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## Trace elements in *Sphagnum* moss waters as indicators of the chemical reactivity of contemporary atmospheric dusts: comparison with peat bog porewaters

Sundas Arooj Butt,  Fiorella Barraza,  Na Chen  and William Shotyk \*

Open-pit mining and other industrial activities generate dusts containing trace elements (TEs) that can be released into aquatic and terrestrial ecosystems. The release of these TEs can be either beneficial or harmful, depending on their concentration, chemical speciation, and toxicity. *Sphagnum* mosses from ombrogenic peatlands have been used for decades to monitor atmospheric deposition of TEs, but there have been few studies of the water they contain. *Sphagnum* fluids and peat porewaters are acidic ( $\text{pH} \leq 4$ ), making both suitable for dust dissolution. Previous studies used near-surface peat porewaters to assess TE bioaccessibility due to open-pit bitumen mining in the past. Here, TEs were determined in waters extracted from living *Sphagnum* mosses collected in bogs from the same mining and remote locations in Alberta, Canada. Trace elements increased in concentration toward industry, reflecting the increased rates of dust deposition from mining. Concentrations were greater in moss waters compared to peat porewaters, likely due to the increase in rates of dust deposition over time. For example, Y, Fe, and Th were enriched  $>100\times$ ; V and Ni, up to  $40\times$ ; and As, Cd, Pb, Sb, and Tl, up to  $20\times$ , in moss waters near mining activities, relative to the reference sites: none of these elements were enriched  $>10\times$  in peat porewaters. *Sphagnum* moss water is a promising and sustainable new tool for estimating TE bioaccessibility in contemporary atmospheric dusts of natural and anthropogenic origin.

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### Environmental significance

Open-pit mining is a significant source of atmospheric dust and trace elements (TEs) that can affect surrounding ecosystems. This study demonstrates that water extracted from living *Sphagnum* moss provides a sensitive indicator of TEs released from dust deposited by open-pit mining and other industrial activities. Elevated concentrations of dissolved TEs in moss waters near industrial sources, relative to peat porewaters, highlight the stronger influence of contemporary *versus* past atmospheric deposition. This approach offers a valuable tool for monitoring present-day airborne contaminants and assessing their ecological impacts.

## 1. Introduction

Concerns are rising globally over dust emissions from open-pit mining and related activities,<sup>1</sup> particularly due to the release of associated trace elements (TEs).<sup>2–4</sup> Open-pit mining is prevalent for extracting gold, base metals, iron and manganese ores, coal, bitumen, gravel, and limestone.<sup>5,6</sup> When these dusts enter aquatic and terrestrial ecosystems, the ecological significance of TEs in the dusts depends on their abundance in the particles,<sup>4,7,8</sup> the chemical reactivity of the dusts themselves,<sup>9–11</sup> the extent to which they are released in bioaccessible and bioavailable forms,<sup>12–14</sup> and their inherent toxicity.<sup>15,16</sup>

Ombrogenic peatlands (peat bogs) are isolated from mineral-rich waters,<sup>17</sup> and their vegetation depends exclusively on rainwater and atmospheric inputs.<sup>18</sup> Due to these characteristics, *Sphagnum* mosses from peat bogs have been used as valuable monitoring tools to study contemporary atmospheric deposition of dust,<sup>19</sup> TEs,<sup>20–24</sup> organic pollutants,<sup>25–27</sup> and microplastics.<sup>28</sup> However, far less attention has been given to the water they contain. *Sphagnum* mosses possess the ability to retain water within their dead hyaline cells,<sup>29</sup> constituting nearly 80% of the overall volume of the stems and leaves of these plants.<sup>30,31</sup> Cellular water, comprising both dead hyaline cells and living chlorophyll cells, constitutes 10–20% of the total water content.<sup>29</sup> The remaining 80–90% of water is primarily located in the pore spaces among the stems, branches, and leaves of individual plants or between plants.<sup>29,32,33</sup> Overall, the presence of dead hyaline cells and extracellular pore spaces enables *Sphagnum* plants to retain water in excess of 2000% of

Department of Renewable Resources, University of Alberta. Edmonton, AB, Canada.  
E-mail: shotyk@ualberta.ca; sundas@ualberta.ca; barrazac@ualberta.ca; na3@ualberta.ca



their dry weight.<sup>34,35</sup> The high cation exchange capacity of *Sphagnum* mosses, coupled with the release of organic acids, contributes to the low pH (3.2–4) of bog waters,<sup>36</sup> creating conditions conducive to the dissolution of chemically reactive mineral phases, such as carbonates, phosphates, and sulphates.<sup>37,38</sup> Given this, *Sphagnum* moss waters could be utilized for monitoring the release of major and TEs due to the reactivity of contemporary dusts deposited on the moss surface. However, to assess the impact of dust deposition, the only metallic element that has been analyzed in *Sphagnum* moss water to date is Ca.<sup>39</sup> No published studies appear to have examined TEs in waters extracted from *Sphagnum* mosses.

In the Athabasca Bituminous Sands (ABS) region of northern Alberta, Canada, large-scale open-pit mining and bitumen upgrading operations are significant sources of anthropogenic dust and aerosol emissions.<sup>40,41</sup> However, the reactivity of dust produced by mining activities, examined through peat porewaters, has shown a modest impact on the abundance of dissolved TEs.<sup>43,44</sup> For these studies, peat porewaters were obtained from excavated pits (30–40 cm) under *Sphagnum* carpets, at the top of the water table in the recharge zone. Age-dated peat cores from these bogs indicate that the top 30–40 cm of peat has accumulated over the past century.<sup>42</sup> The contemporary accumulation rates of acid-insoluble ash (AIA) were higher in the living *Sphagnum* moss layers of these bogs compared to the deeper peat layers that pre-date industrialization, indicating an increase in dust deposition rates since the inception of the mining industry.<sup>42</sup> These findings suggest that peat porewaters likely reflect the chemical reactivity of past atmospheric inputs, but provide little, if any, information regarding current atmospheric deposition.

The present study aims to explore the use of water from living *Sphagnum* mosses to evaluate the chemical reactivity of contemporary dusts by analyzing dissolved TEs (<0.45 μm). The primary objectives are to: (1) determine whether the elevated rates of dust deposition to peat bogs with proximity to open-pit bitumen mines and upgraders have led to elevated concentrations of any dissolved TEs in *Sphagnum* moss waters, (2) determine whether the greater contemporary rates of dust deposition have led to elevated concentrations of TEs in *Sphagnum* moss waters compared to peat porewaters, which likely reflect the impact of atmospheric deposition in the past, (3) determine whether weather conditions could significantly impact the concentrations of TEs in *Sphagnum* moss waters, and (4) evaluate the impact of dust from mining activities on the release of TEs to *Sphagnum* moss waters relative to background TE concentrations in moss waters from remote areas. The hypotheses of this study are: (1) TE concentrations in moss waters increase toward industrial areas due to the higher rates of dust deposition from open-pit mining, and (2) TE concentrations are higher in moss waters than in peat porewater from surface peat layers due to the recent increases in dust deposition.

## 2. Materials and methods

### 2.1. Sampling sites

In September 2015, *Sphagnum* moss samples were gathered from 30 bogs in the ABS region near mining activities, with two

additional bogs, Caribou Mountains Wildland (CMW) and Birch Mountains Wildland (BMW), serving as reference sites (Fig. 1). As described by Mullan-Bourdeau *et al.*,<sup>19</sup> these sites are inaccessible, thus they were approached using a helicopter. Moss samples were collected again, for three consecutive years, in September/October 2019 to 2021, from four bogs in the ABS region, where peat porewaters were also collected:<sup>44</sup> JPH4, McKay (McK), McMurray (McM), and Anzac (ANZ). During the 2019 to 2021 field campaigns, Utikuma (UTK) was used as a reference site (Fig. 1). All these sites, sampled during 2019 to 2021, were accessed by foot, from nearby roads.

To account for the influence of prevailing weather conditions during the sampling years, data on rainfall, temperature, and wind speed and direction were compiled from the Mildred Lake weather station (Fort McMurray) and are presented in Fig. S11. Other factors that could influence moss water chemistry include wildfire events and snowmelt dynamics. Although a major wildfire occurred in the study area in 2016, previous observations indicated that it was a minor contributor to TE deposition relative to ongoing industrial emissions.<sup>45</sup> In temperate bogs, snowmelt typically occurs in spring (April–May). Two subsequent sampling events conducted in June and September 2021 showed negligible variation in TE concentrations (unpublished data), suggesting that snowmelt-related effects had already stabilized prior to sampling. Therefore, these factors are unlikely to have significantly influenced moss water chemistry at our sites and were not considered further.

### 2.2. Moss samples collection and preparation

*Sphagnum* moss samples were collected at 3 locations per bog, from hummocks approximately 3 to 10 meters apart from each other, directly into inverted polypropylene (PP) boxes (21.5 cm × 21.5 cm × 7.2 cm).<sup>46</sup> After collection, the boxes were transported in coolers and stored at –20 °C until further processing. Most of the samples that were collected in 2015 by Mullan-Bourdeau *et al.*<sup>19</sup> were mostly used up in their work. However, a box of unprocessed sample from each bog site had been archived and stored at –20 °C for later use: these were used for the present study. The preferred moss species was *Sphagnum fuscum*; however, at a few sites (9 out of 37), some other moss species were collected as well, including *Sphagnum capillifolium*, *Sphagnum warnstorffii*, *Sphagnum teres*, *Sphagnum magellenicum*, and *Sphagnum russowii*.<sup>19</sup>

Moss samples were thawed at room temperature, and any foreign plant materials were removed using stainless steel (316 L) tweezers. The green, living layer of the moss samples (upper 2–5 cm) was cut using a stainless-steel knife (316 L) and transferred to polyethylene (PE) bags. Inside a metal-free, class 100 clean air cabinet, water was extracted by squeezing the PE bags containing the moss samples. Information regarding the potential impact of pressure changes during squeezing on TE concentrations can be found in the SI (Section 1, Fig. S12). The extracted water is likely a mixture of cellular water (from hyaline and chlorophyll cells) and pore water (from pore spaces among the stems, branches, and leaves of individual plants or between plants). Hereafter, the water expressed by squeezing will be



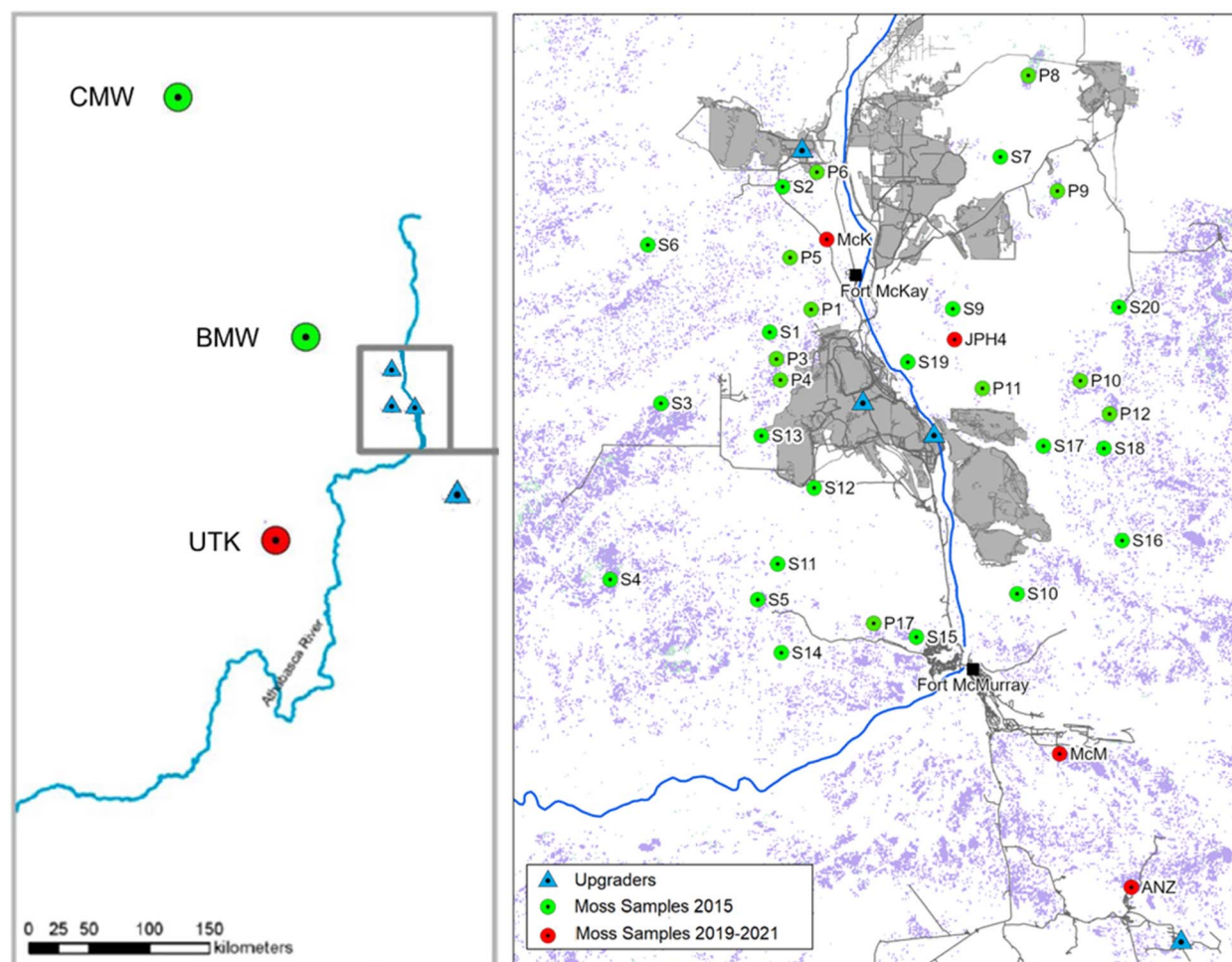


Fig. 1 Map showing the location of bog sites. *Sphagnum* mosses were sampled from bogs in the Athabasca Bituminous Sands (ABS) region, and from Caribou Mountains Wildland (CMW), Birch Mountains Wildland (BMW) and Utikuma (UTK) as reference sites.

referred to as “moss water”. Moss water was collected in centrifuge tubes and then centrifuged at 5780 RPM (equivalent to 5725 RCF) for 20 minutes. This step facilitated the removal of large particles, making the subsequent filtration process easier. Waters were then filtered through acid-cleaned 0.45  $\mu\text{m}$  polytetrafluoroethylene (PTFE) filters into acid-cleaned PP bottles. For TE analyses, samples were diluted (1 : 10) using 2%  $\text{HNO}_3$ . For chloride analysis, unacidified samples were used.

The same procedure was followed for all samples except those collected in the autumn of 2021. For these, water was directly filtered without the centrifugation step. Further, peat porewaters collected from excavated pits (30–40 cm deep) from the same sites on the same day and time, in the autumn of 2021,<sup>44</sup> were used for comparison of TE concentrations in moss water and peat porewater.

### 2.3. Sample analyses

ICP-MS (ICAP RQ, Thermo Scientific) was used to determine the dissolved concentrations of 41 TEs. The detailed methodology for this analysis is described by Shotyk *et al.*<sup>20</sup> To ensure analytical reliability and accuracy, standard reference materials

(SRMs) of natural surface waters, NIST 1640a or NIST 1643f (Elements in Natural Surface Water or Elements in Fresh Water, respectively, from the National Institute of Standards and Technology) and SPS-SW2 (Elements in Surface Water from Spectrapure Standards), were diluted and analyzed together with each set of samples. Furthermore, Sc, In, Ir, and Bi were used as internal standards. The data, including blank values, detection limits, quantification limits, and accuracy, are presented in Tables SI1–SI3. Chloride concentrations were determined using ion chromatography along with NW-LON-18 (Natural Lake water from Environment and Climate Change Canada) as a standard reference material (recovery = 104%).

### 2.4. Presentation of data

To ensure readability and focus on the key findings, this study presents only selected elements representing four geochemical groups: conservative lithophile (Al, Th, and Y), mobile lithophile (Fe, Li, Mn, and Sr), bitumen-enriched (Mo, Ni, and V), and chalcophile (As, Cd, Pb, Sb, and Tl). However, the data regarding other elements could be made available on request.



Concentration maps of TEs were created using packages *ggplot2*<sup>47</sup> and *ggmap*<sup>48</sup> in R 4.3.1.<sup>49</sup>

## 2.5. Statistical analyses

The significance of variation in TE concentrations among moss waters and peat porewaters was assessed using a *t*-test (for normally distributed data) or the Wilcoxon test (for non-normally distributed data). Additionally, the significance of interannual variations in dissolved TE concentrations over three consecutive years (2019–2021) was examined. For normally distributed data, a one-way ANOVA was conducted, followed by post hoc pair-wise multiple comparisons using the Tukey HSD test. If the data was non-normally distributed, the Kruskal–Wallis test was performed, followed by the conover test for pair-wise multiple comparisons. These statistical analyses were conducted using R with a significance level of 0.05.

Linear fit analyses were conducted to explore the correlations between selected elements at the 95% level of confidence, using OriginLab.

## 3. Results

### 3.1. Spatial distribution of TEs in *Sphagnum* moss waters

#### 3.1.1. General trends

**3.1.1.1. Sites at remote locations.** The concentrations of most TEs among the three reference sites (CMW, BMW, and UTK) showed negligible variations (Table SI4). Manganese was the most abundant element, with an average concentration of

approximately 1 mg L<sup>-1</sup> (Fig. 2). On the other hand, the least abundant elements were Y and Sb, each with concentrations of approximately 10 ng L<sup>-1</sup> (Fig. 2).

**3.1.1.2. Sites near open-pit mining.** Contrary to the reference sites, remarkable variations in the concentrations of most TEs were observed among sites in the vicinity of mining activities (Table SI4). Additionally, the most abundant element was Fe (17.5 mg L<sup>-1</sup>), and a chalcophile TE, Cd (10 ng L<sup>-1</sup>), was the least abundant (Fig. 2 and Table SI4). Notably, Fe, Y and Th were elevated to a greater extent near open-pit mining, relative to remote locations, than bitumen-enriched (Mo, Ni, and V) and chalcophile elements (As, Cd, Pb, Sb, and Tl) (Fig. 2).

#### 3.1.2. Spatial distribution

**3.1.2.1. Conservative lithophile elements.** In the ABS region, conservative lithophile elements (Al, Th, and Y) showed a distinct increase in concentrations toward mining activities (Fig. 3). Aluminum increased by a factor of 24×, Th 60×, and Y 234× (Table SI4) at sites close to mine pits relative to the distal sites (Fig. 3 and SI3). In contrast to ABS sites, lower concentrations were observed at the reference sites (Fig. 3 and Table SI4). Anzac, where a bitumen upgrader facility that was shut down in 2016 is located, but no open pit mines exist, was the only site in the ABS region where the concentration of Al was lower than the average of background concentrations at all three reference sites.

**3.1.2.2. Mobile lithophile elements.** Mobile lithophile elements such as Fe and Sr (Fig. 3) and Li (Fig. SI4) also increased toward the center of mining activities. In contrast, the variation in the concentration of Mn was independent of its

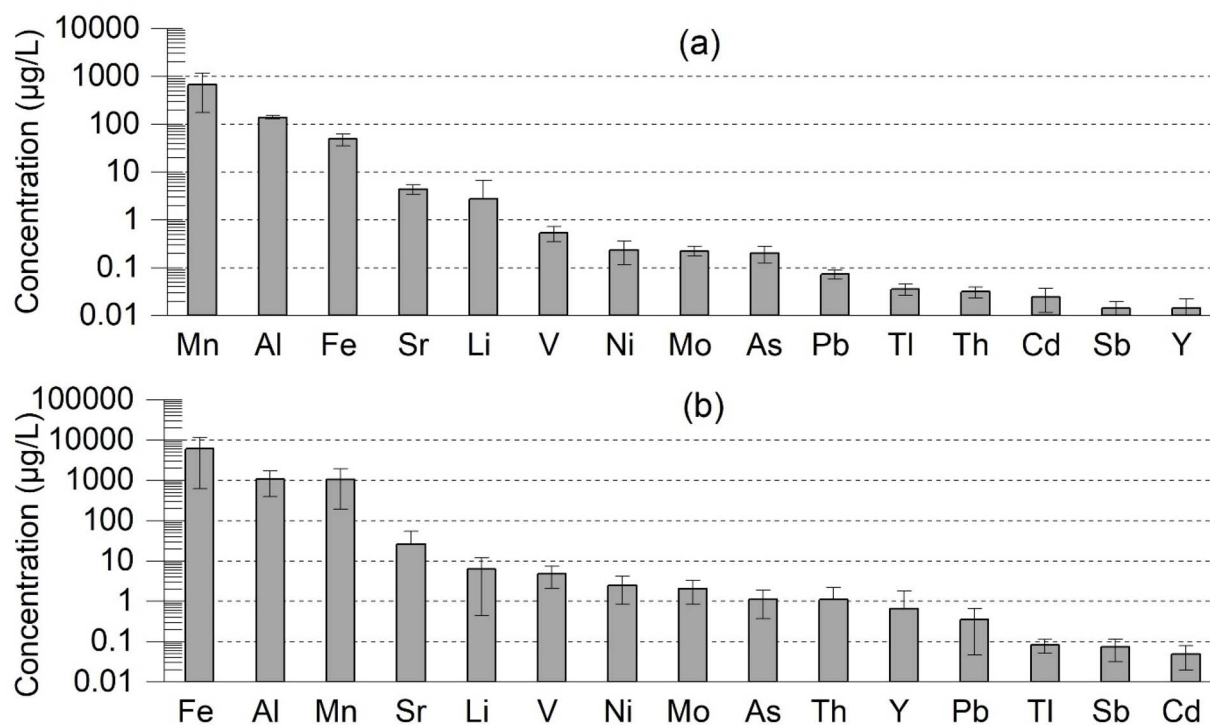


Fig. 2 Average concentrations of TEs in *Sphagnum* moss waters at (a) three remote locations (Caribou Mountains Wildland (CMW), Birch Mountains Wildland (BMW) and Utikuma (UTK)) and (b) thirty-four sites in the vicinity of mining activities in the Athabasca Bituminous Sands (ABS) region.



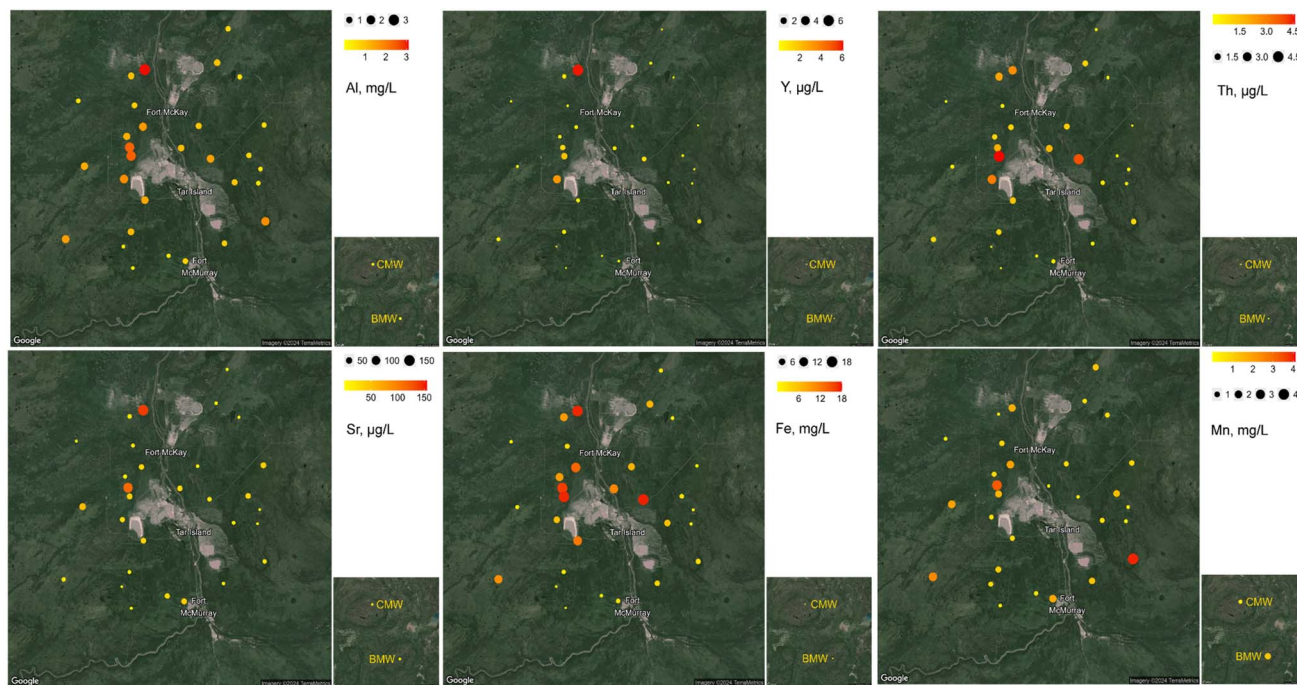


Fig. 3 Spatial variation in the concentrations of conservative (Al, Y, and Th) and mobile lithophile elements (Sr, Fe, Mn) in moss waters, in autumn 2015. Notes: CMW = Caribou Mountains Wildland and BMW = Birch Mountains Wildland. Both CMW and BMW were used as reference sites.

distance from the mining area (Fig. 3 and Table S14). Among mobile lithophile elements, the greatest variation in concentration within the ABS region was observed for Fe, up to  $235\times$ . On the other hand, Li and Sr increased only by a factor of 19 and  $50\times$ , respectively, toward the mining area.

3.1.2.3. *Elements enriched in bitumen.* Bitumen-enriched elements (Mo, Ni, and V) also exhibited increasing trends in concentration with proximity to the mining area (Fig. 4). The concentrations of all elements varied similarly, with a  $17\times$  increase observed for Ni,  $15\times$  for Mo, and  $14\times$  for V (Table S14).

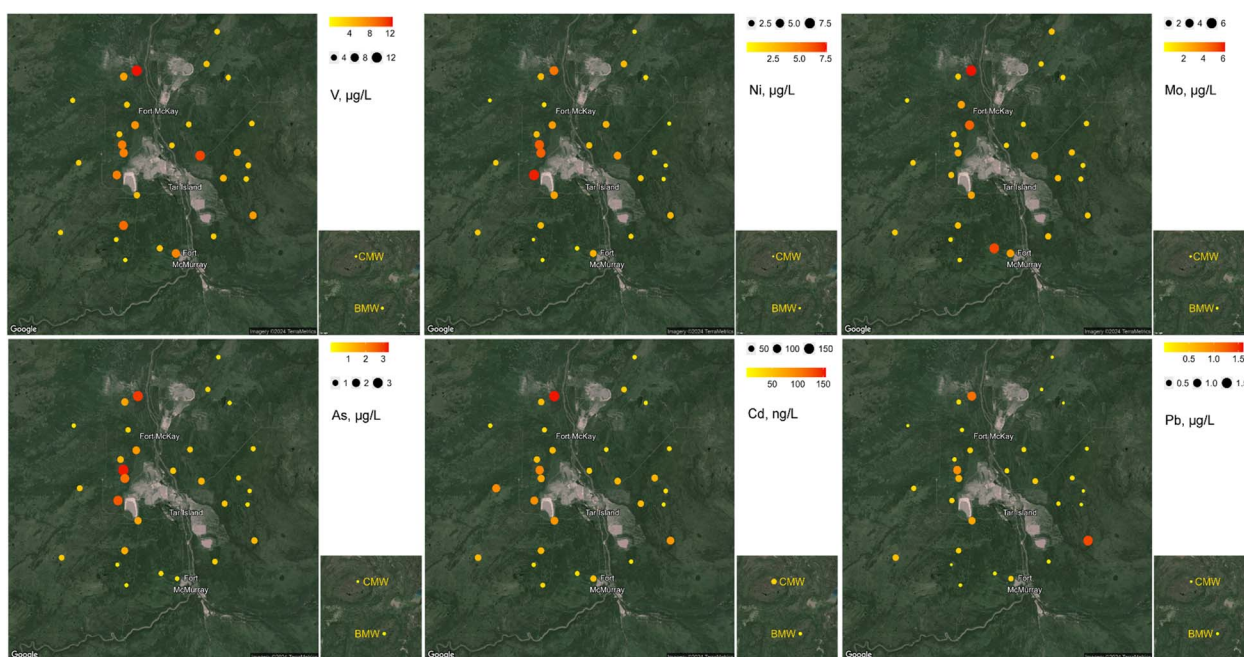


Fig. 4 Spatial variation in the concentrations of bitumen-enriched (V, Ni, and Mo) and chalcophile elements (As, Cd, and Pb) in moss waters, in autumn 2015. Notes: CMW = Caribou Mountains Wildland and BMW = Birch Mountains Wildland. Both CMW and BMW were used as reference sites.



**3.1.2.4. Chalcophile elements.** Chalcophile elements such as As, Cd, Pb, Sb, and Tl also increased in concentration toward the mining area (Fig. 4 and SI4). Lead exhibited a 50× increase toward the center of mining activities, compared to only a 13× increase observed for As (Table SI4). Modest variations with proximity to mining activities were also observed for Cd (16×), Sb (8×), and Tl (6×).

### 3.2. Moss waters vs. peat porewaters

The concentrations of some conservative (Y and Th) and mobile lithophile elements (Fe, Li, and Sr) showed significant variations between moss water and peat porewaters, only at sites in the mining area (Fig. 5). On the other hand, elements such as Al, As, Mn, Mo, Ni, Sb, Tl, and V were more abundant in moss waters compared to peat porewaters at all sites, including the reference site (Fig. 5).

### 3.3. Interannual variation

Compared to the long-term average precipitation in the ABS region, early summer precipitation was relatively low in 2019, but by the end of the growing season (May to August) accumulated precipitation had increased by 18 mm (5%) (Fig. SI1). In 2020, the growing period was relatively wet, with 91 mm (27%) more accumulated precipitation compared to the long-term average in the area. In contrast, 2021 was hot and dry, having 61 mm (18%) less accumulated precipitation compared to the long-term average in the area (Fig. SI1). To estimate the

possible importance of dilution of TEs in moss water by rain, or evaporative concentration of TEs by drought, chloride was used as a surrogate of ionic strength, owing to the conservative behaviour of this element in peat porewaters.<sup>50</sup> Despite the distinct variations in temperature and precipitation (Fig. SI1), the variation in the concentration of chloride over time and space was negligible, except at McK in 2021 (Fig. 6).

Most TEs, such as Al, As, Cd, Li, Mn, Mo, Ni, Pb, Sb, Sr, Tl, and V, were significantly higher in concentration at most sites in the autumn of 2021, compared to the preceding years (Fig. 6, SI5 and Table SI5). Thorium was the only element that showed considerably greater concentrations in 2019 at two sites closer to the mining area compared to the succeeding years (Fig. 6). On the other hand, Y and Fe showed insignificant variations across the monitoring period at most sites (Fig. 6).

### 3.4. Enrichments of TEs in moss waters of the ABS region relative to the reference sites

To evaluate the influence of dusts from mining activities on the relative abundance of TEs in moss waters, the dissolved TE concentrations at sites near mining operations were normalized to the average of TE concentrations at reference sites (CMW and BMW). Trace element enrichments at all sites in the ABS region for 2015 are presented in Table 1. Additionally, to assess the impact of variation in dust deposition, if any, over the study period 2019–2021, TE concentrations in moss waters near mining sites were normalized to their respective concentrations in moss waters from UTK collected in the

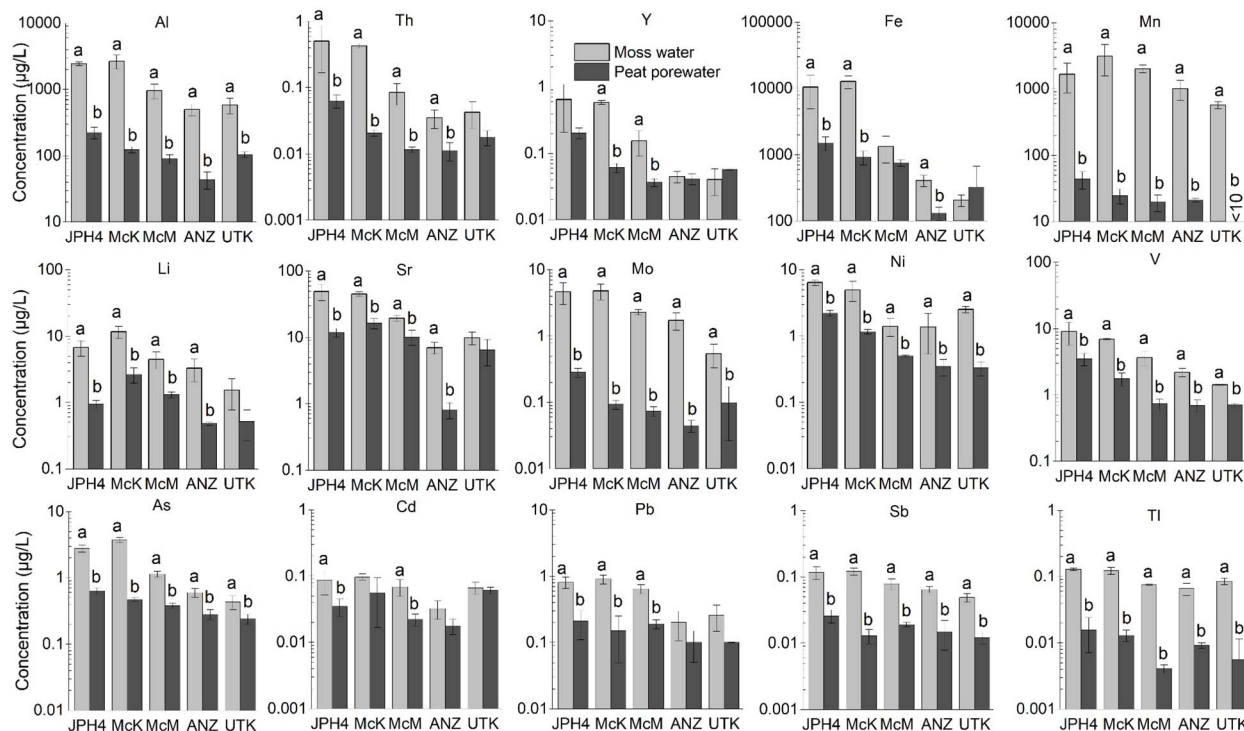


Fig. 5 Relative abundance of selected TEs in moss waters compared to peat porewaters collected from the same sites, in autumn 2021. Notes: error bars represent the standard deviation. Sites are ordered from right to left based on their proximity to the mining area. Bars with letters indicate significant differences in TE concentrations between moss water and peat porewater at that site, while those without letters indicate insignificant differences.



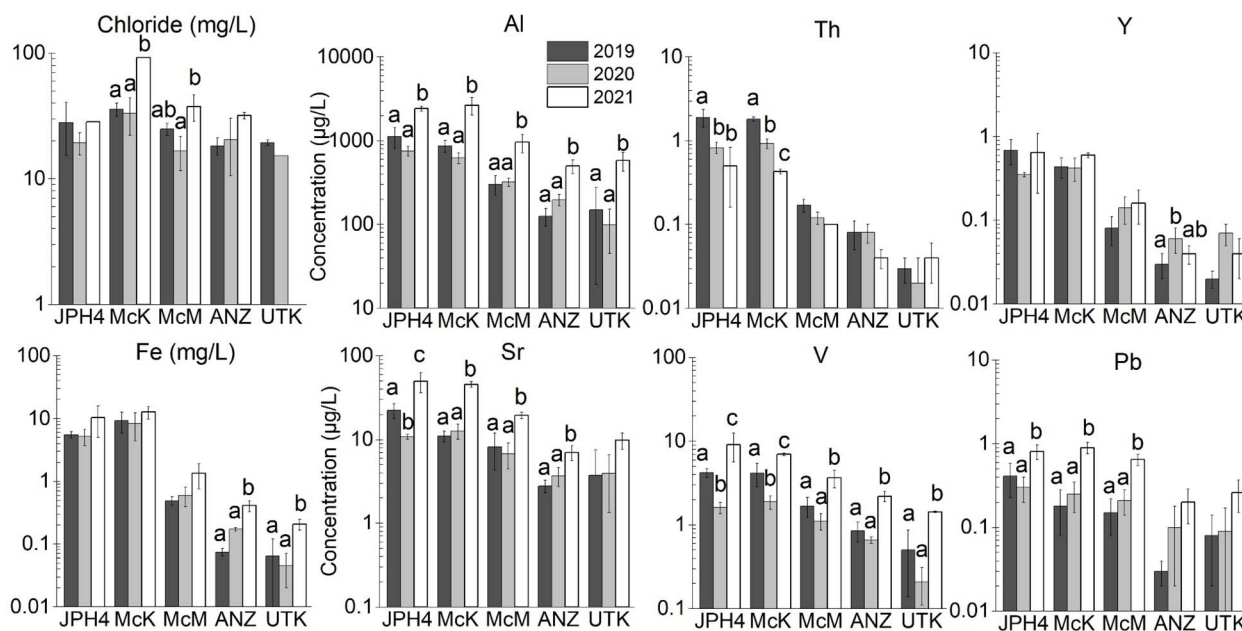


Fig. 6 Interannual variation in the concentrations of chloride and selected TEs in moss waters. Notes: error bars represent the standard deviation. Sites are ordered from right to left based on their proximity to the mining area. Bars having different letters indicate significant interannual variations in concentration at that site, while those sharing the same letter or are without letters indicate insignificant differences.

corresponding year. The TE enrichments from 2019–2021 are presented in Table SI6.

#### 3.4.1. 2015

**3.4.1.1. Lithophile elements.** Relative to the background concentrations of TEs at the reference sites, the top three enriched elements in moss waters near the mining operations were Fe, Th, and Y (Table 1). Overall, Y, Fe, and Th enrichments reached factors of up to 600, 400, and 140, respectively. In contrast, enrichments of other lithophile elements, such as Al, Li, and Sr, were only up to 30 $\times$  (Table 1). Among the 30 bogs studied in the ABS region, enrichments greater than 10 $\times$  relative to the background concentrations were observed at a minimum of 20 sites for Y, Fe, and Th; at 10 sites for Al; and only at 3 sites for Sr.

**3.4.1.2. Bitumen-enriched elements.** Nickel was the most enriched element in moss waters in the vicinity of mining activities (Table 1), showing enrichments up to 40 $\times$ , relative to the reference sites. Most sites showed enrichments greater than 10 $\times$  for Ni, while fewer sites exhibited such high enrichment for V and Mo (Table 1).

**3.4.1.3. Chalcophile elements.** In comparison to the maximum enrichments observed for conservative and bitumen-enriched elements (up to 600 and 40 $\times$ , respectively), enrichments of chalcophile elements were no more than 20 $\times$  (Table 1). Antimony exhibited enrichment greater than 10 $\times$  at 7 sites, whereas As and Pb at only 4 sites near mining activities (Table 1).

**3.4.2. 2019–2021.** In 2019, 9 and 7 out of the 15 selected elements presented here exhibited enrichments >10 $\times$  at the JPH4 and McK sites, respectively (Table SI6). However, in the following years, the number of elements with enrichments

exceeding 10 $\times$  decreased to 3 or 4. Throughout the monitoring period from 2019 to 2021, the most enriched elements were Fe, Th, and Y (excluding Y in 2020), consistent with observations from 2015. In contrast to 2015, Mo became the most enriched element among bitumen-abundant elements at almost all sites (Table SI6). Molybdenum was also one of the 4 elements that showed enrichment >10 $\times$  in 2020.

On the other hand, none of the chalcophile elements (Cd, Pb, Sb, and Tl) demonstrated enrichments >10 $\times$ , except for As in 2019. Overall, the lowest enrichments for most TEs were observed in 2021, compared to the prior years.

## 4. Discussion

### 4.1. Trace elements in moss waters: evidence of dust dissolution

**4.1.1. Conservative lithophile elements.** The ash content of *Sphagnum* mosses is an indicator of the rate of dust deposition, and increases toward industry.<sup>19,46</sup> Conservative lithophile elements (Al, Th, and Y) in moss waters exhibited a positive correlation (Adj.  $R^2 = 0.55$ – $0.66$ ) with the ash content of *Sphagnum* mosses. This correlation, coupled with a gradual increase in the dissolved concentrations with proximity to the mining area (Fig. 3), suggests that their abundance in moss waters is mainly a reflection of enhanced deposition of atmospheric dusts.

Aluminum concentrations near mining activities reached up to 3 mg L<sup>-1</sup> (Tables SI4 and SI5). However, Al concentrations in moss waters remain undersaturated with respect to both gibbsite and amorphous Al hydroxides (Table SI7). Of the industrial sites, note that the lowest concentrations of dissolved Al occur





**Table 1** Enrichments of TE<sub>s</sub><sup>a</sup> in moss waters at industrial sites compared to their concentrations at the reference sites (autumn 2015)

Site	Fe (EF)	Site Y (EF)	Site Th (EF)	Site Ni (EF)	Site Al (EF)	Site V (EF)	Site Mo (EF)	Site Sb (EF)	Site Pb (EF)	Site As (EF)	Site Sr (EF)	Site Tl (EF)	Site Cd (EF)	Site Mn (EF)	Site Li (EF)
P11 398	P6 610	P4 142	S13 42	P6 23	P6 22	P6 26	S2 15	S16 19	P3 14	P6 30	P4 4	P6 6	S16 5	P3 9	
P6 394	S13 334	P11 121	P3 35	P4 18	P11 19	P17 23	P6 13	P6 16	P6 13	P3 25	S12 4	P3 4	P3 4	P6 5	
P4 393	P4 195	S13 95	P4 34	P3 18	S11 16	P1 21	S7 13	P3 13	S13 12	S3 12	S13 3	S3 3	S4 3	S2 3	
P3 371	P3 129	P6 83	P6 30	S13 14	P3 14	S15 14	S13 13	S12 10	P4 10	P4 9	S3 3	S13 3	S3 2	S13 3	
P1 313	P11 93	S2 66	P11 23	S16 14	S13 14	P5 13	P4 12	P4 9	P1 8	S15 8	S7 3	S12 3	P1 2	P4 2	
S12 283	S2 74	P3 59	P1 22	P1 12	P4 14	S12 12	P3 11	S4 8	S2 7	S20 8	S1 3	S16 3	S15 2	P11 2	
S19 252	S11 71	S19 55	S12 21	S4 12	S15 14	P11 12	P1 10	P11 6	S12 7	S12 8	P3 3	P4 3	P6 2	P1 2	
S4 236	S16 69	S12 45	S15 18	P11 11	P1 12	P4 11	S1 9	P1 6	S11 6	P10 8	S11 3	P10 2	P4 2	S4 2	
S2 211	S12 65	S9 38	S9 18	S12 10	S16 11	S17 9	S12 9	S11 6	P11 6	P1 7	S16 3	S11 2	P10 2		
S1 209	S19 64	S7 36	S16 16	S3 10	S2 11	S11 9	S15 8	S15 5	S1 6	S19 7	P11 3	P11 2	S10 2		
S9 162	S4 59	P1 34	S7 16	S1 9	P10 10	S10 9	P11 8	S13 5	S16 5	P17 7	S19 3	S4 2			
S7 162	P1 54	S11 32	S2 16	S11 8	S17 9	P10 9	S9 7	S3 5	S19 4	S13 6	P1 3	P1 2			
S13 140	S1 53	S16 31	S11 15	S19 8	S12 8	P8 9	S10 6	S9 4	S17 4	S2 5	S9 2	S2 2			
S17 137	S9 34	S1 31	S1 15	S7 8	P17 7	S13 8	S11 6	S2 4	S3 4	P11 5	P6 2	S17 2			
S10 89	S7 33	S4 29	S19 15	S2 8	S7 7	S16 8	P5 5	P10 4	S9 4	S4 4	S2 2	S1 2			
S16 84	S17 29	S17 21	S17 13	S9 7	P5 7	S1 7	S5 5	S19 4	S4 4	S16 4	S17 2	S15 2			
P5 78	S3 29	S15 16	S3 11	S17 7	S1 6	S2 7	S6 5	S1 3	S10 4	S1 4	S15 2	S19 2			
S15 61	P10 22	S3 16	S4 11	P5 6	P12 6	S4 7	S16 5	S17 3	P5 3	P5 3	S4 2	S7 2			
P10 61	S10 21	S10 14	P10 10	S10 6	S10 6	P3 7	S17 5	P5 3	S7 3	S11 3	P9 2				
S11 53	S15 21	P5 14	S10 9	S15 6	S19 6	S3 7	S4 4	S10 3	S20 3	S17 3	S6 2				
P8 48	P5 18	P12 10	P9 8	P10 5	S9 6	S20 6	S18 4	S20 3	P10 3	S7 3	P12 2				
S3 43	S6 16	S18 10	P5 8	P8 5	S3 6	S19 6	S3 4	P17 2	P17 3	S10 3	S20 2				
P9 34	S18 15	P9 8	P8 7	S20 4	P8 6	S7 6	S19 4	S14 2	S15 2	S9 3	P10 2				
P17 30	S20 12	P10 8	P17 7	P9 4	S20 6	S18 6	P12 4	S7 2	P8 2	P8 2	S10 2				
S6 28	P12 11	P17 7	S18 6	S6 4	S18 5	S9 6	P8 3	S18 2	P12 2	P9 2					
S20 28	P17 11	P8 7	P12 6	S18 4	P9 5	P9 5	P9 3	P12 2	S6 2	S14 2					
S18 25	P9 10	S6 5	S14 5	P12 3	S6 5	P12 5	P17 3	S18 2	S18 2						
P12 21	P8 8	S20 3	S20 5	P17 3	S4 5	S14 4	P10 3	P9 2	P9 2						
S5 13	S14 6	S14 3	S6 5	S5 2	S5 4	S5 4	S20 2	S5 2	S5 2						
S14 9	S5 5	S5 2	S5 3	S14 2	S14 3	S6 4	S14 2	S14 2	S14 2						

<sup>a</sup> Only sites with TE enrichments  $\geq 2$  are listed, ordered by decreasing enrichment from top to bottom.

at ANZ (Table SI4), even though this site has the lowest pH (Table SI7). This observation indicates that pH is not the dominant factor controlling the Al concentrations. Given that there are no open-pit mines at ANZ, the low concentrations of Al at this location suggest that dust deposition is the most important influence on dissolved Al in bog waters: these findings further support the use of Al in bog waters as an indicator of the extent of dust dissolution.<sup>44</sup>

Heavy minerals such as monazite and zircon, which often contain very high concentrations of Th and Y,<sup>51</sup> were also identified in the bituminous sands of Alberta.<sup>52–56</sup> Thus, the observed increase in dissolved concentrations of Y and Th with proximity to mining sites suggests that either these minerals are dissolving in moss waters or occur in colloidal forms. Considering the low solubility of these minerals, even under acidic conditions,<sup>57–59</sup> it is more likely that the elevated concentrations of Y and Th in moss waters reflect the abundance of colloidal forms of these metals.<sup>44</sup>

**4.1.2. Mobile lithophile elements.** Elevated rates of dust deposition near mining activities have also caused an increase in the dissolved concentrations of Fe in moss water (Fig. 3). While Fe is an essential micronutrient for plants<sup>60</sup> and its concentration in plant fluids can be influenced by biological cycling, a strong positive correlation between dissolved Fe and Y (Adj.  $R^2 = 0.7$ ) indicates that Fe in moss waters is primarily due to dust deposition, which increases toward industry. Chemically reactive hosts of Fe in these dusts include Fe-containing carbonate, sulphide, sulphate, and oxide/hydroxide minerals occurring in the ABS ores, including siderite, hematite, ilmenite, magnetite, pyrite, jarosite, goethite, and wustite.<sup>53,56,61,62</sup> The low pH, abundance of organic ligands, and reducing conditions of bog waters provide ideal conditions for the dissolution of these minerals.<sup>37,63–67</sup> Given the abundance of Fe in moss waters and its sensitivity to rates of dust deposition, combined with the ease with which it can be measured in the laboratory, Fe is a promising indicator of the chemical reactivity of atmospheric dusts.

In the ABS ores, Fe-rich oxides and carbonates also contain Mn<sup>61,62</sup> and thus are its potential sources to bog waters. Nevertheless, no correlation was observed between the distribution of Fe and Mn in moss waters (Adj.  $R^2 = 0.01$ ). The variation in Mn concentration in moss waters was independent of its proximity to the mining area (Fig. 3), similar to the spatial pattern observed for bog vegetation such as lichens, berries, Labrador Tea, and mosses from the ABS region.<sup>46,68–70</sup> While low pH and anoxic conditions promote the dissolution of oxides and oxyhydroxides of both Fe and Mn, the lack of correlation between these two elements in moss waters suggests that some other factor is influencing Mn: this is most likely the efficient biological uptake of Mn by *Sphagnum* mosses, as described elsewhere.<sup>71–73</sup> Thus, Mn is not suitable to be used as a monitor for regional atmospheric deposition, as highlighted by Pakarinen.<sup>74</sup>

The reactivity of dust and the subsequent release of TEs were also underscored by the increase in concentrations of Li (Fig. SI4) and Sr (Fig. 3) toward mining activities, most likely associated with reactive mineral phases such as carbonates and sulphates.

**4.1.3. Bitumen-enriched elements.** Although Ni and V occur predominantly in the bitumen fraction of the ABS,<sup>75</sup> in *Sphagnum* moss collected within this region, they are mainly supplied by mineral dust.<sup>20,46</sup> In moss water, their strong positive correlations with Y (Adj.  $R^2 \geq 0.7$ ; Fig. 7) indicate active dissolution of their mineral hosts. Vanadium and Ni concentrations in the ABS and its fractions<sup>75</sup> indicate V/Ni ratios of 2.6 in bulk ABS, 2.9 in bitumen, and 2.3 in the mineral fraction. Although the average ratio of V/Ni in moss waters (2.2) is similar to the mineral fraction of ABS, the spatial variability of V/Ni ratios across the ABS region (Table SI8) suggests contributions from multiple sources to their concentrations in moss waters. The V/Ni ratios observed in moss waters are also comparable to those reported for geomaterials from the ABS region, including soils ( $3.1 \pm 0.5$ ), overburden ( $2.9 \pm 0.4$ ), road construction materials (type 1 ( $1.8 \pm 0.7$ ) and type 2 ( $3.5 \pm 0.9$ )), and tailings ( $2.4 \pm 0.8$ ).<sup>76</sup> These similarities indicate that these geomaterials likely represent potential sources of fugitive dusts affecting our sampling sites (Fig. SI3).

Despite the increase in Mo concentration toward industry (Fig. 4), its weak correlation with Y (Adj.  $R^2 = 0.3$ ; Fig. 7) suggests that in moss waters, Mo is not primarily controlled by dust-derived inputs. A similar pattern was reported for the acid-soluble fraction of snow collected along the Athabasca River ((Adj.  $R^2$  for Mo–Y = 0.2)<sup>77</sup>), where elevated Mo may reflect its use as a catalyst for hydrocarbon upgrading and refining. Moreover, the markedly lower V/Mo and Ni/Mo ratios in moss waters (2.5 and 1.3, respectively, Table SI8) compared to those calculated for bulk ABS (24 and 9), bitumen (23 and 8), and the mineral fraction (44 and 19)<sup>75</sup> indicate relative enrichment of Mo, further supporting an additional industrial source beyond mineral dust. Regardless of the source, Mo in moss waters still serves as an indicator of local anthropogenic inputs, as suggested by Javed *et al.*<sup>78</sup>

**4.1.4. Chalcophile trace elements.** In the moss plants themselves, strong positive correlations between chalcophile elements (As, Pb, Sb, Tl) and conservative lithophile elements (either Sc, Th, or Y), and their increasing concentrations toward industry,<sup>21,46,79</sup> suggest that they occur mainly in the form of mineral dusts. In moss waters, the moderate correlation between these elements and Y (Adj.  $R^2 \geq 0.6$ ) (Fig. SI6) suggests that some fractions of the dust are dissolving, releasing these elements to solution.

## 4.2. Trace elements in moss water vs. peat porewater: reflections of the changing rates of dust deposition

Significant differences in the abundance of TEs in moss water and peat porewater (Fig. 5) collected from the same sites likely reflect changes in the rates of dust deposition over time. This interpretation is supported by an increase in the cumulative mass of AIA in peat accumulated between 1985 and the time of sampling (2013 and 2014), *versus* the amount of peat accumulated between 1900 and 1960: these two time intervals are representative of the post and pre-industrial periods in the region, respectively.<sup>42</sup> This trend in AIA deposited from the air to the bogs was observed at sites near mining activities in the ABS region: JPH4 (AIA:  $56 \text{ g m}^{-2}$  in the post-industrial period *vs.*  $10 \text{ g m}^{-2}$  in the pre-industrial period).



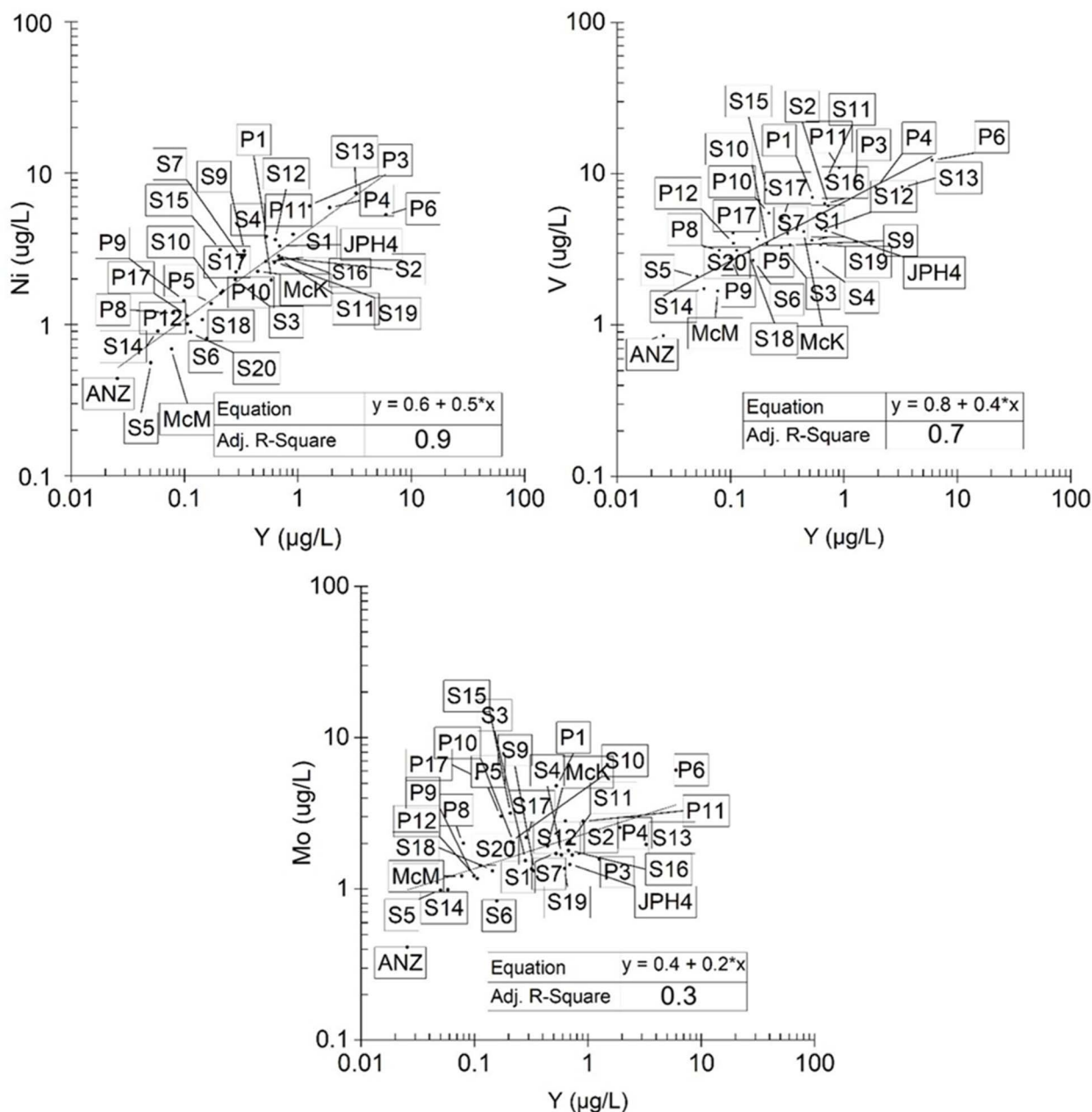


Fig. 7 Correlation between bitumen-enriched elements (Ni, V, and Mo) and Y in moss waters collected from bog sites in the Athabasca Bituminous Sands region.

$\text{m}^{-2}$  in the pre-industrial period), McK (AIA:  $95 \text{ g m}^{-2}$  vs.  $1 \text{ g m}^{-2}$ ), McM (AIA:  $30 \text{ g m}^{-2}$  vs.  $15 \text{ g m}^{-2}$ ), and ANZ (AIA:  $34 \text{ g m}^{-2}$  vs.  $20 \text{ g m}^{-2}$ ), as well as at the reference site UTK (AIA:  $22 \text{ g m}^{-2}$  vs.  $14 \text{ g m}^{-2}$ ). At McK, McM, ANZ and UTK, the depth of the pits excavated for collecting peat porewaters (30–40 cm) is similar to the depth of peat accumulated (25–35 cm) between approximately 1967 and the date of collection (2013 and 2014). At these locations, therefore, TEs in peat porewaters (Fig. 5) reflect interactions between bog waters and atmospheric dusts deposited in the past, when dust deposition rates were lower. Consequently, TE enrichments in peat porewaters near mining activities were only up to  $10\times$  relative to background concentrations at UTK.<sup>44</sup>

#### 4.3. Trace elements in moss waters: effect of weather conditions vs. dust dissolution

Moss waters are exposed to the atmosphere, unlike peat porewaters collected from 30–40 cm deep pits. While the difference in TE concentrations in moss waters and peat porewaters implies greater rates of dust deposition to moss, the possible importance of evaporative concentration in moss water cannot be overlooked. Therefore, further scrutiny was needed to determine whether TEs in moss waters are predominantly influenced by weather conditions.

The variation in chloride concentrations over three consecutive years (Fig. 6) was negligible, irrespective of the weather



conditions (Fig. S11). Thus, the differences in TE concentrations (Fig. 6) cannot be ascribed to evaporative concentration. The exception is the elevated chloride concentration in moss waters at McK in the autumn of 2021, compared to all other sites, which aligns with the spatial distribution of chloride in peat porewaters,<sup>43,44</sup> likely due to road salt inputs.

In the autumn of 2021, significantly higher concentrations of lithophile elements, such as Al, Li, and Sr, were found at all sites in the ABS region compared to prior years (Fig. 6 and SI5). These lithophile elements were observed as indicators of dust dissolution in peat porewaters.<sup>43</sup> Thus, higher concentrations in moss water collected in the autumn of 2021 are likely due to greater rates of dust deposition at that time.

Although most TE concentrations were higher at all sites near mining activities in the autumn of 2021 compared to the preceding years (2019 and 2020) (Fig. 6 and SI5), their enrichments relative to the reference site were lower (Table SI6). This implies that greater dust deposition in 2021 may not be directly linked to increasing industrial development in this area. Instead, it could be due to a rise in windblown fugitive dust emissions from dry surfaces, driven by prevailing dry weather conditions.<sup>80,81</sup> Therefore, TE concentrations in moss waters at both industrial and reference sites were increased in the autumn of 2021 (Fig. 6 and SI5). Overall, the predominant influence of dust deposition on TE concentrations in moss waters suggests that these fluids have great potential as indicators of the impacts of the rates of deposition and chemical reactivity of atmospheric particles.

#### 4.4. Implications of dust dissolution on bog ecosystems near mining activities

Mineral dust dissolution in moss waters closer to open-pit mining areas could impact the bog ecosystem by releasing both essential and chalcophile TEs.

**4.4.1. Aluminum.** At pH levels below 4, Al<sup>3+</sup> becomes the dominant aqueous species,<sup>82</sup> a form which is toxic at micromolar concentrations to plants.<sup>83–85</sup> Aluminum toxicity is a major factor limiting plant diversity in peat bogs, particularly where Al concentration exceeds 0.2 mg L<sup>-1</sup>.<sup>86</sup> Notably, the concentrations of Al closer to mining activities were up to 3 mg L<sup>-1</sup> (Tables SI4 and SI5). Despite these elevated concentrations, moss waters remain undersaturated with respect to gibbsite and amorphous aluminum silicates (Table SI7). The relatively low concentrations of Al (Table SI5), compared to those expected based on moss water pH (Table SI7), suggest two possible explanations. First, other minerals or amorphous phases, rather than gibbsite and amorphous aluminum silicates, may control the solubility of Al. Alternatively, Al liberated by dust dissolution is effectively removed from the aqueous phase by adsorption or surface complexation by *Sphagnum* mosses. The latter explanation is further supported by the increasing trend in Al concentrations in the acid-soluble ash (ASA) fraction of *Sphagnum* mosses, obtained by leaching ash with 2% HNO<sub>3</sub> for 15 min, toward industry.<sup>46</sup> These findings establish a direct link between anthropogenic Al inputs to peat bogs and their accumulation in bog vegetation. However,

they provide limited insight into the potential impact on plant health. Furthermore, in the present study, dissolved concentrations were determined in the conventional way (*i.e.* <0.45 μm), while recognizing the possible importance of Al associated with organic and inorganic colloids.<sup>87</sup> Therefore, further study is required to determine the concentrations of truly dissolved Al (*i.e.* in the form of ions and small molecules) in moss waters receiving substantial dust inputs, and the possible impacts of these forms of Al on the health of bog plants.

**4.4.2. Micronutrients.** Among the studied TEs, essential micronutrients for plants include Fe, Mn, Mo, and Ni. The addition of these micronutrients to bogs, which are naturally nutrient-poor ecosystems, could disrupt the nutrient balance. The abundance of Fe was particularly impacted by dusts from mining activities, showing enrichment up to 400× near mining activities, relative to reference sites (Table 1). Similarly, Ni concentrations in moss waters were enriched close to mining activities by up to 40×. In contrast, Mo, while less affected by dust dissolution, seemed to be influenced by other industrial activities such as bitumen upgrading, with a 20× enrichment observed at sites close to industry. These findings underscore the significant impact of industrial activities on the abundance of micronutrients in bog waters. The increased availability of nutrients could potentially reduce the growth and productivity of *Sphagnum* mosses, which are adapted to nutrient-poor environments.<sup>39</sup> Consequently, regions experiencing elevated dust deposition might see a shift in species composition, with other mosses and higher plant species potentially dominating over *Sphagnum*.<sup>88,89</sup>

**4.4.3. Chalcophile elements.** Although chalcophile element concentrations in bog waters were influenced by dust dissolution, their enrichments were no more than 20×, relative to the reference sites. Among the chalcophile elements studied, only three (As, Pb, and Sb) showed enrichments >10× at a few sites closer to mining activities (Table 1). These findings indicate a more modest impact of industrial development on the release of these chalcophile elements to bog waters in the ABS region. For context, the global average concentrations of these 3 elements (As, Pb, and Sb) in uncontaminated river water are 620, 79, and 70 ng L<sup>-1</sup>.<sup>90</sup> In the moss waters near the bitumen mines and upgraders, the average concentrations are 1128, 350 and 73 ng L<sup>-1</sup>. Considering the profound differences in pH of bog waters (approximately 4) and river waters (approximately 6 to 7), some of these differences in TE concentrations may simply be due to differences in pH. Additional studies of TEs in bog waters from other regions will help to provide further context for the results presented here.

## 5. Conclusions

The reliable determination of TEs in moss waters from ombrogenic peatlands offers a novel approach for quantifying the impacts of differences in the rates of dust deposition and the chemical reactivity of these particles on aquatic ecosystems. Given that TE concentrations are significantly greater in moss waters compared to peat porewaters, the former is a better guide to the



environmental significance of contemporary dust deposition. Further, greater concentrations bring with them more accurate and precise measurements, further improving the value of the data. Therefore, to accurately determine the effects of current dust and aerosol emissions on the surrounding environment, monitoring the water from the living moss layers is preferred.

Monitoring moss waters, as opposed to peat porewaters, allows for the detection of annual variations in atmospheric deposition. This is because moss waters reflect short-term interactions (within a single growing season) between dust particles and aerosols with plant surfaces, plant fluids, and porewaters. Additionally, sampling moss waters is more sustainable in the long term. Extracting peat cores involves disturbing the bog surface, which is not ideal, especially in protected areas where conservation efforts may restrict such activities. Conversely, moss water can be extracted in the field by gently squeezing the moss, without cutting it from the surface.

Contemporary dust emissions from mining activities clearly influence the dissolved concentrations of lithophile elements, but also essential plant micronutrients such as Fe and Ni. They also affect elements such as Al, As, and Pb to a lesser extent. While all of these elements are impacted by mineral dusts, dissolved Mo appears to be more affected by other industrial activities, such as bitumen upgrading. This indicates that moss water serves as an effective medium for studying the bioaccessibility of TEs from diverse sources. Moreover, they hold promises for studying the fate of other significant atmospheric contaminants, such as fallout radionuclides, nanoparticles, and microplastics. The water expressed from *Sphagnum* moss, therefore, represents an exciting new tool for the broader goals of environmental monitoring and atmospheric pollution research.

## Author contributions

S.A. Butt: methodology, data curation, formal analysis, visualization, writing – original draft. F. Barraza: supervision, formal analysis, validation, writing – review & editing. N. Chen: methodology, formal analysis, writing – review & editing. W. Shoty: conceptualization, funding acquisition, investigation, methodology, project administration, supervision, validation, writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Ref. 44 of the main manuscript is also cited in the SI, Fig. S14. Supplementary information: details of an experiment performed to justify our methodology; in addition, several figures and tables which are integral to the research, but were excluded from the main manuscript to maintain clarity and focus on the core message; QA/QC data. is available. See DOI: <https://doi.org/10.1039/d6ea00015k>.

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