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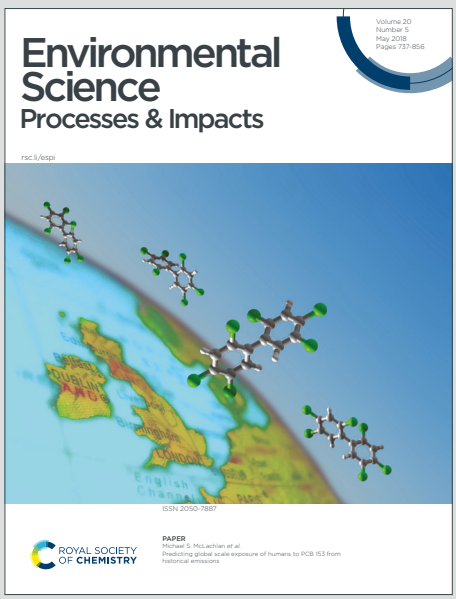

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Environmental Significance Statement:

Industrial activities such as open pit mining are thought to affect the environment due to the presence of trace elements (TEs) in the dusts they emit. Beyond determining TE concentrations, it could be useful to also assess their association to colloids and ionic species. We studied the total, particulate, "filterable", and "truly dissolved" concentrations of TEs in the particulate matter occurring in snow deposited along a boreal river which bisects the Athabasca Bituminous Sands (ABS) region in Canada. The 11 TEs studied were predominantly found in the particulate fraction. The "filterable" fraction was dominated by ionic and small species (below 300 Da). However, the concentrations of TEs in this fraction were extremely low, suggesting limited bioaccessibility to aquatic organisms.

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Size-resolved analyses of trace elements in snow from an open-pit bitumen mining and upgrading region

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ABSTRACT

Dust containing potentially toxic trace elements (TEs) from open pit mining, smelting of metallic ores, aggregate extraction, and road dust is a major concern worldwide. The potential ecological significance of TEs in these dusts, however, depends not only upon their concentrations, but also their physical and chemical forms. Here, dusty snow from the Athabasca River (AR) which bisects an open-pit bitumen mining and upgrading area in Canada was collected to perform size-resolved analysis of selected TEs. Conservative, lithophile (Al, Th, Y), bitumen-enriched (Mo, Ni, V), and chalcophile (As, Cd, Pb, Sb, Tl) elements were overwhelmingly found in the particulate fraction (> 0.45 μm), with concentrations increasing toward industry. The mineralogical composition of this fraction was similar to dusts from natural and anthropogenic sources in the area. In the "filterable" fraction (< 0.45 μm), Al, Mo, and V in snow were elevated near industry. Within the filterable fraction, TEs occur predominantly in the "truly dissolved" fraction (< 300 Da): these are

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assumed to be ionic species and small molecules, and represent potentially bioavailable species. However, the concentrations of TEs in this fraction were extremely low: for perspective, Cd and Pb are similar to values reported for ancient Arctic ice. Within the filterable fraction at midstream sites, up to 30% of Ni and 37% of Y were associated with organic colloids (≈1 kDa) which may be from bitumen and soil-borne sources, respectively. Except for V, TE concentrations in the filterable fraction of snow were below the average values for the AR and the global average for uncontaminated river water. Consequently, the threat to aquatic life in the river by TEs in snowmelt may be limited.

KEYWORDS: trace elements, AF4-ICPMS, ionic species, bioavailability, dust, oil sands

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1. INTRODUCTION

Atmospheric dust is increasing considerably from industrial development, changing land-use activity and climate change-induced drought.[1–3] Anthropogenic dust from wind erosion of land-disturbed areas accounts for approximately 30 to 70% of the total global dust flux.[2] Significant portions of these dusts are from open pit mining of coal,[4,5] iron and base metal mining and smelting,[2,5–7] aggregate extraction,[5,8] and road dust.[6,9] Natural sources include wind erosion of soils, especially deserts in arid and semi-arid regions,[2,10] sea salt spray,[10,11] volcanic emissions,[10,11] and wildfires.[3,10]

Mechanical processes generate coarse dust particles with most of their mass present in the 2.5 to 10 μm diameter size range[12,13]. Fine particles (< 2.5 μm) on the other hand, are generated by combustion processes at high temperatures.[10,13] Fine particles and nanoparticles (1,000 nm) tend to be more toxic than the larger ones due to their smaller size and larger surface area,[4,11] posing environmental risks to living organisms.[10,14] The chemical composition of these dusts also plays a critical role given that they may contain potentially toxic contaminants such as Cd, Pb, and other trace elements (TEs).[2,5,10,14]

In the northern hemisphere, up to one-third of the land is covered with snow for a minimum of three months per year.[15,16] When wet deposition occurs, light absorbing dust particles can darken snow and ice packs[12,17] reducing albedo, accelerating snowmelt and reducing snow cover.[1,17] Snowmelt water is a critical source of freshwater, accounting for 50 to 80% of total runoff.[16] In spring, the concentrations and bioaccessibility of TEs in rivers and lakes receiving snowmelt can fluctuate markedly, presenting challenges for the protection of aquatic organisms[17,18] particularly during the spawning season.

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Previous research has examined the size distribution of particles containing TEs in order to better understand their bioaccessibility and their potential bioavailability to living organisms.[18] These studies include surface waters of large boreal rivers,[19–26] permafrost peatlands,[27] rainfall and snowmelt runoff,[28] and snow[24]. Other studies focused on the analytical challenges posed by available methodologies for size-resolved analysis of TEs such as asymmetric flow field-flow fractionation (AF4) coupled to inductively coupled plasma mass spectrometry (ICP-MS).[29–31]

In the Athabasca Bituminous Sands (ABS) region of northern Alberta, Canada, open pit bitumen mining and upgrading generate considerable amounts of dust.[32–35] Research conducted in the area include studies of total, particulate (> 0.45 μm), and dissolved (< 0.45 μm) TEs concentration in surface waters,[19,20,36,37] moss,[38–40] peat bog porewaters,[41] peat cores,[42,43] lichens,[44,45] berries,[46,47] and snow.[19,37,48–52] More precisely, our previous studies in river waters and snow focused on the spatial[20,36,50] or spatiotemporal variation of TEs,[20,49] the reactivity of TEs in dust deposited on snow,[48,49] the size-resolved analysis of Pb in river waters and snow from peat bogs[19] and the distribution of TEs among colloidal and ionic forms in river waters.[20,25] These publications highlighted the abundance and predominance of TEs in the particulate form, low concentrations of elements of concern in the dissolved fraction (below water quality guidelines), and limited solubility of the dusts containing TEs.

Snowmelt, rainfall, peatland runoff as well as groundwater and inputs from tributary rivers all contribute water to the lower Athabasca River (AR), which bisects the ABS region.[53,54] Given that the AR drains into Lake Athabasca by forming the Peace-Athabasca-Delta (PAD), a UNESCO world heritage site,[55] it is vital to understand how the size and speciation of TEs in dust deposited within the ABS region may affect their bioavailability in the river and its delta. Snow deposited here during the winter months provides a convenient opportunity to address these questions.

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The aim of this research was to determine the significance of dust for TEs in snow. Specifically, to determine the concentrations of TEs that: i) are potentially bioavailable (i.e. ionic species and molecules smaller than 300 Da), ii) occur as colloidal materials within the fraction smaller than 0.45 µm (i.e. "filterable" fraction), and iii) are present in particulate form (i.e. larger than 0.45 µm). For consistency, and to help guide the reader, “dissolved” refers to the < 0.45 µm fraction of a water sample, and “filterable” to the same size fraction in snow; “truly dissolved” refers to the fraction smaller than 300 Da in both sample types. This latter size fraction is assumed to consist of ionic species and small molecules The species in this size range are also assumed to be directly bioavailable to living organisms, as they are capable of passing through cell membranes.[56]

The elements of interest are conservative lithophile elements (Al, Th, Y)[57] which are indicators of mineral dusts, elements enriched in bitumen (Mo, Ni, V),[57,58] and chalcophile TEs (As, Cd, Pb, Sb, Tl)[57] which are of greatest concern. Given that snowmelt provides direct access of TEs to surface waters, the results are also discussed within the context of water quality guideline values for the protection of aquatic life.

2. MATERIALS AND METHODS

2.1 Study area, sample collection, and sample processing

Bulk snow samples representing complete snow profiles were collected between February 24 and March 5, 2016 from 20 sites along the Athabasca River (AR), 5 of its tributaries, and at a reference site, Utikuma (UTK) located 264 km SE of the ABS region (Figure 1). Sites were classified as upstream, midstream, and downstream with respect to their distance to the mid-point

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between the two central bitumen upgraders (Table S1, Supporting Information) as presented in previous studies.[38,51]

Sampling was conducted using ultra-clean procedures, including acid-cleaned consumables (bottles, syringes and filters) as described elsewhere.[50] Details of the collection and photographs of the study area, and some of the samples are provided in Section S1 and Figure S2 respectively. Prior to processing, the bulk samples were thawed overnight in a class-1000 clean room, located in the metal-free, ultraclean SWAMP laboratory (https://swamp.ualberta.ca/). Once the samples had melted, they were placed inside a metal-free class-100 air clean cabinet. Four fractions were obtained from the melted snow: (i) total (unfiltered, acidified); (ii) filterable (filtered, acidified); (iii) colloidal and truly-dissolved (filtered, unacidified) and (iv) particulate (collected on filter membranes). Potential loss of TEs due to adsorption of dust particles to the polyethylene (PE) plastic bags was assessed as described in Section S2. The percentage of these losses is summarized in Table S3.

For total TE concentrations, a 2 mL aliquot was digested in 3 mL of concentrated HNO_3 (sub-boiled twice) using high-pressure microwave-assisted digestion (Ultraclave MLS, Milestone).[38,50] The use of HNO_3 alone may be insufficient to achieve complete sample decomposition, as TEs contained within refractory mineral phases (e.g. quartz, monazite, rutile, titanite, and zircon) are unlikely to be released (see recoveries in Table S2). On the other hand, the addition of other reagents such as HBF_4 to dissolve refractory minerals could contribute to higher blank concentrations[59] and inadequate detection limits for some TEs. Even though the term "quasi-total concentration" is more accurate in this context, "total concentration" is employed here given that this procedure provides good recoveries for most of the TEs of environmental concern.[59] Four certified reference materials (NIST 1643f "Trace Elements in Water", SPS-SW2 "Elements in

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Surface Water", NIST 2709a "San Joaquin Soil", and IAEA-Soil 7; see Table S2), laboratory blanks, and replicates selected randomly were also digested. As noted earlier, the digestion method employed resulted in lower recoveries of some elements (Table S2). For the filterable TE concentrations, approximately 120 ml of sample was filtered through acid-cleaned 0.45 µm polytetrafluoroethylene (PTFE) filter membranes. Half of this volume was collected inside a polypropylene (PP) bottle and acidified with HNO_3 to reach a final concentration of 2%, whereas the other half was collected inside a fluorinated ethylene propylene (FEP) bottle and maintained unacidified.

2.2 Determination of TEs

Selected TEs such as indicators of dust (Al, Th, and Y), those enriched in bitumen (Mo, Ni, V) as well as chalcophile elements (As, Cd, Pb, Sb, and Tl) were determined using an ICP-MS (iCAP RQ, Thermo Fisher Scientific). The limits of detection (LOD), quantification (LOQ), method detection limit (MDL; for total concentrations), as well as the precision (RSD), accuracy (%) and recoveries (%) of the certified reference materials are listed in Table S2. As mentioned in Section 2.1, the digestion method used in this study resulted in low recoveries of some elements. Therefore, the concentration of some TEs may have been underestimated.

To determine the TE concentrations in the particulate fraction (> 0.45 µm), the dissolved fraction was subtracted from the totals.[50]

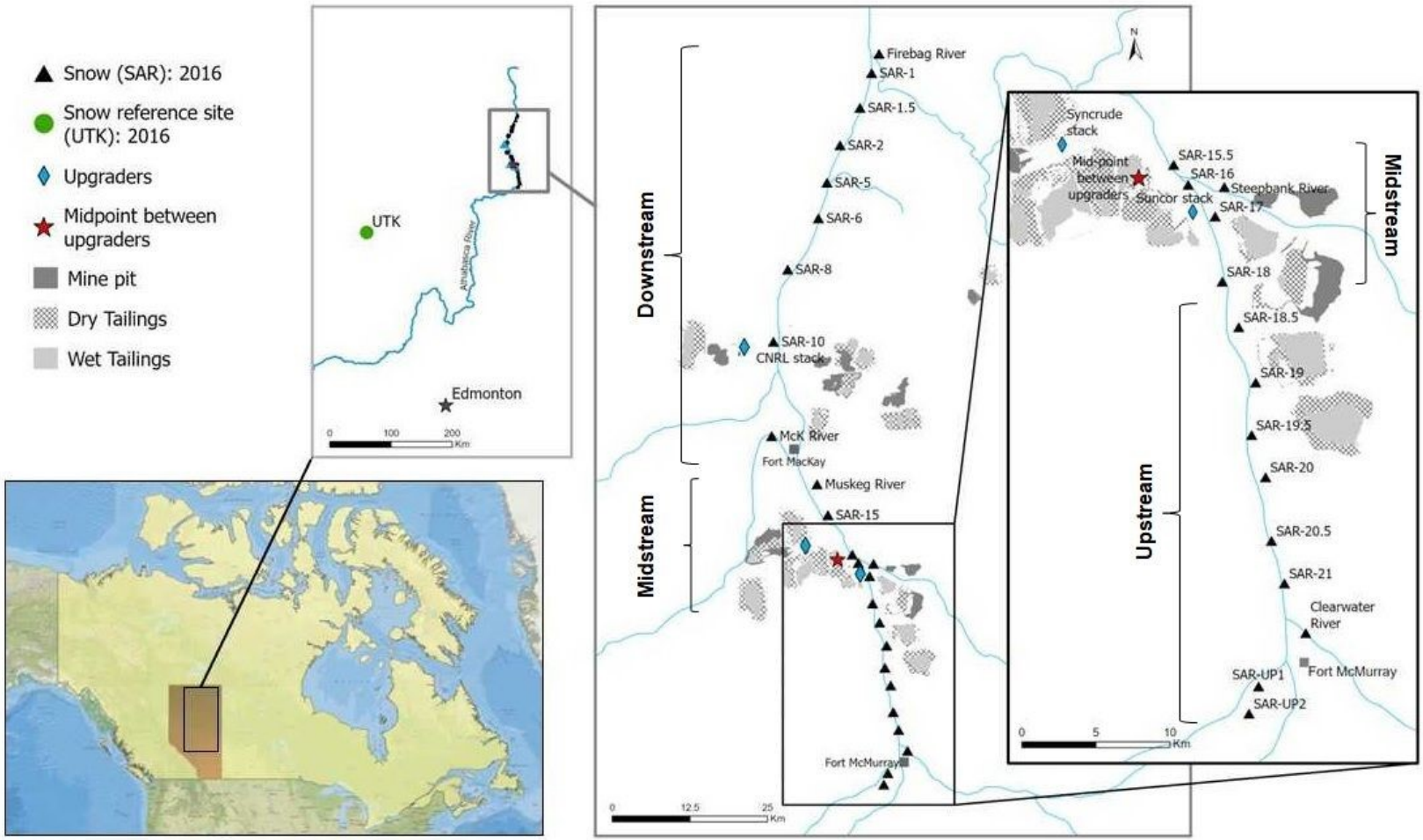

Figure 1. Sampling locations along the Athabasca River (SAR) near the east and west banks, its tributaries, and at the reference site (UTK), winter 2016.

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2.3 Size-resolved analysis of TEs in the filterable fraction of snow

The samples that were filtered (< 0.45 μm) and kept unacidified were analyzed within 24-48 hours after being processed using asymmetrical flow field-flow fractionation (AF4) equipped with an auto injector (AF2000 MF and PN5300, respectively, Postnova Analytics), coupled to a UV-visible absorbance detector (G4212 DAD, Agilent Technologies), and ICP-MS. The UV detector measured the absorbance at a wavelength of 254 nm (A254), which served as a proxy for organic matter (OM) concentrations.

Analytical conditions and settings are described in previous publications,[19,25,60] however a summary is presented in Section S3 and the QA/QC parameters in Table S4. Of the 11 TEs presented here, Sb and Tl were not analyzed because integrable peaks were either absent or small and similar to levels in the blanks as reported in previous study about TEs in the surface waters of the AR.[25]

Four subfractions can be obtained from the filterable snow using this method, each of them associated with a specific retention time (t_r) and corresponding molecular mass (Mp): 1) unretained materials and part of the primarily ionic and small molecular species eluted in the void peak ($t_r \approx$ 445 s, Mp ≈ 300 Da), 2) OM-associated species, co-eluting with organic matter ($t_r \approx 550$ s, Mp ≈ 1 kDa), 3) small inorganic species eluted before the crossflow pump was turned off, with minimal overlap with the organic matter peak ($t_r \approx 900$ s, Mp ≈ 15 kDa), and 4) large inorganic species eluted after the crossflow was shut off ($t_r > 1800$s, Mp > 20.7 kDa). [20,25]

2.4 Scanning electron microscopy (SEM) and X-Ray diffraction (XRD)

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Prior to these analyses, dust particles (> 0.45 μm) from selected locations (Firebag River, SAR-1.5, SAR-5, SAR-10, Muskeg River, SAR-15, SAR-15.5, SAR-16, Steepbank River, SAR-18, SAR-19, SAR-20, SAR-21, Clearwater River, SAR-UP2, and UTK; see Figure 1) were examined. The housing of the filters containing dust particles was cut and opened to remove the filter membranes.[19,48]

The major element composition, morphology, and size of the particulate fraction was determined using an SEM equipped with an energy dispersive X-ray spectroscopy (EDS) system as described in our previous studies.[48] To identify the mineralogical composition of these particles, XRD analyses were performed directly on the filters using a Rigaku Ultima IV X-ray diffractometer in the Earth and Atmospheric Sciences XRD laboratory, at the University of Alberta (https://cms.eas.ualberta.ca/xrd/). Filter blanks were also analyzed to assess the contribution from the PTFE membrane to the diffraction pattern.

2.5 Statistical analysis

The software used for statistical analysis were R 4.2.0 and MATLAB. Linear regressions were conducted using the *lm* function to explore the relationship between selected conservative lithophile elements (Al and Th), elements enriched in bitumen, and potentially toxic TEs. Besides, Spearman correlations were calculated at a p-value of 0.05 for particulate and dissolved TE concentrations, and visualized using the *corrplot* package. An ANOVA test was also performed in order to determine statistical differences of dissolved TE concentrations up, mid, and downstream the ABS region and UTK, the reference site. Finally, statistical fractogram deconvolution of the AF4-UV-ICPMS data was employed to decompose the overlapping peaks into each fraction using MATLAB 2021a.[61,62]

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3. RESULTS AND DISCUSSION

3.1 Distribution of total, particulate, and filterable TEs in snow

3.1.1 General trends

All TEs were predominantly found in the particulate fraction (Figure 2 and 3, Table 1, Table S5 and S7). These results are similar to previous studies in the ABS region[37,50,52] with the exception of Pb and Tl, and Ni and Sb, which were previously reported to be more abundant in the filterable fraction.[37,52] It is also evident that TEs were more abundant in sites located midstream of the industrial area (from Muskeg R. to SAR-18) than at upstream (SAR-18.5 to SAR-UP2) and downstream locations (Firebag River to McK River). These spatial trends have already been observed and are well documented not only in snow [37,48,50–52] but also in vegetation growing in the area.[38,46,63] Trace elements were also more abundant at sites located within the ABS region than at UTK, the reference site, except for Sb (Figure 2 and 3). The pH of the snow samples was slightly acidic to slightly basic, with average values of 6.9 ± 0.6 (upstream), 7.3 ± 0.5 (midstream), and 6.6 ± 0.7 (downstream) (Table S1), similar to snow samples collect in 2017, except at SAR-5 and McK River.[48]

3.1.2 Conservative lithophile elements

a. Snow

The concentrations of total and particulate Al, Th, and Y increased 5 to 6x from downstream to midstream of industry, and 3 to 4x from upstream to midstream (Figure 2). The filterable fraction of these elements represents less than 1% of the total (Table 1). The concentrations of filterable Al increased approximately 8x from downstream to midstream. In addition, filterable Al, Th, and Y

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increased 3 to 4x from upstream to midstream. (Figure 2). The concentrations of Al, Th, and Y in the filterable fraction at upstream and midstream locations in the ABS region were either similar or higher (2 to 5x) that at the reference site, UTK (Figure 2, Table S6). However, significant differences in the concentrations of filterable Al between the ABS area and UTK were only observed at midstream locations (Table S6).

b. Snow vs river water

The filterable concentrations of Al, Th, and Y in snow were 3, 4, and 14x respectively lower than their average dissolved concentrations in the main stem of the AR in autumn of 2014[36] (Figure 2, black dotted line). In addition, the concentrations in snow samples were 5x (Th), 6x (Al), and 9x (Y) lower than the global average dissolved concentrations in river waters (Figure 2, green dotted line).[64] For perspective, Al in the dissolved fraction of the AR (< 0.45 μm) was 2x lower than the global average in river waters(< 0.2 or 0.45 μm)[36,64] (Figure 2).

3.1.3 Elements enriched in bitumen

a. Snow

The concentrations of total and particulate Mo, Ni, and V increased 17 to 26x from downstream to midstream of industry, and 9 to 14x from upstream to midstream (Figure 2). The filterable fraction of these elements represented less than 9% of the total (Table 1). Filterable Mo and V concentrations increased between 2 to 7x toward the centre of industrial activities (Figure 2). Moreover, the filterable Ni, Mo, and V concentrations were 2 to 32x greater upstream and midstream than at UTK. These differences in concentrations were only significant for filterable V at midstream locations (Figure 2, Table S6).

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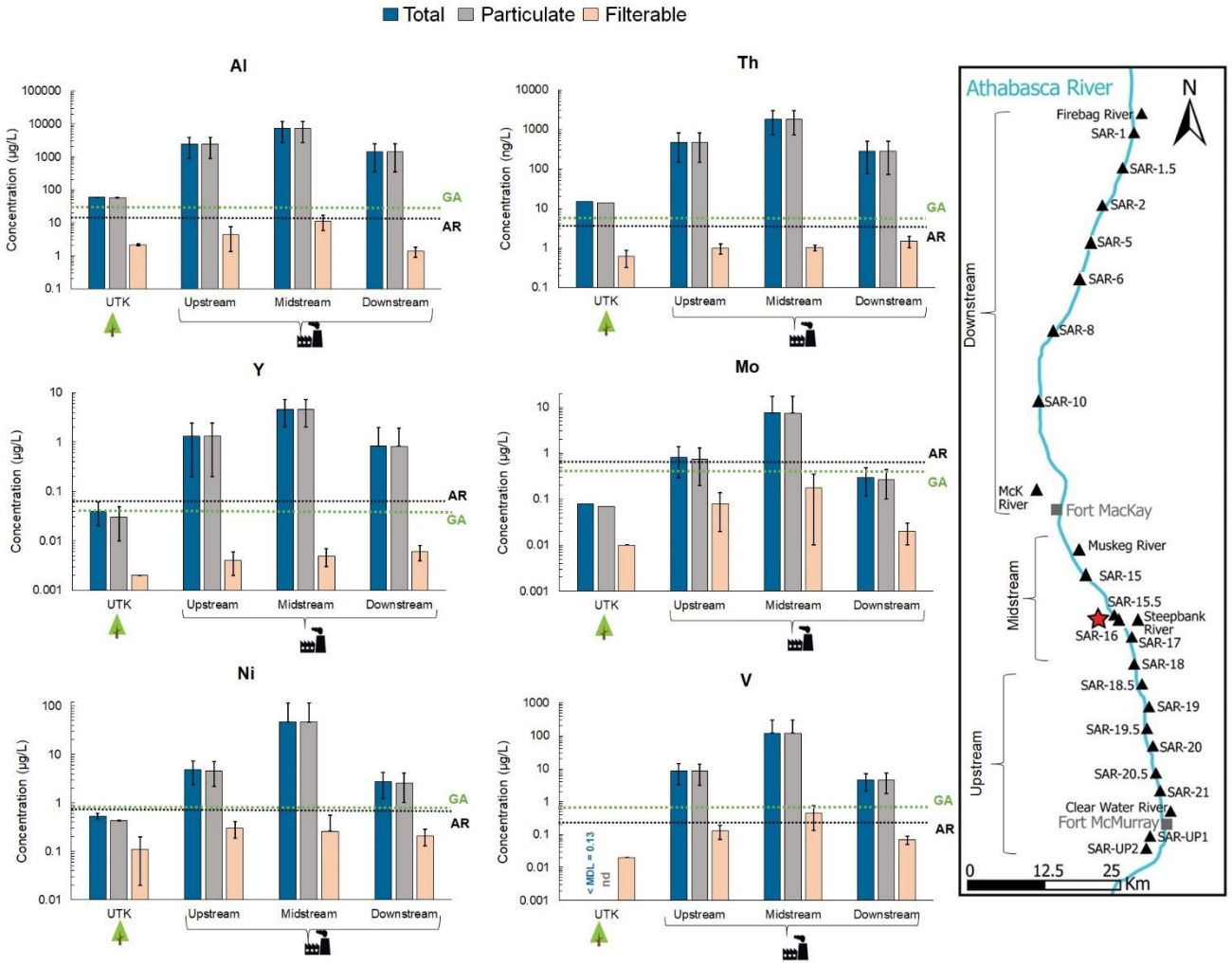

Figure 2. Average concentrations of total, particulate and filterable (< 0.45 µm) Al, Th, Y (conservative lithophile elements), Mo, Ni, and V (elements enriched in bitumen) in snow from upstream, midstream, and downstream locations (with respect to the industry), and at the reference site (UTK), winter 2016. The horizontal black line represents the dissolved TE concentrations in the AR main stem in autumn of 2014[36] whereas the green line represents the global average (GA) dissolved (< 0.2 or 0.45 µm) concentrations of TEs in river water.[64]

Notes: The map on the right side shows the snow sampling locations in the ABS region along the Athabasca River (SAR) and its tributaries. The location of UTK is provided in Figure S1 and Table S1 (Supporting Information). The red star represents the midpoint between bitumen upgraders. Error bars represent one standard deviation. LOD = limit of detection, MDL = method detection limit, nd = not determined. Th and Mo concentrations at UTK are based on one location instead of the average of two.

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b. Snow vs river water

Filterable concentrations of Ni and Mo in snow were 3 and 8x respectively lower than their respective concentrations in the dissolved fraction of the AR.[36] Similarly, the concentrations of Ni, V and Mo in filterable snow were 3x, 4x, and 5x lower than their concentrations in uncontaminated river waters[64] (Figure 2). Again, for context V in the AR was 3x lower than the global average in river waters[36,64] (Figure 2).

3.1.4 Chalcophile elements

a. Snow

The total and particulate concentrations of As, Cd, Pb, Sb, and Tl increased 3 to 6x from downstream to midstream, and 3 to 4x from upstream to midstream (Figure 3). The filterable fraction varied from 1 to 17% of the total (Table 1) and demonstrated the following spatial patterns: (i) no increase toward the centre of industrial operation (Pb and Tl), (ii) a modest increase either from down to midstream (Sb) or in both directions (As), or (iii) no clear trend (Cd) (Figure 3). Of this group of elements, filterable Cd and Pb showed significantly lower concentrations within the ABS region (at the 3 location types for the former, and at upstream and midstream for the latter) than at UTK. By contrast, filterable As and Tl concentrations were significantly greater (up to 5x) at midstream locations compared to UTK (Figure 3, Table S6).

b. Snow vs river water

The concentrations average dissolved concentrations of these TEs in snow were 4 (Cd, Pb, Sb, Tl) to 12x (As) lower than their respective concentrations in the AR[36] (Figure 3). Similarly, the filterable concentrations of Sb and As in snow from the ABS region were 6 to 19x respectively

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lower than in uncontaminated river waters.[64,65] In addition, the dissolved concentrations of these five potentially toxic chalcophile elements were 2 to 6x lower in the AR than in river waters worldwide[36,64] (Figure 3).

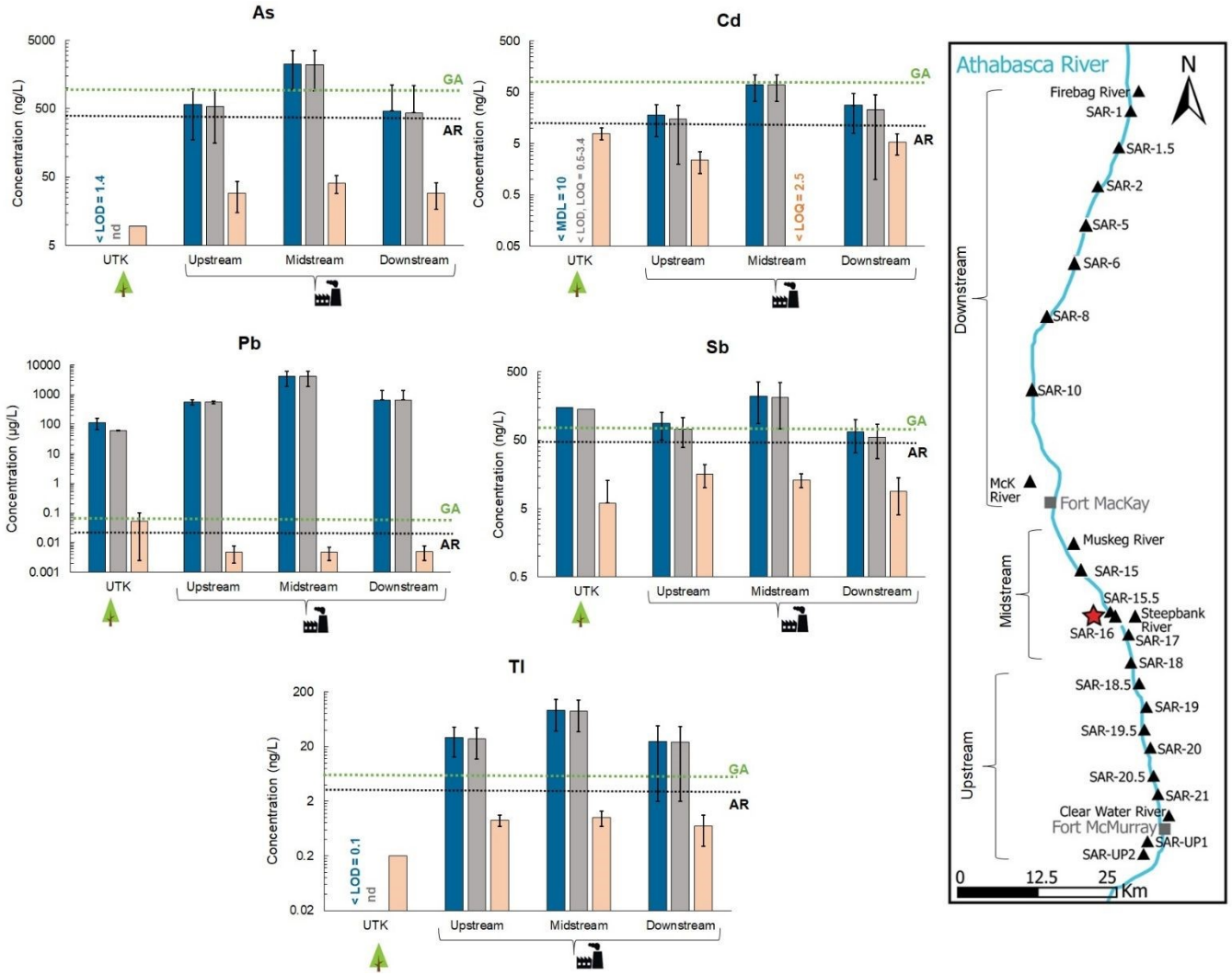

Figure 3. Average concentrations of total, particulate and filterable (< 0.45 µm) As, Cd, Pb, Sb, and Tl (chalcophile elements) in snow from upstream, midstream, and downstream locations (with respect to the industry), and at the reference site (UTK), winter 2016. The horizontal black line represents the dissolved TE concentrations in the AR main stem in autumn of 2014[36] whereas the green line represents the global average (GA) dissolved (< 0.2 or 0.45 µm) concentrations of TEs* in river water.[64]

Notes: The map on the right side shows the snow sampling locations in the ABS region along the Athabasca River (SAR) and its tributaries. The location of UTK is provided in Figure S1 and Table S1 (Supporting Information). The red star represents the midpoint between bitumen upgraders. Error bars represent one standard deviation. LOD = limit

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of detection, MDL = method detection limit, nd = not determined. As and Sb concentrations at UTK are based on one location instead of the average of two. *For Tl, the estimated mean natural concentration in river waters was used.[65]

3.2 Characterization of TEs in the particulate fraction of snow and their potential sources

3.2.1 Mineral characterization and identification using SEM and XRD

Scanning electron microscope analyses performed on PTFE filters (see section 2.4), revealed the presence of particles with irregular shape and microaggregates, ranging from less than 10 to 200 μm (Appendix A, selected images) as reported in our previous studies.[48,49] The elemental composition obtained from the EDS spectra indicated the presence of Si, Al, Ca and Fe, followed by S, Mg, K, Ti, Na, and traces of REEs (La, Ce, Nd) and Zr (Appendix A). The XRD analyses of the same samples indicated the presence of insoluble silicates (quartz; clay, feldspar, and mica-like phases), carbonates (calcite, dolomite, and ankerite), and Ti oxides (anatase and rutile) (Appendix B). Midstream and upstream locations showed more mineral diversity in terms of clays (kaolinite, dickite, nacrite, muscovite), micas (i.e. biotite minerals, but only midstream), feldspars (albite and microcline, only upstream), and other silicates such as enstatite (Appendix B). No mineral phases were identified at UTK, the reference site, simply because the mass of particles on the filter were not sufficient to perform this type of analysis (Appendix B). However, dust particles at UTK are usually smaller (< 30 μm) and less abundant than at the ABS region, and are composed of quartz, feldspars, and clay minerals.[39,40,48] Taking these results together, the composition of the particulate fraction in the AR snows is similar to the mineral fraction of the ABS[66–69] but also with other dust sources such as limestone and aggregate used in the construction of local roads.[44,51,70]

3.2.2 Source assessment using TE ratios, correlations, and linear regressions in the particulate fraction

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Several authors have stated that it is still challenging to separate natural from anthropogenic atmospheric sources of TEs in the ABS region.[34,71–74] Three methods summarized in Figure 4, Figure S3, Figure S4, and Table S8 were used in order to understand the geochemical behaviour and possible sources of TEs in the particulate fraction of the snow from the AR and its tributaries.

a. Trace element correlations

Aluminum, Th and Y are considered as indicators of mineral dusts.[19,38,51] Aluminum is commonly used as an indicator of the abundance of clay minerals,[38,75] whereas the latter pair are enriched in heavy minerals and froth treatment tailings.[76–78] Trace elements in the particulate fraction showed a correlation ($r > 0.8$) with the conservative lithophile elements, except Sb and Mo ($r < 0.8$) (Figure S4). These strong correlations would suggest that TEs in this fraction (> 0.45 μm) have a common mineral source including heavy minerals and clays.

b. Trace element ratios

Trace element ratios have been previously reported in the ABS region not only in snow[49–51] but also in moss[39] and peat bog porewaters.[41] Focus here is placed on Pb and Tl in the particulate fraction of snow given that these elements are vey toxic, they are enriched in bitumen have, and have already been extensively discussed in previous publications.[49,50] Lead and Tl were normalized to Al and Th and compared to their respective ratios at UTK (the reference site), the Upper Continental Crust (UCC),[79] the bulk ABS and its mineral and bitumen fractions,[58] as well as to diverse geomaterials found in the study area (Section S4, Figure S3, Table S8).

Lead /Th ratios at the ABS region were approximately 2x lower than at UTK . The Pb/Th ratios at UTK were similar to those reported in peat cores collected from the same site,[42] which in turn were similar to Pb/Th reported in the cleanest peat cores ever found, dating from pre-industrial times.[80] Unfortunately, Tl was below the LOD at UTK. However, within the ABS location types,

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Pb/Th and Tl/Th were similar upstream, midstream, and downstream of industrial operations (Figure 4, Figure S3, Table S8). In addition, Pb/Th ratios in the ABS region were double their equivalent ratios in the UCC. In contrast, Tl/Th ratios were similar to the UCC.[79] Many possible sources of dust, ranging from dry tailings to road dust maybe be responsible for these TEs in the particulate fraction (Table S8). For example, Pb/Th and Tl/Th in tailings were similar to the ratios in other industrial materials in the area such as petcoke, tailings, and bulk ABS (Figure 4 and Figure S3). Thus, these element ratios cannot be used to ascribe them to a specific dust source, but they are comparable to many of the possible dust sources in the area. A previous study conducted in the same area, suggested that Pb in lichens collected near industry had an overlapping signature with bulk ABS and tailings.[81]

Regarding the other chalcophile element ratios, they were greater in the ABS region than at UTK given that the concentrations of As, Cd, and Tl in the latter were below the LODs or MDLs (see Table S5). In addition, As/Th and Sb/Th in the industrial area were below the ratios for the UCC[79] while the opposite was observed for Cd/Th and Cd/Al (Table S8).The As/Al and As/Th ratios in the ABS region were very similar to their respective ratios in road construction material (Table S8). Previous studies have linked As to three types of sources (road dust, raw oil sand dust. and road salt)[51] while Sb may be associated with fuel combustion, residential wood burning, and waste combustion.[82] Antimony can also be associated with truck brake pads.[83,84]

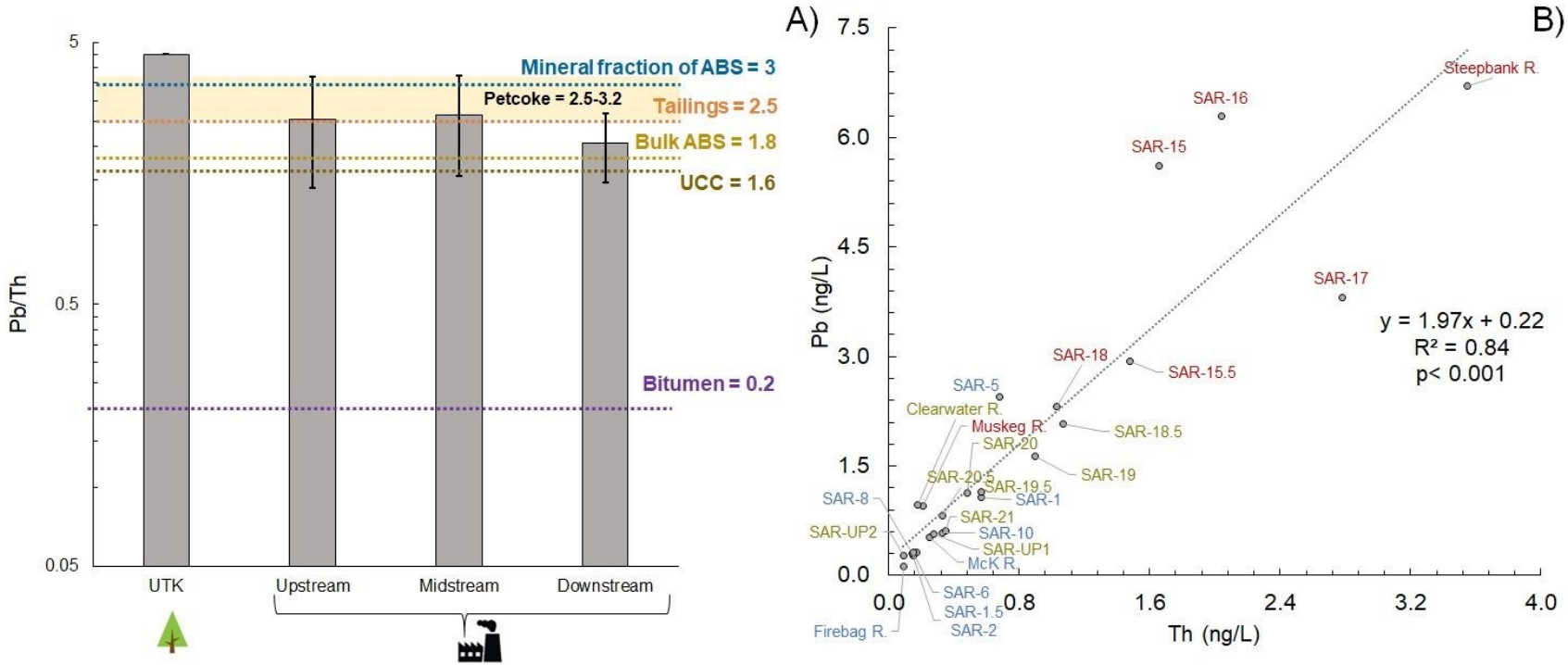

Figure 4. (A) Pb/Th ratios in the particulate fraction of snow from UTK (reference site) and upstream, midstream, and downstream locations (with respect to the industry) in winter 2016. The dashed lines represent the Pb/Th ratios in the Upper Continental Crust (UCC),[79] in the bulk ABS, mineral and bitumen fractions,[58] and in tailings (see Table S7). The yellow area represents the range of Pb/Th ratios in petcoke (see Table S7). **(B)** Linear regression between Pb and Th concentrations in the particulate fraction of snow from the Athabasca River (SAR) and its tributaries.

Notes: sites in green, red, and blue represent upstream, midstream, and downstream locations, respectively. The Pb/Th at UTK was calculated based on concentrations from UTK-1 (See Table S5).

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c. Linear regressions

The increase in the concentrations of particulate Pb and Tl toward industry was proportional not only to the increase of Th (Figure 4B and Figure S3B) but also to that of Al (Table S9), which is in agreement to what was found in the acid-soluble fraction of snow.[49] Arsenic and Sb behaved similarly to Pb and Tl (Table S9). These results indicate that the abundance of these elements in snow of the ABS region reflect the abundance of mineral matter in the samples.

The low R^2 values (0.10 to 0.28) of elements enriched in bitumen vs Al and Th (Table S9) may be explained by specific sites or "hotspots" at midstream (SAR-15, SAR-16 and SAR-17) and downstream locations (SAR-18.5 and SAR-19) that have concentrations that do not follow the spatial trends observed for the other elements (Table S7). Snow collected at some of these sites contained small black particles most likely to be petcoke which is stockpiled in large amounts around the mines [35,49] and is known for elevated concentrations of V and Ni. [85] The poor correlation between Mo, Ni, and V with Al and Th, may reflect the sporadic occurrence of petcoke particles in snow samples.

3.3 Trace element in colloidal and < 300 Da fractions

3.3.1 General trends

In the ABS region, TEs in the filterable fraction of snow were mainly in the < 300 Da fraction (Figure 5, Table S7). However, there are some exceptional elements and sites. For example, at midstream locations, 37.2 % of Y and 30.4% of Ni in this fraction on average were mainly associated with OM. Downstream, the OM fraction ranged from < LOD to 47.5% of the filterable Th, Y, and Ni (Figure 5, Table S7). A study conducted in snow from Western Siberia (from the

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vicinity of Barnaul city to the Ob estuary) reported that OM colloids can originate from thermokarst lakes that freeze solid during winter. These colloids may consist of organic aerosols, humic-like substances, black carbon, and mineral dust coated with organic matter. Freeze-thaw cycles can also contribute by producing large colloidal particles and releasing low molecular weight organic compounds.[24]

At UTK, the reference site, most TEs were also predominantly found in the < 300 Da fraction. The exceptional elements found also in other fractions were Th and Pb (OM: 40.7 and 16% respectively), Mo (small inorganic, 41.4%), and As (large inorganic, 29.6%) (Table S7). According to a previous study, the higher abundance of certain elements in colloidal form in snow is linked to various mechanisms of colloid formation, transformation, and transport in the atmosphere, processes that remain poorly understood. The study points to possible pathways such as the fragmentation of fly ash particles, condensation of volatile compounds from industrial emissions, and the dissolution or dispersion of soil minerals like clays. During winter, both the sources of dissolved elements and the atmospheric processes acting on aerosols may determine the chemical composition of snow water colloids.[24]

The ABS surface-mineable area spans roughly 4,800 km² and is bordered by boreal forest, with numerous lakes and wetlands. In addition, the lower Athabasca River contains many islands, secondary channels, wetlands, and floodplain lakes.[55] Additional features include agricultural land, several urban centers, and wastewater treatment plants.[86] Together, these observations underscore the potential influence and diversity of both natural and anthropogenic sources to the composition of the filterable fraction of the snow. Hypotheses about specific sources will be discussed by class of elements.

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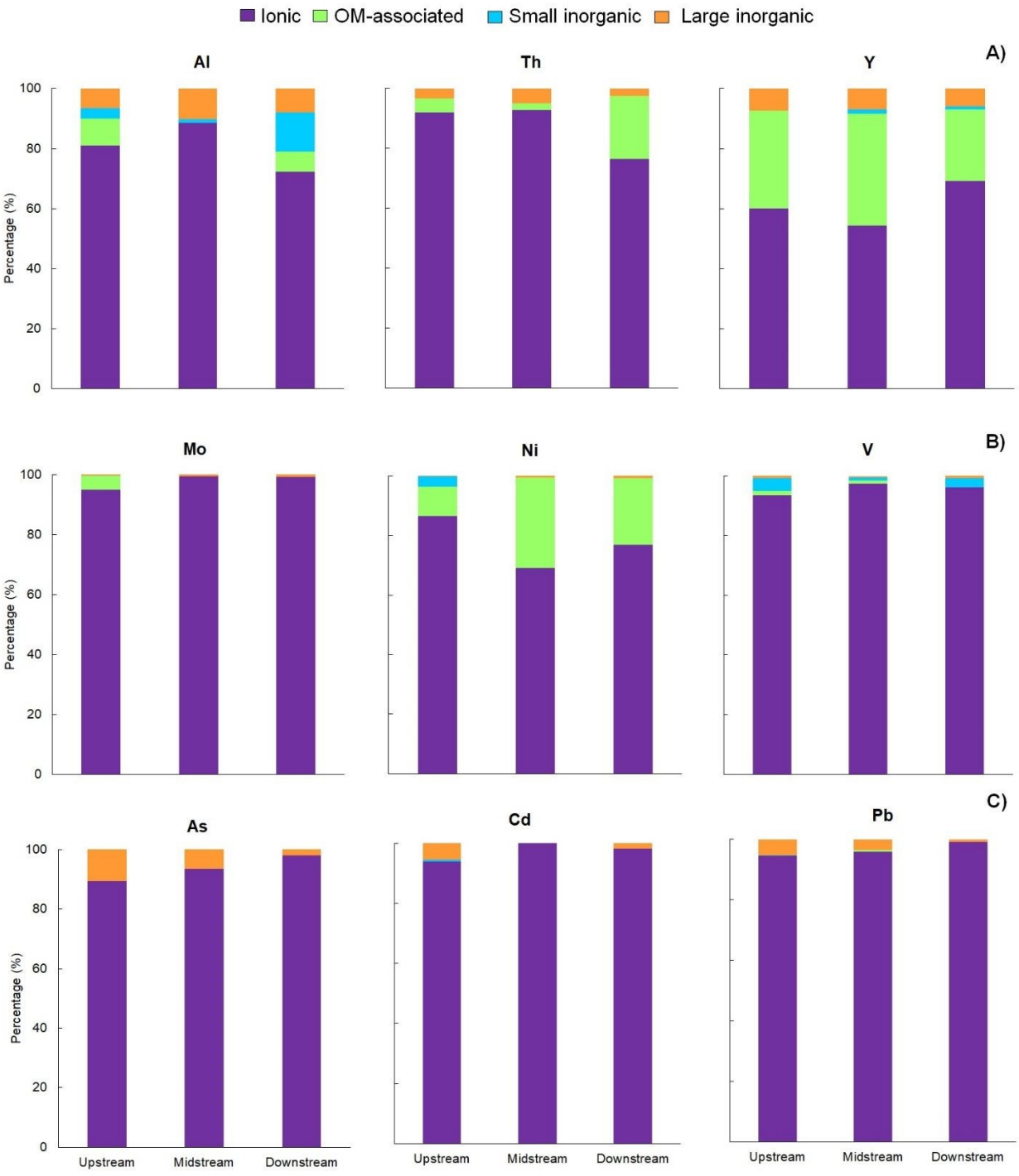

Figure 5. Percentages of filterable A) Al, Th and Y (conservative lithophile elements), B) Mo, Ni, and V (elements enriched in bitumen, and C) As, Cd, and Pb (chalcophile elements) in the "truly dissolved" (< 300 Da), OM-associated (≈ 1 kDa), small inorganic (≈ 15 kDa), and large inorganic (> 20.7 kDa) forms, in selected locations along the Athabasca River (SAR) and its tributaries, winter 2016.

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3.3.2 Conservative lithophile elements

Between 62 to 87% of the filterable Y, Al, and Th in snow occur < 300 Da (Figure 5, Table 1, Table S7). In the case of Al, the second most abundant fractions at downstream and midstream locations were the small and large inorganic forms respectively (Figure 5, Table S7). However, two sites were exceptional (SAR-UP2 and SAR-5) and had considerable amounts of Al associated with OM (Table S7).

At downstream locations, approximately 21% of Th was associated with OM (Figure 5, Table S7). Similarly, and as mentioned above, Y was mainly associated with OM, except at sites SAR-10, SAR-18.5 and SAR-19 where the large inorganic form contributed to 18 to 40% of the filterable fraction in snow (Figure 5, Table S7). The forests of uplands and wetlands, and their soils and sediments, represent important reservoirs of OM in the ABS region. Therefore, the decomposition of plant matter and the formation of metal- and mineral-organic complexes, may help account for the occurrence of organically-bound Y. Yttrium exhibits notable behaviour, in that it occurs in a number of distinct forms in the filterable fraction of the snow, including ionic species and small molecules as well as organic and inorganic colloids. This diversity suggests that number of natural and anthropogenic sources may be contributing to the atmospheric deposition of this element. The lack of large changes in the OM-associated fraction of Y at sites from upstream to downstream suggests that there may be an ubiquitous source of naturally occurring Y in this form (Table S7).

3.3.3 Elements enriched in bitumen

Between 78 to 98% of the filterable Ni, V, and Mo in snow was found < 300 Da (Table 1, Table S7, Figure 5). Up to 51.8% and 35.8% of Ni midstream and downstream of industry

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respectively had an important contribution from organic forms which do not occur at upstream locations (Figure 5, Table S7). Even though V and Ni in bitumen are in the form of porphyrin complexes,[87] and are both enriched in petcoke,[85] Ni is more volatile.[88] We hypothesize that the more volatile Ni porphyrins were more readily released during upgrading and some have ended up in the snow. Another possible explanation could be bacterial and algae activity in snow,[89,90] given that Ni is an essential TE to both organisms.

Table 1. Average percentages and concentrations of TEs in the particulate, filterable, and "truly dissolved" fraction of snow from the AR main stem and its tributaries in winter 2016.

Geochemical group	TE	Total				"Truly dissolved" (< 300 Da)	
		Particulate fraction (> 0.45 µm)		Filterable fraction (< 0.45 µm)			
		%	ng/L	%	ng/L	%	ng/L
Conservative lithophile	Al	99.8	3470 ± 3630*	0.2	5.2 ± 5.2*	80	4.5 ± 4.7*
	Th	99.6	780 ± 894	0.4	1.2 ± 0.4	86.5	1.0 ± 0.2
	Y	99.2	2050 ± 2260	0.8	4.8 ± 2.0	61.8	3.0 ± 1.5
Enriched in bitumen	Mo	90.9	2460 ± 5860	9.1	86 ± 109	97.7	86 ± 109
	Ni	93.3	16 ± 40*	6.7	260 ± 91	78.2	203 ± 83
	V	98.4	38 ± 105*	1.6	200 ± 232	95.5	194 ± 231
Chalcophile	As	91	972 ± 1110	9	32 ± 13	93.5	30 ± 13
	Cd	83	33 ± 34	17	3.3 ± 2.2	97.2	3.3 ± 3.2
	Pb	99	1750 ± 1920	1	4.9 ± 2.5	96.7	4.7 ± 2.4
	Sb	86.6	124 ± 108	13.4	13 ± 5.5	NA	NA
	Tl	96.8	45 ± 43	3.2	0.9 ± 0.3	NA	NA

Notes:
*in µg/L
Please refer to Table S7 for percentages per site.
The filterable percentage was calculated based on data provided in Table S5.
NA= not analyzed.

3.3.4 Chalcophile elements

Between 94 to 97% of the filterable As, Cd, and Pb in snow were found < 300 Da (Table 1, Table S7, Figure 5). As indicated in section 2.3, Sb and Tl were generally below the LOD using

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AF4-UV-ICPMS. A small fraction of Pb (up to 17%, SAR-18.5) and a larger fraction of As (up to 43%, SAR-UP2) were associated with large, inorganic colloids mainly at upstream sites (Table S7): this fraction consists predominantly of oxyhydroxides of Al and Fe. It is well known that Pb and As in soils, sediments and natural waters are often associated with colloidal ferric hydroxide (FeOOHs).[22,25,26,91]

3.4 Broader significance for the protection of the aquatic life of the AR watershed

3.4.1 Importance of the partitioning of TEs into particulate and filtered forms of snow

There is ongoing concern about the water quality of the lower AR watershed, which directly affects the PAD,[55,92] not only from the human health perspective but also in terms of aquatic organisms.[37,72,93–98] It is well known that snowmelt plays a vital role in the AR flow,[54,99,100] however the literature regarding the potential impact of snowmelt to the river is not conclusive. [37,51,52,98,101,102] Water quality guidelines for the protection of aquatic life in Alberta and in Canada[20] are very conservative, and generally consider total concentrations, pH, and hardness,[103,104] although some values are based on dissolved concentrations (e.g. Al[101]; Mn and Zn [100]). By contrast, the European Union and the United States water quality standards respectively for Cd and Pb[105] and As, Cd, and Pb,[106] are based on dissolved concentrations. A previous publication reported that the total concentrations of Cd, Cu, Pb, Hg, Ni, Ag, and Zn in melted snow and/or water from the AR and the dissolved concentration of Cd in snow collected in the ABS region exceeded Canada's or Alberta's guidelines.[37]

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Here, it is clear that the particulate fraction of TEs in snow is the dominant one, similar to what was observed in the AR not only in autumn[36,74] but also in spring.[20] It was reported that the particulate fraction of the AR has limited bioaccessibility.[74,107] It is also expected that TEs in the particulate fraction of snow have limited availability.

When snowmelt occurs, the waters of the AR experience a pH depression, resulting in a short-term acidification of its waters [20,98] which in turn could increase TE concentrations.[108,109] To date, only one publication has reported that of 12 TEs analyzed during acidification episodes in the AR and its tributaries, only Al and Cu may pose a risk to rainbow trout.[98] It has been suggested that the high alkalinity of the river and its buffer capacity, could attenuate the acidification process during early spring[48,86] limiting the availability of TEs.

Regarding the potential bioavailability of TEs, our study shows that in the filterable fraction of snow, between 62 (Y) to 98% (Mo) of the TEs studied were in the < 300 Da form (Table 1, Table S7). Extremely low concentrations were found in this snow fraction, with averages of 30 ± 12, 3.3 ± 3.2, and 4.7 ± 2.4 ng/L for As, Cd, and Pb respectively (Table 1). To put some of these values into perspective, Pb and Cd concentrations from melted and unfiltered snow from the Devon Island ice core (Nunavut, Canada) -which represents snow accumulation from the mid-Holocene- were 5.1 ± 1.4 ng/L [110] and 2.4 ± 0.5 ng/L[111] respectively. Thus, by any measure the concentrations in snow of elements such as Cd and Pb which are < 300 Da and potentially bioavailable, are exceedingly small. In the cases of Sb and Tl, they are too small to be determined, even in a metal-free, ultraclean laboratory.

3.4.2 Bioaccessibility and bioavailability of TEs

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Exposure of TEs to aquatic organisms such as fish occurs via aqueous uptake of water-borne compounds through respiration and/or through ingestion of food and sediment.[112,113] The former pathway considers the conventionally defined "dissolved" fraction, which serves as an indicator of the amount of TEs that could induce a toxic or beneficial effect in a given organism.[18] In contrast, the latter is represented by the particulate material. Based on our findings, it seems as though the low concentrations of TEs found in the < 300 Da fraction of snow (Table 1) upon release to the river as meltwater would have a negligible impact on the health of aquatic organisms. However, bioaccumulation and biomagnification process should also be considered as these increase the concentrations of TEs over time within specific target organs and within the trophic chain. [112,114]

Although some leaching experiments under extreme acidic conditions (pH <1) have been conducted in snow in order to determine the reactivity of TEs in dust particles,[48–50] no studies have assessed their gastric bioaccessibility. *In-vitro* digestion experiments simulating the composition of the gastric fluids in fish[113] could serve as a proxy to better determine the impacts of particulate TEs in snow that enter the AR and contribute to its sediment supply.

4. CONCLUSIONS

A number of studies conducted in the ABS region have now shown that the concentrations of TEs increase toward the centre of the industrial zone, following the general pattern of dust deposition.[37,51,52] Based upon our own work,[48–50] we have further scrutinized the relationships between dusts and the TEs they contain. In snow collected in 2016, TEs of environmental interest, including the chalcophile elements, occur predominantly in the particulate fraction, and exhibited

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strong correlations with Al and Th: this indicates that mineral particles are the dominant carriers. Elemental ratios further suggested contributions from both natural and anthropogenic sources in the area. Here, we show that, within the filterable fraction, TEs were primarily found in the < 300 Da fraction: this fraction represents ionic and small molecules which can cross cell membranes and are readily assimilated by organisms. However, the concentrations of TEs in this fraction are extremely low: for example, Y, Th, Cd, and Pb were all below 10 ng/L. The use of AF4-ICP-MS to obtain size-resolved analyses has provided valuable new insights regarding the chemical forms of TEs found in snow. Having this instrumentation in a metal-free, ultraclean lab facility provides a very important cautionary tale: TEs may occur predominantly in the form of ionic species and small molecules, and yet have limited ecological significance, if they occur at the very low concentrations reported here.

Because TEs in snow from the ABS region are mainly in the form of dusts made up of relatively large, mineral particles, and hosted in stable mineral phases, their release to natural waters is expected to be limited. The extent to which snow in the ABS region contributes to TE loads in the AR depends on two factors: the hydrological significance of snowmelt in the ABS region versus the rest of the AR watershed, and the concentrations of the elements in the snowpack. Hydrological considerations are beyond this scope of our work, but clearly, the concentrations of Mo and Ni (elements enriched in bitumen) and As, Cd, Pb, Sb and Tl (chalcophile elements) in snow of the ABS region are low compared to the dissolved fraction of the AR. Thus, snowmelt in the ABS region would be expected to dilute the concentrations of these elements in the river, not increase them.

In summary, our findings clearly show that mining and upgrading activities have certainly increased TE concentrations in snow toward industry, the environmental significance of these

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elements may be limited, given their association with comparatively large particles of insoluble minerals. While ionic species and simple molecules may dominate the filterable fraction of the snow, their concentrations are extremely low.

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge. Sections 1-4. Materials and Methods. Figures S1-S4. Snow sampling; processing of geomaterials; Tl/Th ratios in the particulate fraction; Spearman correlations. Tables S1-S9. Sample location; ICP-MS QA/QC; Loss of TEs due to absorption; AF4-ICPMS QA/QC; TE concentrations; TE ratios filterable snow and ANOVA results; size-distribution of TEs in percentages; TE ratios geomaterials; linear regressions; Appendix A and B. SEM and XRD selected data (PDF files).

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Captions

Figure 1. Sampling locations along the Athabasca River (SAR) near the east and west banks, its tributaries, and at the reference site (UTK), winter 2016.

Figure 2. Average concentrations of total, particulate and filterable (< 0.45µm) Al, Th, Y (conservative lithophile elements), Mo, Ni, and V (elements enriched in bitumen) in snow from upstream, midstream, and downstream locations (with respect to the industry), and at the reference site (UTK), winter 2016. The horizontal black line represents the dissolved TE concentrations in the AR main stem in autumn of 2014[36] whereas the green line represents the global average (GA) dissolved (< 0.2 or 0.45 µm) concentrations of TEs in river water.[64]

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Figure 3. Average concentrations of total, particulate and filterable (< 0.45µm) As, Cd, Pb, Sb, and Tl (potentially toxic chalcophile elements) in snow from upstream, midstream, and downstream locations (with respect to the industry), and at the reference site (UTK), winter 2016. The horizontal black line represents the dissolved TE concentrations in the AR main stem in autumn of 2014[36] whereas the green line represents the global average (GA) dissolved (< 0.2 or 0.45 µm) concentrations of TEs* in river water.[64]

Figure 4. A) Pb/Th ratios in the particulate fraction of snow from UTK (reference site) and upstream, midstream, and downstream locations (with respect to the industry) in winter 2016. The dashed lines represent the Pb/Th ratios in the Upper Continental Crust (UCC),[79] in the bulk ABS, mineral and bitumen fractions,[58] and in tailings (see Table S7). The yellow area represents the range of Pb/Th ratios in petcoke (see Table S7). (**B)** Linear regression between Pb and Th concentrations in the particulate fraction of snow from the Athabasca River (SAR) and its tributaries.

Figure 5. Percentages of filterable **A)** Al, Th, Y (conservative lithophile elements); **B)** Mo, Ni, V (elements enriched in bitumen); and **C)** As, Cd, and Pb (chalcophile elements) in the "truly dissolved" (< 300 Da), OM-associated (≈ 1 kDa), small inorganic (≈ 15 kDa), and large inorganic (> 20.7 kDa) forms, in selected locations along the Athabasca River (SAR) and its tributaries, winter 2016.

Table 1. Average percentages and concentrations of TEs in the particulate, filterable, and "truly dissolved" fraction of snow from the AR main stem and its tributaries in winter 2016.

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Data availability statement

The data supporting this article have been included as part of the Supplementary Information