Peat Bogs Document Decades of Declining Atmospheric Contamination by Trace Metals in the Athabasca Bituminous Sands Region

William Shotyk,* Peter G Appleby,‡ Beatriz Bicalho,† Lauren Davies,§ Duane Froese,§ Iain Grant-Weaver,† Gabriel Magnan,|| Gillian Mullan-Boudreau,† Tommy Noernberg,† Rick Pelletier,† Bob Shannon,⊥ Simon van Bellen,‖ and Claudio Zaccone‡

1Department of Renewable Resources, University of Alberta, 348B South Academic Building, Edmonton, Alberta T6G 2H1 Canada
2Department of Mathematical Sciences, University of Liverpool, Liverpool L69 3BX, United Kingdom
3Department of Earth and Atmospheric Sciences, University of Alberta Edmonton, Alberta T6G 2E3 Canada
4Département de Géographie, Université du Québec à Montréal Montréal, Québec H2V 2B8 Canada
5Quality Radioanalytical Support, LLC, 123 Cougar Trail, PO Box 774 Grand Marais, Minnesota 55604 United States
6*Department of the Sciences of Agriculture, Food and Environment, University of Foggia Via Napoli, 71122 Foggia Italy

Supporting Information

ABSTRACT: Peat cores were collected from five bogs in the vicinity of open pit mines and upgraders of the Athabasca Bituminous Sands, the largest reservoir of bitumen in the world. Frozen cores were sectioned into 1 cm slices, and trace metals determined in the ultraclean SWAMP lab using ICP-QMS. The uppermost sections of the cores were age-dated with 210Pb using ultralow background gamma spectrometry, and selected plant macrofossils dated using 14C. At each site, trace metal concentrations as well as enrichment factors (calculated relative to the corresponding M/Th ratio of the Upper Continental Crust) reveal maximum values 10 to 40 cm below the surface which shows that the zenith of atmospheric contamination occurred in the past. The age-depth relationships show that atmospheric contamination by trace metals (Ag, Cd, Sb, Tl, but also V, Ni, and Mo which are enriched in bitumen) have been declining in northern Alberta for decades. In fact, the greatest contemporary enrichments of Ag, Cd, Sb, and Tl (in the top layers of the peat cores) are found at the control site (UTK) which is 264 km SW, suggesting that long-range atmospheric transport from other sources must be duly considered in any source assessment.

INTRODUCTION

17,18 Snow and ice cores from the Arctic provide remarkable records of atmospheric Pb contamination extending back in time more than three millennia.19–21 For example, an ice core from Devon Island, Nunavut, Canada, has provided a 15 000 year record of atmospheric Pb deposition, with evidence of anthropogenic inputs dating back to the time of the Phoenicians, followed by the Greek and then Roman civilizations, with notable episodes of intense Pb emissions during the Medieval Period, the Industrial Revolution, and later, from the introduction of leaded gasoline.22,23 Careful analyses of these cores using metal-free, ultraclean lab procedures and protocols also document hemispheric contamination by Ag and Tl,22 Sb,23 as well as As, Bi, Cu, and Zn24...
Figure 1. Map showing the locations of the peat cores described in the text (McK, JPH, MIL, McM, ANZ, and UTK) as well as the year of collection. Also shown for comparison, the locations of the moss samples collected from peat bogs of this region which were also measured for trace metals as well as the locations of bogs from other parts of Canada; the trace metals data for the living layer from these bogs is presented elsewhere. The shaded area in the map shown in the upper right corner refers to the locations of open pit bitumen mines. Also shown are the locations of the bitumen upgraders in the area of the ABS, namely Suncor, Syncrude, CNRL, and Nexen. The locations of the SEBA bog, the coal-fired electricity generating stations near Lake Wabamun W of Edmonton, the bitumen upgrader E of Edmonton, the Ni refinery at Fort Saskatchewan, and the hazardous waste incinerator at Swan Hills, are also shown. Produced using ArcMap. All displayed vector data is derived from either Geogratis Canada, GeoDiscover Alberta, or created by authors.
extending back in time several millennia. Trace metal contamination of polar snow and ice results from long-range atmospheric transport of submicron aerosols generated by high temperature combustion processes.

Ombrotrophic (i.e., rain-fed) peat bogs are also excellent archives of atmospheric deposition of many trace metals, providing the first complete, long-term record (ca. 15,000 years) of atmospheric Pb deposition in Europe where anthropogenic inputs have dominated continuously for more than 3,000 years.

Detailed histories of atmospheric Pb contamination have since been reconstructed using peat cores from bogs across Europe.7–12 Bogs in Europe have also been used in retrospective studies of many other trace elements, including As,13–15 Ag,16 Cd,16 Hg,17–19 Ni,19,20,21 Sb,22,23 and Tl.24 In contrast, there has been only a handful of studies of atmospheric metal deposition using peat cores from bogs in North America, and they have all been undertaken in the northeastern part of the continent.

Based on analyses of snow collected during a single season, it was claimed that open pit mining and upgrading of the Athabasca Bituminous Sands (ABS) in northeastern Alberta (AB) has become a significant new source of atmospheric Pb along with many other chalcophile elements including Ag, Cd, Sb, and Tl.25 To test this hypothesis, Sphagnum fuscum was collected from 22 bogs surrounding mines and upgraders of the ABS area: this moss is the dominant hummock-forming species in bogs and receives metals exclusively from the air.26 Moss has been used for many decades, particularly in Europe, for monitoring atmospheric deposition of heavy metals.27 Vanadium which is known for its enrichment in bitumen28 showed a modest enrichment in the moss samples from the ABS region, but no significant enrichment of Pb was found.29 A follow-up study showed that the concentrations of Ag, As, Bi, Cd, Cu, Pb, Sb, Tl, and Zn in moss from the ABS region of northern AB are comparable to the “background” concentrations reported for forest moss from remote regions of central and northern Norway.29

While moss samples provide an indication of the extent of enrichment (or lack thereof) of trace metals in contemporary atmospheric deposition, they provide no indication of the changing rates and sources of contamination in the past. To fill this knowledge gap, peat cores were collected from five bogs in the vicinity of the open pit mines and bitumen upgraders in the ABS region, as well as a bog 264 km upwind of this increasingly industrialized region. The cores were carefully age dated using the bomb pulse curve of 14C along with 210Pb (and validated using 137Cs and 214Am) and showed that atmospheric Pb contamination has been in decline in northern AB for decades, and has now reached the point where Pb concentrations today are comparable to background values.30 Here, we carefully examine the atmospheric deposition histories of additional chalcophile elements, namely Ag, Cd, Sb, and Tl, using the same set of peat cores, but we also present the concentration profiles of V, Ni, and Mo as these three elements are well-known for their enrichments in bitumen.31 Based on the work by Kelly et al.,32 on trace metals in snow, the concentrations of all of these elements should be increasing over time in the bogs from the ABS region, and these increases should be preserved in the peat cores. Synthetic oil production from mining began in 1967 and increased to more than 50 million m³/yr by 2015.33 Our primary objective is to determine whether or not there has been a corresponding increase over time in atmospheric deposition of Ag, Cd, Sb, and Tl, as one would expect based on the work by Kelly et al.32 To help understand the impact of the oil industry on the environment, we also examine the chronology of atmospheric deposition of V, Ni, and Mo which are the three most abundant trace metals in bitumen.

2. MATERIALS AND METHODS

Peat cores ca. 15 × 15 × 100 cm were recovered from selected bogs (Figure 1) using a modified Wardenaar monolith sampler.34 Sphagnum moss was collected from these and many other bogs in the vicinity of the open pit mines and upgraders of ABS as part of recent studies of contemporary atmospheric metal deposition.35–36 Relative to the midpoint between the Suncor and Syncrude upgraders, the distances to the peat cores collected from these bogs are respectively 11.0 (MLL), 12.4 (JPH4), 24.9 (Mck), 48.7 (McM), 68.4 (ANZ), and 263.8 (UTK) km. The details of sample collection, preparation, and analysis, are all given elsewhere,37 but here in the Supporting Information (SI) we provide the exact location of each coring site (SI Table S1) as well as relevant QA/QC information for the trace metal determinations (SI Tables S2 and S3). The 14C age dates for the samples and standards are presented in SI Tables S4 and S5, respectively, and the 210Pb age dates in SI Table S6.

For comparison with the bogs in northern Alberta and to serve as a second reference site, a peat core was also collected in central Alberta, from the ombrotrophic bog at Seba Beach (SEBA) which is ca. 90 km W of Edmonton (Figure 1). This bog is mined for Sphagnum peat moss used in horticulture, but the core was collected from an undisturbed section of this extensive peatland complex. The pH and EC of the expressed porewaters and ash content of the peat from SEBA (SI Figure S1) are characteristic of continental ombrotrophic Sphagnum bogs.38 Below 60 cm, Pb concentrations are low and effectively constant (SI Figure S1) which indicates that the peat below this depth (older than 400 14C yr BP) is not measurably impacted by human activities.39 In fact, the average Pb concentration in this section of the peat core (0.23 ± 0.05 mg/kg, n = 19) is very similar to the values for the “cleanest” peat samples ever found in the northern hemisphere (0.28 ± 0.05 mg/kg, n = 17), in the Swiss bog “Etang de la Grue” (EGR) and dating from S320 and 8030 14C yr BP,40 (ca. 6000–9000 years old). The average 14C concentrations of Sr and Th in the peat from this depth at SEBA (31.7 ± 3.1 mg/kg and 0.15 ± 0.03 mg/kg, respectively, n = 19) provide a first estimate of the abundance of these elements in ombrotrophic peat from western Canada: Sr is a useful indicator of trophic status and Th a surrogate for the abundance of mineral particles (see below). The average 14C concentrations of other trace elements in this section of the SEBA core (from 69 to 98 cm) are given in SI Table S7. We note here that the concentrations of Ag, Cd, Mo, Ni, Sb, Th, Tl, and V in this section of the SEBA core (SI Table S7) are all within a factor of three of the values presented elsewhere41 for the ancient peat samples from Switzerland which predate the onset of agriculture and mining in central Europe.

3. RESULTS

3.1. Distinguishing between Ombrotrophic and Minerotrophic Zones Using Sr. Strontium is a sensitive indicator of groundwater inputs to peatlands and has been used successfully to distinguish between ombrotrophic (rain-fed) and minerotrophic (groundwater-fed) peats.42 The Sr concentration profiles all show increasing concentrations with depth.

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Figure 2. Sr and Th concentration profiles (mg/kg) for the six peat cores. Vertical dashed lines correspond to the average concentrations of Sr (31.7 ± 3.1 mg/kg) and Th (0.15 ± 0.03 mg/kg) in the peat from 69 to 98 cm at SEBA (n = 19).

Figure 3. Vanadium concentrations and EF versus depth for the five peat cores of the ABS region as well as the background site (UTK). The EF is calculated as the V/Th ratio of each sample, normalized to the corresponding ratio of the Upper Continental Crust. Vertical dashed lines correspond to the average concentrations of V (1.3 ± 0.4 mg/kg) in the peat from 69 to 98 cm at SEBA (n = 19).

3.2. Quantifying the Distribution of Mineral Matter Using Th. Thorium is a conservative, lithophile reference element which serves as a surrogate for the abundance of mineral particles in moss as well as peat. The average Th concentration in the deeper peat layers of the SEBA core (69–98 cm) is 0.15 ± 0.03 mg/kg (n = 19). The peat sample from...
ANZ bog (1.4 mg/kg) is comparable to preindustrial peat from UTK. For perspective, the abundance of V at the top of the peat cores (corresponding to the living vegetation) decline for the trace metal inputs. Therefore provide an upper limit on the significance of dust deposition for the trace metal inputs. Thorium concentrations, all within a factor of 3 of the values for the deeper peat layers in the ABS region do not differ by more than a factor of 3. Moreover the greatest V concentrations in each core are found below the surface which suggests that atmospheric V deposition was greater in the past and has declined over time. Some part of the V concentrations seen in these cores will be due to gas phase emissions from upgraders because of the volatility of V-containing porphyrins, the dominant chemical form of V in bitumen. Because of the volatility of V-containing porphyrins, the dominant chemical form of V in bitumen. (13.1:1) in the surface layers of these peat cores exceeds the corresponding ratio in Th concentrations (5.6:1) by little more than a factor of 2. Moreover the greatest V concentrations in each core are found below the surface which suggests that atmospheric V deposition was greater in the past and has declined over time. Some part of the V concentrations seen in these cores will be due to gas phase emissions from upgraders because of the volatility of V-containing porphyrins, the dominant chemical form of V in bitumen. However, some fraction of the V inputs to the bogs is in the form of dust particles: open pit mines, unpaved roads, coke piles and tailings ponds are all important sources of dusts to the air in this region. To correct the metal concentrations for dust inputs, the enrichment factor was calculated using the V/Th ratio of the peat samples and normalizing to the V/Th ratio of the Upper Continental Crust. These calculations reveal modest EF values for V in the living layer of these bogs: 6 (MIL), 4 (JPH4), 4 (McK), 3 (McM), 4 (ANZ), and 2 (UTK) which are consistent with previous work on V in moss from these locations. Most importantly, the peat cores show considerable declines in V enrichments over time in all of the bogs from the ABS region, with maximum EF values of 49 (MIL), 33 (JPH4), 33 (McK), 10 (McM), and 2 (UTK) which are consistent with previous work on V in moss from these locations. Most importantly, the peat cores show considerable declines in V enrichments over time in all of the bogs from the ABS region, with maximum EF values of 49 (MIL), 33 (JPH4), 33 (McK), 10 (McM), and 13 (ANZ). Notice that both the V concentrations as well as the V EF, have strongly declined with depth in the uppermost section of the peat cores from MIL and JPH4 which are closest to the midpoint between the two central upgraders (Figure 1). Vanadium concentrations in these two cores increased since the mid-19th century, reached their zenith by ~1970, and have since declined (SI Figure S2). Table 1. Comparison of Contemporary and Past Enrichment Factors for Trace Metals

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Values for Pb taken from Shotyk et al.68.
Like V, Ni, and Mo are also enriched in bitumen. However, Ni and Mo also show declines in concentrations and EF with depth in each peat core (SI Figures S3 and S4). Nickel is the second most abundant trace metal in bitumen, after V, and yet both the Ni concentrations as well as the Ni EF have strongly declined at MIL and JPH4 (SI Figure S3), the two bogs nearest the central upgraders (Figure 1). The declines in atmospheric contamination by trace metals are summarized in Table 1 which provides the EF for contemporary samples (living vegetation layer), the maximum EF found in the peat cores as well as the ratio of maximum to contemporary values. In the peat profile from MIL which is nearest to industry, the enrichments of Ni and Mo have declined by a factor of 10 or more, since their zenith in the past. Nickel and Mo concentrations and EFs versus time since AD 1800 are shown in SI Figures S5 and S6, respectively.

### 3.4. Ag, Cd, Sb, Tl.

The concentration profiles for Cd show remarkable declines over time in all of the peat cores (Figure 4). To help put these Cd concentrations into perspective, it is important to note that, in each of the peat cores from northern AB (Figure 4), the Cd concentrations in the surface layers are actually lower than the values (67 ± 13 μg/kg, n = 19) found in the deeper, preindustrial peat layers at SEBA (SI Table S7) which are more than 700 years old. It is also worth noting that the Cd concentrations in the top slice of the peat core from MIL (43 μg/kg), the peat deposit closest to industrial development, is much lower than the Cd concentrations reported for the living layer of peat cores collected across Canada67 which range from 106 μg/kg in northern Quebec to 362 μg/kg in southern Ontario. The EF values in the contemporary samples are much less than the maximum values seen in the past, in some cases (McK) up to 55 times less. Graphs illustrating the chronology of Cd accumulation show that all of the bogs sampled within the ABS region have witnessed declining concentrations and enrichments of Cd in recent decades (SI Figure S7).

Like Cd, the concentrations of Ag and Sb are greater in deeper, older peat layers, revealing declining inputs to the bogs (SI Figures S8, S9). Thallium is slightly more complicated, as it is more abundant in the upper layers at MIL, JPH4 and McK, but not McM or ANZ (SI Figure S10). Silver, Sb and Tl all show declining enrichments as well (SI Figure S8–10). There is no significant enrichment of Tl at the surface of any of the peat cores from the ABS region of northern Alberta (SI Figure S10). The chronology of atmospheric deposition of Ag, Sb and Tl, as reflected in their concentrations and EFs since AD 1800 is shown in SI Figures S11–13.

### 4. DISCUSSION

Based on snowpack sampling, it was claimed that “the oil sands industry releases the 13 elements considered priority pollutants (PPE) under the Environmental Protection Agency’s Clean Water Act, via air, soil, and water, to the Athabasca River and its watershed” and that “all PPE except Se were greater near oil sands developments than at more remote sites”. Our work on moss and peat collected in the ABS region is part of an effort to provide an independent assessment of metal emissions from industry, with the composition of moss a reflection of contemporary inputs, and peat providing insight into atmospheric deposition in the past. If the priority pollutants listed by Kelly et al., namely Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, and Zn, are emitted to the atmosphere in...
4.1. Surface Peat Versus Sphagnum Moss. The trace metal concentrations reported here for the top (living) layer of these bogs are consistent with the published data for trace metals in Sphagnum moss from bogs in this region, even though the living layer is a complex mixture of many plant species including both moss as well as herbs and ericaceous shrubs; some of these materials may represent multiple growing seasons. In contrast, the Sphagnum moss data corresponds to samples that were hand-picked to isolate a single moss species (mainly Sphagnum fuscum) by removing foreign plant matter, and they were sectioned to ensure that only the living portion corresponding to that growing season was selected for analysis. In our study of Sphagnum moss from 21 bogs surrounding the ABS region, we found that (1) the concentrations of Ag, Cd, Pb, Sb, and Tl (determined in the metal-free, ultraclean SWAMP lab) were considerably lower than the values found in the same species of moss from four bogs in southern Germany (determined in the metal-free, ultraclean lab at the University of Heidelberg), (2) the concentrations of these metals in moss from the ABS region showed strong linear correlations with Th, a conservative lithophile element indicative of the abundance of mineral particles in the plants, and (3) that none of these elements was enriched in the plants from the ABS region, relative to the M/Th ratio of ancient peat samples ca. 6000 to 9000 years old, from northern Norway. In a subsequent study, we showed that the concentrations of Ag, As, Bi, Cd, Cu, Ni, Pb, Sb, Tl, and Zn in the same set of moss from the ABS region, but determined at a commercial lab, were comparable to the concentrations reported for forest moss from remote areas of central and northern Norway. Thus, by any measure that we know of, the concentrations of trace elements in the Sphagnum fuscum moss of the bogs surrounding the ABS region, and the surface layers of the peat profiles shown here, are low.

4.2. Lichens and Forest Moss. Early work by Addison and Puckett employing lichens as biomonitors showed decreasing V concentrations with distance from the Suncor operations. The map showing V concentrations at 69 sites (Figure 2) is reproduced here (SI Figure S14) and shows that samples nearest the upgrading operation at that time contained hundreds of mg/kg V. Their V concentration data for selected sites versus distance (Addison and Puckett, Table 1) is reproduced here and shows V concentrations reaching values of 3 mg/kg at a distance of 85 km (SI Figure S14); at the time, 3 mg/kg was considered the “background” abundance of V in the lichens but today, this is the average concentration of V found in Sphagnum moss from the ABS region. It should be noted that the V concentration data of Addison and Puckett was obtained at that time using instrumental neutron activation analysis (INAA), a sensitive, accurate, and precise method for the determination of V in solid samples which is still in use today. In a separate study by the Alberta Research Council, forest moss (Pleurozium schreberi) was collected from numerous sites in the ABS region during 1976, 1983, and 1990, and in addition, the lichen Usnea spp. sampled during 1983 and 1990. The V and Ni concentrations given in the summary of elemental concentrations in that report (Table 4.4) is reproduced here (SI Figure S15) and dramatic declines over time are seen for both metals. In respect to the quality of the analytical data, the lichens had been digested in acid (HNO₃, HClO₄, and HF) and total concentrations of trace metals determined using ICP-AES; however, the authors also analyzed the 1976 and 1983 samples using INAA of solid samples, and the V concentration data obtained by the two independent methods was in excellent agreement (Figure 4.1). Lichen samples (Hypogymia physodes) recently collected around the ABS region by the Wood Buffalo Environmental Monitoring Association (WBEA) and measured for a broad range of trace metals reveal V concentrations more than ten times lower than those reported decades earlier by Addison and Puckett and Pauls. For convenience, we have plotted the average values presented by Edgerton et al. (Table 14.5) for proximal (n = 60) and distal (n = 61) samples for V, Ni, Mo, Cd, Pb, Sb, and Th (SI Figure S16). For elements enriched in bitumen (V, Ni, and Mo), the range in concentrations seen in the contemporary lichens is similar to the range seen in the top layers of the peat cores presented here, and comparable to the concentrations found in Sphagnum moss. The differences between proximal versus distal sites, on average, is approximately 3X for each of these elements, but also for Th which suggests the differences in V, Ni, and Mo are mainly the result of differences in dust loadings, even though all three are enriched in bitumen. Linear regression analyses of this lichen data showed strong correlations between V and Al as well as between Ni and Al (R² = 0.830 and 0.851, respectively, n = 241). According to these authors, road dusts, and overburden contain much greater concentrations of V and Ni than do the tailings sands themselves, leading to the conclusion that the greatest impact on element concentrations in lichen tissues of this region is related to fugitive dust.

4.3. Trace Metals Data in Precipitation. During the late 1970s, fly ash samples from coke combustion at the Great Canadian Oil Sands upgrader (today Suncor) yielded ca. 2.5% V, 1% Ni, and 0.25% Mo with the metals being almost entirely in the stable oxide form. In a subsequent study employing snowpack sampling it was found that the soluble fraction of Al and V was generally less than 1% and 10%, respectively and that their insoluble fraction essentially represents total deposition. In a follow up study also using snowpack sampling, it was found that loadings had decreased substantially because “electrostatic precipitators had been installed in the Suncor power plant in November of 1979 to reduce the emissions of particulate matter.” The relevant maps showing V loadings in snow collected in January of 1978 versus January and February of 1981, are reproduced here (SI Figure S17). Between these two snow sampling campaigns, V loadings had declined by a factor of 10 (SI Figure S17).
Contemporary snow data from Bari et al. show much greater concentrations of trace metals at the WBEA/Mannix sampling location (near development, 7.5 km) than the South site (distant, 68 km) which is used for reference: Ag, Sb, Cd, Pb, Sb, and Tl between these two sites could be explained in their entirety, simply based on the differences in dust concentrations. All of the work published on trace metals to date by WBEA suggests that the single greatest source of metals by far is dust from unpaved roads, tailings pond beaches and dykes, open pit mines, and other bare land surfaces with abundant fine-grained mineral particles. More recent data for metals in snow further supports this view. For example, consider the average total concentrations of V, Ni, and Cr in snow from the ABS region: using this data to calculate the V/Cr and Ni/Cr ratios (1.64 and 0.52), we obtain values which are in good agreement with the corresponding ratios in the Upper Continental Crust (1.51 and 0.52), but far removed from the corresponding ratios in bitumen (174 and 70, respectively, according to Hitchon and Filby, 1983).

4.4. V, Ni, and Mo as Tracers of Anthropogenic Emissions. At MIL, the bog which is nearest the midpoint between the Suncor and Syncrude upgraders, the top slice of the peat core yields an EF for V = 6 (Figure 3). The control site (UTK) which was 264 km SW of this same midpoint yielded an EF for V = 2. So, relative to the UTK site, the maximum enrichment of V in the peat bogs of the ABS region today is only a factor of 3. The contemporary enrichments of Ni in the bogs of the ABS region are in the range 3–7, relative to the crustal ratio of Ni/Th (Table 1), but these are all less than the Ni EF (12) found at the top of the bog at UTK. The contemporary enrichments of Mo in the bogs of the ABS region are in the range 18 to 21, relative to the crustal ratio of Mo/Th (Table 1), but these are all within a factor of 2 of the EF (11) found at the top of the bog at UTK. Even though V, Ni and Mo are all enriched in bitumen, their enrichments in moss and peat are rather modest. The slightly greater enrichment of Mo, relative to V and Ni, may be a reflection of the essential role of Mo in plant nutrition.

By far the most abundant trace metals in bitumen are V, Ni, and Mo, so these are the obvious tracers of anthropogenic metal emissions to the surrounding environment from industrial development. Given that V is the most abundant trace metal in bitumen, the limited extent of V enrichment in moss and peat is remarkable. But if V and Ni are the most abundant trace metals in bitumen, why is the extent of their enrichment so low? First, typical concentrations of V and Ni in bitumen are 190 and 69 μg/kg, respectively. Thus, the V and Ni concentrations in bitumen are only a factor of 3.6 and 3.7 times greater, respectively, than their abundance in crustal rocks. So, even though they are enriched in bitumen, the magnitude of their enrichment is low. Second, the concentrations of V and Ni in bitumen noted above refer to the organic fraction after extraction and isolation. Given that bulk ABS are typically 85% mineral matter, mainly coarse sand with some silt and clays, the concentrations of V and Ni in bulk bituminous sand are “diluted” by mineral material, relative to their abundance in bitumen. Third, in respect to stack emissions from the upgraders themselves, it would appear based on the early work on snowpack sampling (SI Figure S17) as well as mosses and lichens (SI Figure S5), that the installation of electrostatic precipitators, beginning in 1979, have been effective. Of the peat cores studied to date, the greatest V concentrations by far are those from MIL which is the site closest to industry. Even here, however, there have been remarkable declines in V concentrations, from 141 mg/kg at 23 cm to 11 mg/kg at the top of the peat profile (Figure 3). The 210Pb age date for the sample containing the greatest V concentration (MIL 21) is AD 1978 ± 2 yrs (SI Table S6) which supports the view that the electrostatic precipitators installed in 1979 had a profound impact of atmospheric V emissions.

4.5. The Crustal Enrichment Factor. The Enrichment Factor concept, pioneered by Peirson et al., and applied to tropospheric aerosols worldwide by Rahn, has been severely criticized by some: considered to be of doubtful merit and believed to be based on several serious flaws, it was recommended that its indiscriminate use be abandoned. It is possible that the limited extent of enrichment of trace metals in living vegetation and peat presented here is simply being masked by recent increases in dust deposition from the mines, tailings, and roads? This seems unlikely, for three reasons. First, the Th concentration profiles show that the increase in Th concentrations over time near the surface of the peat cores is modest (Figure 2). At JPH4, for example, which is only 12 km from the midpoint between the two central upgraders, Th concentrations have increased only by a factor of 2 since 1979, from 184 to 386 μg/kg, while during the same interval Cd concentrations (Figure 4) have declined by a factor of 7 (from 258 μg/kg to 35 μg/kg at the surface today). Thus, the decrease in Cd EF is being driven more by a decrease in Cd concentrations over time, and less by an increase in Th concentrations. Second, while there is a significant increase in Th concentrations in the surface peat layers with distance toward industry, from 65 μg/kg at UTK to 386 μg/kg at JPH4 (Figure 2), there is no significant change in Cd concentrations. For example, compare the Cd concentrations in the surface layers of UTK (the remote site, with 41 μg/kg Cd) with JPH4 (35 μg/kg, even though it is only 12 km from the midpoint between the two central upgraders): clearly, the increase in dust deposition with distance toward industry has not affected the abundance of Cd in surface vegetation. It is worth noting here that the average concentrations of Cd in lichens presented by Edgerton et al. (Table 14.5) are similar for proximal (n = 60) and distal (n = 61) sites (see SI Figure S16). Third, as we noted earlier, Cd concentrations in the surface layers of these bogs is low (Figure 4): less than the average values for Cd in preindustrial peat from the SEBA core (SI Table S7), and comparable to Cd in contemporary forest moss from remote parts of central and northern Norway. In summary, Th concentrations in the peat cores collected from bogs nearest industry show that dust inputs have indeed increased recently, but Cd concentrations in these profiles have been declining the entire time.

Enrichment factors, when used with caution, can help to distinguish between natural and anthropogenic sources of trace metals to the environment. Here, we have presented both the metal concentration profiles as well as the metal EF profiles,
to provide a more complete picture of the history of atmospheric metal deposition in this region.

4.6. Decades of Declining Atmospheric Deposition of Trace Metals. The maximum enrichment by Ag, Cd, Sb and TI, as well as V, Ni and Mo, is found in deeper, older peat layers from these bogs (Table 1): clearly, the extent of atmospheric metal contamination was greater in the past. In fact, the EF values for Ag, Cd, and Sb in the top layers of the bogs in the ABS region (Table 1) are less than the values reported for the control site (UTK). In respect to Ti, there is no significant enrichment of this metal in the top sample of any of these peat cores. Atmospheric deposition of all these metals, as well as Pb, has been in decline for decades (SI). Taking V as a tracer of atmospheric metal emissions from the industrial development of the ABS, the declining enrichments over time of trace elements in these peat cores is entirely consistent with the results presented in many previous studies.

If we were to completely ignore the EF calculations, out of concern that they have been unduly influenced by recent increases in dust deposition, and were to instead focus exclusively on the metal concentration profiles, we would arrive at the same conclusion. In the two peat cores nearest industry, concentrations of V have been declining for decades (Figure 3), even though V is the single most abundant element in bitumen. Concentrations of Cd, have not only been declining (Figure 4), but it is no more abundant in the surface layers of the bogs near industry than it is at our remote site (UTK), and at the surface of these bogs it is no more abundant than it is in the preindustrial peat from the bog at Seba Beach. The declines in V and Cd concentrations are all the more remarkable, given that oil production from mining operations is currently over 50 million m³/yr. It would appear that the extent of environmental contamination by heavy metals from the industrial development of the ABS, has been exaggerated by a considerable margin.

Compared with the retrospective, peat bog studies of environmental contamination by trace metals cited in the Introduction, the concentrations found in these peat cores, especially in recent layers, are low. For example, the maximum concentration of Sb found in this study (SI Figure S9) is 75 times less than the maximum reported for some Swiss peatlands.21 Times less than that reported for Scottish peat bogs, and 8 times less than the maximum reported for the Myranar peatland on the remote Faroe Islands. In fact, the maximum Sb concentration found in this study is approximately 30 μg/kg which is an order of magnitude less than its abundance in the Upper Continental Crust. There is surprisingly little modern data for trace elements in the ABS, and a detailed assessment is warranted, to help us better understand the limited extent of environmental contamination by potentially toxic heavy metals. In addition, critical examination of particulate emissions are needed, including studies of chemical speciation, to clearly distinguish between submicrometer aerosols and mechanically generated dusts.

4.7. Analytical Challenges Presented by Ag and TI. The method detection limits (MDLs) obtained for the trace metals studied here are shown in SI Table S3. As a general rule, the accuracy and precision of trace metal determinations decrease as concentrations approach the MDL. For V, Ni, and Mo, the median concentrations are far above the MDL (469 μg/kg, 71X, and 83X, respectively). In respect to the potentially toxic chalcophile elements, the ratio of median concentrations found in peat to the MDL decreases in the order Pb (240), Cd (167), Sb (19), Ag (6), and Ti (2). Despite the use of the metal-free, ultraclean lab facilities, related infrastructure, and state-of-the-art quadrupole ICP-MS, Ag and Ti still present a challenge. In the current study of 251 peat samples, Ag and Ti were below the MDL in 15 and 7 samples, respectively. Seventy-five percent of the peat samples contained <30 μg/kg of Ag and Ti. But this is largely to be expected, given that the natural abundances of these elements is also very low: Ag and Ti in the Upper Continental Crust, for example, are only 55 and 75 μg/kg, respectively. To the best of our knowledge, there is no published data for these two elements in bitumen and this is most likely due to their low abundance. From these perspectives, the very low concentrations of Ag and Ti in peat are understandable. But in the context of environmental impacts by mining and upgradings activities in northern Alberta, claims regarding contamination of environmental media by Ag and Ti deserve additional scrutiny, simply because of their very low natural abundances, and the challenges this presents for the analyst, even those with the latest in laboratory equipment and facilities.

ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b04909.

Description of age dating, 14C age dates for samples and standards and 209Pb age dates of all six peat cores; electrical conductivity and pH of the porewaters, as well as ash contents, Sr, Th and Pb concentrations of the peat profile from Seba Beach; for the five peat cores from the ABS region (MIL, JPH4, McK, McM, ANZ) and UTK, the concentration profiles and EF profiles for Ni, Mo, Ag, Sb, and Ti; metal concentrations and EF profiles (V, Ni, Mo, Ag, Cd, Sb and Ti) versus calendar year since AD 1800; V concentrations in lichens, from Addison and Puckett; V and Ni concentrations in moss and lichens from Puckett et al., and Sphagnum moss from Shorty et al. Metal concentrations in lichens from Edgerton et al., V in snow from Barrie and Kovalick, GPS coordinates of peat bogs sampled; QA/QC data for trace metal determinations using ICP-MS; average concentrations of trace metals in peat in deeper layers at Seba Beach (PDF)

AUTHOR INFORMATION

Corresponding Author

Phone: 780-492-7155; fax: 780-492-4323; e-mail: shotyk@ualberta.ca.
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