficients

Metal partitioning coefficients (K_d) were calculated for each sampling period for each wetland:

$$K_d = \frac{\text{Total metal}}{\text{Dissolved metal}}$$

where total metal in soil is in mg kg^{-1} and the total dissolved metal is in mg L^{-1} and the units for K_d are L kg^{-1} . Models, predicting metal partitioning for Al, Fe, Mn, Ni, Cu, Zn, and Co, were then developed using forward stepwise regression and individual sample concentrations. Variables representing DOM quantity and quality (DOC, HIX, and Sr), along with hydrology ($\delta^{18}\text{O}$), acidity (pH), and the SO_4 concentration, were used as potential predictors of metal partitioning in the study sites.

6 Results

Peat chemistry varied considerably among the study sites, with coefficients of variation for all measured parameters ranging from 20 to 94 % (Table 2). Both

Table 2 Summary statistics for peat chemistry at the 18 sites sampled in the Sudbury area

Peat chemistry	Average	St. dev	CV (%)	Median	Minimum	Maximum
Al (g kg^{-1})	8.29	6.64	80.1	5.66	1.66	37.5
Fe (g kg^{-1})	6.65	4.55	68.5	5.33	2.09	24.1
Mn (mg kg^{-1})	70.8	51.1	72.3	54.8	13.7	269
Ni (mg kg^{-1})	610	344	56.3	599	86.9	1829
Cu (mg kg^{-1})	675	451	66.8	630	34.6	1932
Zn (mg kg^{-1})	63.6	35.1	55.1	53.8	15.0	179
Co (mg kg^{-1})	14.6	6.69	45.7	13.0	3.74	44.7
Na (g kg^{-1})	0.55	0.22	39.7	0.51	0.13	1.60
K (g kg^{-1})	0.60	0.36	58.9	0.52	0.10	1.89
Ca (g kg^{-1})	4.52	3.11	68.8	3.96	0.57	14.1
Mg (g kg^{-1})	0.93	0.87	94.3	0.65	0.27	4.65
P (mg kg^{-1})	527	331	62.8	524	0.10	1447
C/N ratio	21.7	4.89	22.5	18.6	16.4	28.9
N (%)	1.90	0.40	20.9	1.86	1.05	2.50
C (%)	39.8	7.59	19.1	41.6	20.8	48.7
S (%)	0.71	0.23	32.6	0.75	0.35	1.13

St. dev standard deviation, CV coefficient of variation

major elements (e.g. Al, Fe, Ca, Mg, and K) and trace elements that are emitted from the smelters (e.g., Cu, Ni, and Co) varied in concentration by between 3- and 15-fold among the 18 sites (Table 2). Maximum concentrations of Ni and Cu in peat exceeded 1800 and 1900 mg kg⁻¹, respectively, at some sites, while other sites had Cu concentrations as low as 34 mg kg⁻¹ (Table 2). Carbon, S, and N were less variable among the study sites, but nevertheless, C content ranged between 21 and 50 % while concentrations of Fe and Al exceeded 24,000 and 37,000 mg kg⁻¹, respectively. The first two axes in a principal component analysis explained approximately 57 % of the variability in peat chemistry (Fig. 2). Axis 1 (38 %), representing primarily an organic-mineral gradient, was positively loaded with C, N, and S and negatively loaded with Al, Fe, and Mg. The two Daisy sites were clearly separated from the remaining sites as they were characterized by having a stronger mineral influence (Al, Mg, and Fe), and much lower carbon content. Both Ni ($R^2=0.72$) and Cu ($R^2=0.88$) concentrations in surface peat decreased with distance from the Copper Cliff smelter (Fig. 3). Concentrations of other metals that are also emitted from the Copper cliff smelter, such as Co, Fe, and Mn, were unrelated to distance from smelter.

Pore water was sampled on three occasions (October 2011, May 2012, and August 2012). The October 2011

campaign followed a period of drought when water table levels fell 20–40 cm below the surface at the six sites with continuous measurements (Fig. 4). During the May 2012 campaign, the water level at all the measured sites was at or above the surface, but in the final campaign (August), samples were collected during a summer drought that was interrupted by several rainfall events resulting in variable water levels among sites during the collection period (Fig. 3). Pore water chemistry exhibited large seasonal and spatial variability (Table 3): The coefficients of variation ranged from 11 % for $\delta^{18}\text{O}$ to over 240 % for Zn and NO_3 (Table 3). Maximum concentrations of Ni (1567 $\mu\text{g L}^{-1}$) and Cu (672 $\mu\text{g L}^{-1}$) greatly exceed provincial water quality objectives (25.0 $\mu\text{g L}^{-1}$ Ni; 1 $\mu\text{g L}^{-1}$ Cu) (Table 3). Pore water DOC concentration was positively related to the carbon content of peat in all sampling campaigns (Fig. 5), and high DOC concentrations were strongly negatively related to spectral slope values and more weakly associated with higher HIX values (Fig. 6).

There appear to be three clearly distinct seasonal patterns in pore water chemistry. The pattern that encompassed the most parameters (pH (H^+), SO_4 , Co, Ni, Ca, Mg, Mn, and spectral slope) is characterized by lower concentrations in the wetter May campaign and the highest concentrations in the late summer and fall. In May, mean pH in pore water at individual sites, for example, was as high as 6.98, while in August, the mean pore water pH could be as low as 3.92. Similarly, mean site SO_4 concentrations were as low as 1.50 mg L⁻¹ in May and as high as 180 mg L⁻¹ in October (Fig. 7). The second pattern is characterized by higher concentrations in May, with lower values in August and includes DOC, Cu, Fe, and HIX values (Fig. 8). Mean Fe concentrations at individual sites were between ~4 mg L⁻¹ in May falling to below detection limits (<0.005 mg L⁻¹) during the August campaign, while mean Cu concentrations at individual sites exceeded 600 $\mu\text{g L}^{-1}$ during the May campaign but were as low as 4.1 $\mu\text{g L}^{-1}$ during August. Both DOC and HIX varied between May and August with higher concentration and more humified DOM occurring in the spring (Fig. 8). The third pattern that includes $\delta^{18}\text{O}$, dissolved inorganic carbon (DIC), and NO_3 is characterized by higher concentrations and increased variability in August with lower values and variability in the October campaign (Fig. 9). Significant positive relationships between distance from the Copper Cliff smelter and pore water Cu, Ni, Co, and SO_4 were only found during the August campaign (Fig. 10).

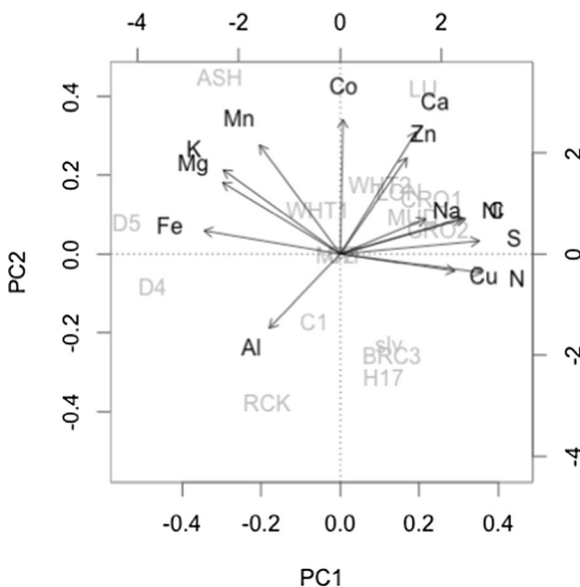
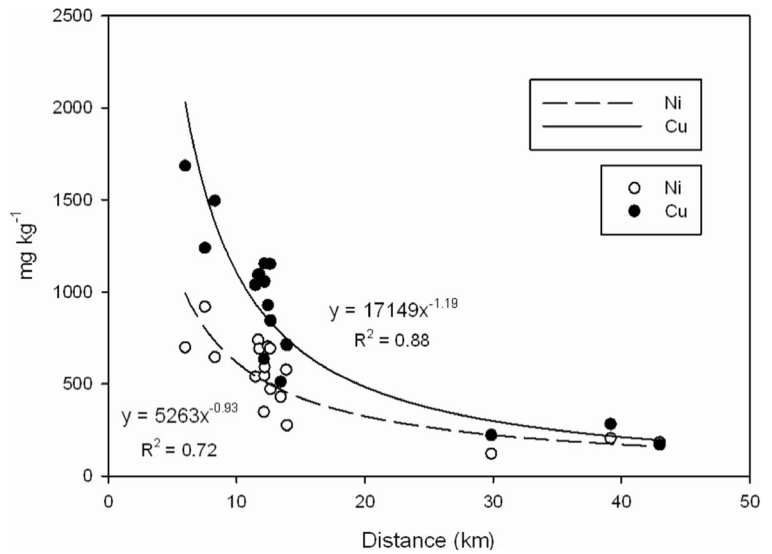


Fig. 2 Principal component analysis for surface peat chemistry at the 18 wetlands showing variable and site loading, $n=18$. These two components explain 57 % of the variance (PC1, 38 %; PC2, 19 %)

Fig. 3 Relationship between mean nickel (a) and copper (b) concentrations in surface (0–30 cm) peat at the 18 sites and distance from the Copper Cliff smelter



Despite the large spatial and temporal variability in pore water chemistry, soil-solution partitioning coefficient ($\log K_d$) of some metals (Ni, Co, Mn) can be explained by pH (H^+) alone (Fig. 11), with $\log K_d$ values increasing with pH. Even though pH alone is a significant predictor for K_d values for Ni, Co, and Mn, models for all three metals could be significantly improved by including SO_4 (Table 4). In addition, 51 % of the

variability in K_d values for Cu could be explained by TOC and $\delta^{18}O$ values (dissolved organic matter and hydrology), while 61 % of the variability in Fe K_d values can be explained by Sr and TOC (dissolved organic matter quantity and quality; Table 4). For Al, 64 % of the variability in K_d can be explained by TOC, pH, and spectral slope (dissolved organic matter quantity and quality and acidity; Table 4).

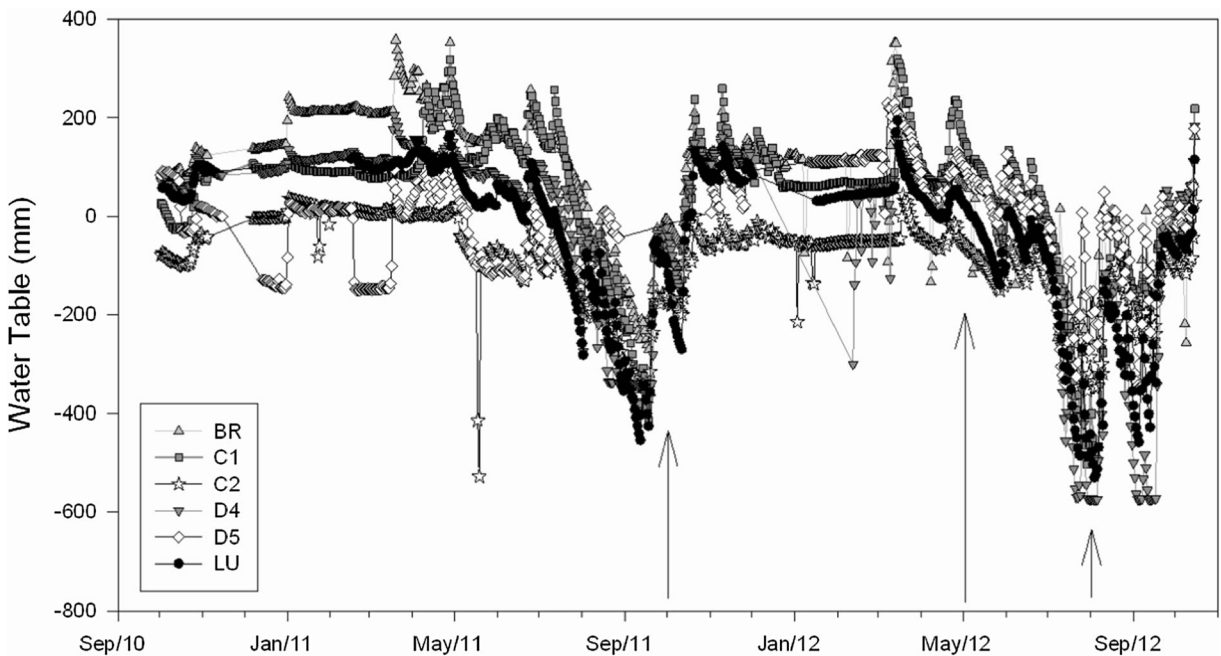


Fig. 4 Water table heights for six of the 18 wetlands over 2 years, with the three sampling times indicated (October 2011, May 2012, and October 2012)

Table 3 Summary statistics for pore water chemistry sampled at the 18 sites in the Sudbury area

Site	Average	St. dev	CV (%)	Median	Minimum	Maximum
pH	5.21	0.86	16.5	5.08	3.80	6.98
Slope Sr	1.07	0.29	27.0	1.00	0.67	2.04
$\delta^{18}\text{O}$	-11.0	1.20	-10.9	-11.3	-14.0	-8.13
HIX	9.89	3.88	39.2	9.50	2.63	34.9
Na (mg L ⁻¹)	5.21	6.24	120	3.19	0.42	47.8
K (mg L ⁻¹)	0.94	0.88	93.3	0.65	0.11	6.24
Ca (mg L ⁻¹)	9.66	8.38	86.7	6.39	1.22	32.3
Mg (mg L ⁻¹)	2.51	2.45	97.5	1.68	0.08	11.3
Al (mg L ⁻¹)	0.30	0.22	74.1	0.24	-0.002	1.07
Fe (mg L ⁻¹)	0.58	0.87	150	0.18	0.03	4.31
Mn ($\mu\text{g L}^{-1}$)	152	146	95.6	111	10.3	672
Ni ($\mu\text{g L}^{-1}$)	312	323	104	177	16.5	1567
Cu ($\mu\text{g L}^{-1}$)	146	127	86.9	123	4.13	724
Zn ($\mu\text{g L}^{-1}$)	236	568	241	90.3	0.39	4643
Co ($\mu\text{g L}^{-1}$)	15.3	13.9	90.8	11.1	0.65	64.8
Cl (mg L ⁻¹)	6.75	11.7	173	1.64	0.09	64.3
SO ₄ (mg L ⁻¹)	37.2	42.4	114	21.6	1.49	179
TP ($\mu\text{g L}^{-1}$)	64.7	150	232	39.7	0.96	1329
PO ₄ ($\mu\text{g L}^{-1}$)	39.4	133	337	16.9	0.92	1238
TOC (mg L ⁻¹)	15.2	12.3	80.8	12.5	1.77	84.3
NO ₃ ⁻ ($\mu\text{g L}^{-1}$)	161	396	246	57.8	2.05	2857
IC (mg L ⁻¹)	2.01	2.17	108	1.15	0.35	17.7
TN ($\mu\text{g L}^{-1}$)	1217	773	63.5	990	167	4914
NH ₄ ($\mu\text{g L}^{-1}$)	543	455	83.7	438	17.6	3318

St. dev standard deviation, *CV* coefficient of variation, *HIX* humification index, *TOC* total organic carbon, *IC* inorganic carbon, *TP* total phosphorus, *TN* total nitrogen

Fig. 5 Peat percent carbon from the October sampling period and total organic carbon in water samples collected during the each of the three sampling periods (October 2011, May 2012, August 2012). Also shown are power relationships between percent carbon and TOC for each of the three water sampling periods

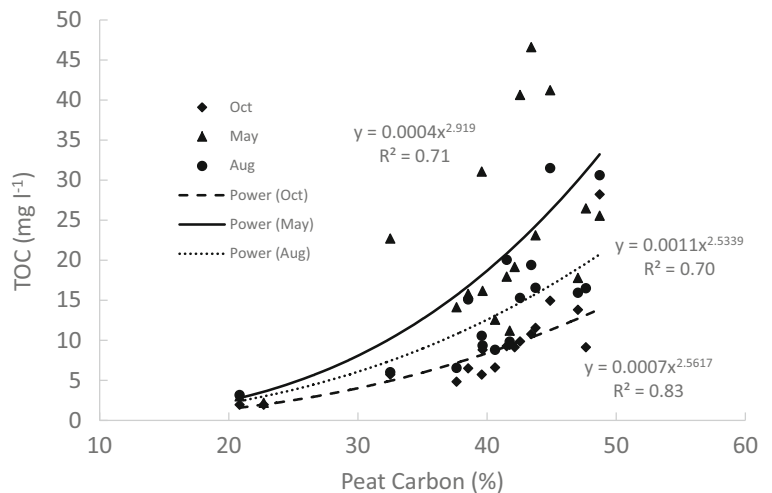
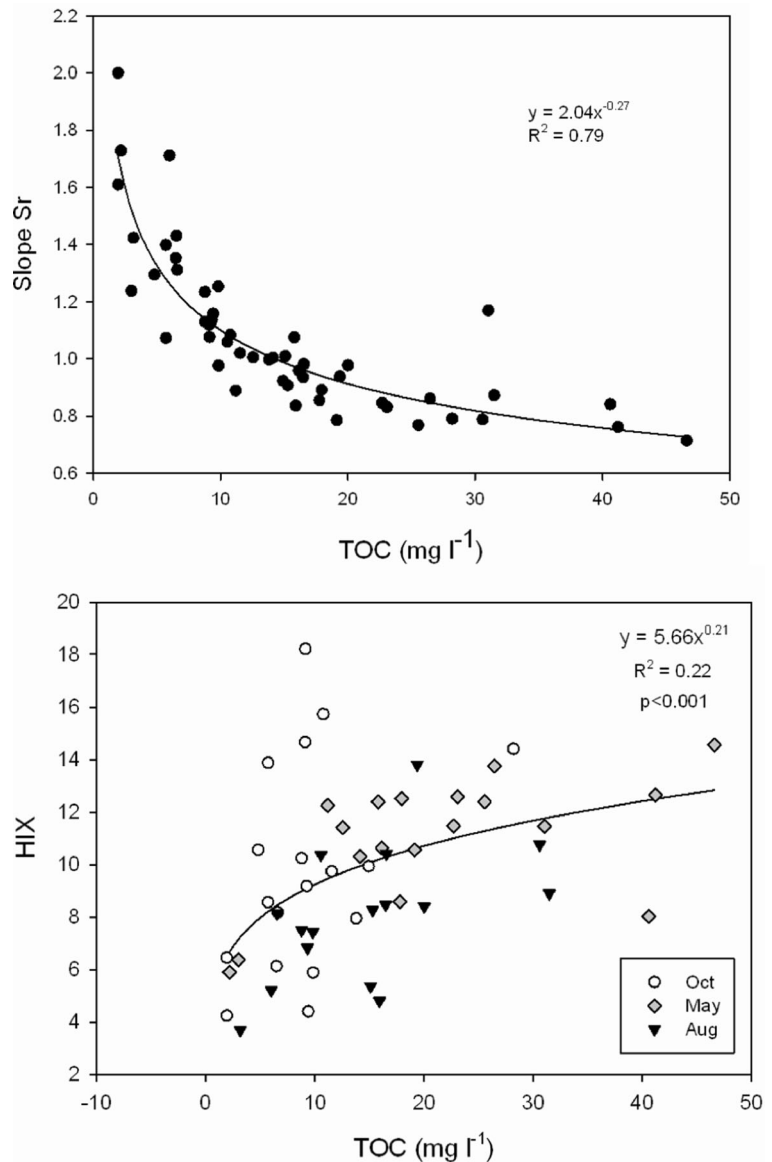


Fig. 6 Relationship between total organic carbon and spectral slope and total organic carbon and humification index in water samples collected for each of the three sampling dates (October 2011, May 2012, and August 2012)



7 Discussion

The geochemistry of peatlands in the Sudbury area is influenced by the deposition of atmospheric metals and the inherent spatial variability in chemical and physical properties and, most importantly, soil organic C content and acidity. Despite the large reduction in acid and metal deposition over the past 40 years, surface peat close to the main smelter remains heavily contaminated with both Cu and Ni. Metal concentrations in the pore

water varied seasonally, and Cu, Ni, and Co concentrations were only related to distance from Copper Cliff during the summer sampling campaign. For the metals of concern (Cu, Co, Ni, Al, and Mn), pore water concentrations could be significantly predicted by a combination of pH (H^+), DOC (quantity and quality), SO_4 , and $\delta^{18}O$ as well as peat metal concentration indicating that multiple processes control metal release to pore water, but the relative influence of each process differs by metal.

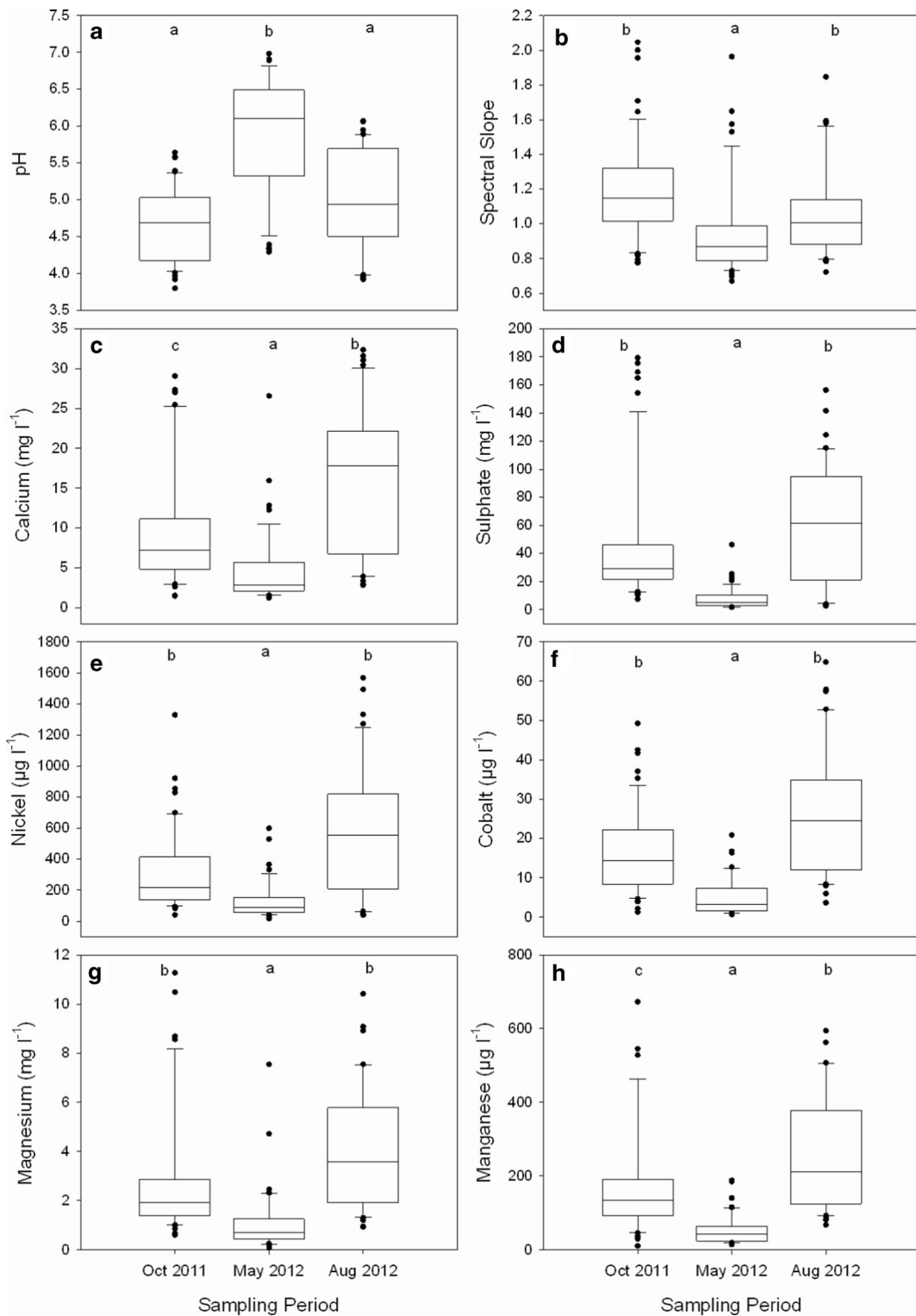


Fig. 7 Seasonal variation in pore water chemistry in 18 wetlands in Sudbury. **a** pH (H⁺), **b** spectral slope, **c** calcium, **d** sulphate, **e** nickel, **f** cobalt, **g** magnesium, and **h** manganese for each of the three sampling times (October 2011 (*n*=54), May 2012 (*n*=56),

and September (*n*=40)). Kruskal-Wallis one-way ANOVA on ranks was run for each variable (**a–h**). Shown on the figure are the results from the post hoc Dunn's test (**a–c**) for differences between each sample time

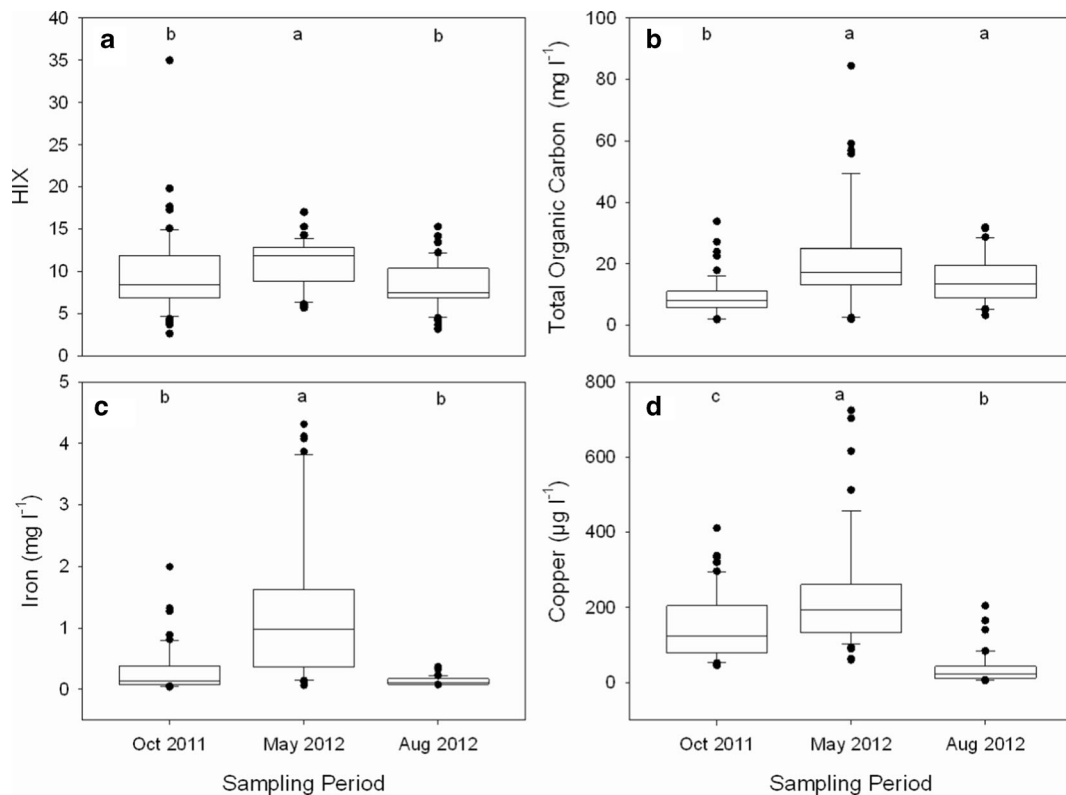


Fig. 8 Seasonal variation in pore water chemistry in 18 wetlands in Sudbury. **a** HIX, **b** total organic carbon, **c** iron, and **d** copper for each of the three sampling times (October 2011 ($n=54$), May 2012 ($n=56$), and September ($n=40$)). Kruskal-Wallis one-way ANOVA

on ranks was run for each variable (a–d). Shown on the figure are the results from the post hoc Dunn's test (a–c) for differences between each sample time

8 Peat Chemistry

In the present study, only Cu and Ni concentrations in surface peat were strongly correlated with distance from the Copper Cliff smelter: concentrations of Cu and Ni close to the smelter were as high as 1932 and 1829 mg kg⁻¹, respectively, but declined to values less than 100 mg kg⁻¹ around 40 km from the main smelter in Sudbury. Freedman and Hutchinson (1980) estimated that approximately 40 % of the Cu and Ni emitted from Copper Cliff fell within a radius of 60 km and many other studies in Sudbury have documented an inverse relationship between Cu and Ni concentrations in precipitation, mineral soil, vegetation, leaf litter, lake sediment, and peat with increasing distance from the Sudbury smelters (Gignac and Beckett 1986; Hazlett et al. 1984; Hutchinson and Whitby 1977). Concentrations of Cu and Ni in surface peat at many of the wetlands are still at potentially toxic levels, well above the provincial soil quality guideline for the soils (150 mg kg⁻¹ for both Ni and Cu) (SARA 2008; CCME 2007).

Copper and Ni are not the only pollutants emitted from smelters in Sudbury. Smelter operations also release relatively large amounts of S, Co, Fe, Pb, Cd, Zn, and Mg (Taylor and Crowder 1983). Concentrations of S, Fe, and Mg in precipitation and lake chemistry have also been shown to decrease rapidly with distant from the smelters (Potvin and Negusanti 1995; Taylor and Crowder 1983). However, as shown in other studies (Adamo et al. 2002; Dudka et al. 1995; Gignac and Beckett 1986), there were no significant relationships between the acidity of the peat or concentration of all other measured elements and distance from the Copper Cliff smelter. The lack of any relationship between peat pH, and other chemical parameters and distance from Copper Cliff is likely because peatland chemistry is also strongly influenced by other factors such as mineral content and groundwater inputs (Gignac and Beckett 1986; Szkokan-Emilson et al. 2014). In particular, mineral soil contains large amounts of Al and Fe and is likely coming into these peatlands through erosion and dust in this highly eroded landscape (Gignac and Beckett 1986).

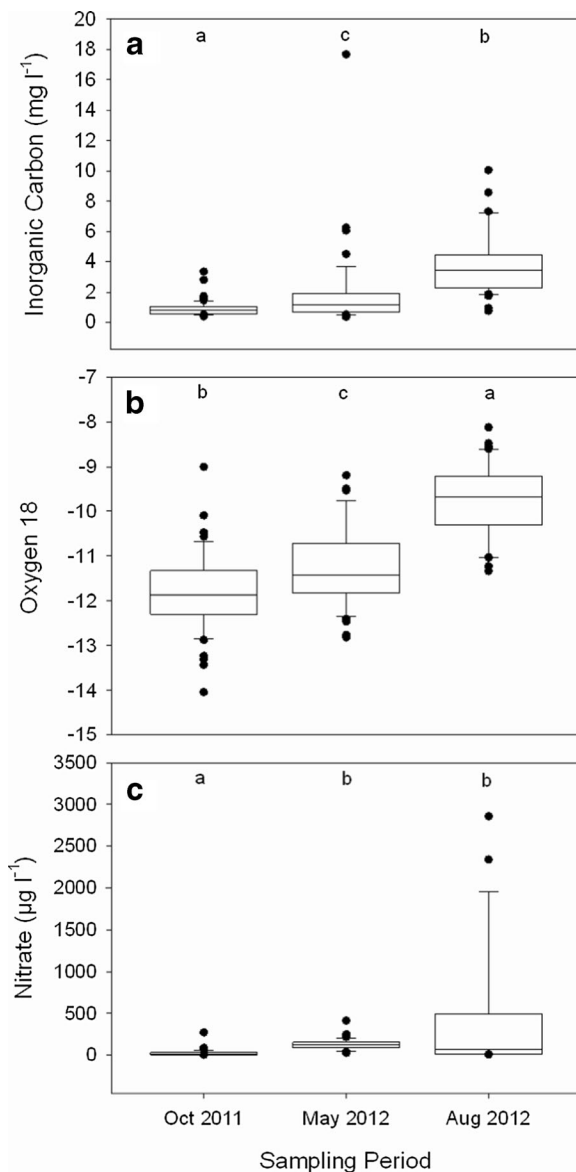


Fig. 9 Seasonal variation in pore water chemistry in 18 wetlands in Sudbury. **a** inorganic carbon, **b** oxygen 18, and **c** nitrate for each of the three sampling times (October 2011 ($n=54$), May 2012 ($n=56$), and September ($n=40$)). Kruskal-Wallis one-way ANOVA on ranks was run for each variable (**a–c**). Shown on the figure are the results from the post hoc Dunn's test (**a–c**) for differences between each sample time

9 Pore Water Chemistry

The chemistry of pore water in the Sudbury peatlands varied considerably among the peatlands and also by season. Differences in pore water DOC concentration among sites can largely be explained by differences in the C content of the soil. Sites having a greater C content

in surface soil also appeared to have a greater DOC concentration in the pore water regardless of the season. The main reason for differences in C content in the surface soil is most likely due to past erosion: Sites with the lowest soil carbon content (Daisy Lake) are surrounded by severely eroded uplands that presumably resulted in substantial mineral inputs to the wetlands. Mineral inputs to the wetlands are reflected by lower peat carbon content, which in turn is reflected as lower DOC concentrations in the pore water of the peatlands. This is particularly important in the Sudbury context as recent work suggested that aquatic productivity is related to carbon inputs from the terrestrial catchment (Tanentzap et al. 2014).

Pore water chemistry varied considerably by season, and this study identified three potential processes that appear to be contributing to the seasonal variability in pore water chemistry in the Sudbury wetlands. The pattern that encompassed the most parameters (SO_4 , H^+ , Ni, Co, Ca, Mg, Mn, and spectral slope) is characterized by considerably lower concentrations and little variability during the warm and wetter May campaign, with the highest concentrations and increased variability occurring during the late summer and fall. Recent studies have reported that following droughts, when water levels rise in the late summer and fall, large spikes in SO_4 , acidity, and metals are transferred into stream water from the substrate (Juckers and Watmough 2014; Szkokan-Emilson et al. 2013). During the drought, S in aerated surface peat is oxidized to SO_4 which is flushed from the peatlands during the fall rain. Acidification is the main cause of these pH-dependent releases of large amounts of Ni, Co, Ca, Mg, and Mn from the cation exchange sites on peat into pore water (Szkokan-Emilson et al. 2013). There was no evidence that wetlands closest to the smelter had greater drought-induced spikes in SO_4 as the seasonal variation was equally evident across all study sites regardless of distance, S, and metal contamination in the peat. Other studies have similarly measured high concentrations of SO_4 in water-draining peatlands at sites remote from local emission sources (Eimers et al. 2007). The acidification of water and metal mobilization resulting from the oxidation of exposed peat during drought conditions may be amplified and of greater concern because of pending climate change (Kerr et al. 2012). Climate change is predicted to increase drought conditions in the Sudbury area (and other northern regions) causing the release of increased amounts of acidic and metal-

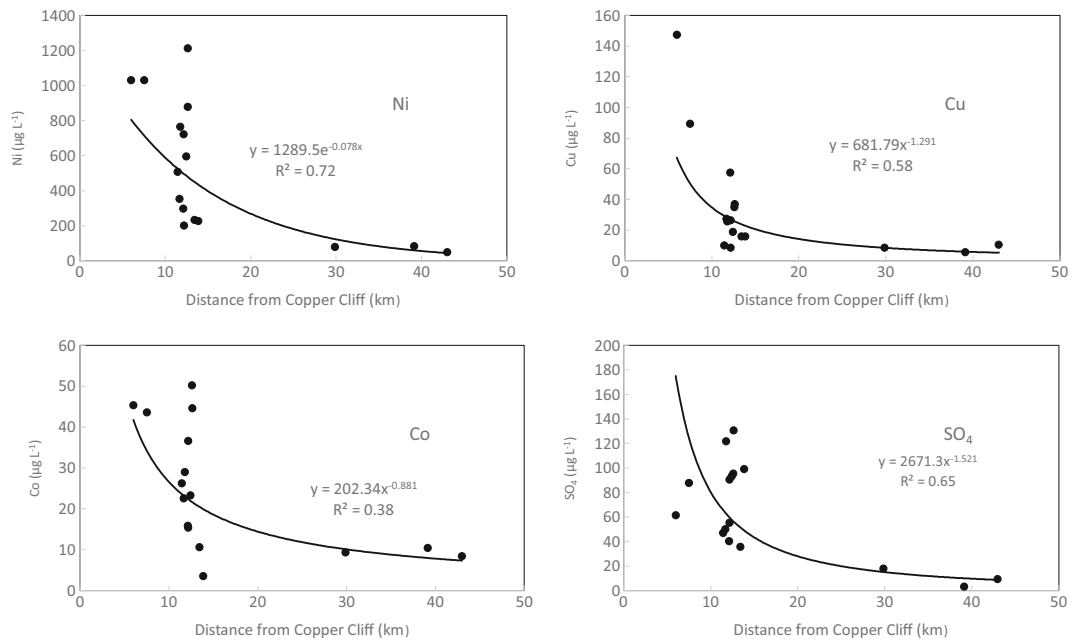


Fig. 10 Relationship between pore water Ni, Cu, Ni, and SO₄ sampled in August and distance from Copper Cliff in the 16 monitored peatlands with available water

contaminated waters from wetlands (Eimers et al. 2007; Szkokan-Emilson et al. 2013). Moreover, the length and overall severity of drought contribute to the level of drawdown and can influence how much S, metals, and acidity are available to be flushed into local streams and lakes (Juckers and Watmough 2014; Szkokan-Emilson et al. 2013).

The highest pore water metal concentrations for Co, Mn, and Ni reached approximately 65, 670, and 1560 $\mu\text{g L}^{-1}$, respectively, with the potential for delivering toxic levels to downstream systems. For example, Co concentrations in relatively pristine areas vary with bedrock type and surface geological conditions but are typically around 1 $\mu\text{g L}^{-1}$ in surface waters (Environment Canada 2013). Toxic levels above 90 $\mu\text{g L}^{-1}$ for most biota, including humans, are known to inhibit various enzymes, causing a reduction in tissue respiration and metabolism (Environment Canada 2013). Invertebrates such as *Hyaella azteca* are essential for primary food organization and are extremely sensitive to high levels of Co: Concentrations of less than 3 $\mu\text{g L}^{-1}$ have been known to be lethal (Norwood et al. 2007). Nickel is considered only moderately toxic to mammals (CCME 1999), with the lowest effect dose being approximately 25 $\mu\text{g L}^{-1}$, and levels associated with harmful effects on most biota range between 300

and 2500 $\mu\text{g L}^{-1}$ (CCME 1999). Toxic levels of Ni were found at many sites and can impede soil microbial processes, affect plant growth, and impede liver functions in most biota (CCME 1999).

The second seasonal pattern identified in this study is characterized by higher concentrations of DOC, Cu, Fe, and HIX with increased variability in May and lower values and less variability during late summer and fall. It is likely this pattern is driven by DOC production during the warmer and wetter May campaign. Under aerobic conditions that occur during the summer when the water table drops, there is a more complete respiration to CO₂ (Wang et al. 2014). Studies have clearly demonstrated that following summer drought (decline in water table and exposure of surface peat to the atmosphere), DOM concentrations in water draining wetlands are low (Neff et al. 2006), which may potentially increase the toxicity of metals to biota (McGeer et al. 2002). Another possibility for declines through late summer and fall could be accredited to the large release of SO₄ from the peat under these drought conditions. The resulting higher acidity may be affecting the ionic strength of the pore waters, which subsequently affects DOC solubility and the overall OM quality (Clark et al. 2012; Jager et al. 2009).

In the present study, DOC levels were highest in early summer (May) with a lower spectral slope value (more

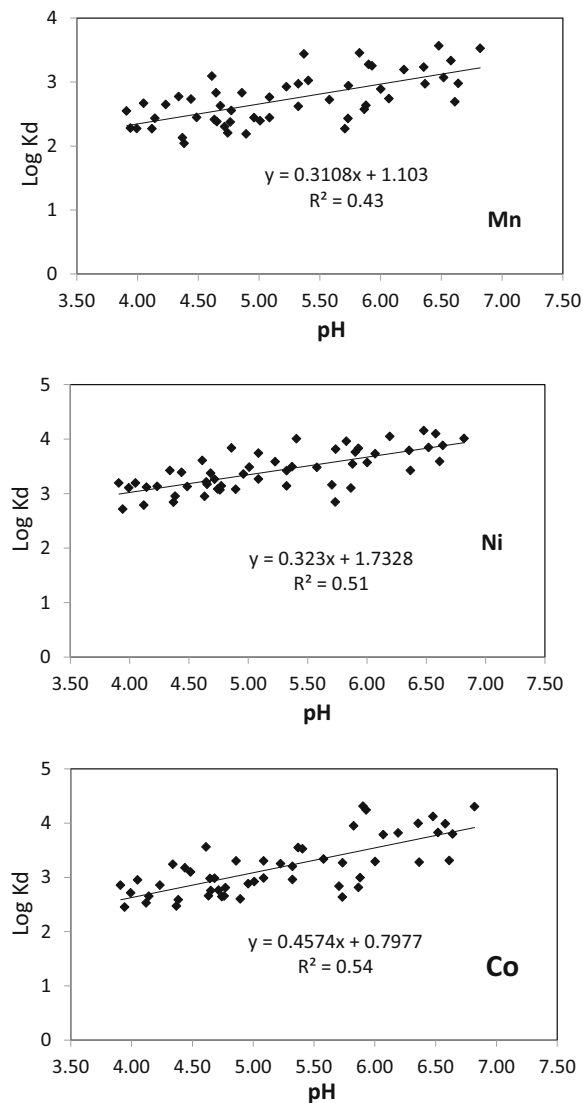


Fig. 11 Relationship between pore water pH and soil solution partitioning coefficient ($\log K_d$) for Mn, Ni, and Co (all three campaigns combined), $p < 0.001$

aromatic and humified DOM). Neff et al. (2006) reported that the DOM concentration in wetlands was very high and originated from a terrestrial source in the spring, while DOM production decreased significantly through the warmer summer months. However, Neff et al. (2006) implied that the DOM was fresher or young in spring, whereas this study found that the increase in DOM during the spring appears to be more humified and may reflect decomposition of peat, whereas DOC produced in the late summer/early fall may be of a more recent origin (e.g., plant exudates, and microbial biomass produced during the summer) (Wong and

Table 4 Forward stepwise regressions run for the estimation of $\log K_d$ pore water contaminants using six potential predictors (pH, slope Sr, HIX, $\delta^{18}\text{O}$, SO_4^{2-} , and TOC)

Metal	Adj R^2	MSE	Model
Ni	0.69	0.04	$2.15 - 4.07\text{E}^{-03} * \text{SO}_4 + 0.27 * \text{pH}$
Co	0.69	0.08	$1.33 - 5.17\text{E}^{-03} * \text{SO}_4 + 0.40 * \text{pH}$
Mn	0.66	0.05	$1.58 - 4.73\text{E}^{-03} * \text{SO}_4 + 0.25 * \text{pH}$
Cu	0.51	0.13	$7.68 + 0.31 * \delta^{18}\text{O} - 2.31\text{E}^{-02} * \text{DOC}$
Fe	0.61	0.13	$3.57 + 1.00 * \text{Sr} - 2.04 \text{E}^{-02} * \text{TOC}$
Al	0.64	0.08	$2.69 + 0.53 * \text{Sr} - 2.03\text{E}^{-02} * \text{DOC} + 0.28 * \text{pH}$

Stepwise regressions were run using Systat SigmaPlot 11.0

MSE mean squared error

Williams 2010). There have not been any studies of changes in DOM composition in response to drought in boreal wetland systems, but similar changes in DOM aromaticity have been observed in laboratory studies of pore water DOM in humic peats from the UK (Clark et al. 2005), and drought-related increases in the protein-like fraction of DOM have been observed in large subtropical rivers as well (Hong et al. 2011). It is also possible that during the post-drought conditions, there is a higher relative contribution of upland versus wetland-derived DOM. Waters draining upland soils tend to have lower DOM that is less aromatic with higher protein-like fractions (Fellman et al. 2009). Fellman et al. (2009) noted similar increases in protein-like fluorescence in wetland-draining stream samples in both the fall and the spring when flows are high, suggesting that these changes may occur as a result of high flow and dilution with upland-derived inputs.

In association with the higher DOC in late spring, the concentrations of many other metals and SO_4 were low and pH was high, suggesting a lack of competition for OM binding sites and that S is being reduced (Benedetti et al. 1996). In contrast, metals that have a strong affinity for DOM (e.g., Cu, Fe, and Al) exhibit the highest concentrations during the May sampling campaign as metal speciation models indicate that the fraction of metals such as Cu and Al in solution bound to DOM increases with increasing DOM (Watmough and Orlovskaya 2015). The higher Fe and Cu concentrations in May could also be due to reducing conditions mobilizing these metals from peat into solution (Reddy and DeLaune 2008). At some sites, Cu concentrations in pore water exceeded $600 \mu\text{g L}^{-1}$ during the May

campaign but could be as low as $4 \mu\text{g L}^{-1}$ during August at other sites. Similar to Fe, Cu is well known to strongly bind to DOM but, under anoxic conditions, can be liberated into pore water (Benedetti et al. 1996). As evident with the decline through summer and fall, most Cu is probably being transferred back into solid phases due to increased competition for binding sites and conditions favorable for reduction of Cu^{2+} (Schiff et al. 1998). Uptake by existing and new growth during the warm summer may also contribute to the decline in Cu found through late summer and fall (Benedetti et al. 1996).

The third process identified in this study suggests a greater hydrology influence on pore water chemistry and includes $\delta^{18}\text{O}$, IC, and NO_3 . Nitrate, $\delta^{18}\text{O}$, and IC are characterized by the highest values in August with lower values during the October and May campaigns. It is also interesting to note that it was only during the August campaign when concentrations of metals emitted from the smelter (Cu, Ni, and Co) and SO_4 (SO_2 also emitted from the smelter) in pore water were significantly related to distance from the main Copper Cliff smelter. During August, water tables were lowest and some sites had dry wells (therefore, no sample), while others had variable amounts of water suggesting that groundwater and rainwater inputs likely vary among sites. There were also rainfall events during the August sampling campaign that lasted over a period of 10 days (rainfall events occurred on 7 of 10 days and were between 0.5 and 4 mm day^{-1}). A greater precipitation influence is also suggested by the high $\delta^{18}\text{O}$ values in pore water, which are higher (less negative) in summer precipitation compared with winter (Peng et al. 2004). It is also possible that, following these rainfall events after an extended dry period, there is some production of sulphuric and nitric acid, leading to higher metal levels similar to what was observed in the previous fall. The high DIC values may reflect high CO_2 production during aerobic respiration in the summer and subsequent accumulation in water following the precipitation events (Estop-Aragonés et al. 2012).

10 Metal Release to Pore Water

In the present study, metal partitioning (K_d) values for Ni, Co, and Mn could be significantly predicted by pH (H^+) alone and $\log K_d$ values increased as pH increased.

Metal pools in the solid phase are much larger than the metal pools in solution and are relatively unaffected by these changes. It is well recognized that pH is a good predictor of solid-solution partitioning in soils: The release of metals into solution is favored under acidic conditions (Watmough et al. 2005). For example, in a survey of the literature, Sauvé et al. (2000) reported average K_d coefficient values in mineral soils of 3000, 17,000, 170,000, and 12,000 for Cd, Ni, Pb, and Zn, respectively, but found that K_d values for a single metal could differ by up to 6 orders of magnitude, mainly as a function of soil pH, total metal content, and soil organic matter content (Sauvé et al. 2000). Few, if any, studies have tested the relationship between pH and K_d in wetland soils, which are expected to be much more strongly influenced by the high organic matter content and changes in redox processes for example. Sauvé et al. (2003) examined the solid-solution partitioning of Cd, Cu, Ni, Pb, and Zn in the organic horizons of a forest soil in Quebec, Canada, and found weak or no relationship with H^+ (over a pH range of 4.0–5.5). However, Tipping et al. (2003) conducted a survey of upland soils in the UK and found that total heavy metal concentrations in soil solution were positively correlated with the soil metal content and dissolved organic carbon (DOC) content and negatively with pH and soil organic matter content (loss on ignition, LOI).

The solid-solution partitioning of Ni, Co, and Mn was improved (r^2 values 0.66–0.69) by adding SO_4 to the models, with K_d values decreasing as SO_4 increases (more metal in pore water when SO_4 is higher), which is consistent with the potentially higher precipitation influence on pore water measured in August and also by the fact that SO_4 production is primarily causing the increase in H^+ , which mobilizes these metals into solution. In contrast, the solid-solution partitioning of Cu, Al, and Fe was best predicted by DOC (highest in spring) or measures of DOC quality (HIX, Sr) (more humified in spring). For Cu, K_d values were lowest when DOC levels were highest and $\delta^{18}\text{O}$ were lower (more negative), reflecting higher Cu levels in solution during the late spring when conditions are wet and DOC production is high. For Al and Fe, DOC concentration, spectral slope, and H^+ (Al only) were significant predictors of solid-solution partitioning, with lower K_d values (more Fe and Al in solution) occurring when DOC levels are highest and spectral slope values and pH (Al) are lowest. This implies that Fe and Al release to pore waters is strongly controlled by DOC but that pH also contributes

to Al mobility but not Fe (Jansen et al. 2003). Importantly, this work shows that metal release to pore waters with widely contrasting physical and chemical properties can be reasonably well predicted in peatlands that vary considerably in the degree of contamination and other physical and chemical properties from a few basic measures of soil and pore water chemistry.

11 Conclusion

Peatlands in the Sudbury area remain heavily impacted by smelting activities as is evidenced by high Cu and Ni concentrations in surface peat close to the main Copper Cliff smelter. However, the release of metals to pore water is determined primarily by differences in acidity and DOC concentrations in pore water in addition to atmospheric deposition and the metal concentration of peat. The concentrations of DOC and H⁺ are controlled by inherent spatial variability in C content and mineral content of the peat most likely caused by past erosional input into these small peatlands. Despite the large variability in pore water chemistry it is possible to predict the release to pore water (and to lakes) using a few basic parameters that include pH, δ¹⁸O, SO₄ concentration, and measures of DOC quantity and quality as well as the metal concentration of the peat.

Acknowledgments We thank the National Sciences and Engineering Research Council of Canada (NSERC), Vale INCO, Xstrata, and the City of Greater Sudbury for financial assistance. We acknowledge the assistance of Liana Orlovskaya, Erik Szkokan-Emilson, Sophie Barrett, Andrew McDonough, Ryan Cant, Myra Juckers, and Andrea Hatton for help with fieldwork and laboratory analysis.

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