Trace Metal Geochemistry of Peatlands

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ABSTRACT

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Peatlands can be found widely across all latitudes and play a significant role in global cycles within the earth's biosphere. The anoxic conditions in peatlands promotes the accumulation of organic matter through decreased rates of decomposition and the storage of certain elements, which have received contaminant loading over the course of human existence, with significant increases occurring during the period of industrialization. We assessed global patterns of metal enrichment in peatlands in 439 cores distributed across 5 continents and 21 countries and measured 35 elements by depth increments and by peatland type. Global patterns in enrichment factors (EF's) were determined for all metals with the majority of metals being found to have a median EF < 2 indicating relatively minor enrichment. Principal component analysis indicated EF's of 6 metals (Cd, Co, Cu, Ni, Pb, and Zn), 2 metalloids (As and Sb) and 1 none metal (Se) in the upper peat horizon had similar spatial patterns among peatlands and these elements had generally the highest EF's with many cores exceeding EF >10 and some having EF values >100. Significant differences in EF's were found for these 9 "pollution" elements by peatland type and to a greater extent by geographic region, with higher EF values typically occurring in Europe and North America. Enrichment factors for most elements exhibited weak but significant positive correlations with modelled [1850 – present] S deposition. Estimated pools for the "pollution metals" within the 0 - 40 cm depth varied considerably, with median global pools in peat ranging from 12.9 mg m^{-2} (Sb) to 439 mg m^{-2} (Zn) for these 9 metals. Climate changes presents a significant risk to global peatland geochemistry due to expected changes in hydrologic regimes, resulting in potentially increased metal mobility though drought-induced peatland acidification, with historic areas previously impacted by industrial activities presenting the greatest risk of metal release to downstream receiving environments. Using a case study, we examined the impact of simulated 30-day drought on pore water chemistry at six sites in a peatland complex in

Elliot Lake Ontario that were historically impacted by uranium (U) mining activities. All sites responded similarly to simulated drought with pore water pH significantly declining. The decline in pore water pH was likely due to increasing sulphate (SO_4^{2-}) concentrations, which accompanied large increases in Al, Ni, Cu, Pb, Zn, and U. Dissolved organic carbon (DOC) increased, which may further enhance Al, Cu, and U mobility as these metals are strongly complexed by organic acids. Metal partitioning (K_d) values could be significantly predicted by pH and DOC although the strength of the relationship varied considerably among sites. Multiple linear regression and the inclusion of SO_4^{-2} improved predictions, indicating that declines in pH as a result of SO_4^{-2} and H^+ production primarily governs metals and U partitioning in peatland soils. The results from both studies show that metal enrichment in global peatlands is highly variable, with northern peatlands in industrialized areas presenting the greatest risk of metal release to downstream surface waters based on expected hydrologic impacts from climate change due to historical and on-going metal and S deposition.

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List of Abbreviations

Al	Aluminum
As	Arsenic
Ba	Barium
C	Carbon
Ca	Calcium
Cd	Cadmium
Ce	Cesium
Co	Cobalt
Cr	Chromium
Cu	Copper
DOC	Dissolved Organic Carbon
Dy	Dysprosium
EF	Enrichment Factor
Eu	Europium
Fe	Iron
Ga	Gallium
Ge	Germanium
K	Potassium
K_d	Partition Coefficient
La	Lanthanum
Li	Lithium
MeHg	Methylmercury
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
N	Nitrogen
Na	Sodium

Nb	Niobium
Ni	Nickel
NO_3^-	Nitrate
Pb	Lead
Rb	Rubidium
S	Sulfur
Sb	Antimony
Se	Selenium
Sm	Samarium
SO_4^{-2}	Sulphate
Sr	Strontium
SQG	Sediment Quality Guideline
Ti	Titanium
TMA	Tailings Management Area
U	Uranium
V	Vanadium
WQG	Water Quality Guideline
Yb	Ytterbium
Zn	Zinc
Zr	Zirconium

1.0 General Introduction

Peatlands are estimated to represent ~3-6% of the earth's terrestrial surface (Leifeld and Menichetti, 2018; Mann and Wetzel, 1995) and have characteristics that favour metal retention through biogeochemical processes such as uptake by plants, bacterial degradation and oxidation, and adsorption to organic substrates (Sheoran and Sheroan, 2006). Localized studies have been conducted on a few trace elements linked to anthropogenic pollution, demonstrating that peatlands can exhibit both high and low levels of contamination, but no global synthesis exists to date. At the same time climate change can significantly impact the natural hydrology and biogeochemical system of peatlands, with the potential to mobilize and release metals into downstream surface water with consequences to both biota and humans. This thesis will investigate the spatial distribution of metal contamination in global peatlands, while utilizing a case study to demonstrate the potential risk of climate induced drought and peatland acidification on metal mobility, expanding our understanding of global patterns, contamination pathways, and processes effecting metal mobility in peatlands.

1.1 Peatland Community Function, Classification, and Global Distribution

Peatlands are unique in the terrestrial biosphere in regard to rates of net primary productivity, which are lower relative to rates of heterotrophic mineralization. This has led to the buildup of deep organic soils making them one of the most important natural resources in the world due to their critical role in maintaining major natural biogeochemical cycles (such as carbon (C) and nitrogen (N)), as well as supporting a wide range of biodiversity that directly and indirectly support human's well-being (Leifield and Menichetti, 2018; Dise, 2009; Zedler and Kercher, 2005; Gorham, 1991). Peatland function related to water can include storage, filtration and supply, mitigation of floods and prevention of erosion (Zielinski et al., 2018). Indirect functions can include nutrient retention, C storage, and sediment retention (Zielinski et al., 2018). Despite the fact that peatlands cover a relatively small area of land, they play a significant role in the global C cycle

(Yu et al., 2011; Charman et al., 2013; Loisel et al., 2014). There are several processes in peatlands where C is involved, such as carbon dioxide (CO_2) exchange with the atmosphere, the emission of methane (CH_4), the production and export of dissolved organic carbon (DOC) (Rydin and Jeglum, 2013; Clymo et al. 1998; Moore et al. 1998). Similarly, through the large accumulation of organic matter in peatland soils, substantial amounts of nitrogen (N), phosphorous (P) and other elements are sequestered (Clymo, 1978).

The type of peatland, and extent to which both services and processes are facilitated is indicative of peatland development, which exist along a gradient of distinct abiotic factors, including topography, climate, hydrologic regime, nutrient status, water chemistry and mineral material (Zoltai and Vitt, 1995). Five distinct peatland types have been widely recognized: bogs, fens, swamps, marshes, and shallow open water (Hook, 1988; Keddy, 2014). Marsh, swamp, and open water weltnads are characterized as highly productive and diverse systems, marked by permanent flooding and seasonal fluctuations in the water table, available nutrients, and abundant vascular plant production (Keddy, 2014). Increased rates of decomposition and poorly developed ground layers caused by water fluctuations, inhibits the production and accumulation of peat (Zoltai and Vitt, 1995). Alternatively, peatlands (bog, fens, and swamps) differ from non-peat forming wetlands, due to the stability of seasonal water levels restricting water flow through the wetland system, causing a shift from tree, shrub, and vascular plant cover to a ground layer dominated by bryophyte communities (Zoltai and Vitt, 1995). Active nutrient sequestering by the bryophyte layer results in decreased rates of decomposition that leads to peat formation (Bayley et at. 1987). The majority of organic matter is decomposed in the upper seasonally saturated layer of peatlands (acrotelm). Only 10% of the litter mass reaches the deeper permanently water-saturated catotelm, where decomposition is slowed due to low temperatures and the growing recalcitrance of remaining peat mass (Beer et al., 2008). The genus *Sphagnum* spp. are particularly important to peatlands in boreal regions, which continually creates cation exchange sites due to the production of uronic acid (Wieder and Vitt, 2010). This process generates decomposition resistant litter that can hold large quantities of water, limiting water flow and nutrient availability (Wieder and Vitt, 2010). The continued invasion of *Sphagnum* and accumulation of peat creates

changes in surface patterns (hummocks and hollows), further limiting the influence of groundwater, affecting nutrient status, and vascular plant abundance resulting in a gradient from minerotrophic fens to ombrotrophic bogs with increasing peat depth (Zoltai and Vitt, 1995; Wieder and Vitt, 2010).

Peatlands occur in all climate zones from the tropics to the tundra, occupying approximately ~3-6% of the earth's surface (Leifeld and Menichetti, 2018; Mann and Wetzel, 1995), although there is some uncertainty in these estimations. Attempts to estimate global area, distribution, and type of peatland have been made using broad-scale approaches, such as remote sensing that vary considerably based on source material and the definition of peatland used in various studies. Studies attempting to estimate global methane (CH_4) emission from peatlands have used estimates of global peatland area that ranged from 5.3-5.7 million km^2 (Mathews and Fung, 1987; Aselmann and Crutzen, 1989; Dugan, 1993), however Gorham (1991) remains the most widely cited and accepted estimate for boreal and subarctic peatlands which he estimated to cover 3.46 million km^2. More recently global estimates using previously published peatland databases have ranged from 1.85-4.23 million km^2 (Lehner and Doll, 2004; Joosten, 2009; FAO, 2012; Xu et al., 2018). Global estimates have been further broken down by continental area and by peatland type, with the vast majority of peatlands being bog and fen systems (60.7%) located in North America (2.07×10^5 - 1.37×10^6 km^2); Asia (5.26×10^5 - 1.62×10^6 km^2) km^2; and Europe (17.1×10^4 - 1.71×10^5 km^2) (Xu et al., 2018; FAO, 2012; Joosten, 2009 Lehner and Doll, 2004; Aselmann and Crutzen, 1989)

1.2 Metal accumulation and enrichment in global peatlands

The ability of peatlands to act as filters for metals and certain elements in water has been recognized as an important ecosystem function, due to the historic contaminant loading over the course of human existence (Sheoran and Sheoran, 2006). Metal and other contamination in peat is greatest close to industrial sources, which can include: burning of fossil fuels, mining and smelting of metalliferous ores, municipal

wastes, sewage, pesticides, and fertilizers (Souch et al., 2002). Key contamination pathways to peatlands systems include direct dumping of waste, surface and groundwater effluent, and airborne or atmospheric transport and deposition (Souch et al., 2002). As a result, metal concentrations can vary drastically depending on peatland type and proximity to point source pollution. Kalbitz and Wennrich (1998) have reported concentrations of 1100 mg kg^{-1} Zn, 800 mg kg^{-1} Cr, 364 mg kg^{-1} Cu, 265 mg kg^{-1} As and 37 mg kg^{-1} Hg in peatland soils in an industrial district of Germany, while concentration of peatlands adjacent to metalliferous mines in China had mean concentrations of 3290 mg kg^{-1} Pb, 4805 mg kg^{-1} Zn, and 5770 mg kg^{-1} Cu (Deng et al., 2004). Similarly, Nieminen et al. (2002) found that an ombrotrophic bog 2.5 km from a Ni-Cu smelter accumulated Cu, Ni and Zn at rates of 149, 64, and 17 mg m^{-2} year^{-1} respectively. Often, a contaminant gradient in peat can be established based on the distance to point sources. Shotyk et al., (2000), found that Pb concentrations showed pronounced regional differences based on distance from industrialized areas, whereby remote alpine peatlands received 10 times less anthropogenic Pb than peatlands closer to pollution sources. Nevertheless, long-range atmospheric transport and subsequent deposition of metals can represent a non-point source of contamination in remote peatlands. Coggins et al. (2006), found Hg, Pb, and Cd accumulation rates in two remote ombrotrophic bogs in Ireland ranged from 6-24 µg, 3-5 mg, and 25-405 µg m^{-2} year^{-1}, respectively, suggesting that the high metal accumulation rates may be the result of long range transport of trace metals from North America due to majority of prevailing winds coming from the southwesterly marine sector oppose from the UK and mainland Europe. Peat is particularly effective at preserving atmospheric metal deposition which has been used to show increases in metal accumulation dating back thousands of years, with the most pronounced increases generally occurring post 1850 (Marx et al., 2010; De Vleeschouwer et al., 2007; Shotyk et al., 2005).

A benefit of metal accumulation, burial, and preservation of metals and elements within peatland soils is the ability to obtain long-term estimates of metal contaminant inputs through dated geochemical profiles. Although stratigraphic records do not provide perfect information, such records provide independent estimates of metal loading and allow insight into lithogenic (natural weathering and erosion) and

anthropogenic inputs through time (De Vleeschouwer et al., 2007; Shoytk, 1996). Studies addressing environmental metal pollution, utilize conservative elements to quantify the amount of individual metals gained, relative to source rock composition, thereby indicating anthropogenic enrichment (Shoytk, 2000; Shotyk, 1996). Typically, Al, Si, Sr, or Ti are used as a conservative element to be compared to heavy metals of interests, such as Pb, Cu, Ni, and Zn, whereby the crustal ratio of metal to conservative element is representative of pre-anthropogenic signatures of soils, allowing the determination of metal enrichment factor (EF) derived from deposition and loading (Shoytk, 2000; Shotyk, 1996). Shotyk (1996) found that conservatively estimated EF in Switzerland *Sphagnum* bogs were approximately 5 times for Cu, 15 times for As, and 30-50 times for Pb Sb, and Zn higher than pre-industrial background values. Nieminen et al., (2002), found that the maximum EF for Cu, Ni, Zn, Pb, and As were 4500, 300, 300, 100, and 300 respectively in surface peat (0 – 14 cm depth) in a ombrotrophic peat bog near a Cu-Ni smelter in Finland. Kylander et al., (2006) and Wedepohl (1995), estimated Pb EFs from average ratio of peats from pre-anthropogenic times dated to 4000 to 5000 years before present that included: the Roman period, present and maximum (industrial) time periods in Spanish bogs that ranged from 5-73, 2-72, and 11-173, indicating a varying degrees of metal enrichment through time.

1.3 Metal removal and immobilization in peatlands

The continued release of metals to the environment from industrial sources has encouraged the development of systems and technologies for removal and mitigation of metal contamination. Traditional active treatment technologies employ processes to remove metals from wastewater such as chemical precipitation, coagulation-flocculation, membrane separation, and electro-treatment that are generally quite costly, inefficient, and unfeasible in certain geographical locations (Kurniawan et al., 2006). As a result, the use of natural and artificially constructed peatlands presents an alternative for the passive treatment of trace and heavy metals that offers advantages in reduced investment and operating costs, often with little to no energy input (Eger, 1994). Research to better understand the specific biogeochemical processes that

facilitate metal removal and immobilization in artificial and natural peatlands can then be used to tailor treatment to a variety of waste waters to decrease the impacts on humans and the environment.

Primary metal removal and immobilization are facilitated through the soil and substrate, hydrology, and vegetation in peatland systems. Hydrology and the permanent or periodic saturation of a peatland area results in anaerobic conditions that helps to facilitate biogeochemical processes, which can be broken into chemical and biological mechanisms of removal (Sheoran and Sheoran, 2006).

Sorption is one of the most important chemical removal processes in both peatlands resulting in the short-term or long-term retention and immobilization of metals. Sorption refers to a group of processes that includes adsorption, oxidation, and precipitation reactions. Heavy metals are adsorbed to soil particles by cation exchange that involves the attachment of positively charged cations (Cu, Ni, Pb, Zn) to the surfaces of clay and organic matter by electrostatic attraction (Sheoran and Sheoran, 2006). The ability of sediment to retain cations is referred to as cation exchange capacity, which increases with increasing clay and organic matter content. Chemisorption is a stronger and more permanent form of bonding, which is highly dependent upon physico-chemical environment, properties of metals and elements, and soluble ligands present (Patrick and Verloo, 1998; Kadlec and Keoleian, 1986; Tipping and Hurley, 1992; Wiebner et al., 2005). Oxidation, reduction, precipitation, co-precipitation and the formation of metal carbonates and sulphides are additional important mechanisms for the formation of insoluble metal precipitates, which greatly limits bioavailability in these systems. Oxidation and hydrolysis of metals, such as Fe, Al, and Mn can occur as a result of changes in pH, oxidation-reduction potential (E_h), and the presence of various anions, with bacteria playing a role in the initial oxidation of ferrous to ferric iron and Mn^{2+} to Mn^{4+}, which can for insoluble compounds in the form of a variety of oxyhydroxides and hydroxides (Sheoran and Sheroan, 2006). The oxidation and reduction or redox state of metals and elements in solution is dependent on the anoxic or oxic conditions of peatlands which drives speciation, toxicity, adsorptive behaviour and transport (Jenne and Luoma, 1977). Precipitation and co-precipitation are chemical processes that are highly

dependent on the solubility product (Ksp) of metal species involved, pH, and the concentrations of metals, elements and anions in solution (Karathanasis and Thompson, 1995; Tarutis and Unz, 1995; Woulds and Ngwenya, 2004). Precipitation from a saturated solution of a soluble metal occurs within a dynamic equilibrium, whereby at equilibrium the rate of metal ion removal in the form of a precipitate is equal to the rate of their dissolution from precipitate (Matagi et al., 1998). Co-precipitation of heavy metals occurs with secondary minerals, such as hydrous oxides of Al, Fe and Mn, which have been found to be normally co-precipitated with Cu, Ni, Pb, Zn, Fe, and Mn etc. The charge of oxides, oxyhydroxides, and hydroxide surfaces is highly dependent on pH, with the co-precipitation and removal of oxyanions (As, Se and Sb) generally occurring under acidic conditions, while the removal of cationic metals (Cu, Zn, and Ni) is better facilitated under alkaline conditions (Brezonik and Arnold, 2011; SenGupta, 2002). The formation of metal carbonates can play a significant role in the initial capture of metals, especially in areas of high bacterial production of bicarbonate or when peatlands are in the flow path of mineral rich waters (Sheroan and Sheroan, 2006). Mercury (Hg) cycling in peatlands has received interest as they constitute a major source of methylmercury (MeHg) to adjacent streams and lakes as a result of anoxic peat soils and availability of electron acceptors such as sulfate which provides optimal conditions for the production of MeHg (Haynes et al., 2017; Coggins et al., 2005; St. Louis et al., 1994). Given Hg semi-volatile state in elemental form, the factors controlling removal, cycling and transport is quite different from base metals.

Biological removal processes represent an important pathway for heavy metal removal and immobilization in wetland systems. Plant uptake being the most widely recognized process, which can occur through the roots and plant tissues. The reduced environment in wetland sediments and peat results in metal forms with different bioavailability and is a result of the complex interaction within the rhizosphere as oxygen transport to plant roots results in changes in pH and redox processes (Jacob and Otte, 2003; Armstrong and Armstrong, 1990). Soluble and exchangeable metals are easily absorbed, while precipitates and complexed metals with humic material are potentially available, and insoluble sulfide metals and crystalline metals are unavailable for root uptake (Gambrell, 1994). Metal removal rates through the roots

and tissues of the plants varies greatly, depending on the plant species, growing rate, and concentration of metals in tissues. In general, the rate of metal uptake per unit area is higher in herbaceous species, through foliar absorption, in which the passive movement of aqueous phase metals through cracks in the cuticle or through the stomata. Similarly, mosses including *Sphagnum spp.* are capable of accumulating metals owing to their large surface to volume ration and their low surface resistance to ion uptake from solutions, due to limited cutin development (Brown, 1982). The rooting zone and rhizosphere of plants can oxidize sediments by translocating oxygen from the shoots to the root rhizomes resulting in the oxidation of sediments that can remobilize metal contaminants and increase exchangeable forms (Moorhead and Reddy, 1988). However, depending on the biogeochemical condition of the rhizosphere and sediments, the oxidative conditions can result in the conversion of ferrous to ferric iron and the precipitation of Fe oxides and hydroxides on the root surface forming plaques, with Mn representing a secondary element due to higher redox potential (Moorhead and Reddy, 1988 Christensen and Sand-Jensen, 1998; Liu and Zhu, 2005). Both Fe and Mn (hydro) oxides possess functional groups that can react and have high adsorption capacity to some cations and anions in soils, which may immobilize metals by limiting metal uptake in plants.

The role of microorganisms in the multiple physico-chemical and biological mechanisms effecting transformations between soluble and insoluble phase of metals in peatlands and wetland sediments has been recognised (White and Gadd, 1996; Sayer and Gadd, 1997; Kosolapov et al., 2004). Biosorption is the passive metabolism-independent sequestration of metals interacting with live or dead biomass though ion exchange, chelation, adsorption, and entrapment and various functional groups (amino acids, sulfonate, phosphate etc.), as well as metal accumulation within the cell that forms amorphous mineral inclusions (Vainshtein et al., 2002). Although these interactions play a role in the enhancement or inhibition via metal transport and transformation, this process does not contribute to the long-term storage of metals within peatlands (Kosolapov et al., 2004). Anaerobic dissimilatory metal-reducing bacteria and archaea are able to reduce metals to a lower redox state by using the metal as a terminal electron acceptor during respiration, decreasing metal mobility through precipitation reactions (Kosolapov et al., 2004). The dissimilatory

reduction of Fe, Cr, U, V, Tc, and Au has been well documented by a diverse group of microorganisms in a variety of environmental conditions (Lloyd, 2003; Lovley, 1993). In addition to direct dissimilatory reduction of metals, bacteria are able to produce sulfide, hydroxide, carbonate and phosphate through diagenetic processes resulting in the formation of highly insoluble precipitates. Sulfur-reducing bacteria (SRB) and the formation of metal sulfides can be considered one of the most important reactions for the long-term immobilization and storage of metals in peatlands (White and Gadd, 1996). Sulfur-reducing bacteria reduction of sulphate and the oxidization of a range of organic compounds or hydrogen results in the formation of hydrogen sulfide which then precipitates with metals such as Fe, Zn, Cu, etc. (Kosolapov et al., 2004). This reaction also results in an increase in pH due to the lowered concentration of sulphate, loss of hydrogen sulfide to the atmosphere and production of bicarbonate (Kosolapov et al., 2004). The lowered acidity in the system causes a shift in equilibrium when sulfate is converted to sulfide, prompting further precipitation of metals as hydroxides (White and Gadd, 1997). In order for S reducing bacteria to effectively immobilize metals in natural and artificial peatlands concentrations of sulfate and C must be sustained (Kosolapov et al., 2004).

1.3 Global Implications of Climate Change

Climate change represents a significant pressure on ecological systems due to projected changes in regional and global temperature, precipitation, and other climatic variables, which will potentially affect the geographic location and function of ecological systems and water resources. The Intergovernmental Panel on Climate Change (IPCC) anticipates a 0.3-4.8°C increase in global average temperature over the next century, with changes in precipitation patterns, and frequency of extreme weather events expected to occur on a regional basis (IPCC, 2014). The extent at which ecosystems will be impacted varies globally and is highly dependent on differences in local environmental conditions, sensitivities to predicted changes and pre-existing stressors on the system (Settele et al., 2014). The impact of climate change on terrestrial systems is projected to occur at a faster rate than plant species can grow, reproduce, and re-establish, with

global areas undergoing shifts in broad vegetation types and a geographic movement towards the poles, resulting in changes in composition, species loss, and new ecosystem establishment (Settele et al., 2014). The tundra, alpine and permafrost systems demonstrates an example of a sensitive ecosystem to the projected implications of climate change, which has warmed more than the global average over the last century (Kaufman et al., 2009). Tundra regions of North America and northern Eurasia have seen increased expansion of woody vegetation and shrub cover due to increased photosynthetic capacity, thawing permafrost, retreat of sea ice, and increased frequency of fire, resulting in a positive feedback for additional woody plant encroachment (May et al., 2020; Goetz et al., 2011; Bhatt et al., 2010). Similarly, inland freshwater ecosystems are already considered among the most threatened systems on the planet, which will be further influenced by altered water temperatures, flow regimes, water levels, and thawing of permafrost at higher latitudes (Dise, 2009; Jiménez Cisneros et al., 2014). Lakes and streams would likely see an increase in flow variability, due to the frequency and duration of large floods and droughts, resulting in changes in water quality, biological productivity, and habitat in streams (Jiménez Cisneros et al., 2014).

Climate change is expected to have clear impacts on the hydrology of peatland ecosystem through changes in temperature, precipitation, and evapotranspiration, which will likely be the indirect agent affecting wetland size, shift of wetland type or outright loss of the peatland system. The plant community's response to drought conditions has been strongly linked to climate, hydrology, geochemistry, and gas exchange (Kuhry et al., 1993; Bubier, 1995). In northern and subarctic peatland communities, increasing temperature will result in the drying of the surface soil and peat layer, initiating secondary succession, whereby the *Sphagnum* dominated moss layer disappears, followed by dwarf-shrubs in nutrient poor locations, while the species composition develops gradually towards upland forest vegetation in nutrient rich systems (Laine and Vanha-Majamaa, 1992; Laine et al., 1996). Similarly, tropical and coastal peatland communities are expected to be impacted by more intense rain events, over a shorter rainy season and sea level rise, which can result in increasing rates of erosion, saline inputs into freshwater systems, altered species composition and extensive loss along coastline areas (Eliot et al., 1999). Climate change and the

shift in plant community composition, will have compounded effects on natural peatland function, geochemistry and cycling, specifically related to water-level drawdowns impact on the C balance. The oxidation of organic matter within peatland soils will increase rates of decomposition, resulting in elevated flux of CO_2 to the atmosphere, suggesting that C storage in higher latitudes could shift from a net sink to source (Gorham, 1991).

1.4 Peatland Acidification

Studies that have investigated the potential impacts of climate change on peatlands primarily focused on C dynamics, cycling, and feedback mechanisms with little consideration to the potential risk of drought induced peatland acidification. Changes in mean precipitation are expected to lead to earlier peak runoff, increased duration of low flow, and the frequency of drought events during the summer (Trenberth 2011). If dry periods are severe enough to result in a lowering of the water table, exposing previously anoxic soils to the air, profound changes on wetland water chemistry and quality are expected to occur. Global sulfur dioxide (SO_2) emissions have risen drastically over the last century, with sources changing both geographically and by sector, with emissions from countries in the North Atlantic basin (United States, Canada, Europe) declining substantially over the last two decades, while contributions from Asia have increased (Smith et al., 2001). Similarly, nitrogen (N) emissions have approximately doubled since the 1960's and is still increasing (Vitousek et al, 1997). The accumulation and retention of S and N compounds in peatland surfaces and soils can be through direct inputs, dry and wet deposition, in addition to fixation of N through plants (Urban et al., 1989; Moore et al., 2005). Under drought conditions reduced sulfur compounds are oxidized to sulphate (SO_4^{2-}) and form H_2SO_4 resulting in a reduction in pH and increases in metal and certain element concentrations in pore water upon rewetting (Juckers and Watmough, 2014; Watmough et al., 2004). The severity of pH depressions has been shown to gradually decline due to the depletion of soil S pools in peatlands by drought (Tipping et al., 2003). However, pH depressions have been shown to be sustained from N deposition, due to the increase nitrification and mineralization of nitrogen-

containing organic compounds under aerobic conditions, with NO_3^- concentrations being shown to increases immediately following prolonged summer droughts (Watmough et al., 2004; Freeman et al., 1993; Williams and Wheatley, 1988). Both NO_3^- and SO_4^{-2} are implicated in environmental and peatland acidification, which can significantly alter metal and DOC export to downstream environments.

The impact of drought on metal mobility and release from bog and fen systems has been well documented in UK and North America, whereby decreasing pH results in higher concentrations of base cations (Ca and Mg) and dissolved metals (Al, Fe, Mn, Ni, Cu, Pb, Cd, Co, and Zn) (Juckers and Watmough, 2014; Tipping et al., 2003; Adkinson et al., 2008). Increasing trends of DOC concentrations in freshwater systems have also been observed in Europe and North America, however there is little consensus on global and mechanistic drivers associated with these trends. The increase in DOC export from wetland systems can further enhance metal pulse dynamics due to complexation to humic substances, with Al, Cu, and U demonstrating a high affinity to organic molecules (Cumberland et al., 2016; Watmough and Orlovskaya, 2015; Wang et al., 2013; Tipping et al., 2003). Explanations on a landscape scale have been linked to increased temperature (Freeman et al., 2001), increased rainfall (Hongve et al., 2004), decreased S deposition (Driscoll et al., 2003) and elevated N deposition (Findlay, 2005). On a more localized scale, the impact of water table drawdowns on DOC production and export has also been debated, with some authors observing increased DOC concentrations in soil leachates proceeding drought periods (Tipping et al., 1999), while others have observed reductions (Freeman et al., 2004) or no change (Blodau and Moore, 2003). Under drought conditions explanations for DOC increases have included 1) changes in DOC export in relation to changes in hydrology and discharge (Eimers et al., 2007; Pastor et al., 2003; 2) changes in peat structure preventing rewetting thereby delaying or inhibiting DOC release (Watts et al., 2001); 3) changes in decomposition, production, and microbial consumption under dry conditions resulting in CO_2 efflux (Freeman et al., 2004; Fenner and Freeman, 2011); and 4) pH influence on DOC solubility by controlling the dissociation and precipitation of organic acids (Clark et al., 2005, 2006). Based on the anticipated increase in the frequency and severity of drought in response to climate change, significant changes in

wetland and peatland geochemistry are expected to occur, which will likely promote metal release and destabilize carbon stores potentially impacting adjacent surface water and biota.

In contrast to other metals, the geochemical behaviour affecting the accumulation, stability and/or remobilization of uranium (U) in peatlands is far less understood due to the complexity of factors and interactions within organic rich sediments and aquatic environments (Cumberland et al., 2016). Uranium exists in four valence states: U^{3+}, U^{4+}, U^{5+} and U^{6+}, but the tetra and hexavalent states are commonly found in the environment. Most mobilization of U occurs during weathering processes in which uranous compounds (generally uraninite) are released from rock and oxidized to the uranyl ion (UO_2^{2+}) by surface waters, which is the principal form in aquatic environments (Bird, 2012; Gascoyne, 1992). Uranyl ion is a large positively charged ionic species similar in size to K, Ca, and Ce, forming complexes with Cl, Fl, PO_4^{3-}, SO_4^{-2}, and CO^{2-}, with Fl complexes predominating below pH 5 and PO_4^{3-} complexes forming between pH 4 and 7.5 (Sheppard, 1980; Langmuir, 1978)). The chemical speciation of U is influenced by water quality variables such as alkalinity, hardness, pH, and organic matter (Markich et al., 2000; Hamelink et al., 1994). Uranium biotic uptake generally correlates with free UO_2^{2+} concentration with increased ligands which can be assimilated along with the metal (Fortin et al., 2004; Markich, 2002).

Major sources of anthropogenic releases of U include mining/milling and refining, combustion of fossil fuels, with atmospheric emissions occurring mainly through burning of wood, peat, coal, metal refining and cement industries. Long-range atmospheric deposition of U is likely minimal, with major inputs generally occurring in close proximity to the point source pollution, such as mining and milling operations from ore and tailings dust (Thomas, 2000; Becket et al., 1982). Alternatively, the majority of U geochemistry and contamination research pertains to the disposal of nuclear fuel, wastes, and remediation of U-contaminated soils, groundwater and aquatic systems that has resulted from downstream discharge and effluent (Krupka and Serne, 2002; Burns and Finch, 1999). Effluents from mines usually enter the epilimnion of the receiving waters, whereby U is rapidly adsorbed to DOM, suspended soils, sediments,

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and algae. The reduction of U(VI) to U(IV) and the subsequent chemical reactions and transformation of U sulfide, carbonate, or other biogenic ore requires strongly reducing conditions (i.e. U(VI) reduces to U(IV) at low EH < -200 mV) (Bird, 2012). In the peat or sediment profile redox conditions change with oxygen being reduced first, followed by denitirification, then by UO_2CO_3 reduction to uraninite and SO_4^{-2} reduction to sulfide (S^{2-}), with U reduction and removal from porewater being related to bacterially mediated sulfate reduction (Bird, 2012). Changes in environmental conditions such as bioturbation, E_h, pH, temperature, salinity, biological activity (SO_4^{-2} reduction is halted) and ligand type and concentrations may affect U speciation, complexation, and consequently mobility and toxicity (Bird, 2012).

1.4 Research Objectives

My MSc research aims to expand on the current knowledge of global peatland geochemistry, and looks to fill knowledge gaps in the current understanding of metal contamination and distribution in peatland systems, which could be significantly altered based on future climate change predictions. Specifically, the first chapter of my thesis will i) investigate metal and element concentrations and enrichment factors in peatlands sampled around the world in an effort to better understand the global distribution of contamination, ii) estimate and attempt to link global peatland enrichment factors to patterns of sulphur deposition as a surrogate pathway for global contamination, and iii) estimate metal and elemental pools in peatlands. The second chapter of my thesis will utilize a case study of peatlands impacted by uranium mining activities in Elliot Lake, Ontario to further examine iv) the impacts of climate change induced drought on wetland geochemistry and metal mobility. Collectively, this research looks to understand metal geochemistry in peatlands by characterizing global patterns and contamination pathways to examining specific processes effecting metal mobility.

1.5 Significance of Research

The implications of climate change on peatlands will vary between regions and among peatland types, with accurate predictions being difficult to quantify due to general uncertainties, lack of geographical data pertaining to climate prediction models, coupled with differential responses by non-climatic related pressures. Based on the level of variability of global metal contamination and enrichment in both pristine and degraded peatland systems, climate induced peatland acidification and metal release represents a significant risk to surface waters and biota, whereby peatland systems could shift from historic sinks to contamination sources. To date, no study has attempted to quantify the extent of metal contamination in peatland systems on a global scale. It is therefore important to better understand the global distribution and patterns of metal contamination, and further evaluate changes in wetland geochemistry in response to drought as predicted responses of climate change becomes more apparent.

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2.0 Global patterns of metal enrichment in peatlands.

Abstract

Peatlands have been used to assess spatial patterns of atmospheric metal deposition and metal enrichment from natural and anthropogenic sources. Previous studies have primarily focused on bogs and a few well documented metals associated with atmospheric metal pollution with much less work on other metals or peatland types, especially outside of Europe and North America. We sampled 439 cores distributed across 5 continents and 21 countries and measured 35 elements by depth increments [10-20, 30-40 and 60-70 cm]. Peatlands were characterized into five widely recognized peatland categories: bog (158), poor fen (128), intermediate fen (38), rich fen (47) and tropical peat swamps (68). Metal and element concentrations in peatlands were highly variable and not normally distributed and concentrations of most metals were highest in rich and intermediate fen peatland types. Elements that had average concentrations >3x the median were Al, As, Ce, Co, Cu, Dy, Eu, Fe, La, Li, Mn, Na, Pb, Rb, Se, Sm, Ti, U, V and Zn. Global patterns in enrichment factors (EF's) were determined for all elements using Zr as a conservative element. The majority of elements had a median EF < 2 indicating minor enrichment. Principal component analysis indicated EF's of 6 metals (Cd, Co, Cu, Ni, Pb, and Zn), 2 metalloids (As and Sb) and 1 non-metal (Se) in the upper peat horizon had similar spatial patterns among peatlands and had generally the highest EF's with many cores exceeding EF >10 and some having EF values >100. Significant differences in EF's were found for these 9 "pollution" metals by peatland type and to a greater extent by geographic region, with higher EF values typically occurring in Europe and North America compared with South America, Africa, Asia and Oceania. Enrichment factors for most "pollution" elements exhibited weak but significant positive correlations with modelled [1850 – present] atmospheric S deposition. Estimated pools for the "pollution metals" within the 0 – 40 cm depth varied considerably, with median global pools in peat ranging from 12.9 mg m^{-2} (Sb) to 439 mg m^{-2} (Zn).

2.1 Introduction

Metals have been emitted into the atmosphere by human activities and subsequently deposited to soils since the discovery of mining and metallurgy more than 2000 years ago (Nriagu, 1996). Natural sources of trace metals and metalloids include wind-borne soil particles, volcanoes, sea-salt spray, and fires, although natural atmospheric deposition fluxes for most metals are small compared with emissions from industrial activities (Nriagu, 1989). Continued global industrialization over the past century has resulted in the rapid increase in anthropogenic metal contributions on local, regional and global scale, which far exceeds 'natural' background concentrations in soils (Pacyna and Pacyna, 2001). Peatlands represent an important ecosystem and receptor of metals due to their global distribution, sensitivity to environmental changes, and ability to act as reservoirs for metals (Sheoran and Sheoran, 2006). The capacity of peatlands to store metals creates natural long-term records that can be used to differentiate and document the temporal trends of natural versus anthropogenic inputs, as well as the magnitude of metal contamination in these systems (De Vleeschouwer et al., 2007; Le Roux et al., 2005; Shotyk et al., 2005).

Metal profiles in ombrotrophic peatlands are most often studied as they are hydrologically isolated from the influence of groundwaters and surface waters, receiving all chemical inputs from atmospheric deposition (Brinson, 1993; Damman, 1986). Peatlands have been shown to be useful archives of changes in atmospheric metal deposition, sometimes extending more than 3000 years (Mighall et al., 2002; Shotyk, 2002a). Most studies have focused on metal contamination in bogs or poor fens in Europe (Roos-Barraclough et al., 2002; Martinez-Cortizas et al., 2002) and North America (Benoit et al, 1994; Pratte et al., 2013). Further, these studies have primarily focused on local and regional sources of a few metals including lead (Pb) (Shotyk, 2002; Vile et al., 1999; Weiss et al., 1999), copper (Cu) (Mighall et al., 2002), mercury (Hg) (Coggins et al., 2006), nickel (Ni) (Krachler et al., 2003), zinc (Zn) (Twardowska et al., 1999) and to a lesser extent arsenic (As) (Ukonmaanaho et al., 2004), mercury (Hg) (Coggins et al., 2006), cadmium (Cd) (Rausch et al., 2005) and cobalt (Co) (Rausch et al., 2005).

To date, there has been no attempt to evaluate metal contamination in peatlands distributed globally among different peatland types, with additional metals linked to anthropogenic sources such as antimony (Sb), chromium (Cr), manganese (Mn), selenium (Se), and vanadium (V)) having been rarely investigated. Improvements in national and regional trace metal emission inventories have been made (Pacyna and Pacyna, 2001; Nriagu 1989), however it remains unclear whether patterns in metal contamination at a global scale can be linked to anthropogenic sources (fossil fuel and coal combustion, metallurgical processing or sulphur (S) deposition). Background metal concentrations can vary naturally, especially among different peatland types due to differences in sedimentary processes, water table fluctuations and surface and groundwater inputs (Gorham et al., 1979). A common way to differentiate natural and anthropogenic inputs is through the use of enrichment factors (EF's), which indicates the number of times an element is enriched in a given sample compared with the abundance of that element in crustal rocks (Jeffries and Snyder 1981; Schütz and Rahn, 1982). A conservative element (e.g. Al, Sc, Ti, Zr) is used to quantify the amount of metals gained relative to source rock [or deep peat] composition through anthropogenic contamination. Enrichment factors within peatlands have been reported to range from 1-100 times higher than pre-industrial levels, with studies generally linking recent fluxes and deposition to local and regional sources of metal pollution (Rausch et al., 2005; Nieminen et al., 2002; Shotyk, 1996; Dunlap et al., 1999).

This study seeks to evaluate metal contamination in global peatlands by evaluating 439 cores distributed across 5 continents and 21 countries. We evaluated 31 metals, 3 metalloids and 1 non-metal concentrations in 3 depth increments [10-20, 30-40 and 60-70 cm] and by peatland categories. For the purpose of this study, all elements analyzed are referred to as metals, as they comprise the majority of the elements in the dataset, with metalloids (As and Sb) and non-metals (Se) demonstrating similar patterns to metals. In order to determine anthropogenic metal contributions over background levels, global patterns in EF's were determined for these 35 metals, using the deepest peat section as "pre-industrial", but recognizing that even at this depth some anthropogenic influence may have occurred (Shoytk, 1988) and metal mobility

within cores of some peat types may also influence EF's. Based on these metals' general association to atmospheric pollution sources, we investigated the relationship of modelled cumulative S deposition to metal enrichment. This study is also the first attempt at estimating metal pools in surface peat in global peatlands using previously published relationships between soil C concentration and bulk density (Hossain et al., 2015). We expected that metal concentrations to exhibit patterns by depth based on lithogenic vs. anthropogenic origin, with intermediate fens exhibiting the highest concentrations do to surface and groundwater inputs. Metals associated to anthropogenic pollution (Cu, Ni, Pb, and Zn) would exhibit the highest EFs, with patterns of enrichment being tied to proximity to point sources with industrial continents (Europe and North America) being found to have higher levels of metal enrichment due to higher cumulative S deposition.

2.2 Methods

2.2.1 Global peatland microbiome project sampling

We sampled 439 peat cores located in 21 countries distributed across five continents (Figure 2.1). For simplicity, sites were divided into five regions to compare differences among metals, although the sites do not necessarily reflect peatland distribution within each region: North America (n=263), South America (n=29), Europe (n=68), Southern Africa (n=10), and Asia (n=58), and Oceania (n=11) (Table 1.) Similarly, we classified peatlands as bogs, poor fens, intermediate fens, rich fens, and tropical peat swamps based on the classification provided by participants and which generally fall along an acidity gradient with pH increasing from peat swamps and bogs to rich fens. The samples used for this study are part of a larger project characterizing the geochemistry and microbial communities in global peatlands, with sampling not specifically designed to test spatial variation recognizing the uneven distribution of peatland types sampled within each region.

Research groups working on the project followed the same set of standardized sampling protocols, whereby three samples were collected from a specific topographic position that would be representative of the site. Participants were instructed to collect one core from each replicated plot or up to three cores for each treatment depending on the study design of plots already under study or experimental manipulation. Coring and collection methods included Russian peat borer, box corer, or sampled by hand using a serrated knife to achieve three depth increments (10-20 cm, 30-40 cm, and 60-70 cm) from each location, while cleaning sampling tools and avoiding compaction. A minimum of approximately 50 g field moist peat was collected per depth and were homogenized in plastic bags. Immediately upon sub sampling at the depth horizons, temperature, von Post, humification, and soil moisture was recorded. Sample materials were frozen to -20° C prior to shipping. Collaborators were instructed to utilize rapid shipping methods and to keep samples on dry ice or ice packs to ensure samples remained frozen when possible.
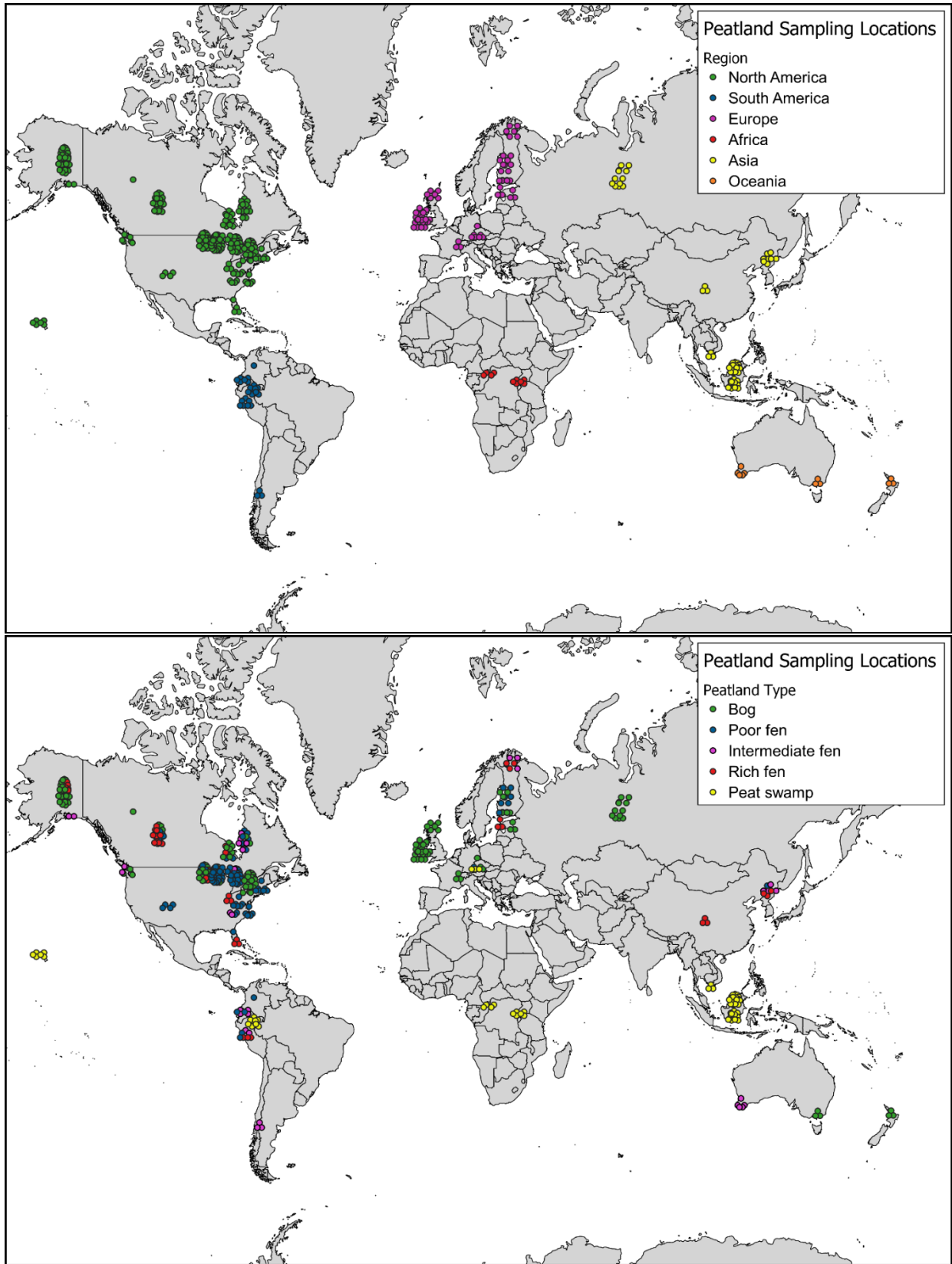
Figure 2.1. Continental distribution of peatland core sampling locations by region (Top) and by peatland type (Bottom).

Table 2.1. Continental sampling sites by each peatland type.

Continents	Countries (n)	Bogs	Poor Fens	Intermediate Fens	Rich Fens	Peat Swamps	Total
North America	Canada, USA	94	111	16	32	10	263
South America	Argentina, Colombia, Ecuador, Peru	-	6	10	3	10	29
Europe	Czech Republic, Estonia, Finland, Ireland, Scotland, Switzerland	46	10	3	6	3	68
Africa	Republic of Congo, Uganda	-	-	-	-	10	10
Asia	Brunei, China, Indonesia, Russia, Vietnam	12	1	4	6	35	58
Oceania	Australia, New Zealand	6	-	5	-	-	11
Total	21	158	128	38	47	68	**439**

2.2.2 Chemical Analysis

Chemical analysis was performed on a subset of each sample, which was oven dried at 60 °C and ground to a fine powder in a ball mill. Milled samples were combusted at 550°C for 6 hours in a muffle furnace before transferring ash into digestion tubes using type I grade purified water for digestion and total elemental analysis on an inductively coupled mass spectrometry (ICP-MS) at the Elliot Lake Field Research Station at Laurentian University. Peat ash in water was first digested at 110 °C for 210 minutes in 10 ml of HF and HCl acid until dry, with this process being repeated twice. For the third digestion, 7.5 ml of HNO_3 acid and HCl was added again at 110 °C for 250 minutes until dry. The final digest was completed by adding 10 ml of HNO_3, 2 ml of HCl and 0.5 ml of HF at 110 °C for 60 minutes and diluted to 50 ml using deionized water. Samples were then diluted within detection limits and analyzed on a Varian 810 ICP-MS for total concentrations for the periodic table. Samples were analyzed in duplicates and two organic standard reference materials were used for every 20 samples to ensure quality standards (spinach and tomato leaves NIST CRM 1570a and 1573a). Samples below detection limits for each analyzed metal was removed from

the data set and statistical analysis. Additionally, values for certain metals are missing from the dataset, resulting in difference in sample size (*n*) for each metal used for global assessment.

2.2.3 Enrichment Factors

Enrichment factors were determined for all metals by quantifying the amount of element gained in the upper profile of the peat cores (10-20 cm), relative to the peat composition found within the lower profile (60-70 cm) of the cores, indicating anthropogenic inputs. It was assumed that 60-70 cm was deep enough to represent background metal concentrations, although the age of peat at these deeper samples likely vary considerably and as such EF should be considered conservative. Enrichment factors were calculated as follows (MI-metal of interest, CE-conservative element in crustal rocks):

$$EF_{Metal\ of\ Interest} = \frac{([MI]/[CE])\ _{Sample}}{([MI]/[CE])\ _{Crust}} \qquad [2.1]$$

Zirconium (Zr) was chosen as the 'conservative' metal as it forms oxides of extremely low solubility, making the metal highly resistant to weathering (Baes and Mesmer 1976).

2.2.4 Cumulative Global Sulphur Deposition

Total cumulative sulphur (S) deposition (Wet and Dry SO_x and SO_4^{2-}) data were used from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), by combining generated multi-model means from decade time slices representative of the period around 1850-1859, 1980-1989, and 2000-2009 on a 0.5° x 0.5° resolution grid (Lamarque et al., 2013). Cumulative S deposition (kg (S) ha) was estimated by summing the interpolated annual rate of S deposition ($mg(S)\ m^{-2}\ yr^{-1}$) determined for time periods from 1850-1979 and 1980-2009, assuming a linear change in deposition on a year to year basis.

2.2.5 Bulk Density

Bulk densities for each wetland core were not recorded and so were estimated for 10-20 and 30-40 cm depth increments using pedotransfer exponential function based on soil organic carbon content (Hossain et al., 2015). The pedotransfer function was developed for organic soils from 0-100 cm depth in Canada's arctic and sub-arctic region. The best fit model for organic soils is as follows ($n = 1376$, $R^2 = 0.98$):

$$BDp = 0.074 + 2.632 \exp(-0.076\ SOC) \qquad [2.2]$$

where, BD_p is predicted bulk density (g cm^{-3}) and SOC is soil organic carbon (% weight). Predicted bulk densities for each respective depth and core was then used for estimating metal pools.

2.2.6 Metal Pools

Soil metal pools (mg m^{-2}) for the 0 - 40 cm layer were calculated for metals shown to have the highest EF's (As, Cd, Co, Cu, Ni, Pb, Sb, Se, and Zn) using the percent metal concentration, predicted bulk density and horizon thickness. The formula is as follow:

$$Metal\ Soil\ Pools = (M\ x\ BDp\ x\ T) \qquad [2.3]$$

where M is metal concentration (% weight), BD_p is the predicted bulk density (g cm^{-3}) and T is thickness of horizon. Using this information, metal pools were calculated by using 10 - 20 and 30 - 40 cm

concentrations for 0 - 20 and 20 - 40 cm respectively to estimate pools from 0 - 40 cm for each peatland core.

2.2.7 Statistical Analysis

To assess spatial relationships among metals in peat, principal component analysis (PCA) was performed on metal concentrations (mg kg^{-1}) at 10 – 20, 30 - 40, and 60 - 70 cm depth increments and enrichment factors (EF). We compared the concentration of 35 metals among peatland types and compared metals shown to have the highest EF among regions and peatland types using Welch's ANOVA due to unequal variances between regions and peatland types. When differences in variable means were found to be significant, a pairwise comparison was conducted using a non-parametric Games-Howell test (p<0.05). Statistical analyses were performed using "R" (R Core Team, 2012). Kendall's Tau ranked correlation was used to determine relationship between EF's for As, Cd, Co, Cu, Ni, Pb, Sb, Se, and Zn to estimated cumulative S deposition since 1850. Summary statistics are presented for estimated global metal pools.

2.3 Results

2.3.1 Metal Concentrations by Depth

Metal concentrations among peatlands varied considerably (Table 2.2). Metals exhibiting the highest median concentrations (>100 mg kg^{-1}) included Al, Ca, Fe, K, Mg, Na, and Ti, with As, Ba, Ce, Co, Cr, Cu, Ga, Ge, La, Li, Mn, Mo, Nb, Ni, Pb, Rb, Se, Sr, V, Zn and Zr had moderate (1-100 mg kg^{-1}) median concentrations, while Cd, Dy, Eu, Sb, U, and Yb had median values < 1 mg kg^{-1}. Concentrations of most metals were not normally distributed; mean concentrations were generally higher than median concentrations, which may be indicative of anthropogenic inputs in localized regions. Metals that had average concentrations >3x the median were Al, As, Ce, Co, Cu, Dy, Eu, Fe, La, Li, Mn, Na, Pb, Rb, Se, Sm, Ti, U, V and Zn (Table 2.2). PCA and varimax normalized rotation of metal concentrations generated three factors for 10-20, 30-40 and 60-70 cm depths, accounting for 63.5, 67.5 and 62.3% of the total variance respectively on the first three axis (Figure 2.2). PC1 generated 17 metals with a loading >0.70 across the three depth increments that included Al, Ba, Ce, Cr, Ga, K, La, Li, Mg, Mo, Na, Nb, Rb, Sm, Ti, V, and Zr. Metals with loadings >90 on PC2 included Dy, Eu, Fe, Ge, Yb, Zn, which only occurred in the 30-40 and 60-70 cm depth increment. Metals generated on PC3 with the highest loadings included As (0.82), Cd (0.80), Cu (0.91), Ni (0.68-0.70), Pb (0.88-0.91), Sb (0.84), with additional metals with lower loadings within the 10-20 cm layer including Co (0.72), Mn (0.85), Se (0.71).

Table 2.2. Summary of metal concentration (mg kg^{-1}), count, mean ($\pm$ SE), median, min and max of total core depth (0-70 cm) from all global peatland cores (n=418).

Analyte	Count (0-70 cm)	Average ($\pm$ SE)	Median	Min	Max
Al	1312	11062 $\pm$ 634	2785	8.7	266000
As	1119	4.94 $\pm$ 0.5	1.31	0.07	267
Ba	1269	114 $\pm$ 5.3	48.3	0.14	1830
Ca	1225	9044 $\pm$ 551	3740	19.8	309000
Cd	920	0.84 $\pm$ 0.1	0.32	0.02	64.6
Ce	1292	13.5 $\pm$ 0.9	3.4	0.03	358
Co	1260	6.2 $\pm$ 1.4	1.1	0.02	1080
Cr	1256	67.3 $\pm$ 3.7	25.3	0.31	1460
Cu	1264	26.4 $\pm$ 3.0	6.4	0.11	2180
Dy	1022	1.1 $\pm$ 0.1	0.28	0.01	47.0
Eu	827	0.52 $\pm$ 0.04	0.17	0.01	12.8
Fe	1292	8661 $\pm$ 556	2600	8.3	227000
Ga	1271	5.2 $\pm$ 0.2	1.9	0.03	77.6
Ge	858	4.0 $\pm$ 0.2	1.9	0.04	91.2
K	1252	2244 $\pm$ 137	781	4.8	59900
La	1273	7.5 $\pm$ 0.6	1.8	0.01	28
Li	1002	4.6 $\pm$ 0.4	1.1	0.01	140
Mg	1293	1792 $\pm$ 92.9	870	9.3	58500
Mn	1248	234 $\pm$ 36.9	34.9	0.13	32600
Mo	375	6.4 $\pm$ 0.3	4.0	1.00	44.8
Na	1267	2028 $\pm$ 170	428	5.07	84800
Nb	725	2.8 $\pm$ 0.2	1.0	0.13	44.8
Ni	913	44.7 $\pm$ 5.6	7.6	0.17	2670
Pb	1308	15.4 $\pm$ 1.2	5.2	0.07	929
Rb	1275	9.4 $\pm$ 0.7	2.7	0.03	326
Sb	918	0.76 $\pm$ 0.10	0.27	0.02	55.7
Se	433	4.9 $\pm$ 0.8	1.4	0.19	217
Sm	1036	1.6 $\pm$ 0.13	0.41	0.01	46.1
Sr	1283	61.5 $\pm$ 3.6	25.8	0.21	2090
Ti	1304	609 $\pm$ 45.4	150	1.2	17600
U	863	1.5 $\pm$ 0.1	0.44	0.03	68.7
V	1120	19.3 $\pm$ 1.1	6.1	0.09	431
Yb	761	0.62 $\pm$ 0.05	0.23	0.01	16.7
Zn	1226	89.7 $\pm$ 19.9	23.1	0.09	13800
Zr	1165	12.1 $\pm$ 0.7	4.2	0.20	325
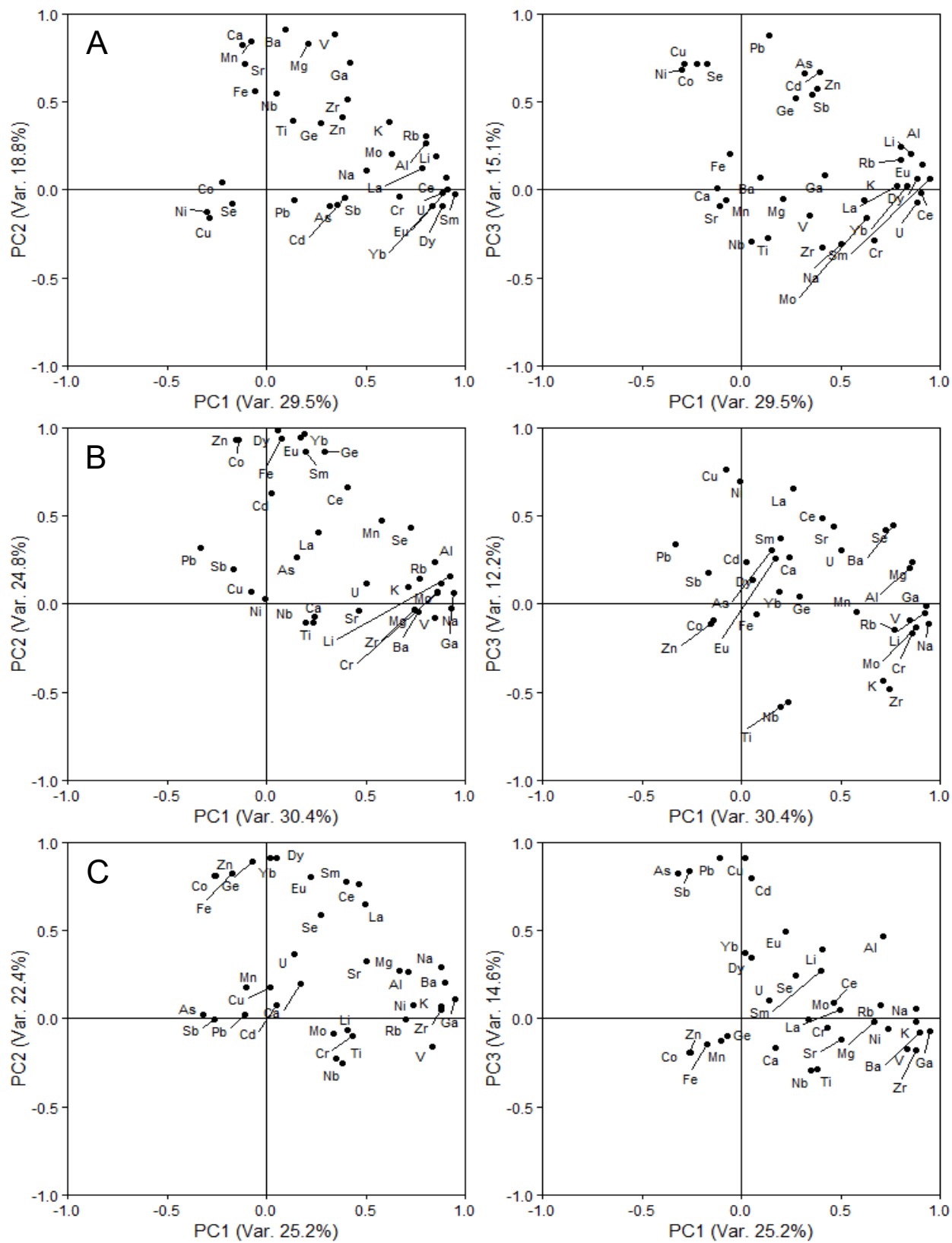
Figure 2.2. PCA of metals concentrations at A) 10 - 20 cm, B) 30 - 40 cm, and C) 60 - 70 cm depths.

2.3.2 Metal Concentrations by Peatland Type

Large differences in metal concentrations were evident among peatland types, with average concentrations of most metals again exceeding median concentration of metals (Table 2.3). In general, bog and tropical peat swamps had the lowest concentrations of metals; especially base cations, Fe, and Al. Average and median metal concentrations were the highest for all metals in intermediate and rich fen systems with the exception of Nb, and Se. Intermediate and rich fens had particularly high concentrations of Al, Ca, Fe, K, Mg, and Na which were 3-15x higher than bog, poor fen and tropical swamp peatland types. Metals shown to have a strong association in the upper depth increment and PC3 included As, Cd, Co, Cu, Ni, Pb, Sb, Se, and Zn were highest in poor and intermediate fens, with the exception of Se (12.1 ± 4.5 mg kg^{-1}) which was greatest in tropical peat swamps. Mean concentrations ranges of these metals in poor and intermediate fens were: As (5.7 ± 1.2 to 15.6 ± 3.5 µg g^{-1}); Cd (1.1 ± 0.2 to 1.8 ± 0.6 µg g^{-1}), Cu (51.9 ± 9.5 to 58.8 ± 10.0 µg g^{-1}), Ni (75.7 ± 21.4 to 87.9 ± 15.4 µg g^{-1}), Pb (15.7 ±2.8 to 21.0 ± 2.8 µg g^{-1}), Sb (0.6 ± 0.2 to 1.3 ± 0.4 µg g^{-1}) and Zn (55.5 ± 6.5 to 210 ± 63.7 µg g^{-1}).

Table 2.3. Summary of mean (± SE) and median of metal concentrations (mg kg^{-1}) of total core depth (0-70 cm) by peatland type.

Metal	Bogs (n=158) Average (± SE)	MED	Poor Fens (n=128) Average (± SE)	MED	Intermediate Fens (n=38) Average (± SE)	MED	Rich Fens (n=47) Average (± SE)	MED	Peat Swamps (n=68) Average (± SE)	MED
Al	6765 ± 734	1850	10129 ± 934	4070	33407 ± 3633	19600	11631 ± 1512	4280	9880 ± 2006	1290
As	2.4 ± 0.2	1.0	5.7 ± 1.2	1.4	15.6 ± 3.5	5.4	5.7 ± 0.9	2.6	1.8 ± 0.2	0.9
Ba	81.6 ± 6.6	33.8	97.0 ± 7.4	58.7	257 ± 31.5	130	190 ± 18.6	146	79.1 ± 12.6	13.5
Ca	4219 ± 219	2990	4700 ± 262	2970	12784 ± 1241	7435	33531 ± 3781	20400	8877 ± 1288	2270
Cd	0.7 ± 0.1	0.3	1.1 ± 0.2	0.4	1.8 ± 0.6	0.4	0.4 ± 0.05	0.3	0.3 ± 0.04	0.2
Ce	7.5 ± 1.0	1.9	18.1 ± 2.2	5.0	38.9 ± 5.6	21.6	9.3 ± 1.0	4.7	6.9 ± 1.1	1.3
Co	1.5 ± 0.1	0.7	13.1 ± 4.6	1.2	11.1 ± 2.5	5.1	4.8 ± 0.6	2.6	1.6 ± 0.2	0.5
Cr	63.5 ± 6.4	23.4	67.9 ± 5.2	30.7	128 ± 22.2	37.3	54.1 ± 6.9	25.2	45.6 ± 6.9	13.2
Cu	9.6 ± 0.6	4.9	51.9 ± 9.5	8.5	58.8 ± 10.0	20.3	13.1 ± 1.5	7.7	8.0 ± 0.7	2.7
Dy	0.6 ± 0.1	0.1	1.6 ± 0.3	0.4	2.7 ± 0.4	1.3	0.6 ± 0.1	0.3	0.4 ± 0.05	0.3
Eu	0.3 ± 0.05	0.1	0.6 ± 0.1	0.2	1.1 ± 0.2	0.6	0.3 ± 0.03	0.2	0.3 ± 0.04	0.1
Fe	3505 ± 281	1600	8578 ± 1136	2820	26164 ± 2793	17850	15436 ± 2185	7770	5967 ± 1324	1440
Ga	3.5 ± 0.3	1.4	4.7 ± 0.4	2.3	12.4 ± 1.3	6.9	6.5 ± 0.6	4.4	5.0 ± 0.8	0.8
Ge	2.4 ± 0.2	1.1	4.4 ± 0.5	1.8	7.2 ± 0.6	4.6	4.5 ± 0.5	2.7	3.3 ± 0.6	1.3
K	1638 ± 173	657	2044 ± 203	961	5034 ± 746	2190	2698 ± 356	940	2079 ± 510	250
La	3.6 ± 0.4	1.0	10.4 ± 1.3	2.9	22.6 ± 4.2	9.9	4.6 ± 0.5	2.4	3.7 ± 0.5	0.9
Li	3.4 ±0.6	0.6	3.0 ± 0.4	0.8	10.2 ± 1.4	6.8	6.8 ± 0.8	2.7	5.2 ± 1.5	1.0
Mg	1386 ± 89.7	831	1083 ± 80.6	653	4718 ± 697	2130	2942 ± 210	2440	1611 ± 299	480
Mn	64.0 ± 5.4	20.3	302 ± 104	45.9	394 ± 101	122	384 ± 57.4	152	302 ± 115	9.1
Mo	7.7 ± 0.9	4.9	5.6 ± 0.5	3.7	9.2 ± 1.0	5.8	4.4 ± 0.4	3.5	5.0 ± 0.5	4.2
Na	968 ± 95.7	387	1156 ± 148	452	6553 ± 924	1850	6129 ± 1119	1080	519 ± 74.4	200
Nb	1.4 ± 0.2	0.8	2.7 ± 0.4	1.1	3.4 ± 0.5	1.8	1.4 ± 0.1	0.8	9.9 ± 1.5	5.0
Ni	10.8 ± 1.0	4.4	87.9 ± 15.4	8.5	75.5 ± 21.4	22.2	23.4 ± 2.5	16.2	15.9 ± 3.0	4.9
Pb	16.6 ± 2.1	5.8	21.0 ± 2.8	7.9	15.7 ± 2.8	6.6	8.4 ± 1.0	3.7	6.4 ± 1.1	1.2
Rb	6.9 ± 0.9	1.9	8.3 ± 1.0	4.0	17.1 ± 2.3	8.0	12.7 ± 1.9	4.2	11.0 ± 2.8	0.6
Sb	0.8 ± 0.2	0.3	0.6 ± 0.2	0.3	1.3 ± 0.4	0.3	0.9 ± 0.1	0.4	0.4 ± 0.1	0.2

Metal	Bogs (*n*=158)		Poor Fens (*n*=128)		Intermediate Fens (*n*=38)		Rich Fens (*n*=47)		Peat Swamps (*n*=68)	
	Average (± SE)	MED	Average (± SE)	MED	Average (± SE)	MED	Average (± SE)	MED	Average (± SE)	MED
Se	4.9 ± 1.4	1.3	3.6 ± 0.5	1.4	3.2 ± 0.5	2.3	2.3 ± 0.7	1.4	12.1 ± 4.5	1.3
Sm	0.9 ± 0.1	0.2	2.0 ± 0.3	0.5	4.0 ± 0.7	2.1	0.9 ± 0.1	0.5	0.8 ± 0.1	0.4
Sr	30.0 ± 1.6	20.1	38.2 ± 3.6	21.3	138 ± 21.5	67.6	175 ± 19.3	73.7	55.6 ± 8.9	17.7
Ti	256 ± 256	98.2	581 ± 82.0	197	1857 ± 280	720	444 ± 51.0	211	913 ± 172	44.8
U	1.1 ± 0.2	0.2	1.7 ± 0.3	0.4	2.7 ± 0.5	1.2	1.6 ± 0.2	0.7	0.9 ± 0.1	0.6
V	11.6 ± 1.2	3.6	14.8 ± 1.4	7.3	53.0 ± 7.2	23.9	22.1 ± 2.6	11.7	21.1 ± 3.1	2.8
Yb	0.5 ± 0.1	0.1	0.8 ± 0.1	0.3	1.1 ± 0.1	0.6	0.3 ± 0.03	0.2	0.3 ± 0.03	0.2
Zn	32.9 ± 3.2	22.2	210 ± 63.7	24.9	55.5 ± 6.5	31.1	50.3 ± 7.0	36.6	15.6 ± 1.7	8.7
Zr	7.2 ± 0.9	2.5	10.8 ± 1.0	6.0	27.0 ± 3.5	12.6	8.2 ± 0.7	5.6	22.8 ± 3.7	4.0

2.3.3 Patterns of Metal Enrichment Factors in Global Peatlands

Metal enrichment factors in the 10 - 20 cm peat depth exhibited similar spatial patterns to metal concentrations, with mean EF's exceeding median values for all metals (Table 2.4). A large proportion (18 of 35 metals; 51%) of metals (Al, Ba, Ca, Ce, Dy, Eu, Ga, La, Li, Mo, Na, Nb, Sm, Sr, Ti, U, V, and Yb) had a mean EF factor ranging between 1.1 and 2.6 (Table 2.4). Metals with the highest mean and maximum EFs included As (4.6 ± 0.7, 163), Cd (4.4 ± 0.6, 83.4), Cu (6.0 ± 0.9, 186), Mn (11.6 ± 1.5, 321), Ni (7.9 ± 1.3, 115), Pb (11.7 ± 1.5, 398), Sb (7.4 ± 1.8, 326), Se (4.7 ± 0.7, 33.2) and Zn (8.5 ± 1.6, 298). The proportion of cores with an EF ≥ 1 averaged 64% of cores sampled, ranging from 43% (Dy) to 84% (K). All metals except Ga, Ti, U and V had at least one peatland core having an EF >10. Metals with the highest number of cores with an EF >10 and >100 includes Mn (90, 6), Pb (87, 4), Zn (53, 4), Cu (36, 2), As (32, 1), Sb (30, 2), Co (21, 0), and K (20, 2) (Table 2.4).

Table 2.4. Summary of metal enrichment factors, count, mean (± SE), median, min and max and number of Cores with EF greater (>) than 1, 10, and 100 in global peatlands (n=418).

Analyte	Count	Average (± SE)	Median	Min	Max	EF >1	EF >10	EF>100
Al	349	1.1 ± 0.04	1.0	0.06	10.3	161	1	-
As	287	4.6 ± 0.7	1.6	0.06	163	198	32	1
Ba	345	1.6 ± 0.1	1.2	0.04	33.7	202	1	-
Ca	333	2.8 ± 0.6	1.4	0.06	193	215	7	1
Cd	217	4.4 ± 0.6	2.1	0.06	83.4	157	15	-
Ce	345	1.2 ± 0.1	0.9	0.04	33.7	148	2	-
Co	345	2.9 ± 0.2	1.5	0.01	34.8	244	21	-
Cr	342	2.7 ± 0.2	1.5	0.1	24.4	243	16	-
Cu	328	6.0 ± 0.9	1.6	0.2	186	238	36	2
Dy	258	1.2 ± 0.1	0.9	0.06	25.4	110	1	-
Eu	195	1.2 ± 0.1	1.0	0.05	12.2	94	1	-
Fe	345	3.2 ± 0.3	1.7	0.06	81.4	266	15	-
Ga	346	1.3 ± 0.05	1.1	0.02	8.1	198	-	-
Ge	197	5.3 ± 1.5	1.6	0.03	244	145	11	2
K	338	4.3 ± 0.7	2.1	0.01	191	283	20	2
La	347	1.2 ± 0.1	0.9	0.04	35.5	152	2	-
Li	258	2.0 ± 0.2	1.1	0.03	45.7	148	5	-
Mg	346	3.0 ± 0.3	1.5	0.1	59.4	244	18	-
Mn	338	11.6 ± 1.5	3.1	0.02	321	274	90	6
Mo	73	1.9 ± 0.3	1.3	0.5	16.6	52	2	-
Na	343	2.0 ± 0.2	1.3	0.03	47.5	223	7	-
Nb	154	1.5 ± 0.1	1.1	0.1	13.1	97	2	-
Ni	224	7.4 ± 1.3	1.3	0.2	115	158	20	3
Pb	349	11.7 ± 1.5	2.5	0.04	398	285	87	4
Rb	346	3.1 ± 0.4	1.8	0.02	91.9	276	13	-
Sb	204	7.4 ± 1.8	1.8	0.04	326	160	30	2
Se	83	4.7 ± 0.7	1.7	0.08	33.2	61	11	-
Sm	254	1.4 ± 0.2	0.9	0.09	27.0	110	3	-
Sr	344	1.8 ± 0.2	1.1	0.03	79.7	207	2	-
Ti	349	1.1 ± 0.03	1.0	0.1	5.5	169	-	-
U	205	1.0 ± 0.06	1.0	0.03	6.8	95	-	-
V	288	1.3 ± 0.07	1.1	0.09	10.0	161	-	-
Yb	175	1.3 ± 0.1	0.9	0.1	14.8	80	1	-
Zn	340	8.5 ± 1.6	2.6	0.02	298	276	53	4

Principle component analysis of metal EF accounted for 72.7% of the total variance within the first three axes of data, which revealed three metal groupings similar to the pattern found among metal concentrations, although patterns are more defined due to higher loadings to each respective component (Figure 2.3). Metal EF with loadings >0.70 on PC1 included Al, Ba, Ga, K, Li, Mo, Rb, Sr, Ti, and V. Metal EF with high loadings (>0.92) on PC2 included Ce, Dy, Eu, La, Mg, Sm, and Yb. PC3 had similarly high loadings (>0.90) which included As (0.95), Co (0.98), Cu (0.96), Ni (0.96), Pb (0.90), and Zn (0.92) accounting for 21.9% of the variance (Figure 2.3).
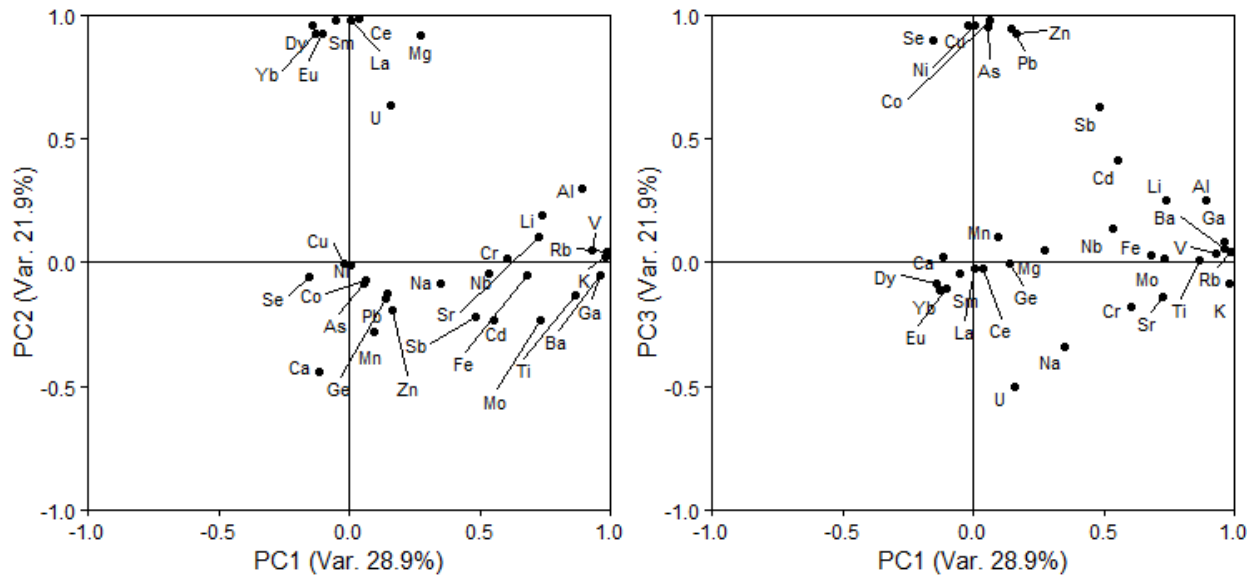
Figure 2.3. PCA of metal enrichment factors.

2.3.4 Metal Enrichment among Peatland Categories

Metal enrichment factors for As, Cd, Co, Cu, Ni, Pb, Sb, Se, and Zn that exhibited similar spatial patterns were among the highest observed in the 10-20 cm depth increment, and EF's for all these metals except Se significantly varied significantly by peatland type (Table 2.5). In general, mean metal EF's increased from peat swamp < rich fens < bogs < intermediate fens < poor fen systems, although median EF's were similar across peatland types for all metals. Poor fens had the highest mean metal EF for As (8.1 ± 2.2), Cu (11.6 ± 2.7), and Ni (6.7 ± 3.5), which was twice the global average and significantly higher

(*p*<0.05) than rich fen and peat swamp systems (Table 2.5). Lead EF's were significantly higher in bog

(12.6 ± 3.2), poor fen (13.3 ± 2.0) and rich fen (13.7 ± 5.7) peatland types and had the highest mean global

EF (11.7 ± 1.5) amongst the tested metals. Rich fens and peat swamps generally exhibited lower (*p*<0.05)

EF across metal with the exception of Zn (17.7 ± 10.0; rich fens) and Se (10.5 ± 4.1; peat swamps) (Table

2.5).

Table 2.5. Mean (±S.E) and median As, Cd, Co, Cu, Ni, Pb, Sb, Se, Zn enrichment factors (EF) of all sampling locations and by peatland type. *P* values indicate results of Welch's ANOVA comparing chemistry across all sites and peatland types. Peatland types with different letters are significantly ($p < 0.05$) different using Games-Howell's post hoc test.

Metal	All (*n*=345)	Bogs (*n*=131)	Poor Fens (*n*=107)	Intermediate Fens (*n*=34)	Rich Fens (*n*=42)	Peat Swamps (*n*=35)	*P*
As	4.6 ± 0.7 (1.6)	3.1 ± 0.5ab (1.3)	8.1 ± 2.2b (1.4)	5.9 ± 1.7ab (1.4)	2.1 ± 0.4a (1.1)	1.6 ± 0.2a (1.2)	*
Cd	4.4 ± 0.6 (2.1)	4.5 ± 0.9a (1.4)	5.4 ± 1.4a (1.7)	4.3 ± 1.0ab (1.6)	3.4 ± 1.0ab (1.3)	1.6 ± 0.3b (1.2)	*
Co	2.9 ± 0.2 (1.5)	1.9 ± 0.2a (1.1)	4.0 ± 0.5b (1.4)	5.4 ± 1.4b (1.2)	1.9 ± 0.3a (1.2)	2.0 ± 0.3a (1.2)	**
Cu	6.0 ± 0.9 (1.6)	3.8 ± 0.6a (1.2)	11.6 ± 2.7b (1.6)	5.8 ± 2.2abc (1.2)	1.6 ± 0.3c (1.0)	2.3 ± 0.4ac (1.0)	***
Ni	7.4 ± 1.3 (1.3)	1.5 ± 0.2a (1.1)	16.7 ± 3.5b (1.6)	8.4 ± 4.0ab (1.1)	1.5 ± 0.3a (1.1)	2.1 ± 0.6a (1.1)	***
Pb	11.7 ± 1.5 (2.5)	12.6 ± 3.2a (1.9)	13.3 ± 2.0a (1.4)	7.9 ± 2.4ab (1.3)	13.7 ± 5.7a (1.7)	4.5 ± 1.1b (1.2)	**
Sb	7.4 ± 1.8 (1.8)	10.0 ± 4.6a (1.4)	8.7 ± 2.3a (1.6)	4.2 ± 1.1ab (1.3)	1.8 ± 0.3b (1.2)	4.3 ± 1.1ab (1.4)	***
Se	4.7 ± 0.7 (1.8	3.3 ± 0.9 (1.2)	5.3 ± 1.4 (1.3)	4.7 ± 2.2 (1.2)	3.1 ± 0.9 (1.2)	10.5 ± 4.6 (1.9)	
Zn	8.5 ± 1.6 (2.6)	8.3 ± 2.5a (1.5)	7.8 ± 1.2a (2.0)	5.3 ± 1.0ab (1.6)	17.7 ± 10.0a (1.4)	3.6 ± 0.7b (1.6)	**

Significance of Games-Howell's hoc test is indicated by: * ($P < 0.05$), ** ($P < 0.01$), *** ($P < 0.001$).

2.3.5 Global Distribution and Regional Differences in Metal Enrichment Factors

Significant differences in mean metal EF was evident across the six geographic regions and these

differences were generally larger than differences among peatland types suggesting location rather than

peatland type has a greater influence on EF of metals associated to pollution (Table 2.6). Peatlands sampled

in North America had significantly higher (*p*=<0.01) average EF for As (5.9 ± 1.1), Cu (8.1 ± 1.4) and Ni

(10.8 ± 2.0) than the other five regions and significantly higher (p=<0.05) average EF for Sb (9.2 ± 2.7) compared with Africa and Oceania (Table 2.6). North America contained the majority of cores sampled with highest proportion of bog (94 of 158 sites (60%)), poor fens (111 of 128 sites (87%)), intermediate fens (16 of 38 sites (42%)), and rich fen (32 of 47 sites (68%)) peatland types that were enriched in these metals. Distribution of cores sampled in this study enriched with these metals are clustered in central Ontario, Canada (Figure 2.4). Peat cores from South America demonstrated the highest mean EF for Co (5.5 ± 2.0), with peatlands in the region being predominately intermediate fen and peat swamp (10 of 29 sites (34%) systems. Peatlands sampled in Europe were predominantly bog systems (46 of 68 sites (68%)), which had the highest mean EF for Pb (16.4 ± 4.7) and Zn (18.4 ± 7.8). Peatlands in Europe and North America had significantly higher Pb and Zn EF's than Africa, Asia and Oceania regions (Table 2.6) and the distribution of Pb and Zn enrichment in Europe and North America is extensive with 13-24% of cores sampled having an EF >10 (Figure 2.4). Similarly, the mean EF for Cd was significantly higher in North America (4.7 ± 0.8) and Europe (4.8 ± 1.6), which were 3-4x higher than Africa and Oceania regions (Table 6). Finally, the mean Se EF in North America (5.4 ± 1.0) and Asia (5.2 ± 3.0) were the highest among regions, although Asia contained the highest proportion of peat swamp systems which were found to be the most elevated in Se among peatland types (Table 2.6).
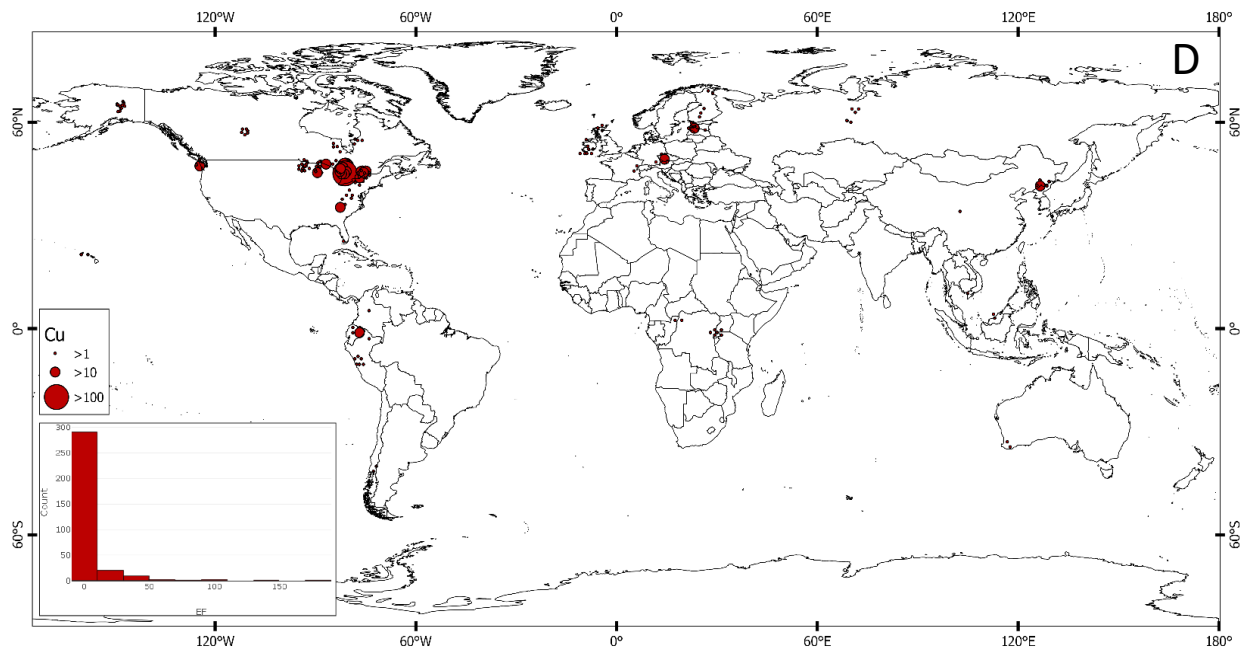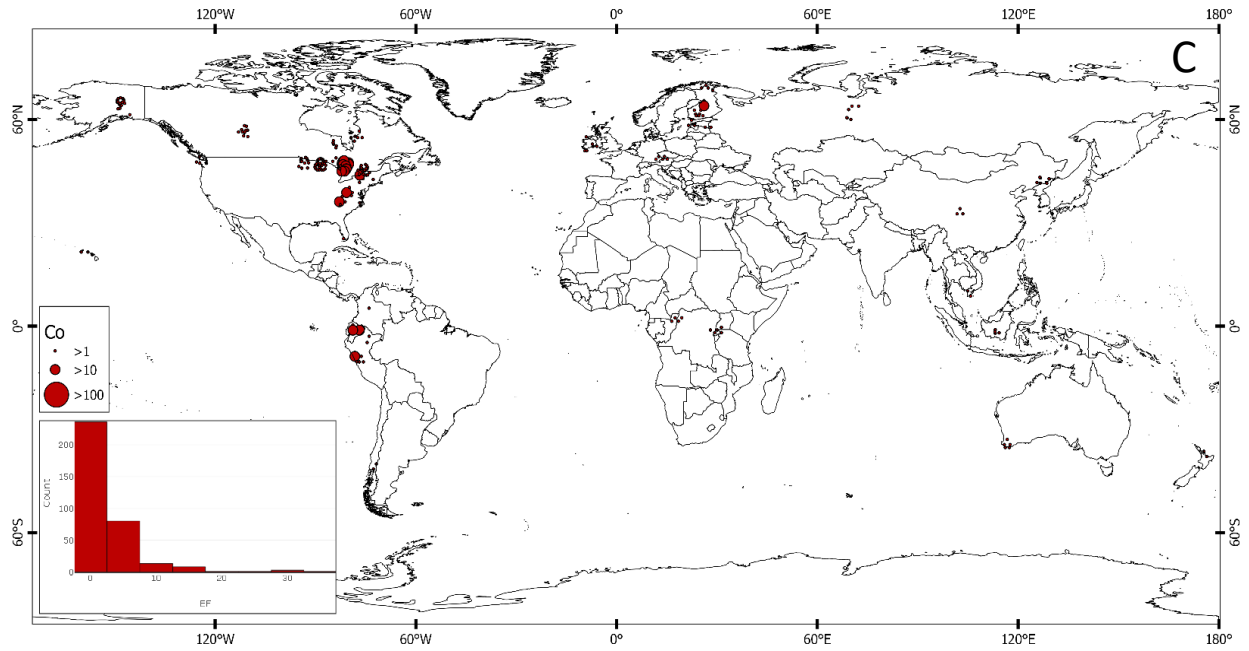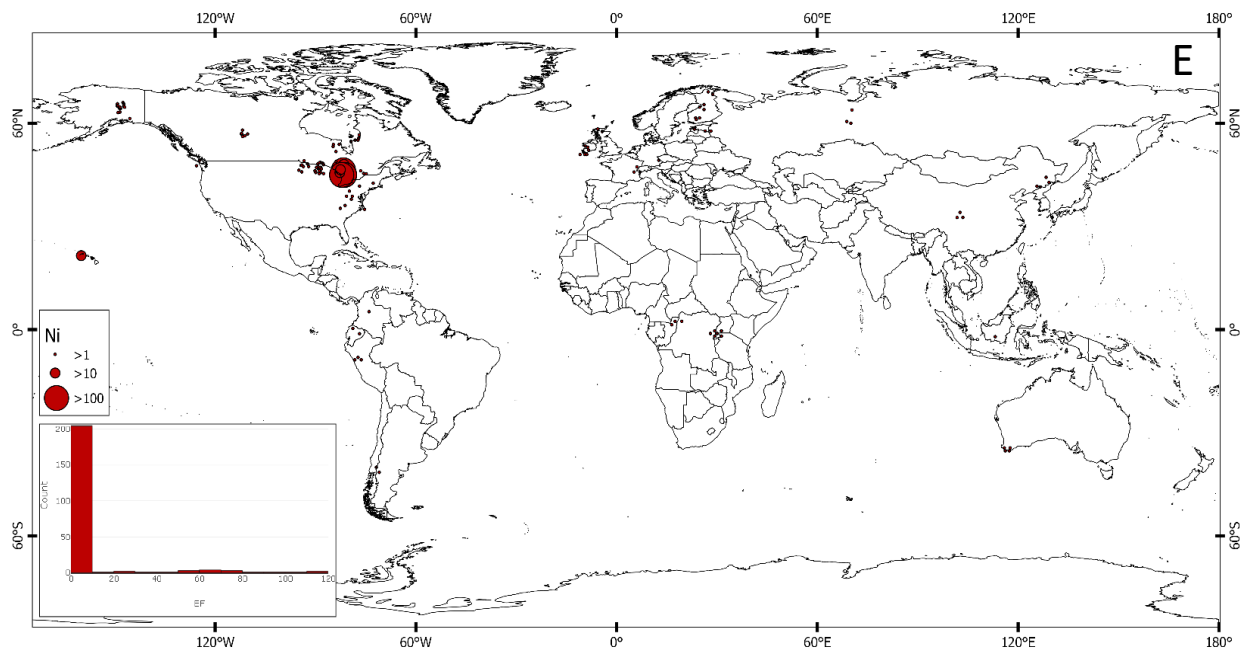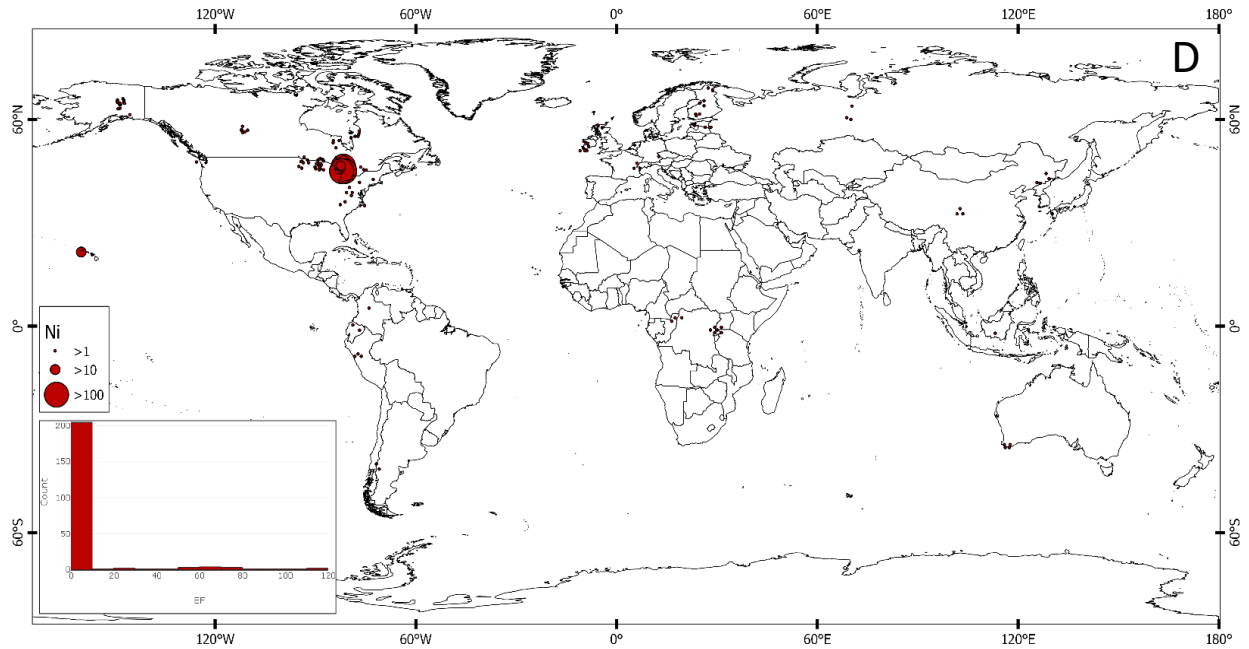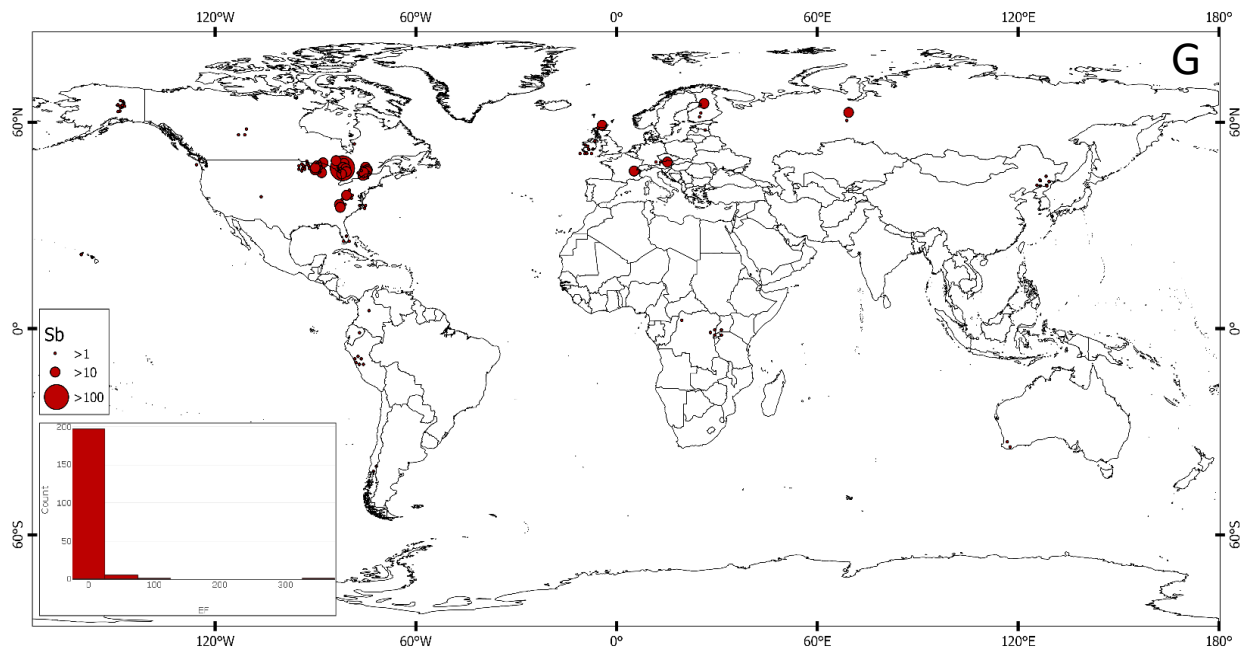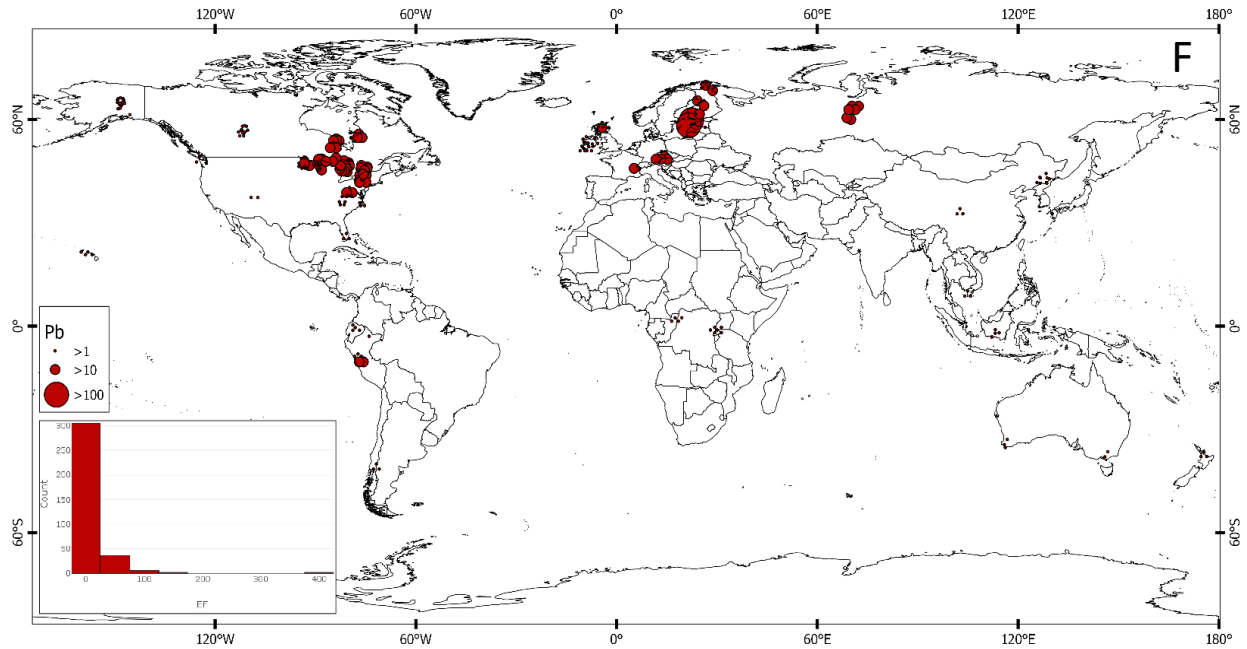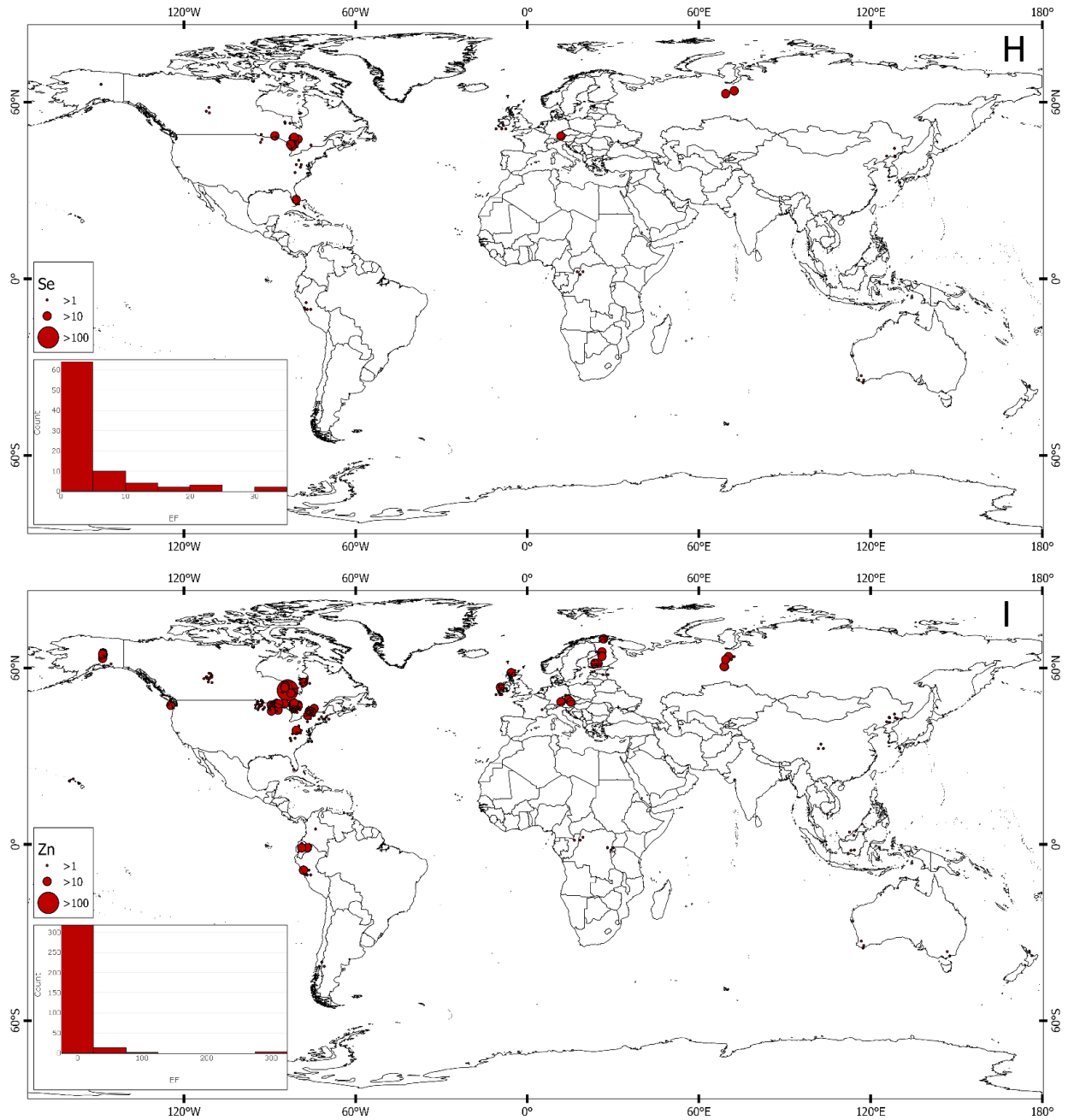
Figure 2.4. Global distribution of enrichment factors of As (A), Cd (B), Co (C), Cu (D), Ni (E), Pb (F), Sb (G), Se (H), and Zn (I).

Table 2.6. Mean (±S.E) and median As, Cd, Co, Cu, Ni, Pb, Sb, Se, Zn enrichment factors (EF) of all sampling locations and by region. *P* values indicate results of Welch's ANOVA comparing chemistry across all sites and regions. Regions with different letters are significantly ($p < 0.05$) different using Games-Howell's post hoc test.

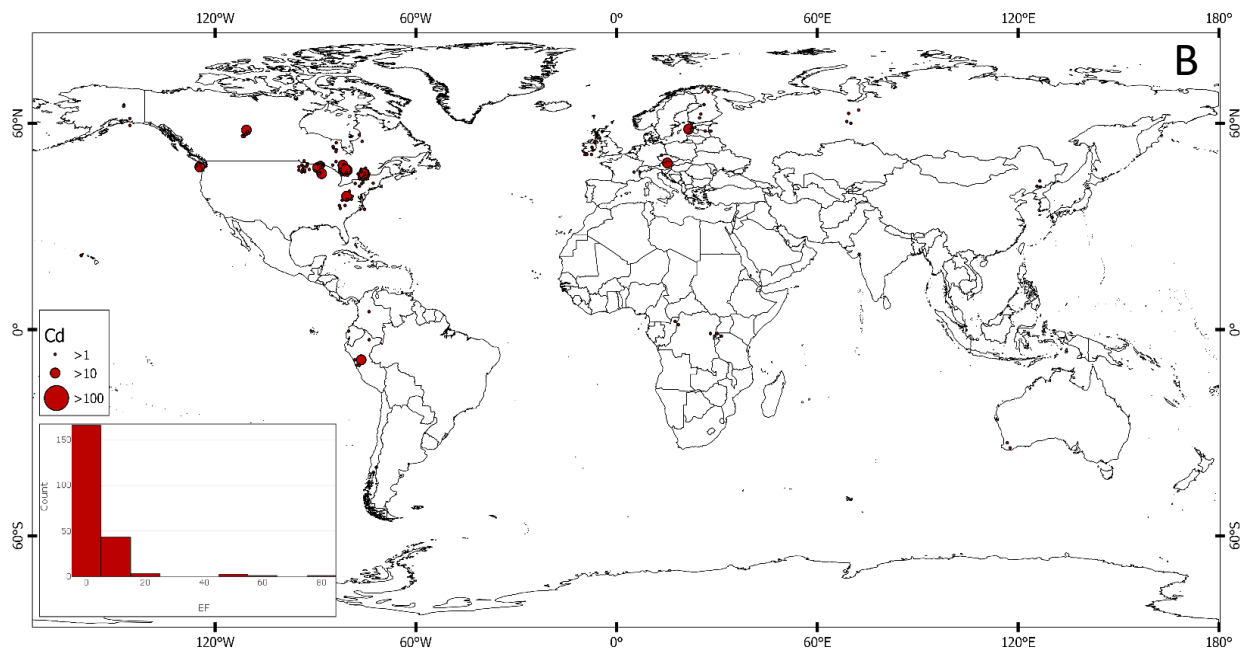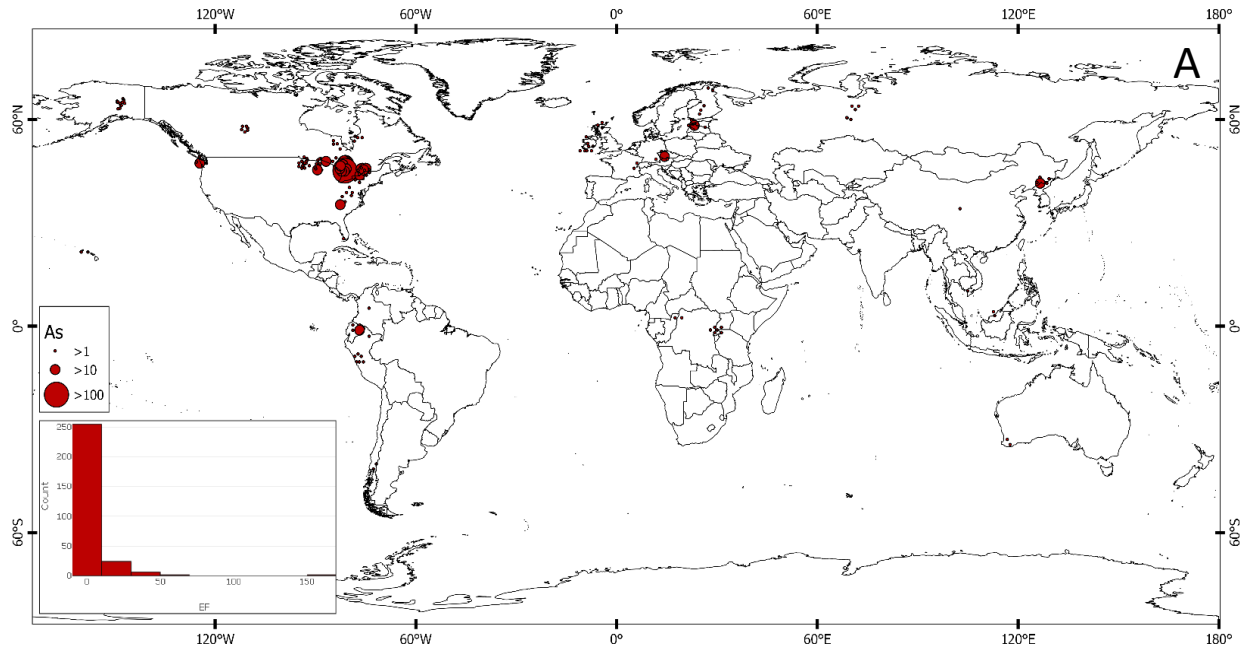| Metal	North America (n=222)	South America (n=19)	Europe (n=55)	Africa (n=10)	Asia (n=31)	Oceania (n=11)	*P*
As	5.9 ± 1.1a (1.7)	3.9 ± 1.6b (1.7)	2.2 ± 0.4b (1.5)	1.8 ± 0.2b (1.7)	2.0 ± 0.5b (1.2)	1.1 ± 0.4b (0.7)	***
Cd	4.7 ± 0.8a (2.3)	3.9 ± 1.0ab (2.3)	4.8 ± 1.6a (2.1)	1.5 ± 0.2b (1.7)	3.0 ± 0.7ab (3.1)	1.1 ± 0.3b (1.0)	***
Co	3.2 ± 0.3a (1.7)	5.5 ± 2.0a (2.0)	1.9 ± 0.3bc (1.1)	2.2 ± 0.3ab (2.3)	1.8 ± 0.3bc (1.3)	1.1 ± 0.1c (1.3)	***
Cu	8.1 ± 1.4a (1.8)	3.2 ± 1.1ab (1.9)	2.4 ± 0.4b (1.2)	2.1 ± 0.7b (1.1)	1.8 ± 0.3b (1.1)	1.3 ± 0.2b (1.4)	***
Ni	10.8 ± 2.0a (1.4)	1.5 ± 0.3b (1.0)	1.8 ± 0.2b (1.2)	2.4 ± 0.5b (1.7)	1.1 ± 0.1b (1.1)	1.0 ± 0.1b (1.0)	***
Pb	13.1 ± 2.1a (3.0)	2.9 ± 0.8b (1.3)	16.4 ± 4.7a (4.2)	2.2 ± 0.3b (2.1)	5.5 ± 1.4b (1.3)	1.4 ± 0.1b (1.2)	***
Sb	9.2 ± 2.7a (2.1)	2.5 ± 0.6ab (1.6)	5.1 ± 1.8ab (1.3)	1.4 ± 0.1b (1.4)	3.3 ± 1.5ab (1.4)	1.0 ± 0.2b (1.0)	*
Se	5.4 ± 1.0a (2.3)	3.0 ± 0.9ab (2.2)	3.9 ± 2.5ab (1.2)	-	5.2 ± 3.0ab (1.3)	1.8 ± 0.4b (1.8)	*
Zn	7.7 ± 1.5a (3.0)	5.0 ± 1.3b (3.2)	18.4 ± 7.8a (2.4)	2.1 ± 0.6b (1.2)	4.7 ± 1.0b (2.0)	1.5 ± 0.3b (1.5)	**

Significance of Games-Howell's post hoc test is indicated by: * ($P < 0.05$), ** ($P < 0.01$), *** ($P < 0.001$).

2.3.6 Cumulative Sulphur Deposition

Global interpolated linear rates of total S deposition increased from 1850-1979, with the highest S deposition areas generally occurring in Northeastern United States, Central Canada, Northern and Southern Europe (Figure 2.5). Post 1980, S deposition decreased in the northern hemisphere and increased in parts of Asia (Appendix, Figure 3). Cumulative S (wet + dry) SO_x and SO_4^{-2} deposition from 1850-2009 was between 6.78 and 5537 kg S ha^{-1} (Figure 2.5).
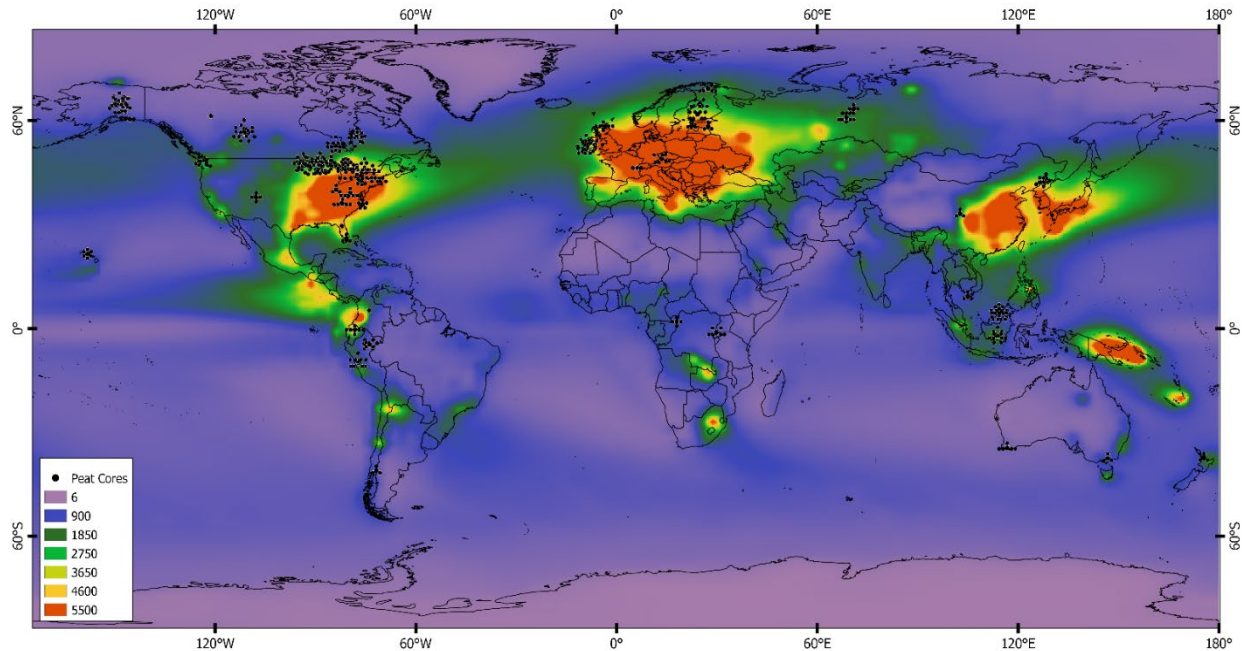
Figure 2.5. Interpolated cumulative total (wet + dry) SO_x and SO_4^{-2} deposition 1850-2009 (kg (S) ha^{-1}).

Metals that demonstrated a strong anthropogenic atmospheric input were significantly (p=<0.01) correlated with cumulative S deposition (kg ha^{-1}) with the exception of Se, but the strength of the relationship varied by peatland type (Table 2.7). Negative correlation coefficients were not included as a increase in cumulative S deposition would not result in a decrease in metal EFs. The majority of correlation coefficients were found to be <0.30, which can be expected as metal deposition is likely to greatly vary within the cumulative S deposition grid resolution (~55km^2). This would also indicate that using cumulative S deposition as a crude surrogate for metal deposition is likely more indicative of industrialization, with multiple other factors contributing to metal enrichment in global peatlands.

Table 2.7. Mann-Kendall correlation between cumulative (wet + dry) SO_x and SO_4^{-2} deposition 1850-2000 (kg (S) ha) and metal enrichment factors by peatland type.

Metal	All (*n*=345)	Bogs (*n*=131)	Poor Fens (*n*=107)	Intermediate Fens (*n*=34)	Rich Fens (*n*=42)	Peat Swamps (*n*=35)
As	0.13**	0.14*	0.04	0.36**	0.21	-
Cd	0.16**	0.21**	0.10	0.35	0.31	-
Co	0.11**	0.06	0.16*	0.28*	0.26*	0.16
Cu	0.23**	0.24**	0.15*	0.15	0.14	0.17
Ni	0.13**	-	0.19*	0.15	-	-
Pb	0.14**	0.10	0.14*	0.21	0.34*	0.46**
Sb	0.12**	0.19*	-	0.41**	-	0.38
Se	0.05	-	0.24	0.19	0.14	0.82*
Zn	0.14**	0.02	0.05	0.34**	0.20	0.51**

Significance of Mann-Kendall correlations is indicated by: * ($P < 0.05$), ** ($P < 0.01$), *** ($P < 0.001$).

2.3.7 Estimated Metal Pools

Estimated metal pools (mg m^{-2}) in the 0 - 40 cm depth layer for metals that exhibited similar spatial patterns and likely have a strong anthropogenic influence varied considerably (Table 2.8). Mean metal pools were 2 – 10 times higher than median concentrations, indicating that a number of peatlands are heavily contaminated with these metals. Median Cu (319 mg m^{-2}) Ni (288 mg m^{-2}), Pb (439 mg m^{-2}), and Zn (1389 mg m^{-2}) pools are among the highest observed with maximum metal pools exceeding >20000 mg m^{-2} for all 4 metals. Median metals pools of As, Cd, Co, Sb, and Se were generally lower ranging from 12.9 to 60.5 mg m^{-2} (Table 2.8).

Table 2.8. Summary of metal pools (mg m^{-2}), count, mean (± SE), median, min, and max from global peatland cores from 10-20 and 30-40 cm depth (n=439).

Metal	Count	Average (± SE)	Median	Min	Max
As	413	377 ± 93.1	60.5	2.4	34591
Cd	359	41.2 ± 4.7	16.0	0.5	1030
Co	431	488 ± 174	52.6	0.4	59207
Cu	436	1765 ± 239	319	3.2	53405
Ni	350	2918 ± 443	288	5.0	65378
Pb	439	1003 ± 83.4	439	5.6	21004
Sb	368	38.7 ± 6.3	12.9	0.5	1524
Se	201	198 ± 37.2	60.5	2.4	4590
Zn	425	2569 ± 271.9	16.0	0.5	77312

2.4 Discussion

In our global data set, metal concentrations varied by both depth increment and by peatland type, with fens demonstrating the highest concentrations. Metal enrichment factors in the 10 - 20 cm peat depth exhibited similar spatial patterns to metal concentrations, with mean EF's exceeding median values for all metals. Principal component analysis of EF's identified three metal clusters. Metals commonly associated with anthropogenic sources (As, Cd, Co, Cu, Ni, Pb, Sb, Se, and Zn) were clustered together indicating generally similar spatial patterns in our dataset. Mean metal EF's were found to be generally highest in poor fen peatlands and in the regions of North America and Europe. Metals traditionally associated with anthropogenic atmospheric inputs were significantly correlated with cumulative S deposition with the exception of Se, indicating that metal enrichment in surface peat is associated with industrial activities. Similarly, estimated mean metal pools in the upper 40 cm peat layer for anthropogenically influenced metals varied considerably ranging from a high of 38.7 mg m^{-2} to 2918 mg m^{-2}.

4.1 Metal Concentrations and Peatland Type

Metal concentrations in peatlands in our global dataset were highly variable. The distribution of elements in peat is related to abundance and mineralogical composition of mineral matter, atmospheric deposition, plant material and behaviours of metals under changing acidity and redox conditions (Shotyk et al., 1989). Metals with some of the highest concentrations of metals in peat included Ca, Fe, K, Mg, and Na, which are essential plant nutrients and have been shown to increase within upper portions of peatlands as a result of plant bioaccumulation and cycling (Severson and Shacklette 1988). The proximity of peatlands to anthropogenic metal sources (Nriagu, 1989; Nriagu and Pacyna, 1988), coastal areas (Shotyk et al., 1990), lithogenic origin from windblown soils, and differences in sediment inputs and underlying till lithology has also been shown to greatly influence metal concentrations in peat profiles (Aubert et al., 2006; Gorham and Janssens, 2005; Krachler et al., 2003; Gorham and Tilton 1978).

While the influence of peatland type on peat metal concentrations cannot be distinguished from other factors, our analysis shows that concentrations of many metals including base cations, Fe and Al are highest in fens consistent with differences in biotic and hydrologic gradients and the influence of mineral inputs within these systems (Shoytk, 1988). Higher concentrations of metals, such as Al, Ca, Fe, Mg, and Na have been observed in fen peatland types compared with bog systems as a result of groundwater and surface water inputs from upland mineral soils, which is limited in bogs due to ombrotrophic conditions (Bendell-Young, 2003; Zoltai and Vitt, 1995). Swamp peatlands occupy a broad classification and environmental gradient, where drastic differences in seasonal water level fluctuations, dominant vegetation communities, and inhibited water flow can alter geochemistry and metal concentrations in peat (Shoytk, 1988). In the present study, swamp peatland types were densely treed or formerly densely treed prior to anthropogenic modification and were found in lowland wet tropical areas. An additional factor for increasing metal concentrations along the hydrologic gradient in fen and swamp peatland types is that these systems occupy the interface between terrestrial and aquatic systems which are subjected to both atmospheric and surface water metal inputs from adjacent land-use and downstream industrial operations (Szkokan-Emilson et al., 2014; Cheng et al., 2015; Denny et al., 1995).

Principal component analysis identified three groupings of metals in peatlands. The first two groupings included the majority of metals and rare earth elements (REE). Higher association of these metals in lower depths within the peat profile can likely be attributed to metals derived from mineral soils and hydrospheric processes, whereby differences in underlying bedrock (ie. granitic or basaltic terrains) have been shown to influence differences in metal abundance (Shoytk 1998; 1996). The third grouping of metals consisted of As, Cd, Co, Cu, Ni, Pb, Sb, and Se that was most apparent in the upper depth increment (10 - 20 cm) that likely reflects more recent biogenic and/or anthropogenic input (Nriagu, 1989; Nriagu and Pacyna, 1988). Although PCA analysis distinguished grouping of metals throughout global peat profiles, based on the inherent variability in global peatland chemistry, the use of EF's factors is likely a better indicator of atmospheric anthropogenic metal deposition.

2.4.2 Metal Enrichment Factors

Mean EF for most metals were higher than median values, indicating that metal concentrations at some sites are more strongly influenced by natural (Shotyk et al., 2016; Nriagu, 1979) and/or anthropogenic point sources (Hwang, 2006; Nieminen et al., 2002; Pacyna et al., 1984). Natural atmospheric enrichment of surface peats have been predominantly linked to lithophilic elements (Al, Fe, Si, and Ti) derived from dust emissions (Weiss et al., 2002), with proximity to point sources such as dry lands, gravel roads, open pit mines, and aggregate quarries having been shown to increase enrichment of these elements associated to the underlying bedrock and soil particles (Shotyk et al., 2016; Bao et al., 2010). Proximity to seawater represents an additional natural point source of halophilic elements such as B, I, Br, Cl, Mg, and S, which have been shown to be enriched in peatlands closer to coastal regions (Gorham and Janssens, 2005). Industrial point sources likely have a more profound increase in metal enrichment in peatlands due to their ability to increase metal loading on local, regional and global scales through atmospheric deposition (Pacyna and Pacyna 2001; Pacyna et al., 1995) and discharges to water and soil (Nriagu and Pacyna 1988).

The majority of metals had a median and mean global EF values < 2 indicating minor enrichment which could reflect continual low-level accumulation from natural sources at many sites. Gorham and Janssens (2005) reported minor enrichment for La, Sm, Sc, Ce, Th, V, and Cr ranging from 1.1-4.2 reflecting their origin from soil. Metals that demonstrated the highest EF's (mean and median) included As, Ca, Cd, Co, Cu, Ge, K, Mn, Ni, Pb, Sb, Se, and Zn. Higher EF's for these metals is the result of the high cation exchange capacity of peat, which can remove a wide range of metallic cations from solutions (Puustjarvi, 1977), resulting in the enrichment of Cu (Walton-Day et al., 1990), U (Read and Hooker, 1989), Cr, Ni, Mn, Pb and, Zn (Shotyk, 1992). Additionally, enrichment of surface peat in plant essential metals (Ca, Fe, K, Mg, and Na) may be the result of plant cycling that concentrates major metals relative to associated waters resulting in enrichment in the upper portion of the peat profile (Casagrande and Erchull, 1977). Manganese for example, had a the highest mean global EF of 11.6, which is likely the result of low

pH (<5.5) and increased redox potential of Mn, whereby Mn-oxides can be easily reduced in soil exchange sites increasing the concentrations of plant available Mn^{2+} (Watmough et al., 2007; Kogelmann and Sharpe, 2006) resulting in plant bioaccumulation and surface enrichment from deposited plant material. Anthropogenic sources of Mn may have also contributed to higher levels of enrichment, with fuel additives being used extensively in the mid-1970s and early 1980s and the use of methyl cyclopentadienyl manganese tricarbonyl (MMT) until 1998 (Zayed, 2001). Lytle et al., (1995) found a strong correlation between soil (0-5 cm) Mn concentration and distance from roadways (0-40 m) with moderate (r=0.915) to moderately high (r=0.932) traffic use with concentrations in plant tissue ranging 13,680 to 42.7 g kg^{-1}, which could also be contributing to the high EF in global peatlands.

Metals that had the highest EF's included As, Cd, Co, Cu, Ni, Pb, Sb, Se, and Zn that are commonly linked to a wide range of industrial activities, which release trace metals to the atmosphere (high temperature production of industrial good, combustion of fuels, incineration of wastes etc.), soil (agriculture, logging, urban refuse etc.) and water (wastewater, base metal mining, manufacturing processes etc.) (Nriagu and Pacyna, 1988). Although estimated natural global emissions of these metals account for only a portion of total emissions to the biosphere (Nriagu, 1989; Galloway et al., 1980), anthropogenic contributions have exceeded natural flux. Rauch and Pacyna (2009) estimated that Cu, Ni and Zn industrial flux represent 48, 48, 33% of natural emissions, respectively, with Pb flux linked to human activities representing 61% of the total Pb flux to the biosphere.

Principal component analysis of EF's identified three metal clusters, similar to those observed for metal concentrations. Metals commonly associated with anthropogenic sources (As, Cd, Co, Cu, Ni, Pb, Sb, Se, and Zn) were clustered together indicating generally similar spatial patterns in our dataset. The significant enrichment of these metals in peatlands have been linked to the proximity to metal smelter and atmospheric sources (Nieminen et al., 2002; Kempter and Frenzel, 2000; Dumontet, 1990; Zoltai, 1988) and to a lesser extent effluent point sources (Humphries et al., 2017; Liu et al., 2003). Rare earth elements

were also grouped (Ce, Dy, Eu, La, Sm, and Yb), but these metals demonstrated minor enrichment in global peatlands compared with metals associated with anthropogenic sources. Mineral weathering constitutes a primary source of REE to soils, with igneous rock and sandstones tending to have higher REE concentrations compared with soils originating from loess and calcareous rock (Hu et al., 2006). Anthropogenic enrichment of REEs has also been linked to proximity to intense agricultural practices and the application of phosphate fertilizers, but enrichment of REE's has also been associated with regions next to polluted sites such as large cities and industrial centers (Xie et al., 2014). Atmospheric deposition of REE is another path into soils, with concentrations of RRE have been reported as high as 1333.7 mg L^{-1} in snow around a fertilizer plant in Russia (Volokh et al., 1990). The minor REE enrichment observed in surface peat can also be linked to RREs bonding to soil organic matter similar to other trace metals, whereby REE concentrations are correlated with DOC concentrations and inversely correlated with soil pH (Pourret et al., 2007). In addition, increased plant uptake and cycling of light REE (Ce, La, Nd, Eu, Sm) can lead to enrichment in the upper portion of peatland soils (Turra et al., 2013). The third group consisted of metals with relatively high EF (Ca, Cr, Fe, Ge, Mn, Na) but different spatial patterns compared to metals associated to anthropogenic pollution or REE, which could be the result of additional factors such as differences in pH, redox conditions, and cycling (Shotyk et al., 1992) along with differences in peatland type. An example can be seen in Mn and Fe that are redox sensitive metals, whereby acidic, anaerobic peat waters can enhance Mn and Fe solubility and plant bioaccumulation resulting in surface enrichment within living tissues and recently deposited litter thereby decreasing concentrations at deeper subsurface layers (Shotyk et al., 1990; Damman, 1978).

2.4.3 Regional and Peatland Type Differences of Metal Enrichment Factors

Enrichment factors of metals with similar spatial patterns that are suggestive of anthropogenic deposition vary significantly by peatland type. The level of metal enrichment will also likely vary based on geographic location and proximity to metal sources. Differences may also be attributed to baseline

geochemistry among peatland types, metal behaviour within the peat profile and influence of peat depth. An example of this is the elevated proton concentrations found in acidic peatland surfaces (bog, poor fen and peat swamps) which promotes mineral dissolution and competes with cation exchange thereby reducing the formation of metal complexes with organic ligands resulting in post-depositional migration of metals such as Cd, Cu, Ni, and Zn (Rausch et al., 2005). Similarly minerotrophic peatland types (fens and peat swamps) are subjected to fluctuating water tables and redox conditions resulting in the enrichment of Fe-Mn oxyhydroxides in subsurface peat which can result in the migration and redistribution of certain metals such as As and Sb (Rothwell et al., 2010; Shotyk et al., 2002). Based on these factors in some cases the 60-70 cm depth increment will not reflect background concentrations and therefore may underestimate the determined EF for the 10-20 cm depth increment available for this study. This is particularly important for fen and peat swamp peatland types as groundwater, the upward diffusion of dissolved elements released by mineral weathering and supply of upland mineral soil are a major source of metals that may mask more recent inputs in the upper portion of peat (Ye et al., 2011; Shotyk et al., 1996; Hill and Siegel, 1991; Shoytk, 1988). There is also the possibility that in some cases peat from 60 -70 cm may not reflect pre-industrial or background values as trace metal enrichment in peat cores measured to a depth of 102 cm representing 2000 years of peat accumulation were found to have peak EF for Pb, Sb, and As between $0 - 40$ cm depth increments dated to 1843 ± 25 to 1979 ± 25 (Shotyk et al., 1996). This would further lead to underestimation of EFs and variability within the global data set as peatland accumulation rates likely vary considerably due to differences in location and peatland type (Robinson and Moore, 1999).

Larger differences in EF among geographic regions than among peatland type were found that is suggestive of a strong influence of anthropogenic metal deposition. In general, EF's of the "pollution" metals (As, Cd, Co, Cu, Ni, Pb, Sb, Se, and Zn) were significantly higher in peat cores sampled in North America and Europe compared with the other 3 regions. North America and Europe contained the majority of cores in this study (331 of 439 sites (72%)), which were predominantly bog and poor fen systems, which were particularly elevated in As, Cu, Ni, Pb, and Zn. Differences in EF's among regions is likely the result

of differences in historical timelines of industrialization and its effect on local and regional metal deposition (Marx et al., 2016). Lead has been extensively used to track historical patterns of metal enrichment from geological archives in lake sediment and peat since it is largely immobile in the environment (Weiss et al., 1999) and can be considered representative of a number of metal pollution based on the extent and magnitude of Pb enrichment (Marx et al., 2014).

In our data set mean EFs in European peatlands were between 1.8 (Ni) and 18.4 (Zn), with 14 and 13 cores exhibiting EF >10 for Pb and Zn respectively. European peatlands were predominantly bog systems (41 of 68 cores (60%)) with the majority of sites located in Ireland, Scotland and Finland. Europe has experienced more than two millennia of metal contamination dating back to Roman Pb-Zn mining and smelting with Pb accumulation and enrichment in peatlands and lake sediment following major phases in metal usage resulting regional scale enrichment yet differing in the magnitude based on location and scale of mining (Marx et al., 2016; De Vleeschouwer et al., 2007; von Storch et al., 2003; Dejonghe, 1998). Peat records indicate drastic metal enrichment with the onset of the industrial revolution whereby Pb contamination increased by 1-2 order of magnitude from background levels (Marx et al., 2016). Lead EF's range from 82.3 to 118 times background levels in Scottish and Swiss peatlands respectively, as the result of advances in smelting techniques and coal burning (Kylander et al., 2009; Shotyk, 1998). Lead enrichment peaked in Europe in the 20th Century due to regional increases in industrial activities and use of leaded gasoline (Cloy et al., 2005; Shotyk et al., 2002b; Shotyk 1998). De Vleeshouwer et al., (2007) reported significant increases in Cu, Ni, and Zn concentrations and an increase of Pb EF's from 39 to 218 between 1835 to 1964 CE. Metal deposition rates post-1970 in Europe began to decline as a result of implementation of pollution controls and emission technologies (Harmens et al., 2007; Pacyna and Pacyna 2001), with the isotopic composition of Pb shifting back to radiogenic values and reducing overall regional metal contamination (Shotyk et al., 1998; Grousset et al., 1994).

North American peatlands demonstrated mean EFs in peatlands ranging from 3.2 (Co) to 13.1 (Pb), with many cores demonstrating EF >10 for As, Co, Cu, Pb, Sb and Zn. North American sites were primarily bog and poor fen peatlands. Similar to Europe, North America has experienced a long history of metal contamination, with Pb and Cu enrichment in lake sediment in Michigan Keweenaw Peninsula dating back to ~6300 to 5000 BP (Pompeani et al., 2013). Metal enrichment followed similar trends to Europe with increased atmospheric deposition occurring as a result regional coal mining, smelting and use of leaded gasoline, with Pb enrichment lake sediments peaking between 1950s and 1980s (Marx et al., 2014). A majority of cores (162 cores of 263 (62%)) sampled in North America are located in northeastern United States and Central Canada, which are high density populated, urban and industrial centers and likely source of trace metals (Martínez and Poleto, 2014; Ajmone-Marsan and Biasioli 2010) with metal EF's typically 1.5-5 times higher than other cores in North America. Anthropogenic metal deposition has been well documented in this area (Pratte et al., 2013; Evans et al., 2005; Carignan et al., 2002) with Simonetti et al. (2003), reporting median EF in snowpack from industrial activities for Pb, Zn and Cu ranging from 292-890, 1000-42000, and 250-980, respectively.

More specifically a small proportion of cores (29 cores of 263 (10%)) are located in close proximity to the Greater Sudbury Area, which has experienced over a century of mining and smelting activities, with pollution sources from logging, acid-mine drainage, smelter emissions, gasoline combustion and drainage of fertilizers (Schindler and Kamber, 2013). Mean EF's for cores located near Sudbury were 42, 49, 39, 8 for Cu, Ni, Pb and Zn, respectively, which fall in the range of EF's for metals in surficial sediment reported by Nriagu et al., (1982). Historical Ni and Cu concentrations in peatlands have ranged from 6912 and 9372 mg kg^{-1} within the immediate vicinity of the smelter to more recent concentration ranges of 1238 – 1685 mg kg^{-1} of Cu and 646 – 920 mg kg^{-1} of Ni within a 10 km radius of the main smelter (Barrett and Watmough, 2015; Taylor and Crowder, 1983). Identifying the origin of targeted metals in an area is difficult given the large number of potential industrial sources, although smelting emission from Sudbury are likely driving the higher reported values of As, Cu, and Ni in North America. Decreased metal deposition and

concentrations in lake sediment have been reported as a result of smelter closures and introduction of the Superstack at Copper Cliff in the 1980s, which could be increasing metal EF in peatlands at greater distances due to long-range transport (Schindler and Kamber, 2013). Decreases in metal deposition beginning in the 1970s as a result of mitigation policies such as the Clean Air Act (1970), phasing-out of leaded gasolines (1976), Convention on Long-range Transboundary Air Pollution (1979), and US Canada Air Quality Agreement (1991) has resulted in lower reported enrichment in these areas and North America (Shotyk and Krachler, 2010; Boutron, 1995).

Peatland cores in South America, Africa and Oceania had mean EF ranging from 1.5 (Ni) to 5.5 (Co), 1.4 (Sb) to 2.4 (Ni) and 1.0 (Ni and Sb) to 1.8 (Se) respectively. Peatland cores sampled from South America, Africa, Asia and Oceania made up a smaller proportion of the dataset (108 of 439 cores (25%)), with South America and Asia demonstrating higher EF than that observed in Africa and Oceania. Higher EF in South America and Asia can be attributed to a longer history of industrial activities. Peatland cores in South America consisted of the hydrologic gradient of fens and peat swamps. South America metallurgical activities have occurred since 2000 BC, although ancient civilization metallurgic production had a negligible impact on metal emissions in region (Uglietti et al., 2015) and local contamination in more remote areas only occurring in the last two centuries (De Vleeshouwer et al., 2014). Mining and industrial activities have been well documented in South America, although metal deposition records in the broader region are less understood. Hong et al., (2004) found metal enrichment dating back to 790 AD, with pronounced increase Cu, Zn, Ag, Cd, and Pb during the 1800's, with De Vleeshouwer et al., (2014) finding local coal-gold rushes and industrialization contributed to local metal contamination in the Karukinka bog in Chile, with Pb enrichment patterns increasing during the industrial period similar to Europe and North America. During this time Pb EF reached a maximum of 25 during the 1950-1970s before declining to 5.4 by 2010 CE. South America had relatively high EF for As, Cd, Co, and Cu which is likely the result of continued mining and smelting in the region, which is second to Asia in non-ferrous metal emissions, as

well as the lack of more advanced emission control technologies (De Vleeshouwer et al., 2014; Pacyna and Pacyna, 2001).

Asian peatlands in our data set had mean EFs ranging between 1.1 (Ni) and 5.5 (Pb), with 7 and 4 cores exhibiting EF >10 for Pb and Zn respectively. Atmospheric metal pollution in Asia has a history equal to that of Europe, with smelting activities associated with Cu, Pb, Ni and Zn dating back to 3000 BC (Lee et al., 2008). Peatlands sampled in Asia were predominantly peat swamp (29 cores of 52 (56%)) in south Asia and bogs (12 cores of 52 (23%)) in eastern Russia. Russian bogs EF were found to be 2-17 times higher for Cu, Pb, Sb, Se, and Zn than other cores sampled in the region. Zhulidov et al. (1997), found peatlands in the Russian arctic impacted by smelting, oil refineries and coal use had concentrations of Cd, Pb, Zn and Cu that were up to 1000 times higher than background concentrations. In the more southern parts of Asia, Mt. Everest ice cores indicate that historical Pb enrichment is minor but peaked at 6.3 in 1994 as a result of rapid industrialization and use of leaded gasoline during the 20th century (Lee et al., 2011). Lee et al. (2008), found that Pb concentration increased by 13.6% in Liangzhi lake sediment in south China following the postwar industrial period (1950s). More recent EFs range from 2-9 for metals such as As, Cd, Cu, Pb, Sb, and Zn in Chinese peatlands as a result of modern large-scale urbanization, vehicle emissions, and annual increase of coal consumption (Bao et al., 2015), which falls within the reported range of EF for Asia peatlands in this study.

Oceania and Africa contained the fewest amount of core samples in the study and had the lowest metal EFs likely due to more recent onset of industrialization and increased atmospheric metal deposition compared with other regions. Peatlands sampled in the Oceania region were solely in Australia and New Zealand, which consisted of bog and intermediate fen peatland types. Australian atmospheric metal pollution and relatively recent industrial history began following European settlement and mining in the 1850's (170 years) (Marx et al., 2010). Metal enrichment in peat cores located in the Australian alps were found to be 2 times higher than background accumulation rates by 1980s and average of ~5 times

background rates by 2006 for Pb, Zn, Cu, As, Cd, Sb, and Zn as a result of increased mineral resource development and smelting, coal production and agriculture (Marx et al., 2014a). Similarly dust aerosols were found to be enriched in Co, Ni, Cu, As, Cd, Sb, and Pb ranging from 15 to >100 compared with background concentrations in the Temple Basin, New Zealand, which were likely derived from anthropogenic sources from Australia (Marx et al., 2014b).

Peat swamps were the only peatland type sampled in Africa, with cores sampled from Uganda and the Republic of Congo. Historical chronologies of Pb contamination in Africa are relatively unknown (Marx et al., 2016), with patterns of metal enrichment being scarce. Similar to the Oceania region, large-scale industrial activities, such as gold mining in South Africa or Pb and Zn smelting in Zambia did not occur until 1886 and 1906 respectively (Alder et al., 2007; Nriagu, 1992). Orr et al. (2018) found that Co, Pb, and Ni showed minor enrichment (>4) in three estuary sediments, with Pb and Cd concentrations drastically increasing during the dry season as a result of fluctuating water table. Similarly, Maina et al. (2019), found that sediment in Lake Naivasha Kenya to have relatively low EF ranging from 0.3-3.2 for Zn, As, Pb, Cu, and Ni as a result of ~50 years of wastewater, fertilizer and pesticides input. Although most literature values are reported for lake sediment in Africa, it would appear that most anthropogenic metal enrichment is relatively minor compared to other regions and similar to values found reported in African peat swamp in this study which coincides with recent metal emission from major sources in Africa being found to be the lowest globally (Pacyna and Pacyna, 2001).

2.4.4 Sulphur Deposition

Although global inventories have been made for metal emissions from both natural (Nriagu, 1979) and anthropogenic (Pacyna and Pacyna, 2001) sources there is currently is no global dataset for metal deposition. Therefore, we used cumulative S deposition as an indicator of industrial activities on a global scale. Cumulative S deposition was also found to be greatest in Europe and North America as a result of a

long history of SO_x emissions from coal, petroleum and natural gas processing and combustion, metal smelting and other industrial processes (Smith et al., 2011), which are also a major source of trace metals (Beavington et al., 2004; Pacyna and Pacyna 2001). A weak positive correlation was found with EF for all metals with the exception of Se supporting some level of anthropogenic influence on metal enrichment in peatlands, although S deposition is not necessarily a good surrogate for metal deposition as S has a longer atmospheric residence time than metals (Hardy et al., 1985; Junge, 1960). It is also important to note natural S emission and deposition are not necessarily from pollution sources with estimated contributions from marine and terrestrial biogenic sources represent 16% and 58% of the total S emissions in the Northern and Southern Hemisphere respectively (Bates et al., 1992; Möller, 1984; Cullis and Hirschler, 1980). When examining cumulative S deposition by peatland type results are far more variable likely due to factors such as geographic location of these peatland types to point source metal emissions. Sudbury for example has released 100 million tonnes of SO_2 since the 1900's (Potvin and Negusanti, 1995) with acid and metal deposition being well documented in bog and poor fen peatlands as a result of Ni and Cu smelting in the area (Gignac and Beckett, 1985; Taylor and Crowder, 1983; Hutchinson and Whitby, 1974), with 40-52% of Cu, Ni, and Fe deposited within a 60 km range from smelters (Freedman and Hutchinson, 1980). Although there is a slightly stronger correlation (0.30) between cumulative S deposition and Ni and Cu EF in the Sudbury area from smelting, weaker relationships are likely more apparent as a result of low S and high metal contributions, such as Pb enrichment from vehicle emissions. Additionally, there is limited resolution of cumulative S deposition ($\sim$55km^2) in this study, which does not account for the rapid changes in metal deposition from point sources as seen in Sudbury (Chan et al., 1984; Hutchinson and Whitby, 1974) and other point sources of metal emissions (Gelly et al., 2019; Chernenkova and Kuperman, 1999).

2.4.5 Metal Pools

Estimated mean metal pools in the 0 - 40 cm depth vary from 38.7 (Sb and Cd) to 6651 (Zn) mg m^{-2} for metals that demonstrated a likely influence of anthropogenic deposition. Globally many studies have

reported metal pools in peat with a wide range in values, primarily due to proximity to metal emission sources. For example in remote locations affected only by long-range transport have considerably lower metal pools, with reported values of 234 mg m^{-2} for As, 784 mg m^{-2} for Cu, 116 mg m^{-2} for Cd, 241 mg m^{-2} for Co, 752 mg m^{-2} for Ni, 4726 mg m^{-2} Pb, and 4808 mg m^{-2} for Zn (Landre et al., 2009; Adkinson et al., 2008). Alternatively, Szkokan-Emilson et al. (2013) estimated metal pools in fen peatlands within 7-13 km from a Cu-Ni smelter in Sudbury to be between 85,000 – 75,000 mg m^{-2} for Co and Zn and Ni and Cu pools to be > 200,000 mg m^{-2}, while Broder and Biester (2015) values ranging from 640 – 1170 mg m^{-2} and 7400 – 24,000 mg m^{-2} for As and Pb respectively in an impacted ombrotrophic bog from historical mining activities. Differences in metal pools are also apparent in land use, with peatland impacted by urban areas demonstrating higher metals pools for Cd, Zn, Pb, and Cu which were 447 mg m^{-2}, 123,000 mg m^{-2}, 18,500 mg m^{-2}, and 5,520 mg m^{-2} respectively (Parker et al., 1978), while agricultural impacted were found to have pools 7.1 mg m^{-2} for As, 1.6 mg m^{-2} for Cd, 130 - 7400 mg m^{-2} for Zn, 31 - 7900 mg m^{-2} for Pb, 22 - 4050 mg m^{-2} for Cu (Bogacz et al., 2019; Teuchies et al., 2013). To our knowledge there has only been one study that has assessed peatland metal pools on a regional scale and has attempted to link metal contamination to broad spatial patterns and pollution sources. Talbot et al., (2017) examined Pb concentrations with depth from 338 peat cores from 127 bogs, fens and swamps located in Ontario, Canada. Estimated Pb metal pools averaged approximately 1200 mg m^{-2} with swamps having the largest value and bogs having the smallest, which contained 54%, 35% and 27% of total Pb in swamps, fens and bogs in the top 50 cm of the profile, respectively, which is similar to the average Pb pools of 1003 mg m^{-2} estimated in our global data. Similar to individual peatland metal pools, spatial patterns to regional contamination of Pb were linked to population density and transport, as well as industrial areas known to be more heavily polluted based on emission data. Metal pools reported in our global estimates falls within the range of reported values estimated by other studies, however presented median values are likely more representative of global peatland metal pools, as mean values are skewed based on a number of peatlands in proximity to metal emission point sources.

2.5 Conclusion

We examined global patterns of metal concentrations and enrichment factors from three depth increments [10-20, 30-40, and 60-70 cm] in peat samples collected from 439 peat cores located in 21 countries across five continents. Metal concentrations were found to differ among peatland types, with fens demonstrating the highest concentrations, likely from minerotrophic conditions. Enrichment factors were found to follow similar, but more pronounced patterns than metal concentrations, with metals likely to be influenced by anthropogenic sources (As, Cd, Co, Cu, Ni, Pb, Sb, Se, and Zn) demonstrating the highest levels of enrichment among the dataset. Additional groupings included minor enrichment of REE and metals with high EF's (Ca, Mn, Fe, and K), but differed in spatial patterns to metals influenced from anthropogenic sources as a result of differences in weathering, peat geochemistry and cycling. Significant differences in anthropogenically influenced metal EF's were observed by peatland type and region, with poor and intermediate fens being found to be more enriched than bog, rich fen and tropical swamp peatland types. North America and Europe exhibited higher levels of enrichment which consisted of primarily bog, poor and intermediate fen systems likely due to the longer history of metal pollution and distribution of sampled peatlands to point sources of "pollution metals". Some level of anthropogenic influence of "pollution" metals was confirmed based on a weak positive correlation (<0.30) with estimated cumulative S deposition. This relationship is likely limited by a number of complex factors including spatial resolution of S deposition, differences in the atmospheric residence time of metal and S emissions, and S deposition likely being a better indicator of industrialization oppose to metal deposition. Estimated metal pools for this global data set varied considerably likely due to proximity to metal emission point sources, with presented median values likely being more representative of global peatland metal pools.

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3.0 Simulated drought impact on uranium and metal mobility in a contaminated peatland complex

Abstract:

Uranium (U) interactions within peatland systems continues to receive interest due to growing production and source contamination. In addition, climate change is expected to alter hydrology of northern peatlands, which may impact U mobility, which is particularly sensitive to changes in pH and redox conditions. This study characterized soil and pore water chemistry at five sites in a peatland complex extending away from a historic tailings breach and one peatland located on the outer limits of tailings impoundment facilities in Elliot Lake, Ontario a region with a long history of U extraction and processing. A 30-day drought experiment was used to evaluate the effect of peatland acidification on metal and U mobility. Baseline geochemistry varied, although downstream sites impacted by historic tailings breach exhibited high peat concentrations of Fe, Mn, Ni, and Pb, with mean U concentrations at the 6 sites ranging from 775 to 1765 mg kg^{-1}. All sites responded similarly to simulated drought with pore water pH significantly declining. The decline in pore water pH was due to increasing sulphate (SO_4^{2-}) concentrations, which accompanied large increases in aluminum (Al), nickel (Ni), copper (Cu), lead (Pb), zinc (Zn) and U which greatly exceeded provincial water quality guidelines. Dissolved organic carbon (DOC) concentrations also increased, which may further enhance Al, Cu, and U mobility as these metals are strongly complexed by organic acids. Metal partitioning (K_d) values in soils could be significantly predicted by pH and/or DOC although the strength of the relationship varied considerably among sites and metals. Multiple linear regression and the inclusion of SO_4^{2-} improved predictions, indicating that declines in pH as a result of SO_4^{2-} and H^+ production primarily governs metals release to pore water, with mean U concentrations in porewater reaching up to 9599 µg L^{-1}. Climate induced droughts may promote metal and U release from peatlands and increased mobilization to surface waters posing a risk to downstream biota.

3.1 Introduction

Peatlands play an important role in global biogeochemical cycles and the balance of carbon (C), nitrogen (N) and sulphur (S) within the earth's biosphere (Gorham, 1991; Limpens et al., 2006; Vile and Novak, 2006). Similarly, the anoxic conditions and accumulation of organic matter (OM) can result in the storage of a wide range of trace metals (Shotyk et al., 1992; Chaney and Hundemann, 1979). The implications of climate change on peatland geochemistry continues to receive interest due to the anticipated hydrologic changes as a result of a warmer climate, which are likely to present shifts in nutrient cycling, microbial activity, and metal mobility (Macrae et al., 2012; Tipping et al., 2002).

The intergovernmental Panel on Climate Change (IPCC) estimates that global temperatures will increase by 1.5 $^{\circ}$C above pre-industrial levels between 2030 and 2052 (IPCC, 2018), which will likely result in the increase incidence of extreme weather events, including changes in overall mean precipitation, peak runoff and the frequency and severity of prolonged droughts during summer months (Trenberth, 2011). When peatlands are subjected to drought conditions, water table drawdowns can expose previously anoxic peat and allow the oxidation of reduced S compounds to form sulphate (SO_4^{2-}) (Dillon et al., 1997). Upon rewetting and re-establishment of normal hydrologic conditions and the formation of sulfuric acid (H_2SO_4) and temporary peatland acidification has been shown to occur (Eimers et al., 2003, 2007; Devito and Hill 1999). The increase in H^+ concentrations compete with metal ion binding sites on peatland soils, resulting in a flux of free metal ions in pore water potentially impacting downstream aquatic life (Sader et al., 2011; Coupal and Lalancette, 1976). Additionally, under these prolonged periods of drought peatland pore water and receiving water have been shown to increase concentrations of dissolved organic carbon (DOC). Explanations for responses in DOC concentrations following drought conditions is highly debated, with increases being related to 'evapo-concentration' (Waiser, 2006), increased biological activity and net DOC production (Paster et al., 2003; Tipping et al., 1999). Alternatively, in some cases lower concentrations of DOC have been recorded post drought that could be due to decreased biological activity and production

(Scott et al., 1998) or DOC consumption by soil biota (Fenner et al., 2005; Pastor et al., 2003). Although acidity is the main control over metal solubility, dissolved organic matter (DOC) can enhance metal complexation and increase metal solubility (Davis and Leckie, 1978), which can further negatively impact water quality in receiving waters downstream of peatland systems (Tipping et al., 2003; Freeman et al. 2001; Macrae et al., 2012).

Uranium (U) interactions within peatland systems has received recent interest due to increased production for nuclear energy and military purposes, resulting in the expansion of mining operations and subsequent source contamination of U and other metals through mining and milling processes (Abdelouas, 2006; Oliver et al., 2007). Peatlands have been shown to be natural sinks for U and other trace metals, with concentrations in peatland soils being reported up to several thousand ppm (Regenspurg et al., 2010; Langmuir, 1978). In our global assessment, both mean and median enrichment factor (EF) for U was 1.0 indicating that U contamination of peatlands is not widespread, although there are localized exceptions (Chapter 2). Uranium naturally occurs in the hexavalent (U(VI)) or tetravalent (UIV)) oxidation states forming a variety of minerals such as oxides or phosphate-, calcium-, silicate- bearing minerals which are stable under anoxic conditions commonly forming poorly soluble mineral uraninite (UO_2) (Langmuir, 1978). U(VI) typically occurs as the uranyl cation (UO_2^{2+}), which is more mobile compared with U(IV) (Langmuir, 1978). The speciation of uranyl is strongly dependent on geochemical conditions including pH, E_h (reduction potential), temperature, and ligand and CO_3^{2-} ion concentrations (Cumberland et al., 2016). The uranyl free cation typically dominates with a pH below 5 that will also readily complex with organic molecules such as acetate, oxalate or humic acids forming aqueous complexes (Haas and Northup, 2004; Stumm and Morgan, 1996; Langmuir 1978), indicating U mobility in peatlands systems may be particularly susceptible to drought conditions and peatland acidification.

To date, the majority of research on the impacts of climate induced drought on biogeochemistry of metals have primarily focused on bog peatland types, located in northern England and Scotland (Clark et

al., 2005; Tipping et al., 2003) and central Ontario, Canada that have been historically impacted by acid deposition and mining activities (Szkokan-Emilson et al., 2013; Adkinson et al., 2008; Eimers et al., 2006). Similarly, metal mobility proceeding drought conditions have focused on metals including Al, Co, Cu, Fe, Mn, Ni, Pb, and Zn, with bench top experiments often being employed to observed changes in pore water chemistry under controlled settings (Watmough and Orlovskaya, 2015; Juckers and Watmough 2014), but are comparable to field measurements (Szkokan-Emilson et al., 2013). A common way to estimate the migration potential of metals present in aqueous solution is to use partition coefficients (K_d), which is the ratio of sorbed metal concentration to dissolved metal concentration at equilibrium. Factors influencing the total metal concentrations in soil solution have included soil metal content, DOC, pH and organic matter content (Watmough and Orlovskaya, 2015; Tipping et al., 2003; Sauvé et al., 2003).

The region of Elliot Lake experienced nearly forty years of U mining that consisted 14 underground mines and 11 associated mills that operated intermittently until 1996 (CEAA, 1996). Decommissioning of Elliot Lake mining operations began in 1992, with twelve permanent tailings management areas (TMA's) being constructed that consisted of underwater storage or vegetated cover based on conditions and feasibility of long-term management of each tailings area (CEAA, 1996). In the 1950's a tailings breach occurred from Denison TMA-2 that released approximately 20,000 tonnes of fine to coarse-grained pyritic uranium tailings into Lower Williams Lake Basin covering an existing fen and bog system. Reclamation of the area occurred in the 1970's, with on-going monitoring of effluent chemistry still occurring today (Paktunc and Davé, 2002; CEAA, 1996).

The objectives of the present study were to evaluate the extent of U and metal contamination in a peatland complex along a distance gradient from a historic tailings impoundment break in Elliot Lake, Ontario to provincial surface water and sediment quality guidelines for the protection of aquatic life. A second objective of this study was to further evaluate the impacts of simulated 30-day drought on pore water chemistry and uranium mobility in soil collected at 6 sites in the peatland complex. A 30-day drought

duration was chosen based on the average of 34 consecutive days of drought per year between 1980 and 2000 in central Ontario, allowing for comparison to other studies (Eimers et al., 2006). The third objective was to evaluate effects of varying physicochemical properties (pH, DOC, SO_4^{2-} and NO_3^-) on U and metal partitioning in soils. We expected that baseline metal concentrations in soil and pore water would be higher in peatlands downstream of historic tailings breach. Following a 30-day drought, we hypothesized that pore water metal concentrations would be greatest at sites impacted by the tailings breach due to higher metal and S content in soils as a result of tailings inputs. Higher S content would generate higher SO_4^{-2} concentrations during drought and upon rewetting would lead to the greater pH depression through production of H_2SO_4, resulting in increased metal and U mobility.

3.2 Methods:

Elliot Lake is located approximately 30 km north of Lake Huron and 130 km west of Sudbury, lying on the Canadian Shield. The grade of pyritic ore processed in Elliot Lake was typically 0.1% U_3O_8 (yellowcake) which was extracted using sulfuric acid and precipitated using ammonia (93% extraction efficiency), which produced tailings and leachate that contained U, radioactive decay products (thorium-230 and radium-266), and residual metals including Cu, Ni, Zn and Pb (Raicevic, 1979). In total, approximately 170 million tonnes of low level radioactive and acid generating tailings were produced, occupying 1250 hectares of land, which were deposited in nearby depressions and lakes (CEAA, 1996, Nicholson et al., 2012; Minnow Environmental Inc., 2017). Permanent underwater storage of tailings, along with control dams, spillways and water treatment facilities were implemented for Qurike, Panel, Denison and Spanish TMAs, which are located approximately 13 km north of Elliot Lake city center (CEAA, 1996; Figure 1). Tailings Management Areas received *in-situ* treatment of lime, with effluent still being periodically treated with sodium hydroxide and barium chloride to manage acidity and remove radium (CEAA, 1996). Water monitoring programs at local and watershed scale continue to track changes in water chemistry and TMA effluent performance to guide long-term water management and environmental protection in the area (CEAA, 1996, Minnow Environmental Inc, 2011).
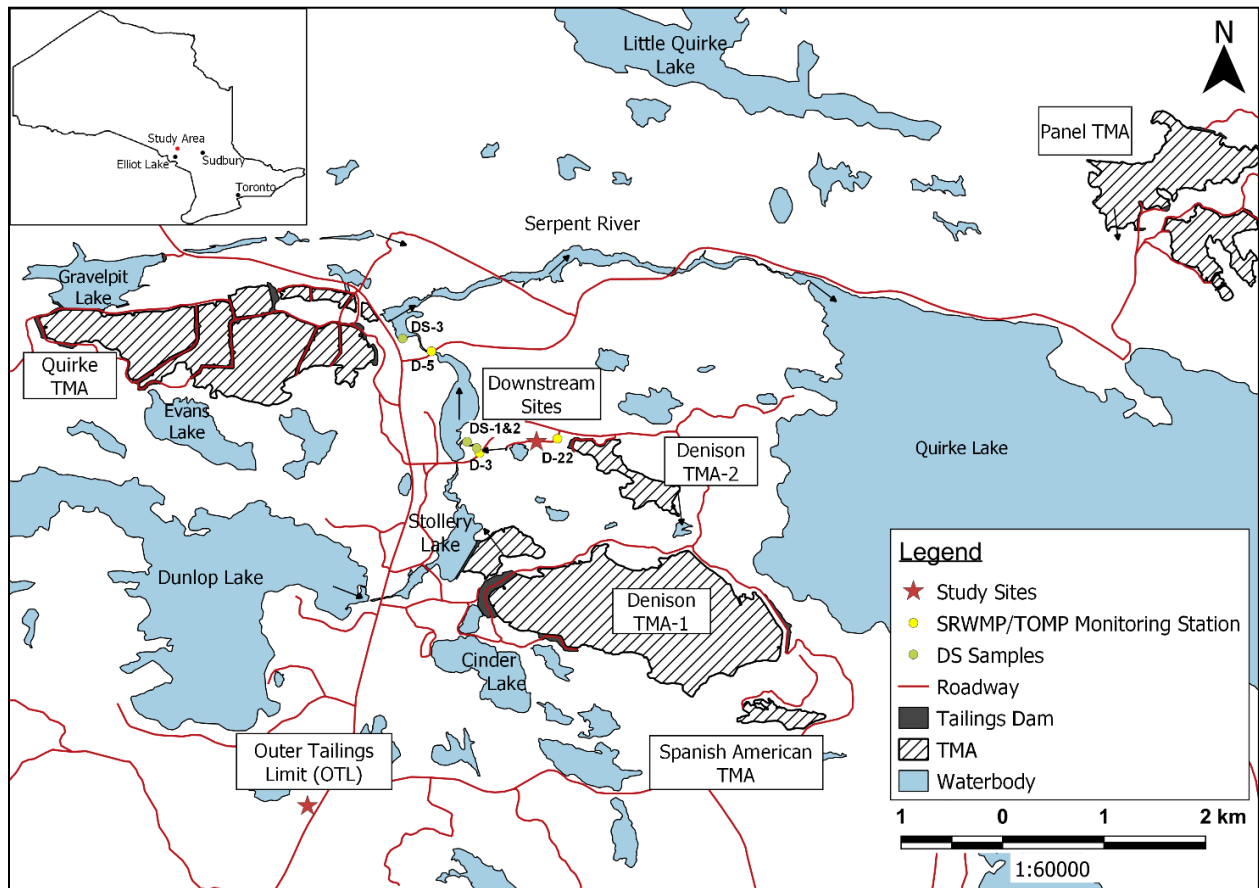
Figure 3.1. Overview of TMAs north of the City of Elliot Lake in relation to sites located downstream of Denison TMA-2 and outer tailings limit (OTL).

3.2.1 Study Sites

Williams Lake tailings basin area was covered by a tailings breach that occurred in the 1950's from Denison TMA-2 (Figure 3.1), covering the existing fen and bog systems to a depth of 0.3 to 1.25 meters (Paktunc and Davé, 2002; Figure 3.1; Figure 3.3). The site was reclaimed from 1976-1977 by creating a sand and gravel barrier layer, limestone application and seed mixture consisting of Red Top (*Agrotis alba*) and Creeping Red Fescue (*Festuca rubra*) grasses, and Bird's Foot Trefoil (*Lotus corniculatus*). A marsh/fen peatland system has since naturally established on the perimeter of Williams Lake and saturated areas within the basin, with a thing layer of newly formed peat.
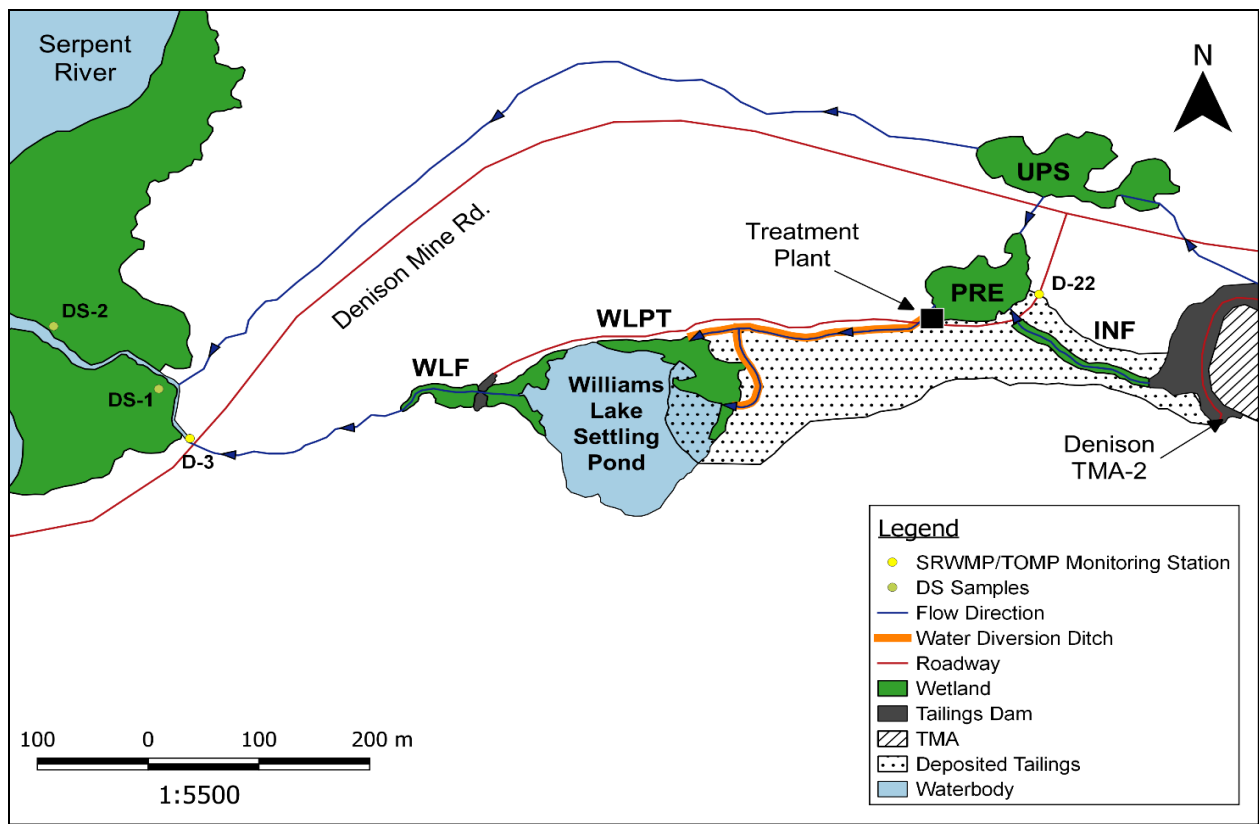
Figure 3.2. Williams Lake tailings area and peatland sampling locations moving downstream from historic tailings spill from Denison TMA-2.
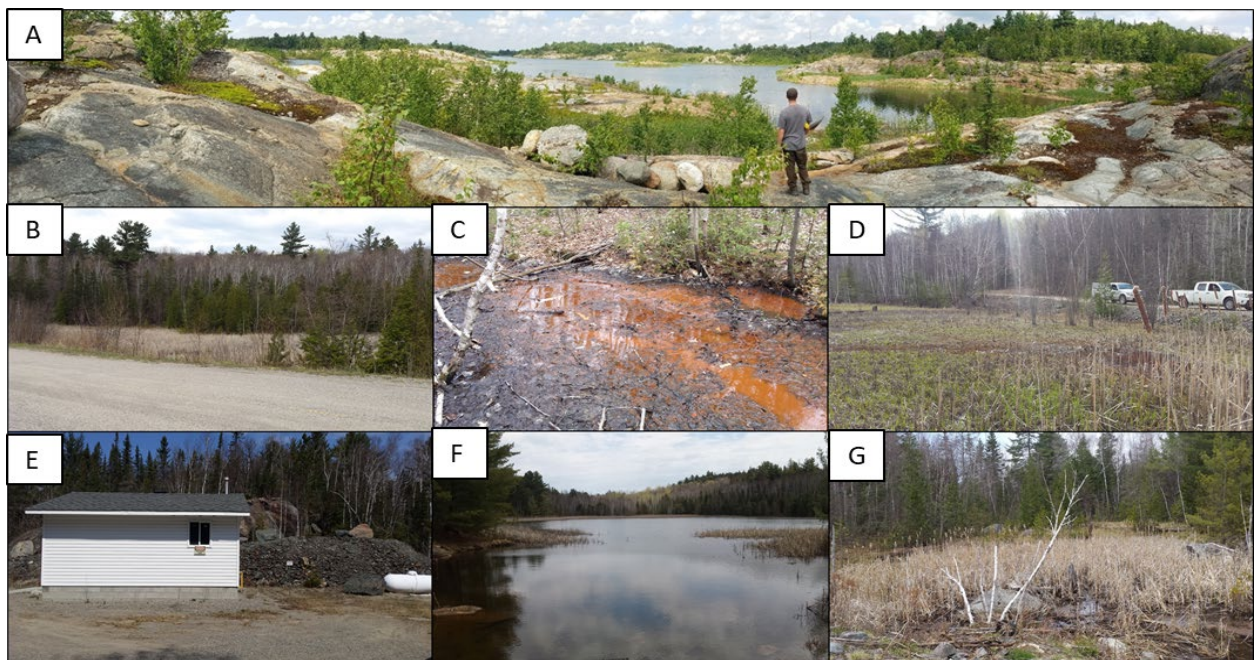
Figure 3. 3. (A) Southern end of Denison TMA-2; (B) UPS; (C) INF; (D) PRE; (E) Treatment plant; (F) Williams Lake; (G) WLF.

Five sites within the peatland complex located in the basin were selected that received tailings effluent and seepage from Denison TMA-2 and collectively drain into the Serpent River. Based on the historic tailings breach and continued input of tailings along flow paths within the complex, some sites contained more organic soil than others. An upstream peatland (UPS; Figure 3.3B) and influent stream (INF; Figure 3.3C) were selected to characterize the outer limit of tailings deposited during the breach and continued tailings seepage from TMA-2 into the Williams Lake basin (Figure 3.2). Effluent from UPS and INF drains into a pre-treatment peatland (PRE; Figure 3.3D) and flows through the Williams Lake Treatment plant, which historically treated water with NaOH and currently treats radium with $BaCl_2$ (Figure 3.3). A geotextile lined diversion ditch also transports water around dry reclaimed tailings into Williams Lake post-treatment peatland (WLPT; Figure 3.2) (Davé, 2011). Williams Lake downstream (WLF) was sampled past the low permeability dam that was installed on the western side of Williams Lake to ensure water cover over wet tailings and increase sediment and water residence time before discharging into the Serpent River (Davé, 2011). Duplicate downstream samples were collected within the peatland beyond WLF in proximity to surface water quality monitoring stations assessed by Denison Environmental Inc, which included DS-1, DS-2 and DS-3 (Figure 3.11 and 3.2). In order to characterize the extent of U and metal contamination from mining activities in Elliot Lake, the final peatland (OTL) was sampled north of the City of Elliot Lake and represent the outer limits of water covered TMAs (Figure 1A).

3.2.2 Sampling

Sites OTL, UPS, INF, PRE, WLPT and WLF and downstream locations (DS1-DS3) were sampled in early August 2018. At each site, ten soil samples (5 samples taken at INF; duplicates take at DS1 to DS3) were collected using a trowel from below the soil surface (5-10 cm) along a transect through the middle of each peatland. Two soil cores were taken from 0-20 cm at the 1st and 10th sampling point along the same transect at OTL, INF, PRE, and WLPT and immediately sectioned at 5 cm increments. Cores were taken to qualitatively assess the distribution of metals in soil and pore water chemistry in peatlands directly

impacted by the historic tailings breach. Samples were placed into 3.8L Ziplock® bags and stored at 4°C in the dark until analysis. A bulk density sample was collected at the 5th sampling point in each peatland and fresh soil samples were classified using the von Post humification scale (Von Post, 1937).

3.2.3 Vegetation Communities

Vegetation species composition and cover was averaged per site by taking two 1 m^2 quadrats between each of the peatland soil sampling locations (Figure 3.2). Peatland sites OTL, UPS, PRE, WLPT, and WLF can be classified as fen/marsh systems based on >50% coverage of robust emergent vegetation (*Typha latifolia*), open water (>8%), and low shrubs (OWES, 2002). Two *Sphagnum* moss species (*Sphagnum fallax* and *Sphagnum fimbriatum*) make up a small percentage of community cover at OTL, UPS, PRE, and WLPT, but were only found along the boundary of each peatland. INF being an influent stream from TMA-2, had the highest coverage of detritus material (46.3%) and open water (33.3%), as well as encroachment of woody species including balsam fir (*Abies balsamea*), speckled alder (*Alnus incana*), white birch (*Betula papyrifera*), and eastern white cedar (*Thuja occidentalis*), with emergent vegetation only occurring at the drainage area of the stream, where water is discharging into PRE peatland site.
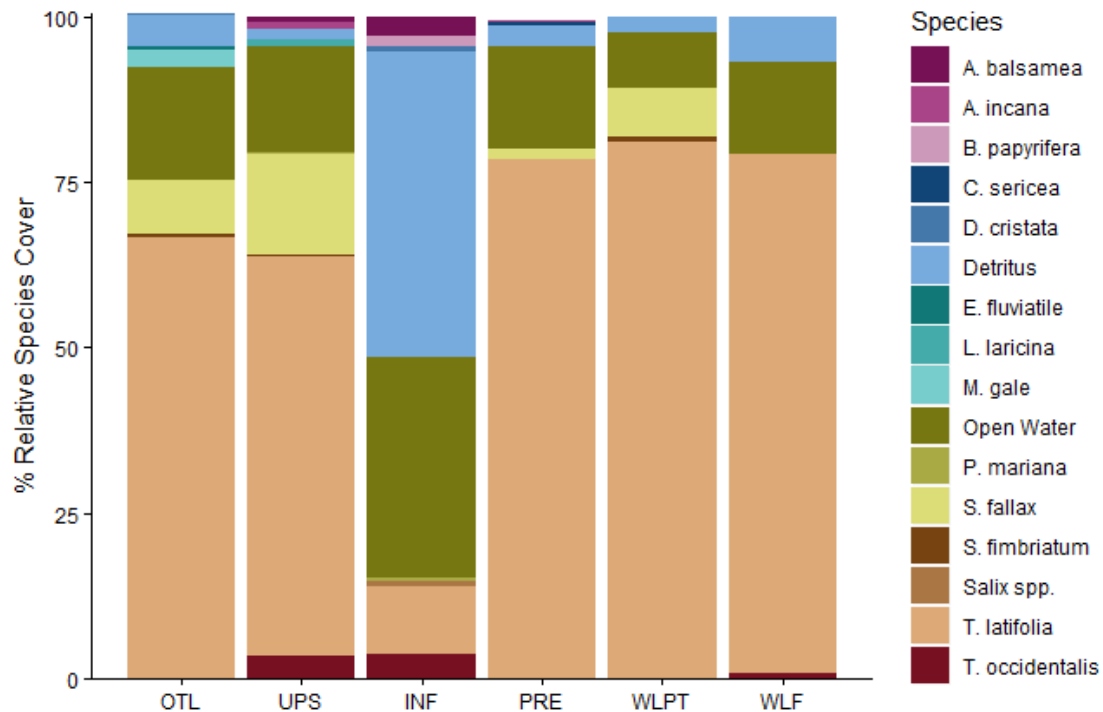
Figure 3. 4. Mean percent (%) relative species cover of vegetation communities found at outer tailings limit (OTL) and peatland sites moving downstream from TMA-2 (n=20).

3.2.4 Baseline Conditions

Moisture content of each sample was measured gravimetrically by drying approximately 5 g of wet soil at 105 °C for 24 h. Organic matter content was estimated by igniting approximately 1 g of oven dried pulverized soil in a muffle furnace at 405°C for 10 h. Oven dried and pulverized peatland soil samples (0.5 g) were cold-digested in 2.5 mL of HNO_3 for 8 h and then digested under reflux at 100 °C for an additional 8 h. Following digestion, samples were filter using FisherBrand™ P8 filter paper and diluted using B-Pure™ to 25 mL. Digests were then analyzed for total metal (Al, Cu, Fe, Mn, Ni, Pb, and Zn), base cation (Ca, K, Mg, and Na), phosphorous (P) and sulfur (S) concentrations using inductively coupled plasma optical emission spectrometry (ICP-OES). Precision of results was confirmed by the analysis of EnviroMAT SS-2 contaminated soil standard and digestion blanks. Total C, N, and S analysis of dried ground soil was weighed within 0.0001 g on a digital balance and approximately 75 mg of peat and 150 mg

of tungsten (VI) oxide powder was placed into a foil capsule and compressed with a pill shaping device. Samples were analyzed using an Elementar CNS Analyzer and precision of results was confirmed using blanks and sulfadiazine for CNS recalibration and QA standard (NIST-1515-SRM apple leaves).

Approximately 100 mL of pore water was extracted from wet subsamples by centrifuging at 5000 rpm for 20 min. Pore water was first analyzed for pH using an OAKTON pH 510 series meter and then filtered using a 25 mm, 0.45 μm nylon syringe filter prior to chemical analysis. Dissolved organic carbon concentrations were analyzed using a Shimadzu TOC-V instrument. ICP-OES was used to measure the concentrations of dissolved metals (Al, Cu, Fe, Mn, Ni, Pb, and Zn), base cations (Ca, K, Mg, and Na) and TP. Concentrations of NO_3^- and SO_4^{2-} were measured on ion chromatography using a Dionex ICS-1100.

3.2.5 Simulated Drought Experimental Design

Soils were left to stabilize in the dark at 4°C for two weeks, before establishing two separate treatments: continually wet (i.e. no drought) and a 30-day drought. For each treatment, approximately 100g of field moist homogenized soils (6 sites/10 samples per site) was added to 120 cm^3 plastic sample container with a screw top lid left ajar to allow air exchange and placed into a Thermo Scientific Precision Economy Incubator 3522 at 26°C. The mass of each sample was recorded at the beginning of the experiment and monitored every three days to maintain field moist conditions of the wet treatment. Proceeding the 30-day drought period, the mass of water loss was added using B-Pure™ and samples were homogenized and left for one day prior to analysis. Soil and pore water were analyzed using the same procedure for baseline geochemistry as described above.

3.2.6 Metal Partitioning Coefficients

Metal partitioning coefficients (K_d) were calculated for each peatland site as follows:

$$K_d = \frac{Total\ Metal}{Dissolved\ Metal} \qquad\qquad [3.1]$$

Where the total metal in soil is milligrams per kilogram and the total dissolved metal is in milligrams per liter. Units for K_d are L kg^{-1}, with low K_d values indicating that there is proportionally more metal in soil solution compared with higher K_d values.

3.2.7 Downstream water geochemistry and provincial water and sediment quality guidelines

Surface water chemistry collected by Denison Mines Inc, as part of a provincial annual report conducted on the Operating Care and Maintenance of decommissioned tailings areas in conjunction with DS-1 to 3 pore water chemistry samples was used to assess water conditions beyond the Williams Lake Tailings basin, within the Serpent River. Monitoring programs assessing water quality objectives within and beyond the Williams Lake Tailings Area, include: Tailings Operational Monitoring Program (TOMP) and the Serpent River Watershed Monitoring Program (SRWMP). Downstream surface water monitoring stations include D-22 (Lower Williams Effluent Treatment Plant), D-3 (Lower Williams final discharge), D-5 (Serpent River between Denison and Quirke TMAs) (Table 3.1). Total metal concentrations found in peatland soils and pore water from baseline conditions and simulated 30-day drought were compared with Canadian sediment and freshwater guidelines for the protection of environmental and human health based on the lowest and severest effect level in sediment and short and long-term exposure in freshwater (Table 3.2).

Table 3.1. Mean surface water pH, SO_4^{2-} (mg L $^{-1}$) and metals (µg L $^{-1}$) moving downstream of TMA-2 and beyond the final discharge point of the Williams Lake Tailings area into the Serpent River at Denison Inc. monitoring stations and Peatlands. (Denison Mines Inc., 2018; Denison Mines and Rio Algom, 2018).

	D-22	D-3	D-5
Sample Size (*n*)	(4)	(4)	(4)
pH	6.70	7.33	6.80
SO_4^{2-} (mg L $^{-1}$)	72	68.2	11.3
Fe (µg L $^{-1}$)	1390	120	70
Mn (µg L $^{-1}$)	186	15	26
U (µg L $^{-1}$)	0.8	4.8	1.3

Table 3.2. Canadian sediment and freshwater guidelines for the protection of environmental and human health for metals found in mining impacted peatlands at Elliot Lake Ontario (CCME, 2001).

Metal	Sediment Quality Guidelines for the Protection of Environmental and Human Health		Freshwater Quality Guidelines for the Protection of Aquatic Life	
	Lowest Effect (mg kg $^{-1}$)	Severest Effect (mg kg $^{-1}$)	Short Term (µg L $^{-1}$)	Long Term (µg L $^{-1}$)
Al	-	-	252	74
Fe	21000	43800	-	300
Mn	460	1100	1900	600
Zn	120	820	-	30
Ni	16	75	150	25
Pb	31	250	7	1
Cu	16	110	4	2
U	33	2000	30	15

See notes in Appendix A for how concentrations were determined.

3.2.8 Statistical Analysis

A non-parametric Kruskal-Wallis test and Bonferroni correction was conducted to assess differences in soil and pore water chemistry across sites. Two-way ANOVAs were conducted to determine the effects and interactions of simulated drought treatment between sites on moisture content and the main factors on pore water chemistry. Prior to analysis, the data were log transformed to meet the assumption of normality and equal variances. When significant F ratios were found, individual means were compared by Tukey's post-hoc test ($p < 0.05$). Relationships between pH and DOC of water extracts, as well as K_d values of pore water metal concentrations (Al, Fe, Mn, Ni, Cu, Pb, Zn, and U) were assessed using linear

regression analysis. Stepwise multiple linear regression model was used to predict the metal concentrations of pore water using pH, DOC, SO_4^{2-} and NO_3^- in RStudio (Rstudio Team, 2020).

3.3 Results

3.3.1 Baseline soil and pore water chemistry

Baseline peatland geochemistry varied considerably across peatland sites, with differences being found to be related to distance from TMA-2 and the influence of tailings input. Pore water pH was significantly higher at sites surrounding TMA-2 ranging from 6.38 to 7.01 before decreasing with distance further downstream of the Serpent River (DS-1 pH 6.43 to DS-3 pH 5.97) (Table 3.4). Base cation (Ca, K, Mg) and P concentrations in both peat and pore water were significantly higher at sites impacted by the historic tailings breach (Table 3.3 and Table 3.4). Nitrate and DOC concentrations varied among peatlands sites, with no apparent trends, while SO_4^{2-} concentrations were significantly higher in downstream peatlands with SO_4^{2-} concentrations ranging from 59.6 to 649 mg L^{-1} (Table 3.4). Physical soil properties also greatly differed among peatlands, as a result of historic and continued tailings input at sites downstream from TMA-2. Peat humification did not differ among peatland sites (H4-H5), although bulk density tended to be higher in sites directly downstream of TMA-2 (0.27-1.50 g cm^{-3}) compared with upstream sites OTL and UPS (0.14-0.18 g cm^{-3}) (Table 3.3). Carbon and N concentrations were significantly higher in OTL site compared with sites effected by the tailings dam breach, which demonstrated concentrations more typically associated to mineral soils with C and N ranging from 57.9 to 143 g kg^{-1} and 3.1 to 6.4 g kg^{-1} respectively (Table 3.3).

Table 3.3. Von post, organic matter content (%), bulk density, and mean (±S.E.) concentrations of carbon, nitrogen, sulphur (g kg^{-1}), base cations (mg kg^{-1}) and metals (mg kg^{-1}/g kg^{-1}) found in bulk peatland soil samples at a depth of 5-15 cm taken from the outer tailings limit (OTL) and at sites downstream of Denison TMA-2. Sites with different letters are significantly different ($P < 0.05$) using Bonferroni post hoc test. Underlined concentrations exceed the Canadian Sediment Quality Guidelines (SQG) lowest effect on environmental and human health (mg kg^{-1}).

	OTL[US]	UPS[US]	INF[DS]	PRE[DS]	WLPT[DS]	WLF[DS]	P	DS-1[S]	DS-2[S]	DS-3[S]
Von Post	H5	H4	H4	H5	H5	H5		H5	H4	H5
Bulk Density (g cm^{-3})	0.18	0.14	1.50	0.27	0.38	0.36		-	-	-
C (g kg^{-1})	374 ± 7.5a	316 ± 16.8b	57.9 ± 11.7c	124 ± 17.7c	143 ± 32.5bc	131 ± 7.4bc	***	36.7	265.5	421.7
N (g kg^{-1})	19.3 ± 0.6a	12.6 ± 0.8b	3.1 ± 0.5c	6.3 ± 0.9bc	7.0 ± 1.7bc	6.4 ± 1.1bc	***	3.3	15.1	24.8
S (g kg^{-1})	5.1 ± 0.2a	19.1 ± 3.0ab	5.2 ± 0.9a	20.3 ± 7.5ab	38.3 ± 3.4b	13.5 ± 2.9a		1.3	4.2	4.2
Ca (mg kg^{-1})	3279 ± 128a	7028 ± 707abc	4644 ± 904ab	7754 ± 1771abc	19144 ± 6823bc	49047 ± 11350c	***	7157	4806	6861
K (mg kg^{-1})	844 ± 94.1a	820 ± 135a	1236 ± 109b	966 ± 215a	567 ± 56.6a	547 ± 82.5a	**	632	361	332
Mg (mg kg^{-1})	892 ± 63.8abc	816 ± 101abc	1292 ± 99.2ac	680 ± 139ab	712 ± 238b	1999 ± 465c	**	761	1416	2218
Na (mg kg^{-1})	1608 ± 142a	473 ± 77.3b	297 ± 32.0b	352 ± 17.2b	409 ± 20.5b	568 ± 56.7b	***	105	761	294
P (mg kg^{-1})	9.5 ± 0.6a	358 ± 26.3b	562 ± 84.9b	535 ± 54.0b	332 ± 56.3b	418 ± 89.9b	***	25.1	17.7	13.4
Al (mg kg^{-1})	6510 ± 5.1ab	5167 ± 736a	6346 ± 504ab	9155 ± 1411ab	9560 ± 2452ab	15458 ± 2632b	**	6149	5433	4288
Fe (g kg^{-1})	19.6 ± 2.1 ac	17.8 ± 2.8c	_107 ± 23.0ab_	_153 ± 19.9ab_	_61.2 ± 10.8ab_	_61.6 ± 14.8abc_	***	73.8	12.8	10.4
Mn (mg kg^{-1})	_138 ± 5.9a_	_548 ± 82.8b_	_7342 ± 2131b_	_2328 ± 692b_	_796 ± 416ab_	_4026 ± 1788ab_	***	_654_	_469_	165
Ni (mg kg^{-1})	_12.4 ± 0.9a_	_16.0 ± 8.1a_	_42.6 ± 16.8ab_	_25.0 ± 5.8a_	_76.7 ± 29.5ab_	_129 ± 23.0b_	***	_20.8_	13.3	9.1
Cu (mg kg^{-1})	_46.3 ± 4.0a_	_29.9 ± 8.4a_	_38.8 ± 3.1a_	_97.7 ± 21.9ab_	_85.3 ± 23.6ab_	_157 ± 28.9b_	***	_82.1_	_33.6_	_23.6_
Pb (mg kg^{-1})	_57.0 ± 4.6ab_	_45.6 ± 7.5a_	_166 ± 30.4ab_	_317 ± 57.0b_	_38.3 ± 8.1a_	_88.9 ± 53.6a_	***	_43.0_	21.4	7.2
Zn (mg kg^{-1})	48.9 ± 5.0a	32.2 ± 15.2a	72.3 ± 29.3ab	71.1 ± 15.1ab	_119 ± 44.1ab_	_239 ± 46.9b_	***	46.7	63.1	59.3
U (mg kg^{-1})	_236 ± 27.2ac_	_162 ± 27.8c_	_1203 ± 168ab_	_1765 ± 226b_	_775 ± 116ab_	_1089 ± 186b_	***	_1405_	_162_	_131_

Significance of Bonferroni post hoc test is indicated by: * ($P < 0.05$), ** ($P < 0.01$), *** ($P < 0.001$).

[b] Site location in relation to TMA-2 is denoted by: [US] – upstream, [DS] – downstream of tailings breach, and [S] – downstream along Serpent River.

Major differences were observed in the level of metal contamination among peatland sites, which were significantly higher in downstream peatlands impacted by the tailings breach. Metal concentrations in peat generally increased moving downstream from TMA-2 (INF, PRE, WLPT, and WLF), with concentrations of Fe, Mn, Ni, Pb, and Zn ranging from 61.2 to 107 g kg^{-1}, 796 to 7342 mg kg $^{-1}$, 25.0 to 129 mg kg $^{-1}$, 71.1 to 239 mg kg $^{-1}$, 38.8 to 317 mg kg $^{-1}$, and 71 to 239 mg kg $^{-1}$ respectively (Table 3.3). Pore water metal concentrations followed similar, but less pronounced trends as peat metal concentrations (Table 3.4). Uranium concentrations were 1.5 to 10 times higher in downstream sites compared with upstream sites; concentrations in peat were between775 and 1765 mg kg $^{-1}$, while pore water concentrations ranged from 69 to 208 μg L $^{-1}$ (Table 3.3 and Table 3.4). All sites were found to have concentrations of metals that exceeded both the SQG lowest effect on environmental and human health and WQG for the long-term protection of aquatic life, with concentrations being generally higher at sites directly downstream of TMA-2. Uranium was found to be 4 to 18 times higher than the WQG including peatlands located further downstream along the Serpent River (Table 3.4 and Table 3.2), indicating metal and U contamination has occurred within the general mining area north of the city of Elliot Lake.

Table 3.4. Mean (±S.E) pH, dissolved organic carbon (DOC mg L^{-1}), total dissolved nitrogen, nitrate (NO$_3$-N mg L^{-1}), sulfate (SO$_4^{2-}$ mg L^{-1}) , base cations (mg L^{-1}) and metals (μg L^{-1}) concentrations found in bulk peatland soil samples at a depth of 5-15 cm taken from the outer tailings limit (OTL) and at sites at varying distances downstream of Denison TMA-2. Sites with different letters are significantly different ($P < 0.05$) using Bonferroni post hoc test. Underlined concentrations exceed the Canadian Freshwater Quality Guidelines (WQG) for the protection of aquatic health for indefinite exposures (μg L^{-1}).

	OTL^{US}	UPS^{US}	INF^{DS}	PRE^{DS}	WLPT^{DS}	WLF^{DS}	P	DS-1	DS-2	DS-3
pH	5.74 ± 0.08a	7.23 ± 0.1bc	6.91 ± 0.1b	6.85 ± 0.1bc	6.38 ± 0.1b	7.01 ± 0.1c	***	6.43	6.37	5.97
DOC (mg L^{-1})	34.5 ± 7.2	38.6 ± 10.7	14.4 ± 5.0	16.6 ± 3.1	26.3 ± 4.3	25.9 ± 2.8	0.08	24.7	19.0	72.5
NO$_3$-N (mg L^{-1})	0.1 ± 0.01a	5.7 ± 5.1b	12.8 ± 11.4b	0.1 ± 0.02a	0.3 ± 0.09a	0.2 ± 0.03a	***	0.2	0.1	0.1
SO$_4^{2-}$ (mg L^{-1})	6.6 ± 1.3a	318 ± 98.8b	146 ± 89.8ab	59.6 ± 15.0a	649 ± 117b	136 ± 21.5b	***	6.2	19.5	1.3
Ca (mg L^{-1})	5.9 ± 0.7a	55.0 ± 11.3a	159 ± 4.0b	81.8 ± 7.9b	226 ± 33.4b	73.6 ± 5.5a	***	38.0	11.6	22.3
K (mg L^{-1})	7.4 ± 2.9a	13.2 ± 3.2b	15.1 ± 1.3b	15.8 ± 2.0b	17.5 ± 3.2b	8.6 ± 2.0a	*	5.1	1.1	2.4
Mg (mg L^{-1})	1.1 ± 0.2a	8.5 ± 1.7bc	16.0 ± 0.4bc	10.3 ± 0.9bc	17.5 ± 1.9b	7.8 ± 0.7ac	***	4.4	1.4	2.5
Na (mg L^{-1})	83.9 ± 4.2a	9.9 ± 1.7b	8.3 ± 0.1b	8.5 ± 0.2b	10.3 ± 1.3b	7.4 ± 0.6b	***	45.3	11.7	48.0
P (μg L^{-1})	1.6 ± 0.001a	62.2 ± 19.7b	51.6 ± 23.1b	41.8 ± 13.2b	59.9 ± 18.9b	42.3 ± 13.4b	***	0.1	0.1	0.1
S (mg L^{-1})	2.4 ± 0.4a	28.6 ± 9.0ac	132.4 ± 3.3b	31.7 ± 9.4abc	116 ± 20.7bc	28.9 ± 4.3bc	***	2.2	1.3	5.8
Al (μg L^{-1})	504 ± 91.5a	124 ± 39.4b	118 ± 53.0b	126 ± 39.8b	161 ± 50.8ab	119 ± 37.8b	***	149.3	864	172
Fe (μg L^{-1})	6953 ± 2954a	3215 ± 1016a	122 ± 54.7b	4741 ± 1499a	7170 ± 2268a	557 ± 176b	***	11226	9778	2935
Mn (μg L^{-1})	314 ± 87.0a	3570 ± 1129b	384 ± 172a	3443 ± 1089b	2476 ± 783b	4167 ± 1318b	***	3782	90.3	2368
Ni (μg L^{-1})	1.6 ± 0.4a	9.9 ± 3.1ab	6.2 ± 2.8ab	5.1 ± 1.6ab	15.1 ± 4.8b	4.9 ± 1.6ab	***	10.0	14.3	8.52
Pb (μg L^{-1})	5.6 ±1.9	2.1± 0.7	2.5 ± 1.1	4.2 ± 1.3	2.1 ± 0.7	1.3 ± 0.4	0.12	3.9	109	0.8
Cu (μg L^{-1})	15.6 ± 1.7a	40.6 ± 3.4b	27.8 ± 0.9ab	26.2 ± 6.3a	34.0 ± 3.49b	15.6 ± 1.36a	***	9.5	26.0	10.4
Zn (μg L^{-1})	66.1 ± 27.6a	23.8 ± 7.5a	5.9 ± 2.6b	4.5 ± 1.4b	4.7 ± 1.5b	3.0 ± 0.9b	***	5.8	73.2	6.3
U (μg L^{-1})	83.3 ± 36.3a	64.1 ± 20.3a	69.1 ± 30.9a	80.4 ± 25.4a	208 ± 65.9b	60.7 ± 19.2a	**	272	241	50.5

Significance of Bonferroni post hoc test is indicated by: * ($P < 0.05$), ** ($P < 0.01$), *** ($P < 0.001$).

[b] Site location in relation to TMA-2 is denoted by: [US] – upstream, [DS] – downstream of tailings breach, and [S] – downstream along Serpent River.

3.3.2. Soil Core Baseline Chemistry

Soil chemistry varied throughout the soil profile at each of the sites, but patterns were notably different at sites directly impacted by the historic tailings breach (INF, PRE, WLPT) compared with OTL (Table 6). Organic matter content was higher throughout the soil profile at the OTL site decreasing from 81.7 to 73.6% with depth compared with INF, PRE, and WLPT sites that had much lower OM at the deeper (>10cm) depths, with values as low as 4.5 percent at 15-20 cm within the soil profile (WLPT) (Table 6). Similarly, metal concentrations were higher throughout the profile at INF, PRE, and WLPT compared to OTL, although there were generally no observed patterns with depth (Table 3.5).

Table 3.5. Mean metal concentrations (g kg^{-1}/mg kg^{-1}) found in peatland soil cores at a depth of 0-20 cm taken from the outer tailings limit (OTL) and peatland sites impacted by historic tailings breach downstream from TMA-2 (n=2).

Core ID	Depth (cm)	OM (%)	Fe (g kg^{-1})	Mn (mg kg^{-1})	Ni (mg kg^{-1})	Cu (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})	U (mg kg^{-1})
OLT	0-5	81.7	11.4	143	13.9	62.5	57.7	77.0	139
	5-10	76.3	10.8	131	11.2	44.5	53.5	87.7	128
	10-15	74.2	8.1	114	12.4	50.5	57.3	86.2	103
	15-20	73.6	8.2	117	11.9	50.6	62.3	86.7	100
INF	0-5	40.5	118	5252	12.0	36.6	120	27.0	887
	5-10	24.5	143	488	14.2	152	401	44.6	923
	10-15	8.2	157	1047	64.5	184	276	129	952
	15-20	41.5	82.1	2150	13.6	59.5	135	18.3	450
PRE	0-5	81.2	1943	2502	11.0	30.7	50.1	94.0	1124
	5-10	63.4	217	648	4.9	150	322	59.7	1459
	10-15	62.4	129	152	49.5	153	744	79.4	834
	15-20	67.5	68.6	48.8	7.1	68.9	572	9.1	363
WLPT	0-5	85.5	73.0	369	39.6	75.2	36.6	77.7	645
	5-10	47.5	75.4	288	79.3	164	77.5	157	920
	10-15	4.3	119.6	1520	109	261	162	147	1147
	15-20	4.5	62.8	1566	66.9	120	431	81.1	439

Pore water chemistry differed among cores, although the chemistry of pore water was more consistent throughout the profile compared with bulk soil (Table 3.6). The pore water pH and SO_4^{2-} concentration at OTL was much lower than sites downstream from TMA-2 (Table 3.6). In general, Al, Ni, and U concentrations in pore water were higher at downstream sites, whereas concentrations throughout the profile of other metals were not notably different across sites.

Table 3.6. Mean pH, sulfate (SO_4^{2-} mg L^{-1}) and metal concentrations (μg L^{-1}) found in pore water peatland cores at a depth of 0-20 cm taken from the outer tailings limit (OTL) and peatland sites impacted by historic tailings breach downstream from TMA-2 (n=2).

Core ID	Depth (cm)	pH	SO_4^{2-} (mg L^{-1})	Fe (μg L^{-1})	Mn (μg L^{-1})	Ni (μg L^{-1})	Cu (μg L^{-1})	Pb (μg L^{-1})	Zn (μg L^{-1})	U (μg L^{-1})
OLT	0-5	5.43	20.2	148	2723	0.7	8.1	5.1	222	27.8
	5-10	5.40	19.6	160	2367	0.2	11.4	7.0	117	22.7
	10-15	5.29	17.1	144	2918	0.7	10.9	10.4	193	32.9
	15-20	5.19	15.3	161	2944	0.7	13.2	6.5	325	32.1
INF	0-5	5.12	370	2185	2170	2.0	C_L	1.0	3.2	48.1
	5-10	5.06	329	2458	840	7.6	C_L	1.5	1.4	55.9
	10-15	5.59	1258	79.5	409	2.5	C_L	1.0	0.7	69.1
	15-20	6.19	363	28.9	175	5.1	C_L	0.5	1.2	35.1
PRE	0-5	6.35	239	6839	2572	6.6	C_L	3.0	8.4	97.0
	5-10	6.24	209	2629	1448	6.1	C_L	2.5	11.7	12.8
	10-15	6.46	299	60803	3513	21.5	C_L	12.0	20.7	765
	15-20	6.08	544	1848	5248	3.5	C_L	2.0	19.3	45.8
WLPT	0-5	7.20	263	10514	2295	32.0	C_L	4.5	19.4	162
	5-10	7.09	159	13810	225	14.0	C_L	7	11.4	165
	10-15	6.99	186	14417	215	6.6	C_L	5	10.2	126
	15-20	7.89	227	1110	274	19.0	C_L	5.5	43.1	62.7

3.3.3. Effects of simulated drought on pore water chemistry

In the simulated drought experiment, pore water chemistry significantly differed among treatments and sites, although there was no interaction for any variables, indicating that despite differences in baseline chemistry concentrations among sites, pH and concentration of DOC, SO_4^{-2}, nutrients (Ca, K, Mg, Na, and P, metals (Fe, Mn, Ni, Cu, Pb, Zn, and U) responded similarly to the 30-day drought treatment. The initial moisture content of peatland soils ranged from 85.2 to 93.0% (Figure 3.5). Following the 30-day simulated

drought, moisture content decreased by an average of 26% across all sites with the greatest loss occurring at WLPT and WLF.
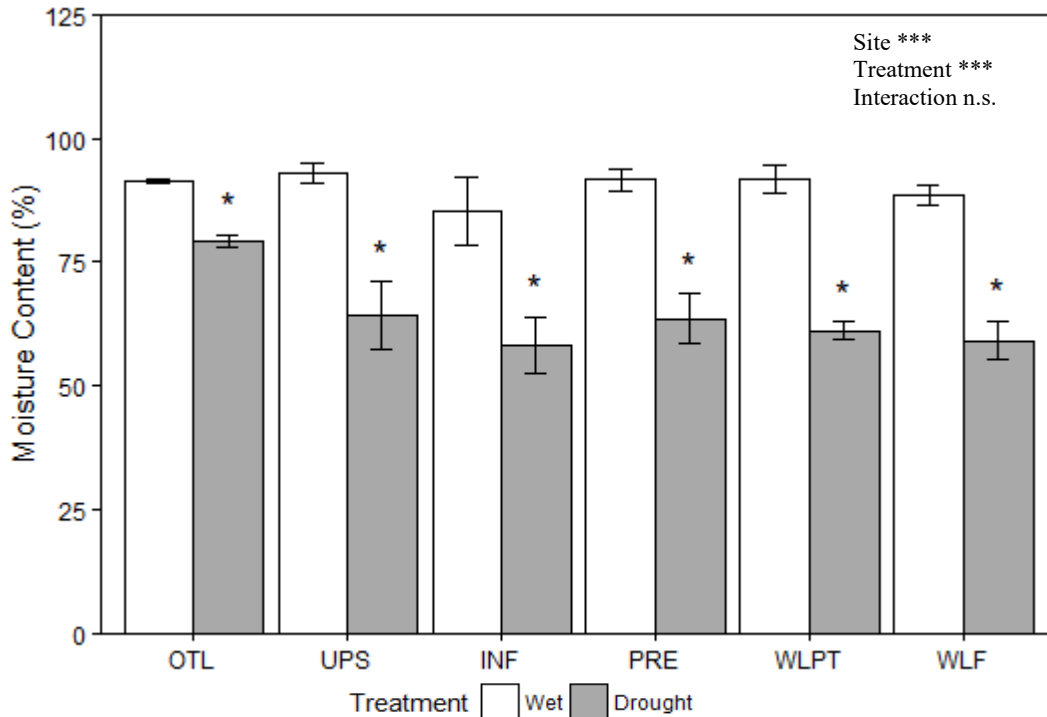
Figure 3.5. Mean (±S.E.) moisture content (%) from microcosms with peatland soil collected from the outer tailings limit (OTL) and peatland sites at varying distances downstream of TMA-2, subjected to two treatments: 30 day drought (dark grey bar) and wet (white bar). Statistical significance: *, $p < 0.05$, **, p <0.001, ***, $p < 0.001$; n.s., no significance.

Following the 30-day simulated drought all sites exhibited a significant (Tukey Test, $p < 0.001$) decline in pH and increase in DOC relative to the peat that was kept continually moist (Figure 3.5). The decline in pH ranged from 0.21 and 2.47 and DOC increased by 4.2 and 43.4 mg L^{-1} (Figure 3.5). The response of other analytes to drought conditions was more variable. Some analytes exhibited little change (K, Na, S and NO_3^-), while other such as SO_4^{-2} demonstrated large treatment effect with concentrations 1.5-18 times higher than the wet treatment (Figure 3.6). Treatment effects were demonstrated for all metals, but there were large variations among sites, with the greatest increases in pore water metal concentrations occurring at UPS, PRE and WLPT sites. At these sites Al, Ni, Cu, and Pb concentrations were found to be

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7 to 440 times greater than wet treatments. Uranium concentrations in porewater followed similar increases as other metals with concentrations being 3 to 10 times higher proceeding drought conditions (Figure 3.6). In general, the highest release of metal concentrations in pore water corresponded to the greatest decrease in pH and increase in DOC concentrations proceeding drought, which occurred at sites UPS, PRE and WLPT (Figure 3.6; Figure 3.4), thereby increasing metal concentrations in pore water well above water quality guidelines.
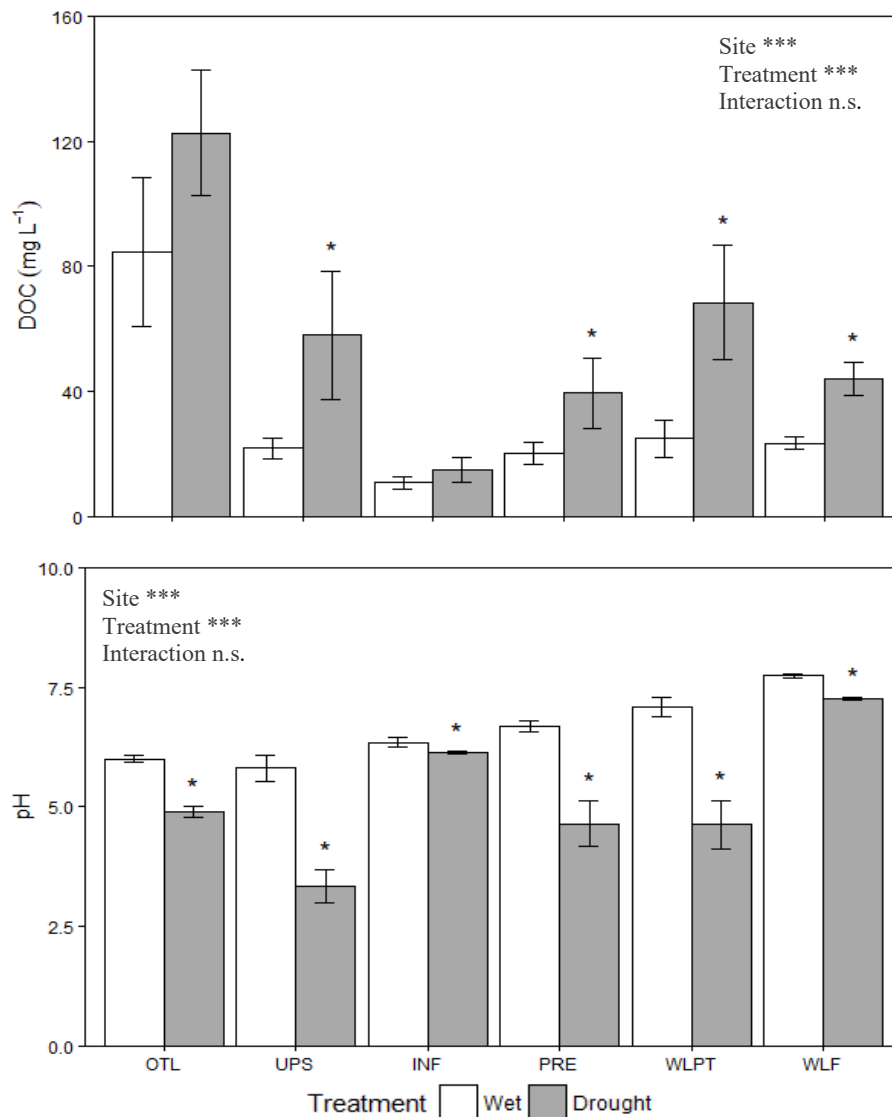
Figure 3.6. Mean (±S.E.) pH and DOC concentrations of pore water extracted from microcosms with peatland soil collected from the outer tailings limit (OTL) and peatland sites at varying distances downstream of TMA-2, subjected to two treatments: 30 day drought (dark grey bar) and wet (white bar). Statistical significance: *, $p < 0.05$, **, $p < 0.001$, ***, $p < 0.001$; n.s., no significance
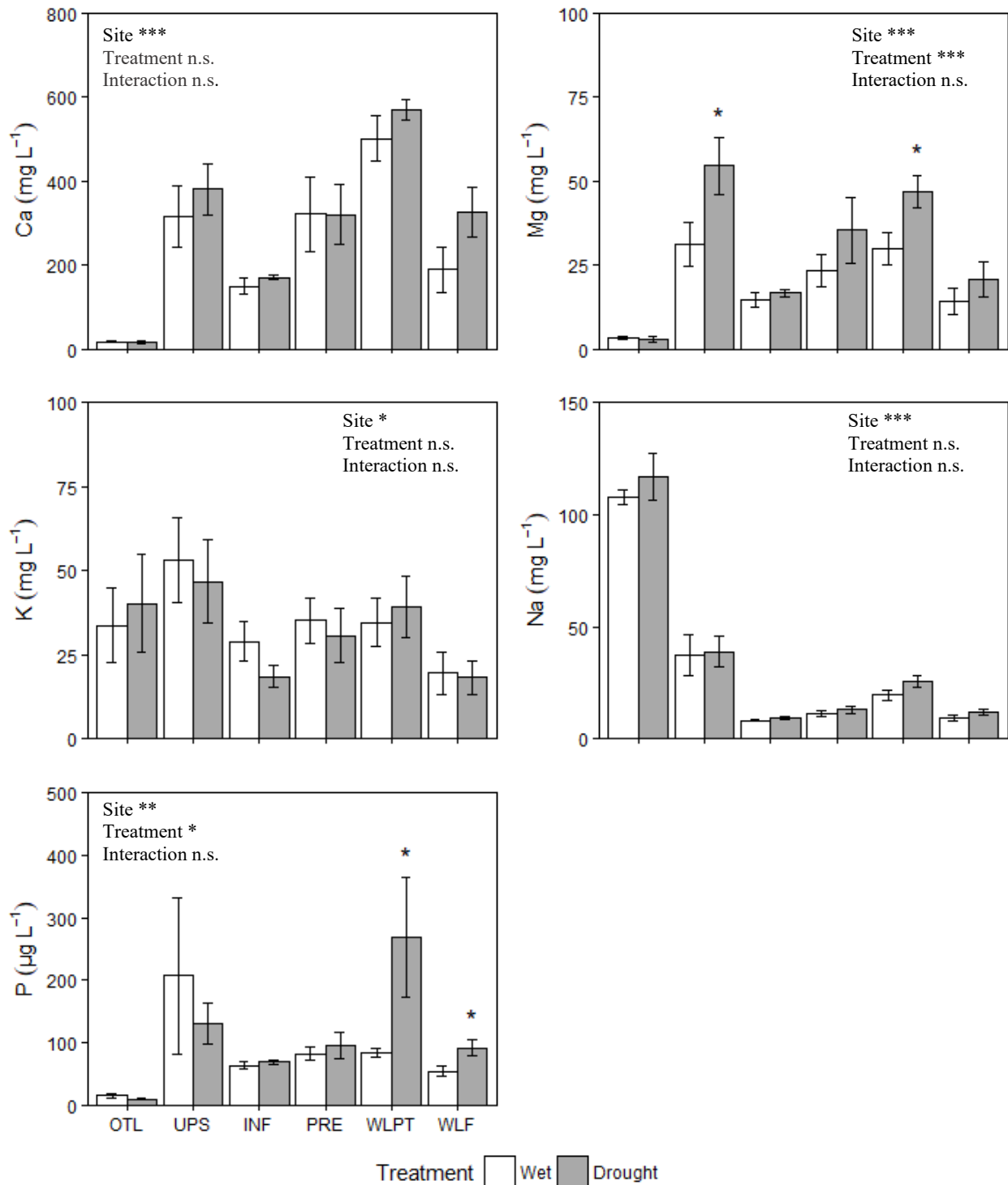
Figure 3.7. Mean (±S.E.) Ca, Mg, K, Na, and P concentrations of pore water extracted from microcosms with soil collected from the outer tailings limit (OTL) and peatland sites at varying distances downstream of TMA-2, subjected to two treatments: 30 day drought (dark grey bar) and wet (white bar). Statistical significance: *, $p < 0.05$, **, $p < 0.001$, ***, $p < 0.001$; n.s., no significance.
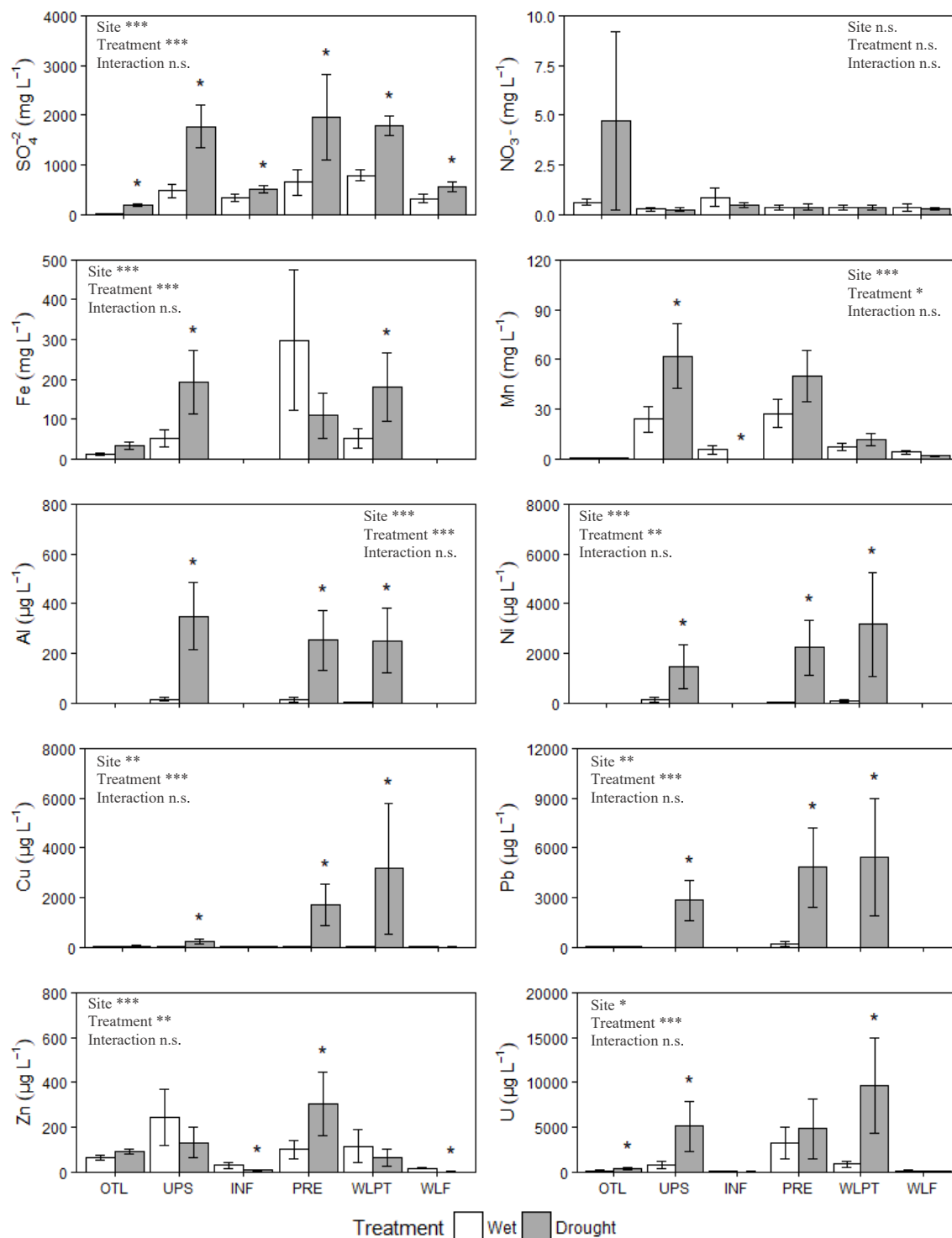
Figure 3.8. Mean (±S.E.) SO_4^{2-}, NO_3^-, Fe, Mn, Al, Ni, Cu, Pb, Zn and U concentrations of pore water extracted from microcosms with soil collected from the outer tailings limit (OTL) and peatland sites at varying distances downstream of TMA-2, subjected to two treatments: 30 day drought (dark grey bar) and wet (white bar). Statistical significance: *, $p < 0.05$, **, $p < 0.001$, ***, $p < 0.001$; n.s. no significance.

3.3.4 Metal partitioning coefficient (Kd)

Metal partitioning (K_d) Al, Fe, Mn, Cu, Ni, Pb, Zn, and U could be significantly predicted by a positive log-linear relationship with pH and $\log_{10}$ DOC (Figure 3.7). Despite the varied response to drought among sites, across all sites K_d demonstrated a stronger relationship with pH than $\log_{10}$ DOC, which was significant for all metals with the exception of Mn (Figure 3.7), while $\log_{10}$ DOC was found to have a weak significant ($r^2 < 0.15$) relationship for combined data set for Al, Ni, Pb, and Zn (Figure 3.7).
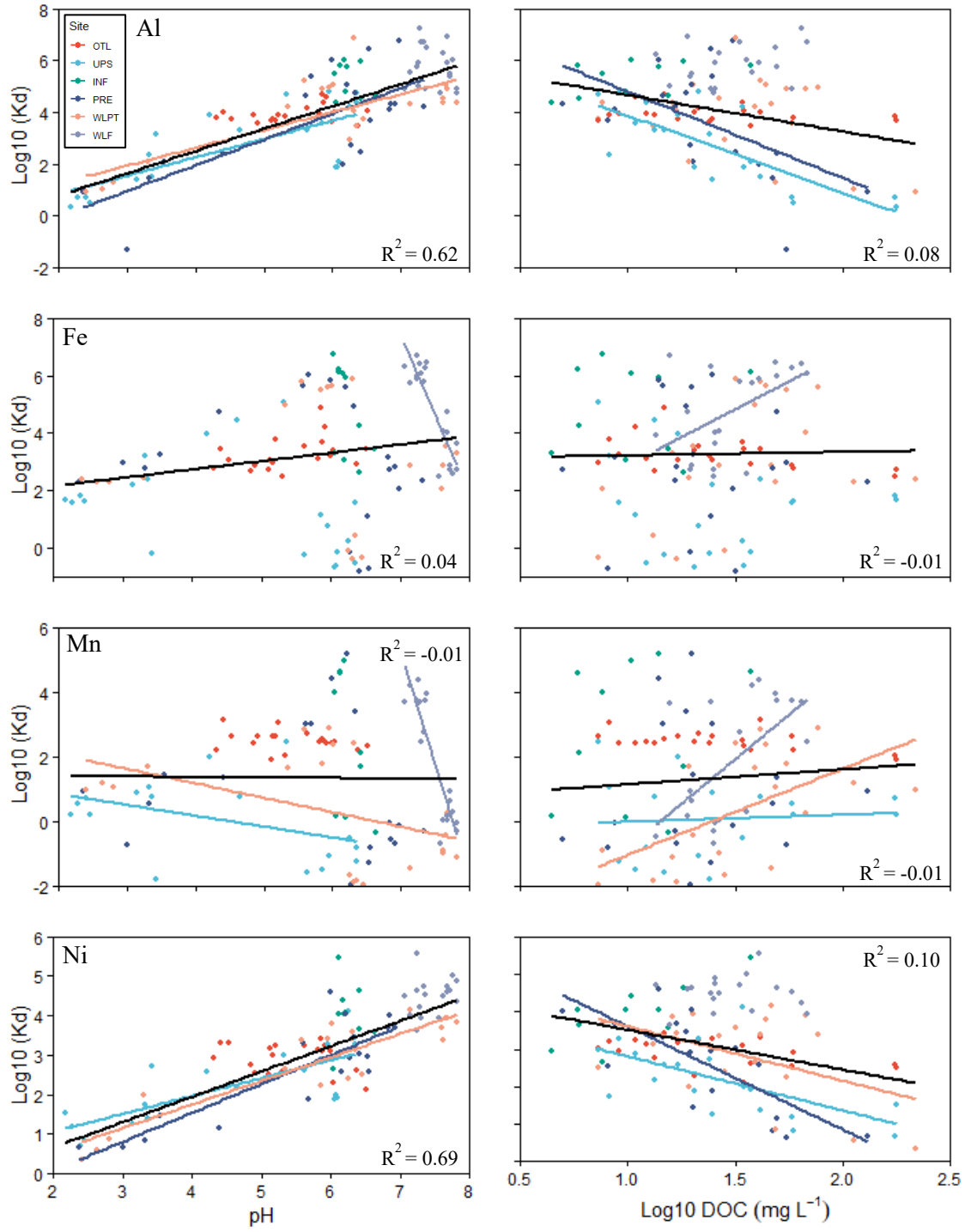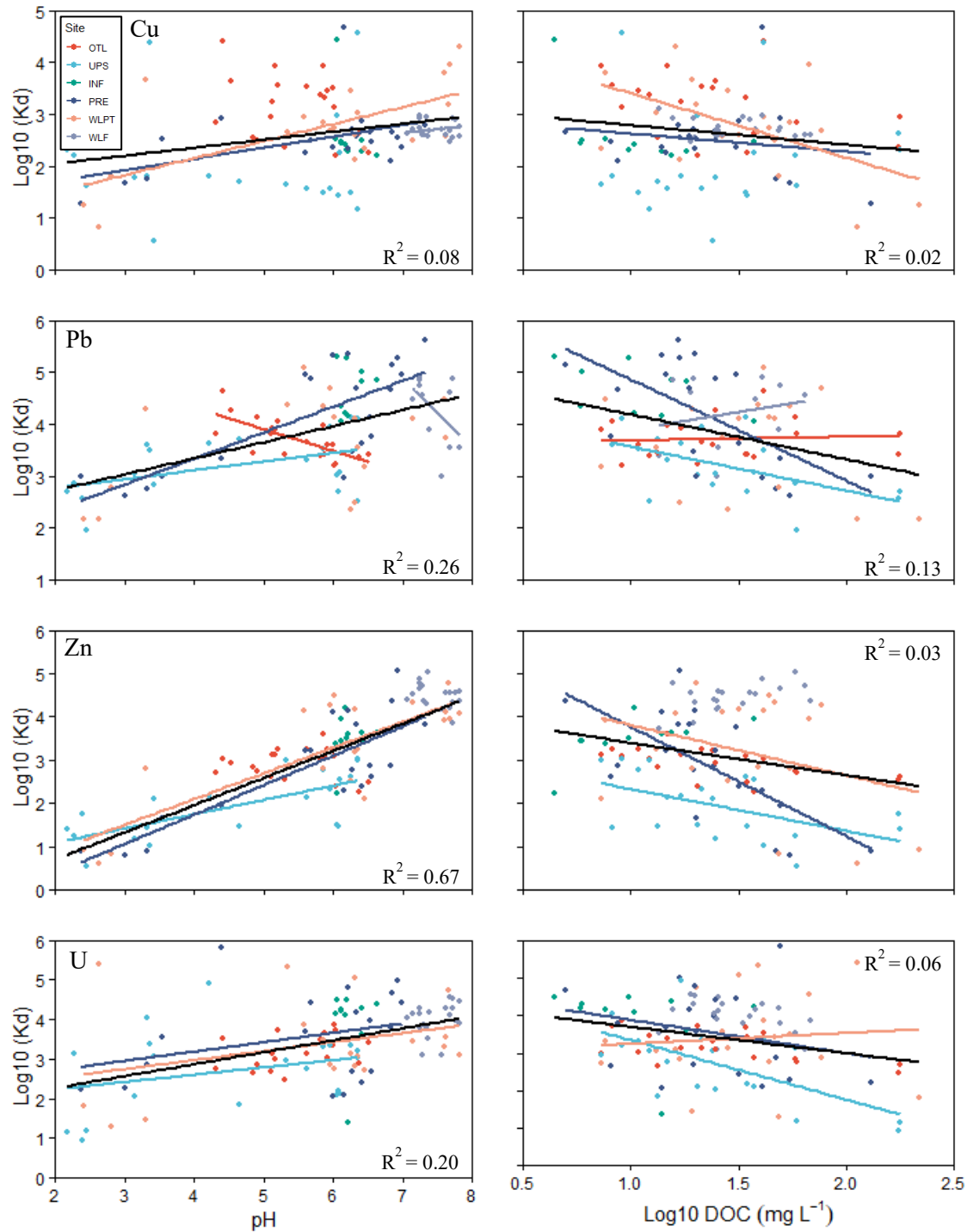
Figure 3.9. Regression relationships between pH and log10 DOC to K_d for six peatlands (OTL; red, UPS; light blue, INF; green, PRE; dark blue, WLPT; pink, WLF; purple lines), and for combined dataset (black line). R^2 values are shown for combined dataset. Lines indicate significant trend.

3.3.5 Predicting metal concentrations in pore water

Metal partitioning of all metals (Al, Fe, Mn, Ni, Cu, Pb, Zn, and U) could being predicted using pH, SO_4^{-2}, NO_3^- and log_{10} DOC, although the strength of the relationship varied by metal ($r^2 = 0.89$ for Al to 0.17 for Cu) (Table 3.8). Pore water concentrations of metals were found to increase with decreasing pH (3 of 8 metals) and increasing concentrations of DOC (5 of 8 metals) and SO_4^{-2} (6 of 8 metals), while pore water Cu concentrations increased with increasing NO_3^- concentrations. Metal log K_d values ranged from -1.3 to 7.1 for Al, -1.0 to 6.7 for Fe, -2.5 to 5.2 for Mn, 0.4 to 5.6 for Ni, 0.5 to 4.7 for Cu, 2.0 to 5.6 for Pb, 0.6 to 6.4 for Zn and 0.9 to 6.8 for U.

Table 3.7. Multiple linear regression models of metal partition coefficient (K_d) and pH, concentrations of log_{10}DOC, SO_4^{-2} and NO_3^- (mg L^{-1}) using combined dataset from all peatland sites.

Metal	Multiple Linear Regression Model	R^2	*P*
Al	$-0.198 + 6.275[SO_4^{-2}] + 0.574[DOC]$	0.89	<0.001
Fe	$0.622 - 0.647 [pH] + 1.440[DOC] + 7.765[SO_4^{-2}]$	0.32	<0.001
Mn	$1.201 - 1.113[pH] + 1.266 [DOC] + 8.382[SO_4^{-2}]$	0.35	<0.001
Ni	$-0.103 + 0.361 [pH] + 2.005[SO_4^{-2}]$	0.74	<0.001
Cu	$2.071 - 0.149[pH] + 0.528[NO_3^-]$	0.17	<0.001
Pb	$2.681 + 2.159[SO_4^{-2}]$	0.44	<0.001
Zn	$-1.093 - 2.211[SO_4^{-2}] + 0.376[pH] + 0.567[DOC]$	0.73	<0.001
U	$2.222 + 2.183[SO_4^{-2}]$	0.28	<0.001

3.4 Discussion

Baseline peat and pore water chemistry varied across the peatland complex, although the level of metal contamination was significantly higher at some sites downstream of the historic tailings breach. Despite varying degrees of metal contamination, all sites were found to be in exceedance of both SQG and WQG of a least one or more metals. Simulated drought resulted in the acidification of pore water of peatlands and the release of metals, although impacts were not necessarily greater at sites historically impacted by the tailings breach which demonstrated higher peat metal (Al, Fe, Mn, Ni, Cu, Pb, Zn and U) concentrations than those upstream and outside mining activities. Metal partitioning was significantly related to decreasing pH and increasing DOC concentrations in pore water and metal K_d values could be significantly predicted for all metals using pH, SO_4^{-2}, NO_3^- and/or DOC. These results would indicate that the expected increase in frequency of drought may lead to short-term metal pulses that can negatively affect downstream aquatic environments and biota.

3.4.1 Baseline Conditions

Soil and pore water chemistry in a peatland complex varied with distance downstream of mine water influent and historic tailings breach from TMA-2. Higher concentrations of Al, Mn, Ni, Cu, Pb, Zn and U closer to the contamination source is consistent with other peatland systems located along a distance gradient in industrial mining areas (e.g. Gignac and Beckett, 1986; Taylor and Crowder, 1983). Similarly, differences in other physical and chemical properties (e.g. BD, %OM, total C and N, of Ca and SO_4^{2-}) among sites are likely the result of shallow tailings deposits, periodic lime treatment and tailings derived groundwater which has been observed in other peatland systems in the area (Davé, 2011; Davé, 1993). Metal concentrations were generally lower in peatlands upstream of TMA-2, as well as at sites further downstream along the Serpent River, however concentrations were found to still exceed provincial sediment and water quality guidelines for the protection of aquatic life, indicating the likely widespread

contamination from historical mining operations in the greater TMA. Despite the tailings breach occurring several decades ago, peat core metal and U concentrations would indicate a high degree of contamination in the surface layer of the peatland complex (0 – 20 cm), which is likely influenced by the continual seepage from TMA-2. Based on the reports of Paktunc and Davé (2002), tailings and metal contamination likely extend deeper to a depth of 1.25 m, especially in low-lying areas in the basin, including Williams Lake and other water covered areas.

Clulow et al. (1998), found that U concentrations in lake water and sediment surrounding the region of Elliot Lake ranged from 1-35 µg l^{-1} and 4.1-133 µg g^{-1} respectively. Further, Clulow et al. (1998) also reported elevated levels of radionuclides including ^{210}Pb that was attributed to mine water and tailings leachate. Similarly, Beckett et al., (1982) found that the effective radius for U pollution from mining and milling operations at Elliott Lake was 22 km with mean U concentrations of 25 µg g^{-1} found in *Sphagnum spp*. which decreased rapidly with distance from mining operations. More recently, Clulow (2018) found that metal concentrations and radionuclides are on the decline in sediment downstream of Quirke Lake in the Serpent River which drains to Lake Huron, with U concentrations decreasing from 500 µg g^{-1} to background concentrations of 5 µg g^{-1} in Lake Huron as a result of improved tailings management. Overall, while metal and U contamination is observed over a large region, sites closest and downstream of the tailings breach tend to have higher concentrations than sites located down along the Serpent River. Similarly, Clulow (2018) reported concentrations of Pb, Ni, Cu, and Zn in sediment downstream of Quirke Lake in the Serpent River to Lake Huron ranging from approximately 30 µg g^{-1} to 275 µg g^{-1}, 10 µg g^{-1} to 400 µg g^{-1}, 1 µg g^{-1} to 260 µg g^{-1}, and 1 µg g^{-1} to 10,000 µg g^{-1} respectively, with concentrations likely influenced by additional industrial sources.

3.4.2 Peatland Acidification during simulated drought

Simulated drought significantly increased SO_4^{-2} concentrations in pore, which has been consistently observed in other field and laboratory studies (Juckers and Watmough; 2014; Fenner and Freeman, 2011; Watmough et al., 2004; Eimers et al., 2007) as a result of the oxidation of reduced S compounds, releasing H^+ upon rewetting leading to peatland acidification (van Breeman et al., 1983). Despite the wide range in S content of soil among sites (5.1-38.3 g kg^{-1}), all peatlands responded with a significant increase in SO_4^{-2} concentrations proceeding 30-day drought similar to the findings of Juckers and Watmough (2014). Alternatively, NO_3^- concentrations did not significantly increase at any of the peatlands after rewetting which can be linked to the longer processes of nitrification and disruption of N mineralization and cycling during the drought period (Larsen et al., 2011; Freeman et al., 1993; Williams and Wheatley, 1988). An example of this can be seen in Juckers and Watmough (2014) and Freeman et al., (1993) who saw a 256-777 and 340-fold increase in pore water NO_3^- concentrations, which was more pronounced proceeding a 60 and 42 day drought period, respectively. The acidification of peatlands due to the release of SO_4^{-2} is not necessarily related to the quantity of S in the soil, with acidification being shown to occur in both impacted (Juckers and Watmough, 2014) and undisturbed peatlands (Eimers et al., 2007; Adkinson et al., 2008). However, in the present study SO_4^{-2} concentrations in pore water were highest at UPS, PRE and WLPT, which had nearly two times the average S content in soils, indicating that greater S content may result in greater and more sustained pH decline proceeding drought conditions. Higher S content in peat and SO_4^{-2} production proceeding drought conditions at these sites may be related to tailings content in the in samples. Paktunc and Davé (2002) reported variable concentrations of pyrite content up to 6.3% wt%, which is a ubiquitous sulfide mineral producing SO_4^{-2} and ferrous iron under oxidation (Chandra and Gerson, 2010).

Porewater DOC concentrations in porewater also increased following simulated drought. The mechanisms responsible for DOC changes in waters following drought have been intensely debated with DOC concentrations decreasing (Eimers et al., 2008b; Szkokan-Emilson et al. 2013; Clark et al., 2005;

Fenner et al., 2005) or showing no change in both soil and stream waters (Blodau and Moore, 2003; Eimers et al., 2008a) post drought. Decreases in DOC proceeding drought conditions have been shown to be the result of increased biological activity and consumption of DOC, improving carbon metabolism and production of CO_2 rather than DOC (Clark et al., 2012; Freeman et al., 1993) or reduced solubility of DOC in response to increased acidity and ionic strength (Clark et al., 2012). Explanations for increases in DOC proceeding drought has been shown to be the result of increased biological activity and net DOC production, where more DOC is released during decomposition than is consumed and respired by soil biota (Pastor et al., 2003; Tipping et al., 1999) or DOC is produced and either released directly to pore waters or is absorbed during drought periods and subsequently released upon peat rewetting (Clark et al., 2009). Differences have also been shown to be related to vegetation communities due to changes water table depth, temperature, microbial assemblages, root exudates and litter quantity and quality (Armstrong et al., 2012). Armstrong et al., (2012) found that peatlands dominated by *Calluna* and sedges had higher DOC concentrations than *Sphagnum* communities, as a result of lower water table depth and higher rates of decomposition from greater assemblages of soil fauna. Vegetation communities within the Elliot Lake peatland complex were dominated by *Typha latifolia*, tree and shrub species, likely resulting in higher rates of DOC production. Regardless of the mechanisms, the significant increase in DOC following drought and the concurrent decrease in pH results in an increase in dissolved metal concentration in pore waters, especially those with strong affinities for organic matter including U.

3.4.3 Metal Release to porewater following simulated drought

Concentrations of base cations (Ca, Mg) and metals (Fe, Mn, Al, Ni, Cu, Pb, Zn) greatly increased in pore water following simulated drought, which was the most pronounced at UPS, PRE, and WLPT sites (Figure 5 and 6). The release of metals corresponds with the drought-induced acidification and competition by H^+ ions for binding sites on organic molecules, resulting in the mobilization of metals from peat and depletion of base cations (McLauglin and Webster, 2009; Brown et al., 2000; van Hasesebroeck et al.,

1997). These mechanisms would explain the highest observed metal concentrations in pore water in UPS, PRE, and WLPT proceeding drought conditions, which demonstrated the greatest decrease in pH and increase in SO_4^{-2} concentrations.

Uranium concentrations followed similar trend to other metals increasing by 6.4, 1.5 and 10 times following 30-day drought at UPS, PRE and WLPT sites respectively (Figure 6). The main mechanisms of U-remobilization have been linked to the chemical composition of pore water (e.g. the presence of other heavy metals competing for sorption sites, redox potential (Eh), temperature and pH (Winde, 2011). Kochenov et al. (1967) and Owen and Otton (1995) have suggested that sorption and immobilization of U is reversible under oxidizing conditions, which generally promotes the transformation of reduced U^{4+} to the more soluble U^{6+} further increasing concentrations in pore water (Winde, 2011). Further the presence of sulphates and the formation of sulfuric acid has been shown to aid in the liberation of sorbed U from soil (Tipping et al., 2003; Sikora and Keeney 1983), with Zielinski and Meier (1988) finding that H_2SO_4 can leach approximately 75% of U at a pH of 1.5, as it provides a strong complexing agent (sulfate) for dissolved U^{6+}, indicating that U is equally susceptible to peatland acidification and release as other metals that have been previously studied. It was notable that there was enormous site-to-site variability in metal release to pore water following drought, which was not necessarily highest in sites closest to the breach because metal release to pore water is controlled by multiple factors.

3.4.4 Metal Partitioning in Peatlands

In our study, metal partitioning coefficients (K_d) of all metals (Al, Mn, Ni, Cu, Pb, Zn, and U) could be significantly predicted in all six peatlands by the pH of pore water and DOC, with pH typically demonstrating a stronger relationship to metal partitioning for the combined, whereby decreasing pH and increasing DOC resulted in higher concentrations of metals in pore water. However, the strength of the relationship varied across individual sites and by metal indicating additional factors other pH and DOC

influence metal mobility in solution. In the present study, pH pre and post drought values ranged from approximately 2.2-8.1, with a stronger relationship between metal K_d and pH being found at site UPS, PRE, and WLPT, which demonstrated the greatest decrease in pH following simulated drought. Pore water pH is generally regarded as the strongest predictor of metal partitioning in soils, with the release of metals into solution being favoured under acidic conditions (Watmough et al., 2005). 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, indicating that K_d values for a single metal could differ by up to 6 orders of magnitude as a function of soil pH, total metal content, and soil organic matter content. Similarly, Watmough and Orlovskaya (2015) and Pennington and Watmough (2015) found that Ni, Mn and Zn metal partitioning could be predicted by pH alone.

Significant relationships between U K_d and pH were found at UPS, PRE and WLPT (0.35-0.38), with a combined dataset r^2 value of 0.21. The sorption of U is strongly dependent on the pH of solution, due to predominant presence of the uranyl cation (UO_2^{2+}) under acidic conditions (98.6% at pH <4) which demonstrates weak sorption to soils (Aide, 2018; Cumberland et al., 2016; Langmuir, 1978). Schöner et al. (2016) found that U was predominantly distributed in labile, moderately labile (acid-extractable) and organically bound ($Na_4P_2O_7$-extractable) fractions within peatland soil profiles, indicating that an environmental change resulting in a shift in pH or Eh may release labile U from peatland sediments. Uranium mobility may also be increased at circumneutral pH, as the fraction of U that is complexed by carbonates increases, further enhancing U mobility from soils. In a study by Echevarria et al. (2001), soil pH (4-9) had a greater influence on sorption ratios for UO_2^{2+} than either soil OM or clay content, which demonstrated a significant linear relationship ($r^2 = 0.89$), with the amount of sorption of UO_2^{2+} on soil decreasing with increasing pH, thereby enhancing the potential for U mobility. This could explain the significant increase in U pore water concentrations proceeding drought as UPS, PRE, and WLPT which had an average pH ranging from 3.33 to 4.64 falling in a pH range that promotes the presence of highly mobile UO_2^{2+} and soluble uranyl-carbonate complexes (Vandenhove et al., 2007; Langmuir, 1978).

The relationship between metal K_d and DOC was sometimes stronger than pH, whereby higher concentrations in DOC resulted in higher metal concentration in pore water. This was observed with metals that exhibit a strong affinity to DOC (e.g., Al, Cu, Fe and U), with the stronger relationships generally being observed at sites UPS, PRE, WLPT, and WLF which exhibited the greatest increase in DOC concentrations following drought conditions. Pennington and Watmough (2015) found that 51, 61 and 64% of the variability in K_d values for Cu, Fe, and Al respectively could be explained by dissolved organic matter quantity and quality, hydrology and acidity, with speciation models indicating a higher fraction of Al and Cu in solution being bound to dissolved organic matter (DOM) (Watmough and Orlovskaya 2015). A significant relationship between U K_d and log10 DOC were found at OTL, UPS, and PRE (0.22-0.60), with a combined dataset r^2 value of 0.05. Functional groups such as humic and fulvic acids are recognized as important substances in facilitating bonding and ion exchange with polyvalent cations such as U^{6+} (Denham and Looney, 2004; Gosset et al., 1986), as well as the complexation of UO_2^{2+} by carboxyl groups and the formation of insoluble uranyl humates which collectively contributes to U retention in peat (Owen and Otton, 1995). Therefore, the release of DOC to downstream receiving environments after drought conditions would likely result in the release of these complexes (Wang et al., 2014).

Between 17 and 89% of the variability in K_d for the metals could be predicted by using a stepwise multiple linear regression model that included pore water pH and concentrations of SO_4^{-2}, log_{10} DOC, NO_3^-. Metal K_d predictions would indicate that metals are most strongly influenced by pH and SO_4^{-2} concentrations, as both parameters are connected to the same process as the oxidation of organic and inorganic S to SO_4^{-2}, increases net H^+ production resulting in decrease in pH and increase of cations in pore water (MacLaughlin and Webster, 2009; Cirmo et al., 2000; Urban and Bayley, 1986). Uranium K_d could be significantly predicted by SO_4^{-2} concentrations alone, which is likely linked to increased H^+ exchange and declines in pH, but may also be the related to the formation of sulfuric acid upon rewetting, which forms soluble complexes of uranyl-sulfates in dilute sulfuric acid solutions and is why sulfuric acid is used

for much of the extraction and purification procedures used in commercial acid-leaching of U ores (Cumberland et al., 2016; Zammit et et al., 2014; Zielinski and Meier, 1988; Langmuir, 1978).

The release of metals is of concern due to significant exceedances in federal quality guidelines (CCME, 2001). Baseline concentration of all metals exceeded guidelines with the exception of Ni and Zn, which ranged from 1.6-15.1 and 3.0-23.8 μg L $^{-1}$, respectively, but exceeded surface water quality guidelines by 1-127 and 2-10 times proceeding 30-day drought. Even greater exceedances were observed for Fe, Pb, Cu and U specifically at UPS, PRE, and WLPT, which exceeded guidelines by 362-642, 2830-5457, 117-1584 and 325-640 times, respectively. The CCME (1991), indicates a trigger response range for total phosphorus of 10-100 μg L $^{-1}$ based on the increasing trophic status from Mesotrophic to Hyper-eutrophic waterbodies. Proceeding 30-day drought, P concentrations ranged from 92-268 μg L $^{-1}$ nearing and exceeding hyper-eutrophic status, reaching concentrations that exceed average concentrations in extreme rich fen peatlands (Zoltai and Johnson, 1987). The mobilization of high concentrations of metals and P has the potential to adversely affect aquatic biota due to the high diversity and abundance in littoral zones of lakes and near stream outflows via metal toxicity and eutrophication (Schindler et al., 1996). Government requirements for on-going monthly monitoring of surface water discharge to the surrounding environment at sites D-22, D-2, and D5 (Figure 3.1 and 3,2) would indicate that metal and U concentrations generally fall below provincial WQG (Table 3.2). However short-term pulses of metals proceeding drought conditions would not be captured from this low-level monitoring program, with metal and U concentrations likely exceeding these guidelines. Further, this presents a long-term risk as the release of stored metal pools in peatlands may be sustained for several years, especially in areas effected by S deposition and industrial activities, such as mining environments (Juckers and Watmough, 2014; Szkokan-Emilson et al., 2013).

3.5 Conclusion

Baseline peat and pore water chemistry varied across peatlands with the level of metal contamination being found to be significantly higher at sites downst4ream of historic tailings breach. All sites within the study area were found to be in exceedance of both SQG and WQG of at least one or more metals. Simulated drought resulted in the acidification of pore water of Elliot Lake peatlands impacted by a historic mining activities and uranium tailings management area breach, with the highest changes in pore water concentrations of Al, Ni, Cu, Pb, Zn and U corresponding to the greatest decrease in pH and increase in DOC concentrations proceeding drought conditions. The post-drought increase in DOC concentration in pore water may further enhance export of metals with a strong affinity to DOC (e.g. Al, Cu, and U). Metal partitioning was significantly related to pH and $\log_{10}$ DOC concentrations in pore water, although the strength of the relationship varied among six sites. Metal partitioning predictions further improved with the inclusion of SO_4^{-2}, which likely corresponds to the increase in net production of H^+ in soil solution. This study would indicate that U is equally susceptible to drought induced acidification and the potential impact of climate change on peatlands may be widespread and potentially exacerbated by increased industrial activities.

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4.0 General Conclusion

This work expands on the current knowledge of trace metal geochemistry in peatlands. The first chapter showed that metal concentrations differ among peatland types globally, with fens demonstrating the highest concentrations of most metals compared with bogs and tropical peat swamps. Metal concentrations were found to not necessarily reflect patterns in peatland contamination. Enrichment factors were calculated and three distinct grouping of metals were identified, with As, Cd, Co, Cu, Ni, Pb, Sb, Se, and Zn being identified as metals with common patterns of enrichment in surface peat. Significant differences were found for these nine metals by peatland type and geographic area, with higher EFs typically occurring in poor and intermediate fens and higher levels of enrichment occurring in North America and Europe due to the longer history of metal pollution and distribution of sampled peatlands to metal point sources. Estimated metal pools varied tremendously, but median values ranged from 13 (Sb) to 439 (Pb) mg m^{-2} which is likely more representative of global peatland metal pools based on other reported values within existing literature.

A limitation of the global dataset in calculating EFs is the assumption that 60-70 cm was deep enough to represent background metal concentrations. Although the age of peat at these deeper samples is likely to vary considerably and our estimated EF were considered conservative, future recommendations to strengthen information of metal enrichment in global peatlands would be to incorporate Pb isotope dating of peatland cores profiles within this dataset. Bog peatland types represent the majority of cores within the global dataset (36%) and have been used as relatively high-resolution archives of Pb pollution levels for the past 12 000 years (Shotyk et al., 1998). To date, most archives have been extensively studied in Europe and include the U.K. (Farmer et al., 1997), Sweden (Renberg et al., 2000), Switzerland (Weiss et al., 1999; Shoytk et al., 1998), and the Czech Republic (Novak et al., 2003). Although 10 cm peat core depth increments would not allow for full reconstruction of the pollution history, isotopic analysis of cores would

give approximate age of peat cores to better evaluate metal EFs, provide metal accumulation rates, and generate more accurate sources of metal pollution by evaluating Pb isotopic ratios (i.e. ^{204}Pb, ^{206}Pb,^{207}Pb, ^{208}Pb) that could be used to fingerprint Pb contamination to local and regional origin and more recent Pb pollution recent (i.e. coal burning and leaded gasoline) to be linked to even continental sources, aiding in a better understanding of metal contamination globally (Le Roux et al., 2005, Shotyk et al., 2005; Novak et al., 2003).

It is clear that metal contamination in global peatlands is widespread. Climate change is predicted to have significant impacts to peatland hydrology, which can result in drought induced peatland acidification, potentially releasing stored metals to downstream environments. The second chapter further strengthened the understanding of metal contamination in peatlands impacted by historical industrial activities, with the results from the study indicating that U is equally susceptible as other metals (Al, Cu, Ni, Pb, and Zn) to drought induced peatland acidification. Proceeding drought conditions all metals were found to greatly exceed both sediment and water quality guidelines by several orders of magnitude. Metal partitioning coefficients (K_d) of all metals (Al, Mn, Ni, Cu, Pb, and Zn) could be significantly predicted in all six peatlands by the pH of pore water and DOC, with pH typically demonstrating a stronger relationship to metal partitioning for the combined dataset, whereby decreasing pH and increasing DOC resulted in higher concentrations of metals in pore water. Uranium partitioning in soils was found to be primarily driven by declining pH through the oxidation of S compounds and release of H$^+$ upon rewetting. Individual sites response to drought and subsequent release of metals to pore water varied considerably, which may be linked to differences in S content in peat. Uranium partitioning demonstrated a weak significant relationship with pH (r^2=0.20) and DOC (r^2=0.06), which was marginally improved by including SO_4^{-2} (r^2=0.28) in a step-wise multi-linear regression. Based on the complexity of U behaviour due to the presence of several U species and a multitude of other factors (mineral, organic, and inorganic constituents, and role of microbial processes) few studies have evaluated U K_d in organic soils. The inclusion of E_h, OM and

additional ions (OH$^-$, CO$_3^{2-}$, PO$_4^{3-}$, SiO$_4^{4-}$) could further improve models in predicting U partitioning and mobility in peatlands (Cumberland et al., 2016).

This work shows that globally peatlands are contaminated with many metals that demonstrate patterns and groupings linked to anthropogenic pollution and peatland type, with metal enrichment being most evident in North America and Europe due to a long history of metal emissions. While peatlands are typically considered to be effective at storing metals over the long-term, predicted changes in climate may lead to more pronounced droughts that can mobilize metals in surface horizons and release potentially toxic concentrations of metal to downstream receiving environments. This is of particular importance in boreal and temperate climates in the northern hemisphere, where the majority of peatlands are located, and where anticipated impacts of climate change are expected to be the greatest.

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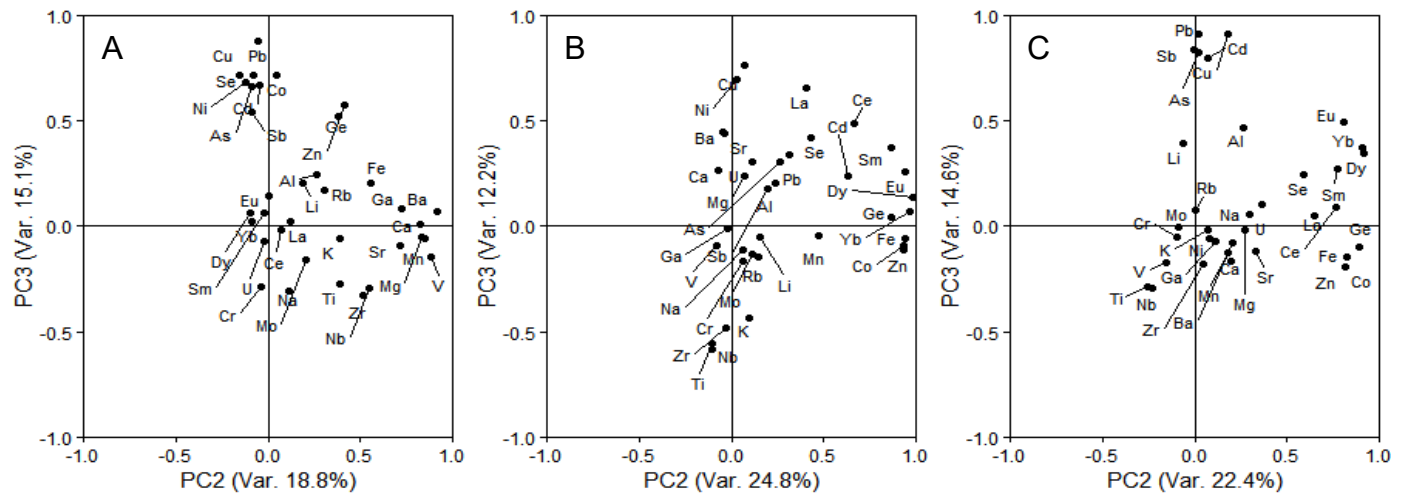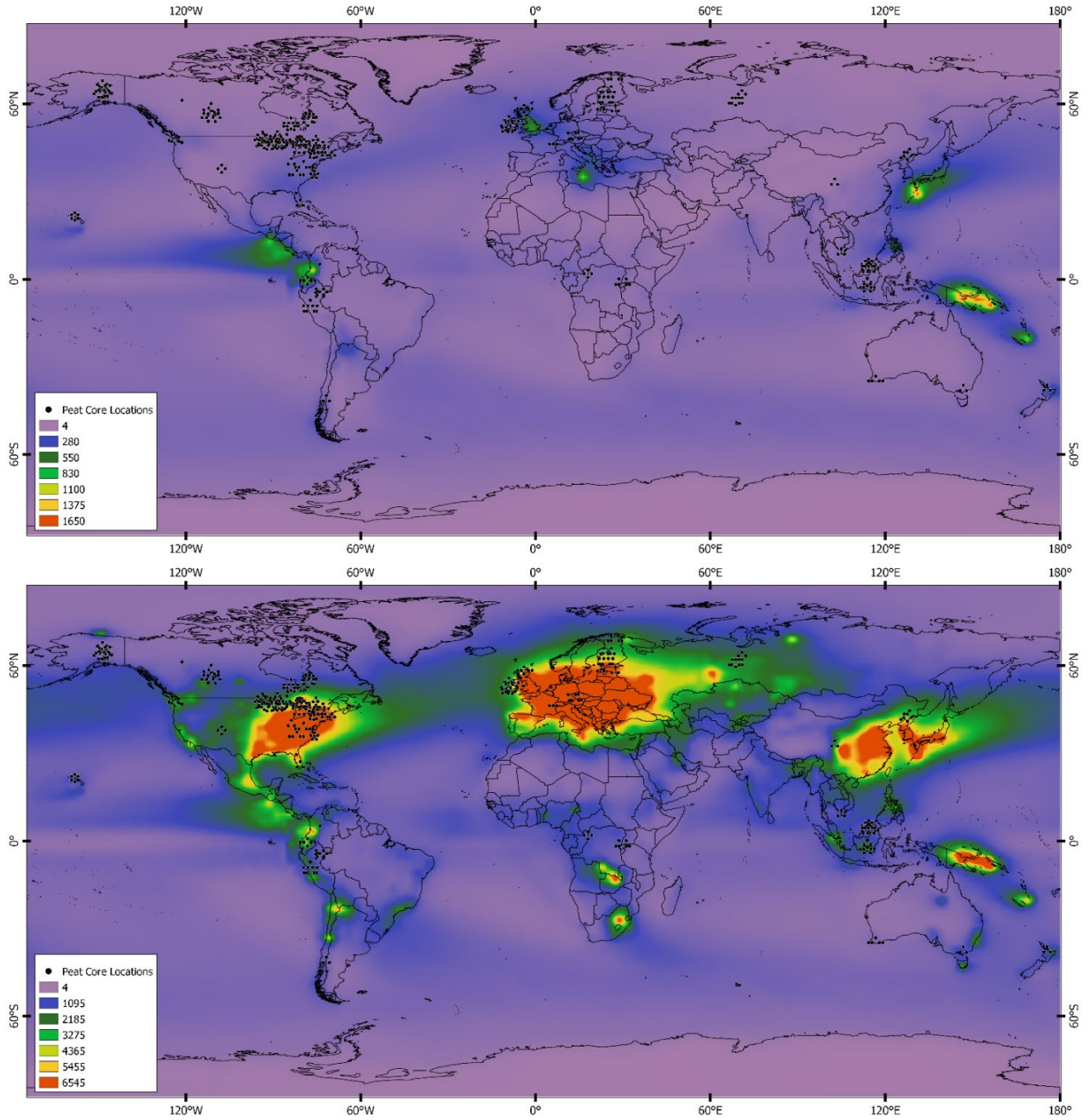Appendix A: Supplementary results for Chapter 2

Figure 1: PCA of metals concentrations loadings PC2 and PC3 for A) 0-20 cm, B) 20-50 cm, and C) 50-70 cm depths.
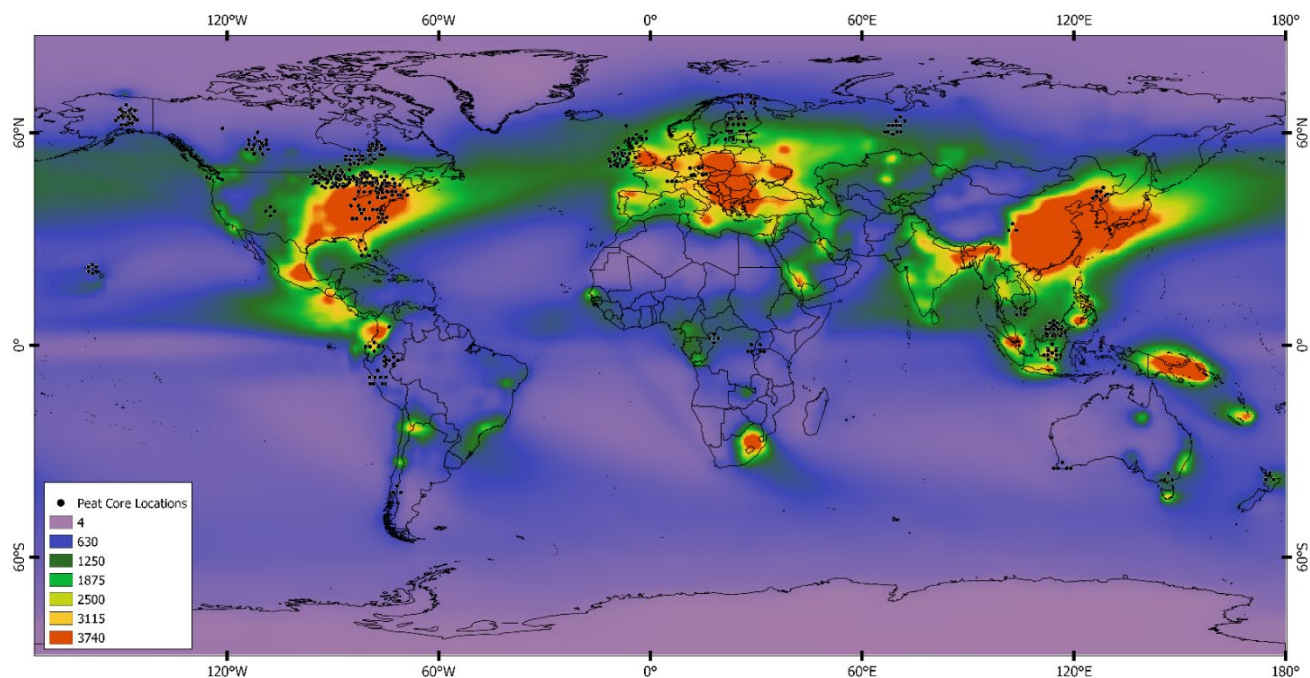
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Figure 2: Total (wet + dry) SO_x and SO_4^{-2} deposition 1850-2009 (mg(S) m^{-2} yr^{-1}). Top row shows 1850-1859, 1980-1989 and 2000-2009.

Cumulative S deposition extracted from peatland cores averaged 898 ± 33.1 kg ha^{-1} across all peatland sampling locations, which were highest in Europe (1452 ± 112 kg ha^{-1}) and North America (915 ± 38.9 kg ha^{-1}), with South America and Asia having similar pools of 531 ± 81.7 and 580 ± 35.1 kg ha^{-1}, respectively. Regions Africa and Oceania had the were the lowest S deposition, averaging $259 + 15.6$ kg ha^{-1} and 282 ± 45.0 kg ha^{-1}, respectively, which were 3x lower than the global average. Poor fen and bog peatland types had the highest extracted cumulative S deposition with 1128 ± 52.3 kg ha^{-1} and 981 ± 55.2 kg ha^{-1} respectively, followed by intermediate fens (701 ± 88.9 kg ha^{-1}), rich fens (642.7 ± 86.6 kg ha^{-1}) and peat swamp (556 ± 96.8 kg ha^{-1}) systems.
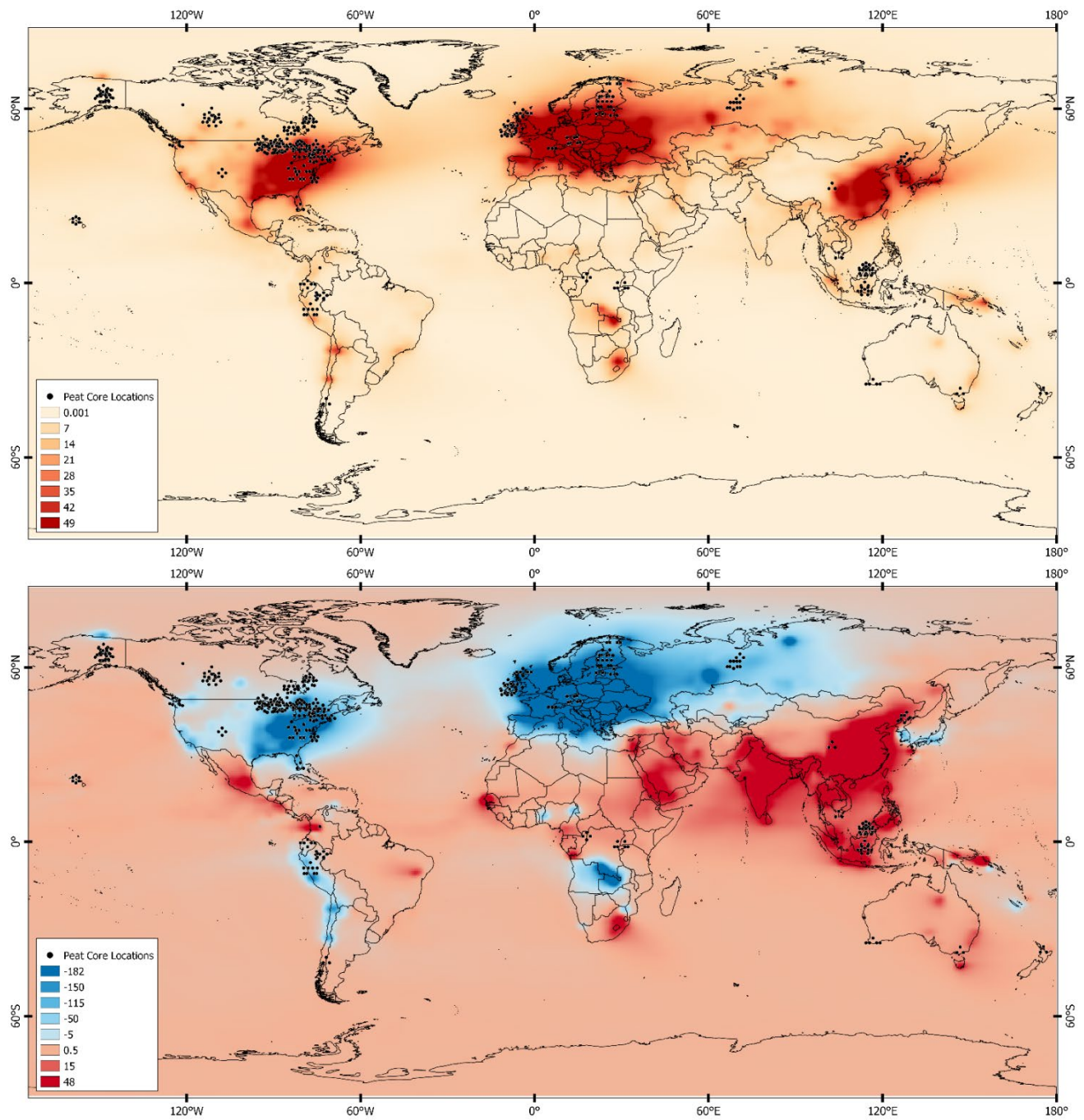
Figure 3: Interpolated linear annual S deposition (mg(S) m^{-2} yr^{-1}) between 1850-1979 (Top) and 1980-2009 (Bottom).

Appendix B: Supplementary results for Chapter 3

Table 1: Canadian sediment and freshwater guidelines for the protection of environmental and human health for metals found in mining impacted wetlands at Elliot Lake Ontario.

Metal	Sediment Quality Guidelines for the Protection of Environmental and Human Health		Freshwater Quality Guidelines for the Protection of Aquatic Life	
	Lowest Effect (mg kg $^{-1}$)	Severest Effect (mg kg $^{-1}$)	Short Term (µg L $^{-1}$)	Long Term (µg L $^{-1}$)
Al	-	-	252	74
Fe	21000	43800	-	300
Mn	460	1100	1900	600
Zn	120	820	-	30
Ni	16	75	150	25
Pb	31	250	7	1
Cu	16	110	4	2
U	33	2000	30	15

Notes: Ranges for sediment quality guidelines (SQG) represent the Lowest Effect Level is calculated as the 5th percentile of the Species Screening Level Concentrations (SSLCs). Each SSLC is the calculated 90th percentile of the concentration distribution for that species. The Screening Level Concentration (SLC) is a plot of the concentration distribution of all the SSLCs for that compound. The Severe Effect Level has been calculated as the 95th percentile of the Species Screening Level concentration distribution (Ceqg-rcqe.ccme.ca, 2018). Uranium sediment quality guidelines are based on the limiting pathway of direct contact with contaminated sediments on commercial properties ranging from impacts to environmental health to human health impacts. Concentrations for Water Quality Guidelines for the Protection of Aquatic Life (WQG) represent short-term to long-term exposure. Short-term exposure guidelines represent severe effects and to protect most species against lethality during intermittent and transient events (e.g., spill events to aquatic-receiving environments, infrequent releases of short-lived/non-persistent substances (CCME.ca, 2018). In contrast, long-term exposure guidelines are meant to protect against all negative effects during indefinite exposures (CCME.ca, 2018). Total aluminum WQG was determined based on lowest and highest concentration for the protection of freshwater life based on pH and dissolved organic carbon (DOC mg L $^{-1}$) (CCME.ca, 2018). Total manganese WQG was determined to be 600 and 1900 µg L $^{-1}$ based on chronic and acute toxicity data at a water hardness (CaCO$_3$) of 0-325 mg L $^{-1}$ respectively (Reimer, 1999). Total nickel, lead, and copper WQG for short term and long term was determined based on an unknown water hardness and a hardness >180 mg L $^{-1}$ respectively.

Table 2: R-squared for linear regressions for each metal (Al, Fe, Mn, Ni, Cu, Pb, Zn, U) at each wetland (OTL, UPS, INF, PRE, WLPT, WLF), between pH, Log10 DOC, and K_d.

Metal	Site	pH (Log10 K_d) R^2	DOC (Log10 K_d) R^2
Al	OTL	0.03 n.s.	0.04 n.s.
	UPS	0.52 ***	0.57 ***
	INF	-0.50 n.s.	0.14 n.s.
	PRE	0.51 ***	0.25 *
	WLPT	0.58 ***	0.04 n.s.
	WLF	-0.05 n.s.	0.05 n.s.
	All	0.62 ***	0.08 **
Fe	OTL	0.01 n.s.	0.18 *
	UPS	0.01 n.s.	-0.01 n.s.
	INF	0.22 n.s.	-0.12 n.s.
	PRE	-0.03 n.s.	-0.05 n.s.
	WLPT	-0.05 n.s.	0.15 n.s.
	WLF	0.65 ***	0.22 *
	All	0.04 *	-0.01 n.s.
Mn	OTL	0.02 n.s.	0.24 *
	UPS	0.26 *	-0.06 n.s.
	INF	0.14 n.s.	-0.08 n.s.
	PRE	-0.03 n.s.	-0.05 n.s.
	WLPT	0.16 *	0.29 **
	WLF	0.79 ***	0.31 **
	All	-0.01 n.s.	-0.01 n.s.
Ni	OTL	0.03 n.s.	0.18 *
	UPS	0.56 ***	0.32 **
	INF	-0.11 n.s.	0.53 *
	PRE	0.73 ***	0.53 ***
	WLPT	0.81***	0.18 *
	WLF	0.02 n.s.	-0.06 n.s.
	All	0.69 ***	0.10 **
Cu	OTL	0.02 n.s.	0.12 n.s.
	UPS	-0.54 n.s.	-0.04 n.s.
	INF	0.07 n.s.	0.19 n.s.
	PRE	0.20 *	-0.03 n.s.
	WLPT	0.41 **	0.24 *
	WLF	-0.03 n.s.	0.03 n.s.
	All	0.08 **	0.02 n.s.
Pb	OTL	0.49 ***	-0.05 n.s.
	UPS	0.17 *	0.26 *
	INF	-0.08 n.s.	0.17 n.s.
	PRE	0.51 ***	0.35 **
	WLPT	0.14 n.s.	-0.02 n.s.
	WLF	0.27 *	-0.05 n.s.
	All	0.26 ***	0.13 ***
Zn	OTL	-0.05 n.s.	0.29 **
	UPS	0.49 ***	0.23 *
	INF	-0.05 n.s.	0.33 *
	PRE	0.67 ***	0.42 **
	WLPT	0.65 ***	0.06 n.s.
	WLF	0.12 n.s.	0.22 *
	All	0.67 ***	0.03 *
U	OTL	0.12 n.s.	0.25 *
	UPS	0.35 **	0.60***
	INF	-0.04 n.s.	-0.10 n.s.
	PRE	0.38 **	0.22 *
	WLPT	0.35 **	-0.04 n.s.
	WLF	-0.05 n.s.	0.08 n.s.
	All	0.21 ***	0.05 **

n.s. no significance
* < 0.05
** < 0.01.
*** < 0.001.