Archives of Environmental Contamination and Toxicology (2024) 86:125–139
https://doi.org/10.1007/s00244-024-01051-3

Global Patterns of Metal and Other Element Enrichment in Bog and Fen Peatlands

Chetwynd Osborne[1] · Spencer Gilbert-Parkes[1] · Graeme Spiers[2] · Louis James Lamit[3] · Erik A. Lilleskov[4] · Nathan Basiliko[5] · Shaun Watmough[6] · Global Peatland Microbiome Project

Received: 21 August 2023 / Accepted: 2 January 2024 / Published online: 10 February 2024

Abstract

Peatlands are found on all continents, covering 3% of the global land area. However, the spatial extent and causes of metal enrichment in peatlands is understudied and no attempt has been made to evaluate global patterns of metal enrichment in bog and fen peatlands, despite that certain metals and rare earth elements (REE) arise from anthropogenic sources. We analyzed 368 peat cores sampled in 16 countries across five continents and measured metal and other element concentrations at three depths down to 70 cm as well as estimated cumulative atmospheric S deposition (1850–2009) for each site. Sites were assigned to one of three distinct broadly recognized peatland categories (bog, poor fen, and intermediate-to-moderately rich fen) that varied primarily along a pH gradient. Metal concentrations differed among peatland types, with intermediate-to-moderately rich fens demonstrating the highest concentrations of most metals. Median enrichment factors (EFs; a metric comparing natural and anthropogenic metal deposition) for individual metals were similar among bogs and fens (all groups), with metals likely to be influenced by anthropogenic sources (As, Cd, Co, Cu, Hg, Pb, and Sb) demonstrating median enrichment factors (EFs) > 1.5. Additionally, mean EFs were substantially higher than median values, and the positive correlation (< 0.40) with estimated cumulative atmospheric S deposition, confirmed some level of anthropogenic influence of all pollutant metals except for Hg that was unrelated to S deposition. Contrary to expectations, high EFs were not restricted to pollutant metals, with Mn, K and Rb all exhibiting elevated median EFs that were in the same range as pollutant metals likely due to peatland biogeochemical processes leading to enrichment of these nutrients in surface soil horizons. The global patterns of metal enrichment in bogs and fens identified in this study underscore the importance of these peatlands as environmental archives of metal deposition, but also illustrates that biogeochemical processes can enrich metals in surface peat and EFs alone do not necessarily indicate atmospheric contamination.

Peatlands occupy every continent, covering approximately 3% of the global land area (Turetsky et al. 2015; Page and Baird 2016; Khan et al. 2019; Kumar et al. 2020; Watmough et al. 2022). Despite the global prevalence and onset of the industrial revolution, the global spatial extent and causes of metal enrichment in peatlands is still poorly known. Most studies have focused on peatland contamination in Europe (Khan et al. 2019; Miszczak et al. 2020; Pech et al. 2022), Asia (Pratte et al. 2018; Pulunggono et al. 2021), and North America (Pratte et al. 2013; Barrett and Watmough 2015; Souter and Watmough 2016; Talbot et al. 2017). These studies report mainly on local and regional sources and enrichment of a few metals including copper (Cu), cobalt (Co), nickel (Ni), lead (Pb), arsenic (As), antimony (Sb), cadmium (Cd), iron (Fe), manganese (Mn), zinc (Zn), and mercury (Hg). To date, there has been no attempt to evaluate metal enrichment in bog and fen peatlands distributed globally, with additional metals and some rare earth elements (REE) that may be linked to anthropogenic sources such as cerium

✉ Shaun Watmough
swatmough@trentu.ca

[1] Environmental and Life Sciences Graduate Program, Trent University, Peterborough, ON K9L 0G2, Canada

[2] Laurentian University, Sudbury, ON, Canada

[3] Department of Biology, Syracuse University, Syracuse, NY, USA

[4] USDA Forest Service, Northern Research Station, Houghton, MI, USA

[5] Natural Resources Management, Lakehead University, Thunder Bay, ON P7B 5E1, Canada

[6] School of the Environment, Trent University, Peterborough, ON K9L 0G2, Canada

(Ce), dysprosium (Dy), europium (Eu), and samarium (Sm). Although global inventories have been made for metal emissions from both natural and anthropogenic sources there is currently no global dataset for metal deposition (Pacyna and Graedel 1995; Pacyna and Pacyna 2001). Therefore, we used cumulative atmospheric S deposition (1850–2009) as an indicator of industrial activities on a global scale. Atmospheric S deposition takes place over long ranges, affecting human health and ecosystems across continents, hence its usefulness as a predictor of anthropogenic sources of metal enrichment on a global scale (Horb et al. 2022).

Peat types and associated biogeochemical and physicochemical characteristics can influence how metal deposition is captured in surface peat. Ombrotrophic peat bogs are regarded as better environmental archives of metal deposition since they are solely fed by wet and dry deposition from the atmosphere (Pratte et al. 2013; Souter and Watmough 2016; Miszczak et al. 2020). Studies by Allan et al. (2013) have reported that ombrotrophic bogs may serve as an excellent and accurate archive of metals such as As, Cu, Ni, and Pb. However, reliable records of historical changes in metal deposition may also be derived from minerotrophic fens that are fed by a combination of rainwater and groundwater (Cole et al. 1990; Ali et al. 2008; Souter and Watmough 2016; Newman et al. 2023). To account for inherent differences in peatland chemistry, enrichment factors (EFs) are often used, which provide insights into the quantity of anthropogenic versus natural emissions of metals (Hanif et al. 2016). Although EFs have been widely used, it is important to recognize that they can be affected by the choice of a reference value such as average crustal (i.e., natural geological source) values. Additionally, metal enrichment in surface peat may not be solely caused by atmospheric deposition because biogeochemical processes in peatlands may lead to enrichment of metals in surface soil horizons (Reimann and De Caritat 2000). Metal in peatlands also serve as key enzyme cofactors (e.g., Ni, Cu, Fe, Mb) and low levels can constrain microbial activity (Glass and Orphan 2012; Bear et al. 2021). On the other hand, high concentrations of metals can be toxic to plants and microbes, reducing their abundance and productivity (Glass and Orphan 2012; Glass 2015) or altering their community composition (Fiałkiewicz-Kozieł et al. 2015; Luke et al. 2015; Bear et al. 2021). Therefore, understanding the range of metal concentrations in peatlands is a good foundation for exploring the importance of natural and anthropogenic drivers of peatland plant communities, biogeochemistry, and microbiology.

Industrial activities have led to high levels of metal emissions resulting in near-global contamination (Kabir et al. 2012), but concentrations and surface enrichment of metals such as As, Cu, Cd, Pb, Zn, and Ni in peatlands are typically much higher close to point sources due to their different atmospheric behavior in particulate form rather than gaseous form (Poikolainen et al. 2004). For example, Borgulat et al. (2018) and Nieminen et al. (2002) found high enrichment of Cd, Cu, Ni, Pb, and Zn near point sources (smelters, metal processing). Mercury is a notable exception as some studies have indicated enrichment of Hg in peatlands close to industrial sources (Fitzgerald et al. 2018; Chen et al. 2021), while other studies indicated Hg enrichment farther away from emission point due to its distinct atmospheric behavior in the gaseous phase (Pearson et al. 2019; Floreani et al. 2020). Therefore, Hg recorded in peatlands may originate from local or regional sources. Additionally, there is limited information on the enrichment of REE (Ce, Dy, Eu, La, Sm, Yb) in peat cores. The increasing usage of REE in agricultural applications and industries, is cause for concern given the potential effects on the environment (Han et al. 2017). The widespread application of REE in agriculture and various industries is increasing the release of these elements in the environment (Balaram 2019). Factors such as pH, distribution of REE in bedrocks, and adsorption ability of organic matters in weathering profiles partly control REE enrichment (Han et al. 2017).

To address these knowledge gaps, this study seeks to evaluate the global patterns of metal enrichment in bogs and fens using a global peat dataset. In this study, all analyzed elements are referred to as metals, since they constitute most of the elements in the dataset, but metalloids (e.g., As and Sb) and transition metals (e.g., Hg) are also included. Further, we refer to "pollutant metals" (As, Cd, Co, Cu, Hg, Pb, and Sb) as those that have commonly been shown to be enriched in surface peat in numerous studies (Shotyk 1996) and "surface peat" refers to the 10–20 cm depth layer. Determination of metal EFs were based on site-specific measurements, while recognizing the variability of peat age at greater depth, thereby rendering EF as conservative in this case. The objectives of this study were (1) to characterize EFs for 34 metals in bog and fen (poor to moderately rich) peatlands distributed globally and (2) to identify if EFs of known pollutant metals in a global dataset are related to cumulative atmospheric S deposition (1850–2009). We expected that most metals will have EFs ~ 1.0 but that median EFs for established pollutant metals such as Pb, Zn, Cd, Cu and Ni will be higher than other metals and EFs of these metals globally will be positively related to each other and to atmospheric S deposition.

Materials and Methods

Studied Area and Sampling

The study on bog and fen (poor to moderately rich) peatlands used data collected by a network of researchers as part of a larger project looking at the characterization of geochemistry and microbial communities in peatlands at a global scale (Global Peatland Microbiome Project; Lamit and Lilleskov

et al. unpublished; Watmough et al. 2022). This dataset does not include tropical lowland peat swamps. To classify habitats, sites were grouped into categories based on pH ranges put forth by Rydin and Jeglum (2013); bog pH < 4.2, poor fen pH = 4–5.5, intermediate and moderately rich fen pH = 5–7. Standardized sampling approaches were applied for data collection from 368 peat cores across the regions of Asia, Europe, North America, Oceania, and South America (Fig. 1). In most cases, three cores from topographic positions representative of the average conditions of a site were collected. Typically, distance between core samples within a site range from ca. 1–500 m. A box corer, hand sampling with a serrated knife, or a Russian peat borer was used to target depths of 10–20, 30–40, and 60–70 cm per site (although not all depths were always obtained), while cleaning sampling tools and avoiding compaction. Approximately 50 g of field moist peat was collected at each depth increment, followed by homogenization in plastic bags. In situ measurements of humification, soil moisture, temperature, and von Post were recorded for each depth horizon. Rapid shipping methods with samples on dry ice or ice packs, when possible, to maintain frozen conditions, were utilized. Samples were catalogued and stored at −20 °C before analysis. It is important to note that the global peatland microbiome project set out to generate a common data set across peatlands robust enough to facilitate comparisons at a global scale, with enough flexibility for direct data usage at the local scale by researchers from each participating site. Based on this premise, sampling sites and specific core locations are in keeping with the individual needs of each research team in accordance with their local knowledge of hydrology, peat chemistry, and vegetation.

Chemical Analysis

A subset of each sample was oven dried at 60 °C and ground to a fine powder in a ball mill prior to chemical analysis. A muffle furnace was used to combust milled samples at 550 °C for 6 h. The resultant ash was transferred into digestion tubes using type I grade purified water for digestion and analysis of total elements on an inductively coupled plasma-mass spectrometry (ICP-MS) at the Elliot Lake Field Research Station at Laurentian University. The first digestion of peat ash in water was done at 110℃ for 210 min in 10 ml of HF and HCl until dry, with this process being repeated twice. The third digestion was conducted at 110 °C for 250 min in 7.5 ml of HCl and HNO_3 until dry. The final digestion was completed at 110 °C for 60 min in 2 ml of HCl, 0.5 ml of HF and 10 ml of HNO_3 followed by dilution to 50 ml with deionized water. Dilution of samples within detection limits was done to facilitate analysis on a Varian 810 ICP-MS for total concentrations of metals. Samples were analyzed in duplicates, with two organic standard reference materials for every 20 samples to maintain quality standards (spinach and tomato leaves NIST CRM 1570a and 1573a).

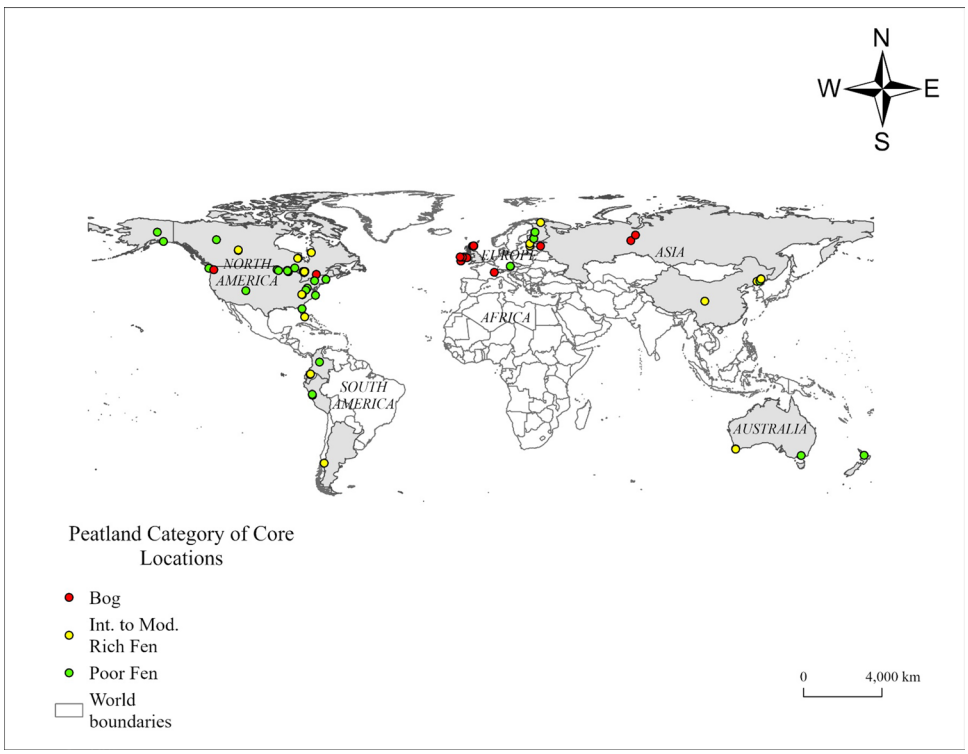

Fig. 1 Global distribution of core sampling locations by peatland type

Dried unground peat subsamples were ground to fine fraction with a mortar and pestle to improve homogeneity. Total Hg concentration was measured with a Direct Mercury Analyzer (DMA-80) by thermal decomposition, amalgamation, and atomic absorption spectrometry. Samples were heated to 900℃ to reduce Hg species to elemental Hg, which was loaded onto an amalgamator. Subsequent heating of the amalgamator resulted in the release of Hg vapors into a single beam, fixed wavelength atomic absorption spectrophotometer. Sample masses ranged from 0.5000 to 1.0000 g and NIST 1515 was used as the certified reference material. Quality control of Hg measurements was assured by the inclusion of blanks at the start and end of each experimental run (40 samples) and recovery ≥ 93% was considered acceptable. Samples were analyzed in duplicates and total Hg measurements were provided in mg kg^{-1} units. A small amount of Hg may also have been lost during our drying procedure as Smeds et al. (2022) reported that the median loss of Hg in samples dried at 60 °C was 4.1% compared with freeze dried samples. However, recovery in our analysis was within the same range of other elements measured in this study (> 93%), so any differences in Hg enrichment most likely reflects the unique behavior of Hg in the environment rather than an artifact caused by our analysis. The missing values for certain elements in the dataset accounts for differences in sample size (n) for global assessment.

Analysis of C and N was done with dried ground peat weighed to within 0.0001 g on a digital balance. A formed tin foil capsule was packed with ca. 75 mg of peat along with 150 mg of tungsten (VI) oxide powder. Samples were sealed by folding over tin foil followed by compression in a pill-shaping device. An Elementar VarioMacro CNS Analyzer was used to analyze the packed samples and results precision was confirmed with the inclusion of blanks and sulfadiazine for CNS recalibration and QA standard (NIST-1515-SRM apple leaves).

Cumulative Global Sulphur Deposition

Total cumulative atmospheric 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° × 0.5° resolution grid (Lamarque et al. 2013). Cumulative S deposition (kg S ha^{-1}) was estimated by summing the interpolated annual rate of S deposition (mg(S) m^{-2} yr^{-1}) determined for time periods from 1850 to 1979 and 1980–2009, assuming a linear change in deposition on a year-to-year basis.

Statistical Analysis

Given the dominance of poor fens, intermediate-to-moderately rich fens, and bogs, these peat cores (n = 368) (Fig. 1) were the focus for statistical analysis. Statistical analysis was conducted with R version 4.0.4 (R Core Team 2021), at an acceptable α-level of 0.05. Descriptive statistical analysis was conducted with R statistical package. Enrichment factors were calculated for all metals by quantifying the amount of metal gained in the upper profile of the peat cores (10–20 cm), relative to the amount found within the lower profile (60–70 cm) of the cores, indicating anthropogenic inputs. Comparisons were made between peat sample and background based on the following formula (Loring 1991; Williams and Antoine 2020):

$$EF = \frac{\left(\frac{M}{Zr}\right)_{sample}}{\left(\frac{M}{Zr}\right)_{background}} \quad (1)$$

where M background and M sample are metal concentrations in reference background and sample respectively, while 'conservative metal (zirconium, Zr)" background and Zr sample are the concentrations in reference background and sample respectively. Zirconium (Zr) was the targeted 'conservative' metal since it forms oxides of extremely low solubility; hence high resistance to weathering (Baes and Messmer 1976). Sample concentrations were from the upper profile of peat cores (10–20 cm); while it was assumed that the lower profile of peat cores (60–70 cm) was deep enough to represent background concentrations. Because the rate of peat formation will vary among peatland, we recognize that different time periods may be captured by our sampling approach, but the intent of this study is to compare relative patterns in enrichment among metals within our data set rather than characterize temporal changes in metal accumulation at individual sites. Mann–Kendall correlation was used to determine if enrichment factors of established pollutant metals (As, Cd, Co, Cu, Hg, Ni, Pb, and Sb) are related to cumulative atmospheric S deposition. A correlation matrix was also computed for enrichment factors of established pollutant metals.

PCA with Missing Values

The results computed from the principal component analysis (PCA) helped with the assessment of interrelations among the studied metals and exploration of probable clusters of metals in bog and fen peat systems. Data from sampled bog and fen peat cores are included, but samples

with missing values for any of the parameters have been treated with an iterative PCA algorithm. This PCA algorithm is based on an imputation method that facilitates the estimation of principal axes and components despite the presence of missing values (skipping of missing values). The imputation is executed with the R package *missMDA*, by simultaneously considering the similarities between individuals and the relationships between variables (Josse et al. 2011; Josse and Husson 2016).

Results

Metal Concentrations and Enrichment Factors by Peatland Type

Metal concentrations varied considerably among peatland types based on the average distance from the mean (Table 1). Generally, bogs had the lowest concentrations of most metals, especially base cations–Al and Fe. Intermediate-to-moderately rich fens had particularly high concentrations of Al, Ca, Fe, K, Mg, and Na which were > 3 × higher than in bogs and poor fens. The concentration of mineral metals (Co, Cu, K, Mg, Mn, and Zn) and REE (Ce, Dy, Eu, La, and

Table 1 Summary of mean (± SE) and median of metal concentrations (mg kg^{-1}) from all three sample depths by peatland type

Metal	Bog (n = 65)		Poor Fen (n = 223)		Int. to Mod. Fen (n = 80)	
	Average (± SE)	Median	Average (± SE)	Median	Average (± SE)	Median
Al	4702 ± 1246	919	5388 ± 683	1860	16,502 ± 2639	4660
As	3.04 ± 0.82	1.13	7.04 ± 2.01	1.10	5.48 ± 0.91	2.80
Ba	37.5 ± 6.23	16.9	61.3 ± 4.87	38.2	178 ± 28.2	96.0
Ca	2946 ± 473	1710	3680 ± 222	2990	16,032 ± 1527	12,000
Cd	0.50 ± 0.10	0.28	0.88 ± 0.12	0.35	0.61 ± 0.10	0.39
Ce	6.59 ± 2.32	0.99	7.24 ± 1.66	1.98	14.1 ± 2.03	5.61
Co	0.93 ± 0.20	0.44	4.69 ± 1.25	1.02	5.12 ± 0.65	3.33
Cr	71.1 ± 18.1	18.5	62.0 ± 6.93	26.3	73.0 ± 13.5	28.9
Cu	7.09 ± 1.34	3.64	68.0 ± 15.9	7.10	32.5 ± 8.83	13.2
Dy	0.97 ± 0.45	0.14	0.84 ± 0.31	0.18	0.86 ± 0.12	0.43
Eu	0.51 ± 0.22	0.11	0.39 ± 0.12	0.15	0.38 ± 0.05	0.20
Fe	2470 ± 452	1215	5863 ± 738	2680	16,549 ± 2304	7855
Ga	1.91 ± 0.38	0.73	2.55 ± 0.27	1.28	7.56 ± 1.06	3.20
Ge	1.46 ± 0.47	0.64	3.50 ± 0.44	1.55	4.89 ± 0.57	3.39
Hg	0.12 ± 0.03	0.07	0.08 ± 0.01	0.06	0.09 ± 0.01	0.09
K	1193 ± 241	673	1438 ± 99.0	992	3434 ± 535	1110
La	2.90 ± 0.92	0.49	3.58 ± 0.61	1.00	7.02 ± 1.00	3.04
Li	3.19 ± 1.02	0.61	2.11 ± 0.42	0.70	6.59 ± 0.91	2.99
Mg	1100 ± 122	766	965 ± 47.3	780	3136 ± 384	1905
Mn	76.8 ± 21.6	15.8	230 ± 76.8	64.0	385 ± 78.1	162
Na	729 ± 130	456	581 ± 44.0	372	4863 ± 936	1040
Nb	0.98 ± 0.15	0.79	1.38 ± 0.18	0.77	2.97 ± 0.78	1.17
Ni	7.00 ± 1.58	3.10	122 ± 30.1	7.45	51.0 ± 14.9	17.5
Pb	20.5 ± 3.34	12.0	26.2 ± 4.81	6.10	11.7 ± 1.54	6.65
Rb	4.85 ± 1.24	1.86	5.56 ± 0.50	3.41	13.9 ± 2.33	5.11
Sb	0.62 ± 0.16	0.32	1.14 ± 0.41	0.27	0.63 ± 0.12	0.37
Sm	1.04 ± 0.44	0.15	0.96 ± 0.25	0.32	1.33 ± 0.18	0.61
Sr	26.1 ± 4.60	16.6	23.0 ± 1.50	16.9	123 ± 17.7	65.0
Ti	170 ± 27.6	63.1	215 ± 22.9	102	1028 ± 217	183
U	1.59 ± 0.65	0.26	0.61 ± 0.11	0.31	1.03 ± 0.17	0.57
V	7.64 ± 1.97	2.74	7.90 ± 0.80	4.89	31.2 ± 5.48	12.7
Yb	0.84 ± 0.45	0.14	0.50 ± 0.15	0.18	0.47 ± 0.07	0.24
Zn	25.6 ± 2.53	19.6	82.8 ± 33.3	32.6	60.5 ± 11.7	36.8
Zr	6.18 ± 1.56	1.68	5.39 ± 0.48	2.75	15.2 ± 2.72	6.01

Sm) also tended to be considerably higher in intermediate-to-moderately rich fens compared with bogs and poor fens.

Median EFs for all metals were between ~ 1.0 and 3.3 and the magnitude of enrichment for individual metals were surprisingly very similar in bogs and fens (all groups), despite being retrieved from different locations (Fig. 2). In contrast to our expectation that pollutant metals would exhibit the highest median EF's, Mn exhibited the highest median EF followed by Pb, Zn, Cd, and K. Most other metals had median EFs < 1.5 (Fig. 2), while most of the pollutant metals such as As, Cd, Co, Cu, Hg, Pb, and Sb had median EFs > 1.5 (Fig. 2).

Generally, EF values < 10 are not considered significant, given the potential for such small enrichments to arise from differences in the sample location geology and background values utilized in the calculations (Pekey 2006; Williams and Antoine 2020). Based on this premise, significant enrichment (EF > 10) in some peat cores was evident for most metals sampled across bog and fen peat cores (Table 2). Peat cores with EFs > 10 accounted for 6% of sampled cores in this study and mostly included pollutant metals (As, Cd, Co, Cu, Hg, Ni, Pb, and Sb) and several mineral metals (Ca, Fe, K, Mg, Mn, Na, and Zn) and to a much lesser extent REE (Ce, Eu, and Sm).

For all metals mean EFs exceeded median values (Table 2), but in general mean EFs were highest for pollutant metals although there were still notable exceptions including Mn, K, and Ge. Metals with the highest mean EFs included As (4.97 ± 0.80), Cd (4.72 ± 0.66), Cu (6.53 ± 1.02), Ge (5.57 ± 1.73), Hg (4.59 ± 0.89), K (4.59 ± 0.81), Mn (12.55 ± 1.67), Ni (8.13 ± 1.49), Pb (12.80 ± 1.70), Sb (7.76 ± 1.92), and Zn (9.10 ± 1.70) (Table 2). Metals with the highest number of cores with an EF > 10 included Mn (88, 29%), Pb (87, 28%), Zn (52, 17%), Cu (36, 12%), As (32, 12%), Sb (30, 16%), Co (20, 6%), K (20, 7%), Ni (19, 10%), and Mg (17, 5%) (Table 2). Pollutant metals such as As, Cu, Ni, Pb, and Sb with EF > 100, were also evident in a few cores in areas such as Sudbury, Ontario (Canada).

The PCA analyses of metal EF accounted for ca. 50% of the total variance within the first four axes of data. PC1 was positively loaded by As, Cd, Co, Cu, Hg, Ni, Pb, Fe, Sb, and cumulative S deposition and accounted for 21.50% of the total variance (Fig. 3). The EF of these pollutant metals showed

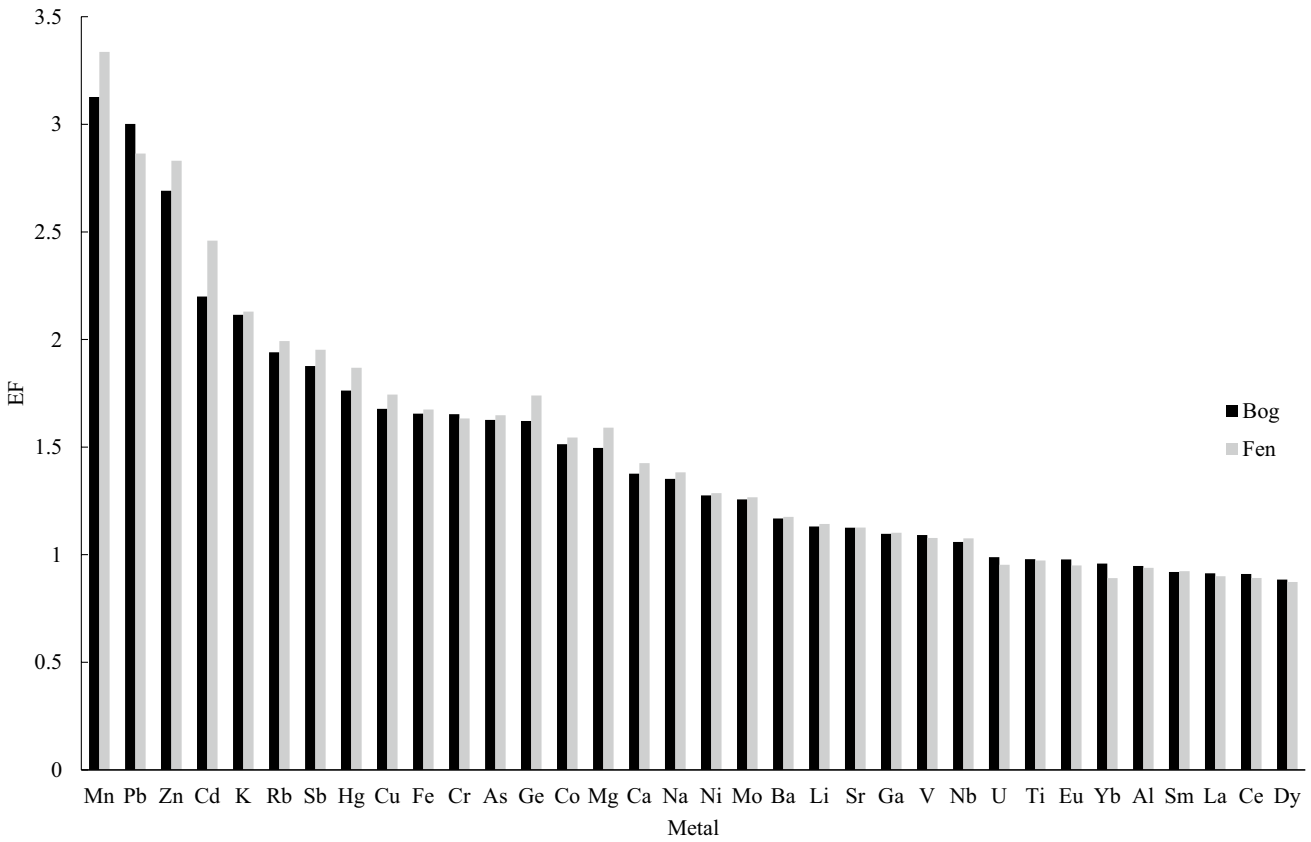

Fig. 2 Median element enrichment factors (EF) by peatland type. Fen refers to all fen types (poor, intermediate to moderate)

Table 2 Summary of metal enrichment factors (EF), count, mean (± SE), median, and number of cores with EF greater (>) than 10 in bog and fen peatlands distributed globally (n = 368)

Metal	Count	Average (± SE)	Median	EF > 10 (% sites)
Al	314	1.04 ± 0.03	0.96	
As	257	4.97 ± 0.80	1.66	32 (12)
Ba	311	1.60 ± 0.12	1.18	1
Ca	307	2.32 ± 0.20	1.43	6
Cd	195	4.72 ± 0.66	2.40	15 (8)
Ce	310	1.05 ± 0.05	0.92	
Co	311	3.02 ± 0.25	1.51	20 (6)
Cr	312	2.71 ± 0.20	1.63	15 (5)
Cu	295	6.53 ± 1.02	1.72	36 (12)
Dy	234	1.07 ± 0.06	0.87	
Eu	177	1.15 ± 0.09	0.95	1
Fe	312	3.31 ± 0.35	1.66	15 (5)
Ga	311	1.33 ± 0.06	1.11	
Ge	175	5.57 ± 1.73	1.62	10 (6)
Hg	118	4.59 ± 0.89	1.94	11 (9)
K	306	4.59 ± 0.81	2.11	20 (7)
La	312	1.03 ± 0.05	0.91	
Li	231	2.05 ± 0.26	1.15	5
Mg	311	3.09 ± 0.32	1.57	17 (5)
Mn	305	12.55 ± 1.67	3.24	88 (29)
Na	313	2.05 ± 0.22	1.37	7
Nb	139	1.51 ± 0.13	1.10	2
Ni	198	8.13 ± 1.49	1.27	19 (10)
Pb	314	12.80 ± 1.70	3.01	87 (28)
Rb	313	3.23 ± 0.38	1.94	13
Sb	191	7.76 ± 1.92	1.93	30 (16)
Sm	229	1.22 ± 0.13	0.92	2
Sr	313	1.82 ± 0.27	1.14	2
Ti	314	1.11 ± 0.04	0.99	
U	177	1.03 ± 0.06	0.96	
V	255	1.31 ± 0.07	1.08	
Yb	161	1.14 ± 0.08	0.90	
Zn	309	9.10 ± 1.70	2.71	52 (17)

some relationship to cumulative S deposition, which is an indicator of anthropogenic air pollution (Table 3). PC2 accounted for 14.64% of the total variance, with positive loading on Ce, Dy, Eu, La, Sm, U, Yb, and pH (Fig. 3). These REE were prevalent in intermediate-to-moderately rich fens where pH was high. PC3 and PC4 explained 8.19% and 6.45% of the variation in the dataset, respectively. Clustering of variables into three groups was evident from the PCA, where variables belonging to one group were highly correlated (As, Cd, Co, Cu, Hg, Ni, Pb, and Sb) (Fig. 3 and Table S1). High correlation was also evident among K, Mg, Mn, and Rb, with more association to higher C content and lower pH that are characteristics of bogs (Fig. 3).

Metal Enrichment Factor and Cumulative Sulphur Deposition

Globally, cumulative S deposition increased from 1850 to 1979, with the highest S deposition areas generally occurring in eastern North America, north and central Europe, and eastern China (Fig. 4). Cumulative S deposition over the 170-year period was between 135 and 4123 kg S ha^{-1}. Metals that have been shown to be emitted from anthropogenic pollution sources were significantly ($p < 0.01$) correlated with cumulative S deposition, except for Hg (Table 3). Correlation coefficients were < 0.40, which can be expected as metal deposition is likely to vary considerably within the cumulative S deposition grid resolution of ca. 55 km^2 and high S deposition is possible without much metal deposition and vice versa. Therefore, the use of cumulative S deposition as a crude surrogate for metal deposition is likely more indicative of industrialization, with several other factors contributing to metal enrichment in bog and fen peatlands globally.

The pattern of Hg enrichment differed from that of the other pollutant metals (Fig. 4a). Mercury showed high enrichment (EF > 10) in regions such as Europe (Ireland), North America (Canada and USA), and South America (Ecuador). In regions such as Asia (China and Russia), Europe (Czech Republic, Estonia, Finland, Ireland, Scotland, and Switzerland), Oceania (Australia), North America (Canada and USA) and South America (Ecuador and Peru), metals such as As, Cd, Co, Cu, Ni, Pb, and Sb showed high enrichment (EF > 10) (Fig. 4). Significant positive correlation was evident among enrichment factors of pollutant metals, except Hg and Ni (Table S1).

Discussion

In our global dataset, the relative enrichment of metals in surface (10–20 cm) peat in bogs and intermediate to poor fens exhibited very similar patterns. Overall, we identified 3 general groupings in metal EFs in our dataset; (1) primarily pollution influenced metals (As, Cd, Co, Cu, Hg, Ni, Pb, and Sb), (2) metals that are enriched in surface peat primarily because of peatland biogeochemical processes (K, Mg, Mn, and Rb) and (3) metals that are generally immobile in peat and experience relatively little enrichment in surface peat from atmospheric deposition (Al, Ce, Dy, Eu, La, Ti, Sm, U, and Yb). Given the differences in biogeochemistry, metals that were most enriched in surface peat were not constrained to known pollution metals, with Mn, K, Rb and Ge having median EFs that were in the same range as known pollution metals such as Pb, Cd, Ni, Cu, As, Hg. Most REE and other metals such as Al and Ti had median EFs close to one indicating relative

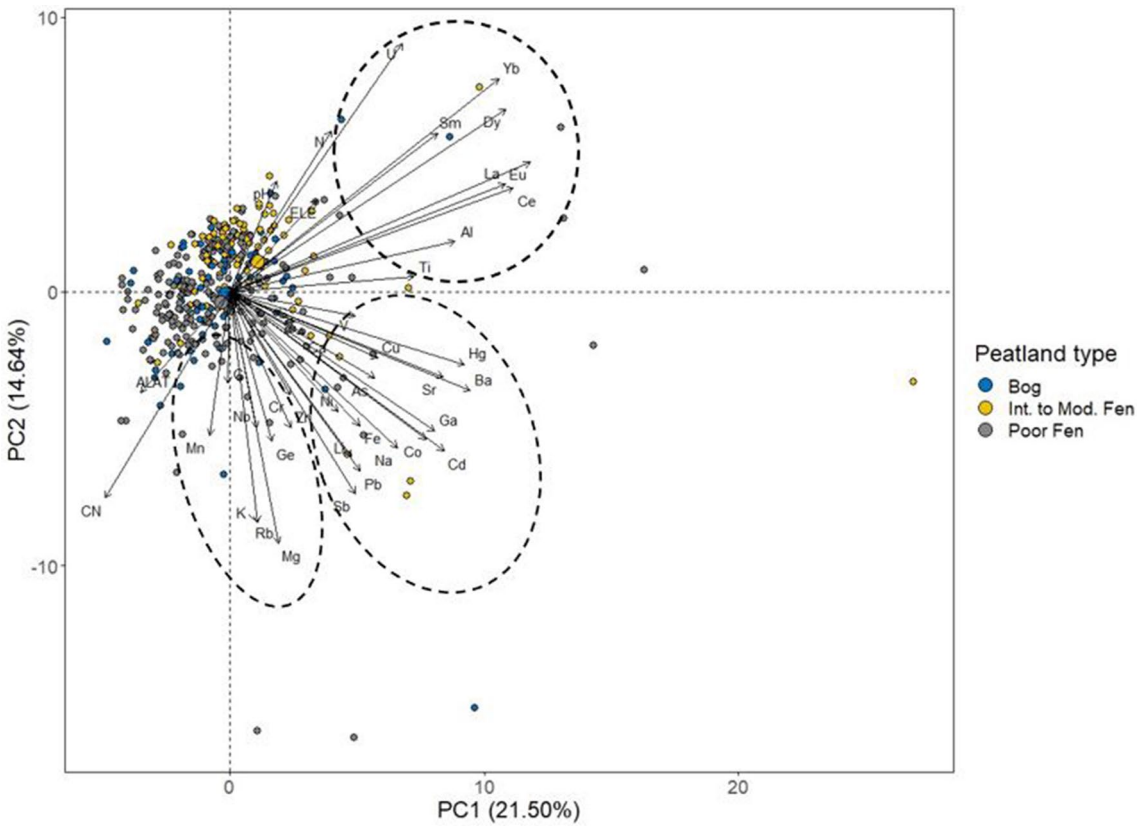

Fig. 3 Multivariate statistical representation of metals in bog and fen peatlands sampled globally and loadings on two principal axes (PC1 and PC2), with standardized pH values, cumulative S deposition, elevation (ELE), absolute latitude (ALAT), nitrogen (N), carbon/nitrogen ratio (CN), and carbon (C). Arrows show the scale and direction of correlation vectors for parameters

Table 3 Mann–Kendall correlation between cumulative (wet + dry) S deposition 1850–2009 (kg S ha^{-1}) and element enrichment factors (EF)

Element	Count	All (n = 368)
As	257	0.120**
Cd	195	0.114*
Co	311	0.118**
Cu	295	0.213***
Hg	118	n.s
Ni	198	0.156**
Pb	314	0.104**
Sb	191	0.109*

Significance of Mann–Kendall correlations is indicated by: *($p < 0.05$), *

consistency in peat cores down to a depth of 70 cm. Additionally, mean EFs were generally higher than median EFs indicating that higher values were present in a few cores most likely caused by local contaminant sources. Enrichment factors of most pollutant metals were positively correlated with cumulative atmospheric S deposition, with the notable exception of Hg.

Bog and Fen Geochemistry

The structure and composition of peat in terms of mineralogy, geochemistry, atmospheric deposition, acidity, and redox conditions facilitates the binding of metals (Smieja-Król et al. 2010; Nsaka et al. 2018). This binding ability can influence the concentration and enrichment of metals in bogs and fens. Even though bogs are described as the best type of peatland to act as environmental archives of atmospheric deposition of airborne pollutants, fens have also been used (Talbot et al. 2017; Miszczak et al. 2020). The results from this study showed that the concentrations of most metals and REE were considerably higher (typically 3–5 times) in intermediate-to-moderately rich fens compared with poor fens and bogs. Higher metal concentrations in intermediate fens is primarily attributed to inputs from groundwater that is rich in mineral elements including metals (Krumins et al. 2016). Klavins et al. (2009) indicated that enrichment due to retention of metals but loss of C and N in peat through decomposition could contribute to higher metal concentrations in intermediate fens. Metals also naturally occur in peat soils, with varying concentrations based on parent materials. Therefore, it is critical to distinguish between geogenic

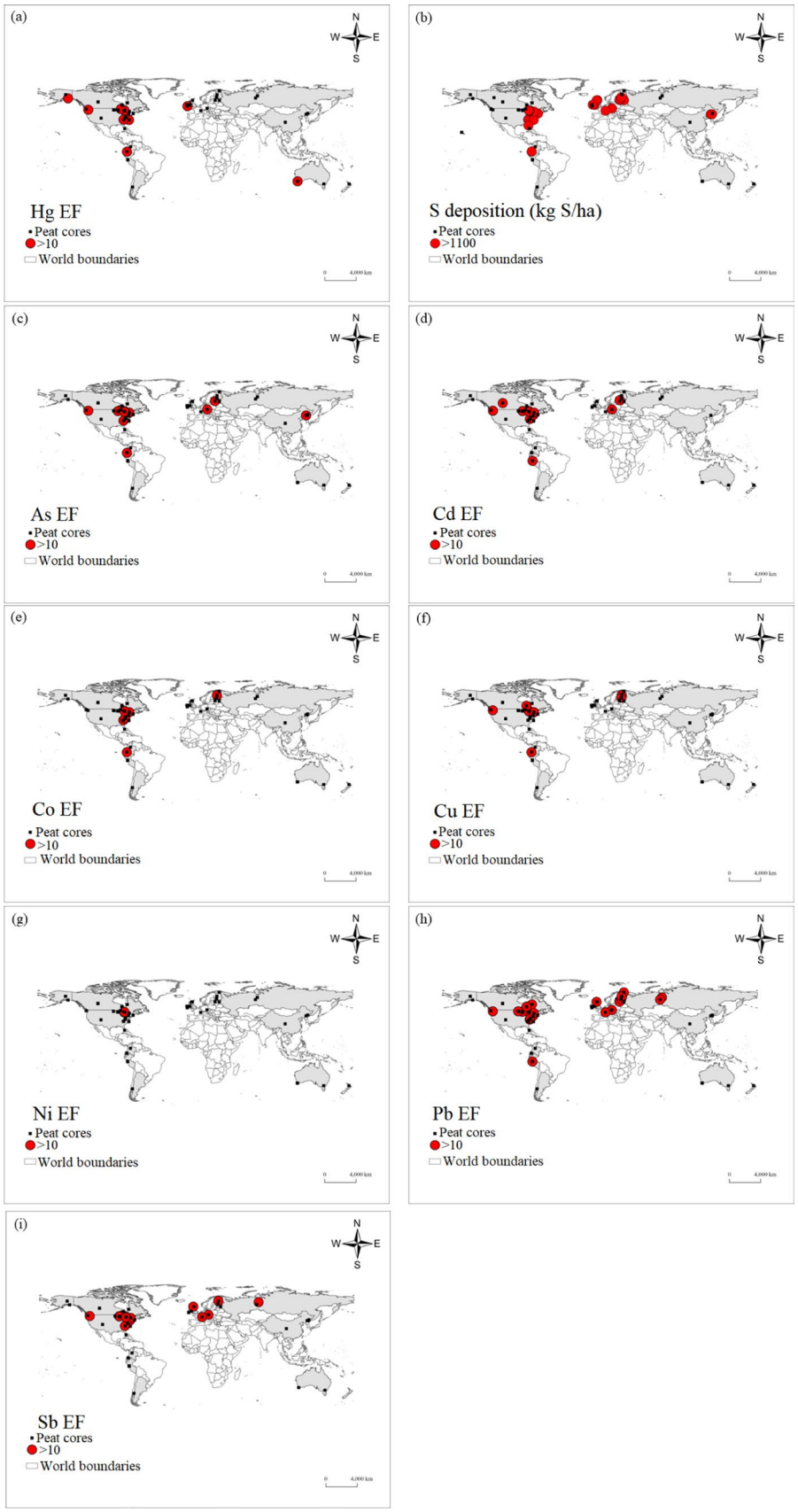

Fig. 4 Global distribution of cumulative atmospheric S deposition and enrichment factors of Hg, As, Cd, Co, Cu, Ni, Pb, and Sb across sampled locations

levels and anthropogenic inputs and the use of EF has been widely adopted (Ghrefat et al. 2011; Barbieri 2016; Williams and Antoine 2020). This index can provide critical insights into the presence and intensity of anthropogenic metal deposition on peat soil (Barbieri 2016), even though its use has been brought into question by Reimann and De Caritat (2000).

Global Metal Enrichment Patterns in Bog and Fen Peatlands

Fens (intermediate, moderate, and poor fens) and bogs showed very similar EFs among metals indicating both types of peatlands may be useful for characterizing metal enrichment in surface peat when baseline differences in peatland chemistry are removed by calculating EF using an immobile element such as Zr, Ti or Al (Shotyk 1996). Other studies have similarly found that bogs and poor fens can be used as environmental archives of deposition of some metals (Newman et al. 2023). Reimann and De Caritat (2000) argued however, that the use of EF's is flawed if crustal values are used as they do not consider natural differences in peat chemistry and biogeochemical process in peatlands. In this study we used the chemistry measured in our deepest peat sample (60–70 cm) to capture inherent variability in peat chemistry. Additionally, while the relative ranking of metal EFs was almost identical in bogs and fens, several of the metals with high median EFs are not known pollutant metals, suggesting that peatland biogeochemical processes that can lead to enrichment in surface peat are occurring in both peatland types, supporting the concerns raised by Reimann and De Caritat (2000). Therefore, it is crucial to differentiate the different classes of metals in terms of mobility in peat.

Although the location of peat cores near pollution sources may explain the enrichment of pollutant metals in this study, the high enrichment of metals such as Mn, K, Rb, Ge, and Fe may be linked to other biogeochemical processes (Reimann and De Caritat 2000). High enrichment of K, Mn, and Rb was associated with high peat C concentrations and low pH values that are characteristics of bogs. This suggests that vegetation characteristics and/or redox rather than anthropogenic activities are the primary cause of enrichment in surface peat for these metals (Gucia et al. 2012). Some studies have shown that the enrichment of K may be linked to nutrient uptake and cycling by standing biomass, while Fe and Mn enrichment may suggest limited oxygenation within peat cores, because reduced forms of these metals are more soluble than oxidized forms (Martínez et al. 2007; Lawson et al. 2014). Natural enrichment in peat depends on the compositional and mineralogical characteristic of geological source material (Barbieri 2016). For example, studies have shown that K can often be limited in bogs (Wieder 2022), and so tight internal cycling by vegetation can lead to enrichment in surface peat. Because Rb may be substituted for K in plant tissues (Nyholm and Tyler 2000), this likely explains the similar patterns of enrichment of these metals in surface peat. Fewer studies have examined Ge in peatlands, but it is present in coal and emitted from industrial activities and is known to bind to lignin-derivative organic compounds that are found in peat (Bernstein 1985) so its enrichment may be caused by natural processes or anthropogenic activities. Regardless of the mechanisms, enrichment in surface peat is influenced by peatland biogeochemistry in addition to anthropogenic inputs in deposition so EFs must be interpreted with caution.

A second grouping of metals included the REE (Ce, Dy, Eu, La, Sm, Yb) and several other metals such as Ti and Al that were associated and highest in intermediate-to-moderately rich fens with higher pH. In general, the median EFs of this group of metals was close to one indicating that these metals are mostly immobile in peat and currently experience relatively little influence from elevated atmospheric deposition or peatland biogeochemical processes. Other studies have shown that metals such as Ti and Al are immobile in peat and have used these metals to estimate EF's (Shotyk 1996). In contrast, Krachler et al. (2003) evaluated a peat core from a Swiss bog and reported that enrichments of REE calculated using Sc as a reference element exceeded unity, relative to the Upper Continental Crust. Overall, EF in all peat samples ranged from 1.96 for Sm to 2.34 for Gd, with considerably lower EF for Ce (1.82) and Eu (1.44), respectively. Krachler et al. (2003) argued that the concentration profiles of REE were similar but not identical to those of other lithogenic, conservative reference elements such as Sc, Y, Al, Zr and Ti. As a result, we cannot exclude the possibility that localized enrichment of REE may occur in some locations and mean EFs in our data set were higher than median values indicating that some cores exhibited EFs > 1.0. Anthropogenic enrichment of REE has also been linked to proximity to intense agricultural practices and the application of phosphate-based fertilizers, but the enrichment of REE has also been associated with regions near to polluted sites such as large cities, *e*-waste dump sites, and industrial centers (Balaram 2019). Dust has also been identified as a major atmospheric source of REE deposition (Kolawole et al. 2021). In this study, while some cores exhibited slight enrichment, we found little evidence of substantial enrichment of REE's in our global peatland dataset, and there was only one case were EF exceeded 10 suggesting any contamination is likely localized to sources or any recent increases in REE deposition are not captured in the 10–20 cm depth of peat.

The third grouping of metals included metals such as As, Cd, Co, Cu, Hg, Pb, Ni, and Sb, which are commonly associated with anthropogenic sources. This correlation suggests that these pollutant metals have common sources, or are

subjected to certain control factors, or common dependence and similar transport behavior (Cheng et al. 2012, 2015). In the absence of chronological data for peat cores analyzed, it is challenging to definitively identify the responsible sources for increased concentrations of pollutant metals in bogs and fens. However, the use of average rates of enrichment in peat facilitates broad relations of increased pollutant metal deposition in peat with anthropogenic activities. These anthropogenic activities increase pollutant metal enrichment in peatlands, given their ability to increase loading on local, regional, and global scales because of atmospheric deposition (Pacyna et al. 2010; Bear et al. 2021).

Relationship between Pollutant Metals and Cumulative Sulphur Deposition

Pollutant metals in the third grouping (except for Hg) were generally enriched and significantly ($p < 0.01$) positively correlated with cumulative S deposition, indicating pollution influence at the global scale, although we recognize that peatland biogeochemical processes are also likely influencing EFs, and our groupings of metals are not mutually exclusive. Studies by Pratte et al. (2013) for example, indicated that Zn enrichment in peat bogs is commonly linked to bioaccumulation by living plants. Additionally, while a positive correlation with S deposition was observed for most of the pollutant metals these correlations are generally weak, most probably because of the influence of natural processes, and because S deposition is not a perfect surrogate for metal deposition. Although global inventories have been made for metal emissions from both natural and anthropogenic sources, there is currently no global dataset for metal deposition (Pacyna and Graedel 1995; Pacyna and Pacyna 2001). Therefore, we used cumulative S deposition as an indicator of industrial activities on a global scale, which has its inherent challenges. For example, natural S emission and deposition also comes from marine and terrestrial biogenic sources, which represents 16 and 58% of the total S emissions in the Northern and Southern Hemisphere respectively (Bates et al. 1992; Hidy and Blanchard 2016). Cumulative S deposition was also found to be greatest in Europe and North America because of a long history of SO_x emissions from coal, petroleum and natural gas processing and combustion, metal smelting, and other industrial processes, which are also a major source of metals (Pacyna and Pacyna 2001; Smith et al. 2011). However, SO_x emissions have changed spatially over the past 160 years. Sources in Europe dominated anthropogenic SO_2 emissions prior to 1900, but this changed between 1900 and 1960, with emission sources from North America becoming dominant (Smith et al. 2011; Hidy and Blanchard 2016). More recently, emissions in China have dominated at the global scale. The use of consistent depths (10–20 cm and 60–70 cm) may therefore capture peak emissions in some regions but not others. This may impact whether areas are identified as being particularly enriched in our dataset but will not affect the relative enrichment of metals in peat cores, which is the goal of this study. Additionally, there is limited resolution of cumulative S deposition (ca. 55 km^2) in this study, which does not account for the rapid changes in metal deposition from point sources as seen in Sudbury and other point sources of metal emissions (Szkokan-Emilson et al. 2014; Barrett and Watmough 2015; Gelly et al. 2019; Bear et al. 2021).

Despite these limitations we found that several cores had EFs > 10 and those with very high EFs were mostly close to known pollution sources such as Sudbury (history of smelting and mining activities in Canada), Atlantic Mine (USA), Europe (history of natural gas extraction and metal mining and smelting), and South America (history of coal/gold rushes and industrialization) (Barbieri et al. 2014; Barrett and Watmough 2015; Luke et al. 2015; Maus et al. 2020; Bear et al. 2021). Zhou et al. (2022) documented the high impacts of Pb–Zn smelting on the environment, where heavy metal(loid)s (Cd, Cu, Pb) were mainly deposited within a 2 km distance of smelters. Barrett and Watmough (2015) found that sites closer to the main Copper Cliff smelter in Sudbury were greatly enriched in Cu and Ni, leading to adverse impacts of industrial activities on bog and fen peat cores close to smelters. Souter and Watmough (2016) also referenced the possible linkage of Cu and Pb enrichment in peat cores to nearby mining and smelting activities. These findings also corroborate with Pratte et al. (2013), which found greater trace metal contents and accumulation rates (As, Cd, Ni, and Pb) in cores closer to point sources of urban and industrial centers in eastern Canada and the U.S. Mid-West. Mean EF for all metals exceeded median values, indicating that metal concentrations at some sites are more strongly influenced by natural (Shotyk et al. 2016) and/or anthropogenic point sources (Nieminen et al. 2002). Localized high levels of contamination near major pollution sources also accounts for mean EF of pollutant metals being higher than median values.

However, the spatial pattern of Hg differed from the other metals most likely due to several reasons including its unique characteristics that facilitates long-range transport in its gaseous elemental form and volatile nature and several authors have reported elevated Hg in peat far from emission sources (Pearson et al. 2019; Floreani et al. 2020). Areas such as Sudbury and Whispering Firs Bog (USA) showed high enrichment of Hg (EF > 10). The proximity of pollution sources such as Sudbury (historical metal deposition impacts) to peatlands (Barrett and Watmough 2015) can explain the high enrichment of Hg. However, the high enrichment of Hg recorded in the preservation area of Whispering Firs Bog that is far from known pollutant sources may be linked to the persistent nature of Hg in the

environment and its high atmospheric mobility over long distances following release from anthropogenic sources such as coal burning and smelting activities (De Simone et al. 2014). Additionally, a major source of Hg emission is from artisanal gold mining that occurs primarily in tropical regions, which is distinct from major sources of S and metal emissions (Streets et al. 2019). Finally, Hg exhibits different geochemical behavior in peat, whereby sulphate-reducing bacteria mediate the conversion of ionic mercury (Hg^{2+}) to bioaccumulating and highly toxic methylmercury (Selvendiran et al. 2008; Hu et al. 2020). Such conversion could also explain the different behavior of Hg in peatlands compared to other pollutant metals that are not subjected to methylation and more related to localized sources.

Conclusion

Global patterns of metal enrichment were examined in bog and fen peat samples collected from 368 peat cores distributed across six continental-scale regions. Metal concentrations differed among peatland types, with intermediate-to-moderately rich fens demonstrating the highest concentrations, likely from minerotrophic conditions and higher rates of organic matter mineralization and overall soil mass loss than in poor sites. Median EFs were similar among bogs and fens (all groups), with metals likely to be influenced by anthropogenic sources (As, Cd, Co, Cu, Hg, Pb, and Sb) demonstrating median EFs > 1.5. Contrary to expectations, high EFs were not restricted to pollutant metals, with Mn, K and Rb all exhibiting elevated median EFs that were similar to pollutant metals likely due to peatland biogeochemical processes leading to surface enrichment of these elements. Additional groupings included minor enrichment of REE and mineral metals with high EFs within intermediate-to-moderately rich fens but differed in spatial patterns to metals influenced by anthropogenic sources due to differences in weathering, peat geochemistry and cycling. Europe and North America exhibited higher levels of enrichment likely due to the longer history of metal pollution and distribution of sampled peatlands in proximity of point sources. Some level of anthropogenic influence of pollutant metals was confirmed based on a weak positive correlation (< 0.40) with estimated cumulative S deposition. This relationship is likely limited by several 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 as opposed to metal deposition.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00244-024-01051-3.

Acknowledgements The authors also acknowledge the assistance of many field and lab assistants including Moira Hough, Kevin Adkinson, Schylur Deraaf, and Bryce Robinson who made this work possible. Grateful for the Sustainable Guyana Program, a partnership between Trent University and the University of Guyana funded by CGX Energy Inc. and Frontera Energy Corporation.

Members of the Global Peatland Microbiome Project consortium that contributed peat to the analyses presented in this paper include Roxanne Andersen (NSERC and INTERACT-TA), Rebekka E. Artz (RESAS SRP and NERC), Brian W. Benscoter, Luca Bragazza, Suzanna L. Bräuer, Michael A. Carson, Xin Chen, Rodney A. Chimner, Bev R. Clarkson, Andrea S. Enriquez (CONICET), Samantha P. Grover, Lorna I. Harris, Christina Hazard, John Hribljan, Sari Juutinen, Evan S. Kane, Klaus-Holger Knorr (DAAD and DFG), Randy Kolka, Anna M. Laine, Tuula Larmola (Academy of Finland), Carmody K. McCalley, Jim McLaughlin, Tim R. Moore, Nadia Mykytczuk, Anna E. Normand, David Olefeldt, Virginia Rich, Nigel Roulet (NSERC), Danielle L. Rupp, Jasmine Rutherford, Christopher W. Schadt, Oliver Sonnentag (Canada Research Chair), Leho Tedersoo, Carl C. Trettin, Eeva-Stiina Tuittila, Merritt Turetsky (Univ Colorado, NSF), Zuzana Urbanová, Ruth K. Varner, Mark P. Waldrop, Meng Wang (National Natural Science Foundation of China), Zheng Wang, Magdalena M. Wiedermann, Shanay T. Williams, Joseph B. Yavitt, and Zhi-Guo Yu.

Author's Contribution Conceptualization SW, SG-P, COe; Data curation GSp, LJL, EAL, NB; Formal analysis SG-P, CO, NB, LJL, EAL; Writing–original draft SW, CO; Writing–review and editing SW, CO, NB, LJL, EALilleskov.

Funding Funding came from Natural Sciences and Engineering Research Council of Canada Grants to Shaun Watmough (#311794) and Nathan Basiliko (#341381). Funding was also provided by the USDA Forest Service Northern Research Station Climate Change Program, the US National Science Foundation [grant number DEB-1146149] to E.S. Kane and E.A. Lilleskov. Funding through the Sustainable Guyana Program to C. Osborne, a partnership between Trent University and the University of Guyana funded by CGX Energy Inc. and Frontera Energy Corporation. The funders had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript.

Data Availability All data are mentioned in the body of manuscript, tables, and figures.

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

References

Ali AA, Ghaleb B, Garneau M et al (2008) Recent peat accumulation rates in minerotrophic peatlands of the Bay James region, Eastern Canada, inferred by 210Pb and 137Cs radiometric techniques. Appl Radiat Isot 66:1350–1358. https://doi.org/10.1016/j.apradiso.2008.02.091

Allan M, Le Roux G, De Vleeschouwer F et al (2013) High-resolution reconstruction of atmospheric deposition of trace metals and metalloids since AD 1400 recorded by ombrotrophic peat cores in Hautes-Fagnes, Belgium. Environ Pollut 178:381–394. https://doi.org/10.1016/j.envpol.2013.03.018

Baes CF, Messmer RE (1976) The hydrolysis of cations. John Wiley & Sons Inc, New York

Balaram V (2019) Rare earth elements: a review of applications, occurrence, exploration, analysis, recycling, and environmental impact. Geosci Front 10:1285–1303. https://doi.org/10.1016/j.gsf.2018.12.005

Barbieri M (2016) The importance of enrichment factor (EF) and geoaccumulation index (Igeo) to evaluate the soil contamination. J Geol Geophys 5:1000237. https://doi.org/10.4172/2381-8719.1000237

Barbieri M, Sappa G, Vitale S et al (2014) Soil control of trace metals concentrations in landfills: a case study of the largest landfill in Europe, Malagrotta, Rome. J Geochem Explor 143:146–154. https://doi.org/10.1016/j.gexplo.2014.04.001

Barrett SE, Watmough SA (2015) Factors controlling peat chemistry and vegetation composition in Sudbury peatlands after 30 years of pollution emission reductions. Environ Pollut 206:122–132. https://doi.org/10.1016/j.envpol.2015.06.021

Bates TS, Lamb BK, Guenther A et al (1992) Sulfur emissions to the atmosphere from natural sourees. J Atmos Chem 14:315–337. https://doi.org/10.1007/BF00115242

Bear SE, Seward JD, Lamit LJ et al (2021) Beyond the usual suspects: Methanogenic communities in eastern North American peatlands are also influenced by nickel and copper concentrations. FEMS Microbiol Lett. https://doi.org/10.1093/femsle/fnab151

Bernstein LR (1985) Germanium geochemistry and mineralogy. Geochim Cosmochim Acta 49:2409–2422. https://doi.org/10.1016/0016-7037(85)90241-8

Borgulat J, Mętrak M, Staszewski T et al (2018) Heavy metals accumulation in soil and plants of polish peat bogs. Polish J Environ Stud 27:537–544. https://doi.org/10.15244/pjoes/75823

Chen X, Su Q, Chen H, Xue D (2021) A high–resolution accumulation record of arsenic and mercury after the first industrial revolution from a peatland in Zoige. Qinghai-Tibet Plateau Land 10:1241. https://doi.org/10.3390/land10111241

Cheng Q, Wang R, Huang W et al (2015) Assessment of heavy metal contamination in the sediments from the Yellow River Wetland National Nature Reserve (the Sanmenxia section), China. Environ Sci Pollut Res 22:8586–8593. https://doi.org/10.1007/s11356-014-4041-y

Cheng Q, Wang W, Wang H et al (2012) Investigation of the heavy metal contamination of the sediments from the Yellow River Wetland Nature Reserve of Zhengzhou, China. Iran J Public Health 41:26–35

Cole KL, Engstrom DR, Futyma RP, Stottlemyer R (1990) Past atmospheric deposition of metals in Northern Indiana measured in a peat core from Cowles Bog. Environ Sci Technol 24:543–549. https://doi.org/10.1021/es00074a013

De Simone F, Gencarelli CN, Hedgecock IM, Pirrone N (2014) Global atmospheric cycle of mercury: a model study on the impact of oxidation mechanisms. Environ Sci Pollut Res 21:4110–4123. https://doi.org/10.1007/s11356-013-2451-x

Fiałkiewicz-Kozieł B, Smieja-Król B, Ostrovnaya TM et al (2015) Peatland microbial communities as indicators of the extreme atmospheric dust deposition. Water Air Soil Pollut 226:97. https://doi.org/10.1007/s11270-015-2338-1

Fitzgerald WF, Engstrom DR, Hammerschmidt CR et al (2018) Global and local sources of mercury deposition in coastal New England reconstructed from a multiproxy, high-resolution, estuarine sediment record. Environ Sci Technol 52:7614–7620. https://doi.org/10.1021/acs.est.7b06122

Floreani F, Barago N, Acquavita A et al (2020) Spatial distribution and biomonitoring of atmospheric mercury concentrations over a contaminated coastal lagoon (Northern Adriatic, Italy). Atmosphere (basel) 11:1280. https://doi.org/10.3390/atmos11121280

Gelly R, Fekiacova Z, Guihou A et al (2019) Lead, zinc, and copper redistributions in soils along a deposition gradient from emissions of a Pb-Ag smelter decommissioned 100 years ago. Sci Total Environ 665:502–512. https://doi.org/10.1016/j.scitotenv.2019.02.092

Ghrefat HA, Abu-Rukah Y, Rosen MA (2011) Application of geoaccumulation index and enrichment factor for assessing metal contamination in the sediments of Kafrain Dam, Jordan. Environ Monit Assess 178:95–109. https://doi.org/10.1007/s10661-010-1675-1

Glass JB (2015) Microbes that meddle with metals: Microorganisms depend on numerous metal cofactors; these requirements in turn depend on microbial species, type of metabolism, and environmental conditions. Microbe 10:197–202. https://doi.org/10.1128/microbe.10.197.1

Glass JB, Orphan VJ (2012) Trace metal requirements for microbial enzymes involved in the production and consumption of methane and nitrous oxide. Front Microbiol. https://doi.org/10.3389/fmicb.2012.00061

Gucia M, Jarzyńska G, Rafał E et al (2012) Multivariate analysis of mineral constituents of edible Parasol Mushroom (Macrolepiota procera) and soils beneath fruiting bodies collected from Northern Poland. Environ Sci Pollut Res 19:416–431. https://doi.org/10.1007/s11356-011-0574-5

Han G, Song Z, Tang Y (2017) Geochemistry of rare earth elements in soils under different land uses in a typical karst area, Guizhou Province, Southwest China. Can J Soil Sci 97:606–612. https://doi.org/10.1139/cjss-2017-0043

Hanif N, Eqani SAMAS, Ali SM et al (2016) Geo-accumulation and enrichment of trace metals in sediments and their associated risks in the Chenab River, Pakistan. J Geochem Explor 165:62–70. https://doi.org/10.1016/j.gexplo.2016.02.006

Hidy GM, Blanchard CL (2016) The changing face of lower tropospheric sulfur oxides in the United States. Elem Sci Anthr 4:000138. https://doi.org/10.12952/journal.elementa.000138

Horb EC, Wentworth GR, Makar PA et al (2022) A decadal synthesis of atmospheric emissions, ambient air quality, and deposition in the oil sands region. Integr Environ Assess Manag 18:333–360. https://doi.org/10.1002/ieam.4539

Hu H, Wang B, Bravo AG et al (2020) Shifts in mercury methylation across a peatland chronosequence: from sulfate reduction to methanogenesis and syntrophy. J Hazard Mater 387:121967. https://doi.org/10.1016/j.jhazmat.2019.121967

Josse J, Husson F (2016) missMDA: a package for handling missing values in multivariate data analysis. J Stat Softw 70:1–31. https://doi.org/10.18637/jss.v070.i01

Josse J, Pagès J, Husson F (2011) Multiple imputation in principal component analysis. Adv Data Anal Classif 5:231–246. https://doi.org/10.1007/s11634-011-0086-7

Kabir E, Ray S, Kim KH et al (2012) Current status of trace metal pollution in soils affected by industrial activities. Sci World J. https://doi.org/10.1100/2012/916705

Khan UA, Kujala K, Nieminen SP et al (2019) Arsenic, antimony, and nickel leaching from northern peatlands treating mining influenced water in cold climate. Sci Total Environ 657:1161–1172. https://doi.org/10.1016/j.scitotenv.2018.11.455

Klavins M, Silamikele I, Nikodemus O et al (2009) Peat properties, major and trace element accumulation in bog peat in Latvia. Baltica 22:37–49

Kolawole TO, Olatunji OS, Ajibade OM, Oyelami CA (2021) Sources and level of rare earth element contamination of atmospheric dust in Nigeria. J Heal Pollut 11:210611. https://doi.org/10.5696/2156-9614-11.30.210611

Krachler M, Mohl C, Emons H, Shotyk W (2003) Two thousand years of atmospheric rare earth element (REE) deposition as revealed by an ombrotrophic peat bog profile, Jura Mountains, Switzerland. J Environ Monit 5:111–121. https://doi.org/10.1039/b208355h

Krumins J, Klavins M, Seglins V (2016) Fen peat properties and metal accumulation in it. In: Proceedings of the 15th International Peat Congress. International Peatland Society, Kuching, pp 646–651

Kumar P, Adelodun AA, Khan MF et al (2020) Towards an improved understanding of greenhouse gas emissions and fluxes in tropical peatlands of Southeast Asia. Sustain Cities Soc 53:101881. https://doi.org/10.1016/j.scs.2019.101881

Lamarque JF, Shindell DT, Josse B et al (2013) The atmospheric chemistry and climate model intercomparison Project (ACCMIP): overview and description of models, simulations and climate diagnostics. Geosci Model Dev 6:179–206. https://doi.org/10.5194/gmd-6-179-2013

Lawson IT, Jones TD, Kelly TJ et al (2014) The geochemistry of Amazonian peats. Wetlands 34:905–915. https://doi.org/10.1007/s13157-014-0552-z

Loring DH (1991) Normalization of heavy-metal data from estuarine and coastal sediments. ICES J Mar Sci 48:101–115. https://doi.org/10.1093/icesjms/48.1.101

Luke S, Preston MD, Basiliko N, Watmough SA (2015) Microbial communities, biomass, and carbon mineralization in acidic, nutrient-poor peatlands impacted by metal and acid deposition. Water Air Soil Pollut 226:19. https://doi.org/10.1007/s11270-014-2265-6

Martínez CE, Yáñez C, Yoon SJ, Bruns MA (2007) Biogeochemistry of metalliferous peats: sulfur speciation and depth distributions of dsrAB genes and Cd, Fe, Mn, S, and Zn in soil cores. Environ Sci Technol 41:5323–5329. https://doi.org/10.1021/es070555v

Maus V, Giljum S, Gutschlhofer J et al (2020) A global-scale data set of mining areas. Sci Data 7:289. https://doi.org/10.1038/s41597-020-00624-w

Miszczak E, Stefaniak S, Michczyński A et al (2020) A novel approach to peatlands as archives of total cumulative spatial pollution loads from atmospheric deposition of airborne elements complementary to EMEP data: priority pollutants (Pb, Cd, Hg). Sci Total Environ 705:135776. https://doi.org/10.1016/j.scitotenv.2019.135776

Newman JE, Levasseur PA, Beckett P, Watmough SA (2023) The impact of severe pollution from smelter emissions on carbon and metal accumulation in peatlands in Ontario. Can Environ Pollut 320:121102. https://doi.org/10.1016/j.envpol.2023.121102

Nieminen TM, Ukonmaanaho L, Shotyk W (2002) Enrichment of Cu, Ni, Zn, Pb and As in an ombrotrophic peat bog near a Cu-Ni smelter in Southwest Finland. Sci Total Environ 292:81–89. https://doi.org/10.1016/S0048-9697(02)00028-1

Nsaka NC, McCrindle RI, Ambushe AA (2018) Levels of potentially toxic metals in water, sediment and peat from Wonderfontein-spruit, North West Province, South Africa. J Environ Sci Heal Part A 53:907–914. https://doi.org/10.1080/10934529.2018.1462894

Nyholm NEI, Tyler G (2000) Rubidium content of plants, fungi and animals closely reflects potassium and acidity conditions of forest soils. For Ecol Manage 134:89–96. https://doi.org/10.1016/S0378-1127(99)00247-9

Pacyna EG, Pacyna JM, Sundseth K et al (2010) Global emission of mercury to the atmosphere from anthropogenic sources in 2005 and projections to 2020. Atmos Environ 44:2487–2499. https://doi.org/10.1016/j.atmosenv.2009.06.009

Pacyna J, Graedel T (1995) Atmospheric emissions inventories: status and prospects. Annu Rev 20:265–300

Pacyna J, Pacyna E (2001) An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environ Rev 9:269–298. https://doi.org/10.1139/a01-012

Page SE, Baird AJ (2016) Peatlands and global change: response and resilience. Annu Rev Environ Resour 41:35–57. https://doi.org/10.1146/annurev-environ-110615-085520

Pearson C, Howard D, Moore C, Obrist D (2019) Mercury and trace metal wet deposition across five stations in Alaska: controlling factors, spatial patterns, and source regions. Atmos Chem Phys 19:6913–6929. https://doi.org/10.5194/acp-19-6913-2019

Pech P, Wojtuń B, Samecka-Cymerman A et al (2022) Metals in plant functional types of ombrotrophic peatlands in the Sudetes (SW Poland). Arch Environ Contam Toxicol 82:506–519. https://doi.org/10.1007/s00244-022-00928-5

Pekey H (2006) The distribution and sources of heavy metals in Izmit Bay surface sediments affected by a polluted stream. Mar Pollut Bull 52:1197–1208. https://doi.org/10.1016/j.marpolbul.2006.02.012

Poikolainen J, Kubin E, Piispanen J, Karhu J (2004) Estimation of the long-range transport of mercury, cadmium, and lead to northern Finland on the basis of moss surveys. Arctic, Antarct Alp Res 36:292–297. https://doi.org/10.1657/1523-0430(2004)036[0292:EOTLTO]2.0.CO;2

Pratte S, Bao K, Shen J et al (2018) Recent atmospheric metal deposition in peatlands of northeast China: a review. Sci Total Environ 626:1284–1294. https://doi.org/10.1016/j.scitotenv.2018.01.183

Pratte S, Mucci A, Garneau M (2013) Historical records of atmospheric metal deposition along the St. Lawrence Valley (eastern Canada) based on peat bog cores. Atmos Environ 79:831–840. https://doi.org/10.1016/j.atmosenv.2013.07.063

Pulunggono HB, Zulfajrin M, Irsan F (2021) Distribution of nickel (Ni) in peatland situated alongside mineral soil derived from ultrabasic rocks. Sains Tanah J Soil Sci Agroclimatol 18:15–26. https://doi.org/10.20961/stjssa.v18i1.45417

R Core Team (2021) R: a language and environment for statistical computing

Reimann C, De Caritat P (2000) Intrinsic flaws of element enrichment factors (EFs) in environmental geochemistry. Environ Sci Technol 34:5084–5091. https://doi.org/10.1021/es001339o

Rydin H, Jeglum JK (2013) The biology of peatlands. Oxford University Press, Oxford, Second

Selvendiran P, Driscoll CT, Bushey JT, Montesdeoca MR (2008) Wetland influence on mercury fate and transport in a temperate forested watershed. Environ Pollut 154:46–55. https://doi.org/10.1016/j.envpol.2007.12.005

Shotyk W (1996) Peat bog archives of atmospheric metal deposition: geochemical evaluation of peat profiles, natural variations in metal concentrations, and metal enrichment factors. Environ Rev 4:149–183. https://doi.org/10.1139/a96-010

Shotyk W, Appleby PG, Bicalho B et al (2016) Peat bogs in northern Alberta, Canada reveal decades of declining atmospheric Pb contamination. Geophys Res Lett 43:9964–9974. https://doi.org/10.1002/2016GL070952

Smeds J, Öquist M, Nilsson MB, Bishop K (2022) A simplified drying procedure for analysing Hg concentrations. Water, Air, Soil Pollut 233:216. https://doi.org/10.1007/s11270-022-05678-7

Smieja-Król B, Fiałkiewicz-Kozieł B, Sikorski J, Palowski B (2010) Heavy metal behaviour in peat - a mineralogical perspective. Sci Total Environ 408:5924–5931. https://doi.org/10.1016/j.scitotenv.2010.08.032

Smith SJ, Van Aardenne J, Klimont Z et al (2011) Anthropogenic sulfur dioxide emissions: 1850–2005. Atmos Chem Phys 11:1101–1116. https://doi.org/10.5194/acp-11-1101-2011

Souter L, Watmough SA (2016) The impact of drought and air pollution on metal profiles in peat cores. Sci Total Environ 541:1031–1040. https://doi.org/10.1016/j.scitotenv.2015.09.137

Streets DG, Horowitz HM, Lu Z et al (2019) Global and regional trends in mercury emissions and concentrations, 2010–2015. Atmos Environ 201:417–427. https://doi.org/10.1016/j.atmosenv.2018.12.031

Szkokan-Emilson EJ, Watmough SA, Gunn JM (2014) Wetlands as long-term sources of metals to receiving waters in mining-impacted landscapes. Environ Pollut 192:91–103. https://doi.org/10.1016/j.envpol.2014.05.009

Talbot J, Moore TR, Wang M et al (2017) Distribution of lead and mercury in Ontario peatlands. Environ Pollut 231:890–898. https://doi.org/10.1016/j.envpol.2017.08.095

Turetsky MR, Benscoter B, Page S et al (2015) Global vulnerability of peatlands to fire and carbon loss. Nat Geosci 8:11–14. https://doi.org/10.1038/ngeo2325

Watmough S, Gilbert-Parkes S, Basiliko N et al (2022) Variation in carbon and nitrogen concentrations among peatland categories at the global scale. PLoS ONE 17:e0275149. https://doi.org/10.1371/journal.pone.0275149

Wieder RK (2022) Element stoichiometry and nutrient limitation in bog plant and lichen species. Biogeochemistry 160:355–379. https://doi.org/10.1007/s10533-022-00968-y

Williams JA, Antoine J (2020) Evaluation of the elemental pollution status of Jamaican surface sediments using enrichment factor, geoaccumulation index, ecological risk and potential ecological risk index. Mar Pollut Bull 157:111288. https://doi.org/10.1016/j.marpolbul.2020.111288

Zhou Z, Peng C, Liu X et al (2022) Pollution and risk assessments of heavy metal(loid)s in the soil around lead-zinc smelteries via data integration analysis. Int J Environ Res Public Health 19:9698. https://doi.org/10.3390/ijerph19159698