

1 Peat Bogs Document Decades of Declining Atmospheric 2 Contamination by Trace Metals in the Athabasca Bituminous Sands 3 Region

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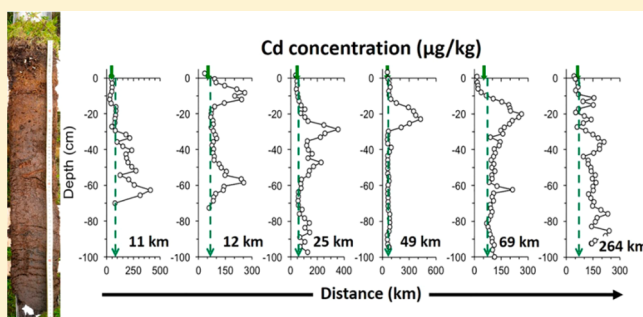
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13 **S** Supporting Information

14 **ABSTRACT:** Peat cores were collected from five bogs in the
15 vicinity of open pit mines and upgraders of the Athabasca
16 Bituminous Sands, the largest reservoir of bitumen in the
17 world. Frozen cores were sectioned into 1 cm slices, and trace
18 metals determined in the ultraclean SWAMP lab using ICP-
19 QMS. The uppermost sections of the cores were age-dated
20 with ²¹⁰Pb using ultralow background gamma spectrometry,
21 and selected plant macrofossils dated using ¹⁴C. At each site,
22 trace metal concentrations as well as enrichment factors
23 (calculated relative to the corresponding M/Th ratio of the
24 Upper Continental Crust) reveal maximum values 10 to 40 cm
25 below the surface which shows that the zenith of atmospheric
26 contamination occurred in the past. The age-depth relationships show that atmospheric
27 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
28 greatest contemporary enrichments of Ag, Cd, Sb, and Tl (in the top layers of the peat cores) are found at the control site
29 (UTK) which is 264 km SW, suggesting that long-range atmospheric transport from other sources must be duly considered in
30 any source assessment.



31 **■** INTRODUCTION

32 Potentially toxic “heavy metals”, in particular the chalcophile
33 elements (Ag, As, Bi, Cd, Cu, Ni, Pb, Sb, Te, Tl and Zn) which
34 are enriched in sulfide minerals and the ore deposits where they
35 are concentrated^{1,2} have been emitted to the environment from
36 human activities for thousands of years.³ Environmental
37 contamination with metals probably began with the discovery
38 of cupellation which gave rise to mining and metallurgy,⁴ with
39 much interest generated by the silver obtained from lead
40 ores.^{5–7} Retrospective studies using lacustrine sediments have
41 documented environmental contamination by several of these
42 elements, Pb and Hg in particular, extending back in time many
43 millennia in the Middle East,^{8,9} South America^{10–15} and Asia.¹⁶
44 The history of environmental contamination from mining and
45 metallurgy in North America has received less attention, but
46 recent studies of sediments from the Michigan Peninsula
47 suggest copper mining and metallurgy may have given rise to
48 environmental Pb contamination starting as long as 8,000 years

ago.^{17,18} Snow and ice cores from the Arctic provide remarkable
49 records of atmospheric Pb contamination extending back in
50 time more than three millennia.^{19–21} For example, an ice core
51 from Devon Island, Nunavut, Canada, has provided a 15 000
52 year record of atmospheric Pb deposition, with evidence of
53 anthropogenic inputs dating back to the time of the
54 Phoenicians, followed by the Greek and then Roman
55 civilizations, with notable episodes of intense Pb emissions
56 during the Medieval Period, the Industrial Revolution, and
57 later, from the introduction of leaded gasoline.²¹ Careful
58 analyses of these cores using metal-free, ultraclean lab
59 procedures and protocols also document hemispheric con-
60 tamination by Ag and Tl,²² Sb,²³ as well as As, Bi, Cu, and Zn²⁴ 61

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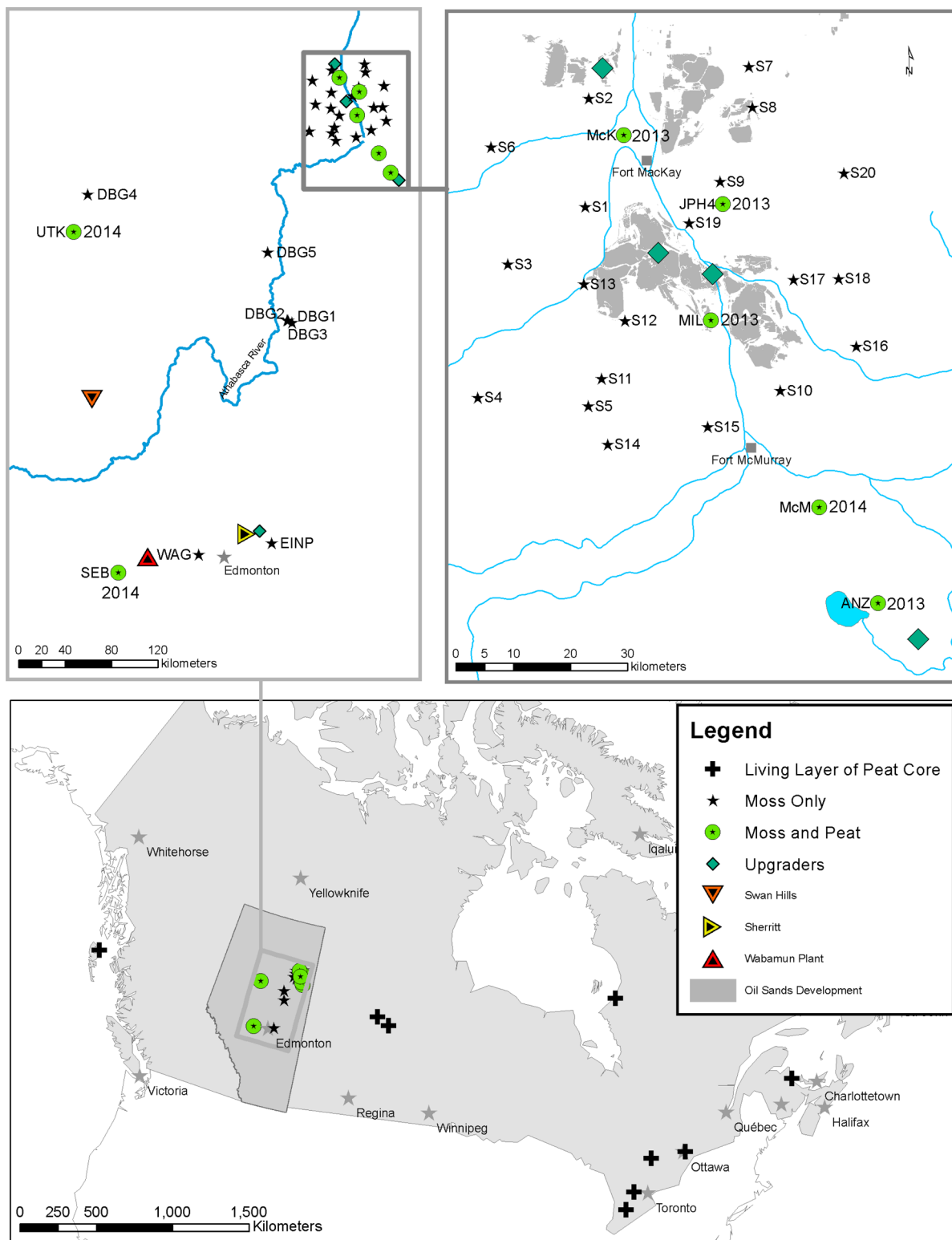


Figure 1. Map showing the locations of the peat cores described in the text (McK, JPH4, MIL, McM, ANZ, and UTK) as well as the year of collection. Also shown for comparison, the locations of the moss samples collected from peat bogs of this region which were also measured for trace metals^{66,67} as 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.⁶⁷ 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.¹⁰⁰ All displayed vector data is derived from either Geogratis Canada,¹⁰¹ GeoDiscover Alberta¹⁰² or created by authors.

62 extending back in time several millennia. Trace metal
63 contamination of polar snow and ice results from long-range
64 atmospheric transport of submicron aerosols generated by high
65 temperature combustion processes.

66 Ombrotrophic (i.e., rain-fed) peat bogs are also excellent
67 archives of atmospheric deposition of many trace metals,
68 providing the first complete, long-term record (ca. 15 000
69 years) of atmospheric Pb deposition in Europe where
70 anthropogenic inputs have dominated continuously for more
71 than 3000 years^{25,26} Detailed histories of atmospheric Pb
72 contamination have since been reconstructed using peat cores
73 from bogs across Europe.^{27–42} Bogs in Europe have also been
74 used in retrospective studies of many other trace elements,
75 including As,^{43,44} Ag,⁴⁵ Cd,⁴⁶ Hg,^{47–49} Ni,^{50,51} Sb,^{36,43,52,53} and
76 Tl.⁴⁵ In contrast, there has been only a handful of studies of
77 atmospheric metal deposition using peat cores from bogs in
78 North America, and they have all been undertaken in the
79 northeastern part of the continent.^{54–61}

80 Based on analyses of snow collected during a single season, it
81 was claimed that open pit mining and upgrading of the
82 Athabasca Bituminous Sands (ABS) in northeastern Alberta
83 (AB) has become a significant new source of atmospheric Pb
84 along with many other chalcophile elements including Ag, Cd,
85 Sb, and Tl.⁶² To test this hypothesis, *Sphagnum fuscum* was
86 collected from 22 bogs surrounding mines and upgraders of the
87 ABS area: this moss is the dominant hummock-forming species
88 in bogs and receives metals exclusively from the air.⁶³ Moss has
89 been used for many decades, particularly in Europe, for
90 monitoring atmospheric deposition of heavy metals.⁶⁴ Vanadium
91 which is known for its enrichment in bitumen⁶⁵ showed a
92 modest enrichment in the moss samples from the ABS region,
93 but no significant enrichment of Pb was found.⁶⁶ A follow up
94 study showed that the concentrations of Ag, As, Bi, Cd, Cu, Pb,
95 Sb, Tl, and Zn in moss from the ABS region of northern AB are
96 comparable to the “background” concentrations reported for
97 forest moss from remote regions of central and northern
98 Norway.⁶⁷

99 While moss samples provide an indication of the extent of
100 enrichment (or lack thereof) of trace metals in contemporary
101 atmospheric deposition, they provide no indication of the
102 changing rates and sources of contamination in the past. To fill
103 this knowledge gap, peat cores were collected from five bogs in
104 the vicinity of the open pit mines and bitumen upgraders in the
105 ABS region, as well as a bog 264 km upwind of this increasingly
106 industrialized region. The cores were carefully age dated using
107 the bomb pulse curve of ¹⁴C along with ²¹⁰Pb (and validated
108 using ¹³⁷Cs and ²⁴¹Am) and showed that atmospheric Pb
109 contamination has been in decline in northern AB for decades,
110 and has now reached the point where Pb concentrations today
111 are comparable to background values.⁶⁸ Here, we carefully
112 examine the atmospheric deposition histories of additional
113 chalcophile elements, namely Ag, Cd, Sb, and Tl, using the
114 same set of peat cores, but we also present the concentration
115 profiles of V, Ni, and Mo as these three elements are well-
116 known for their enrichments in bitumen.⁶⁶ Based on the work
117 by Kelly et al.,⁶² on trace metals in snow, the concentrations of
118 all of these elements should be increasing over time in the bogs
119 from the ABS region, and these increases should be preserved
120 in the peat cores. Synthetic oil production from mining began
121 in 1967 and increased to more than 50 million m³/yr by 2015.
122 Our primary objective is to determine whether or not there has
123 been a corresponding increase over time in atmospheric
124 deposition of Ag, Cd, Sb, and Tl, as one would expect based

on the work by Kelly et al.⁶² 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.⁶⁹ *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.^{66,67} Relative to the midpoint
between the Suncor and Syncrude upgraders, the distances to
the peat cores collected from these bogs are respectively 11.0
(MIL), 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,⁶⁸ 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.⁷⁰ 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.⁶⁸ 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 Gruère” (EGR) and dating from 5320
and 8030 ¹⁴C yr BP.²⁵ (ca. 6000–9000 years old). The average
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
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 elsewhere⁴⁶ 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.²⁶ The Sr concentration profiles all show increasing concentrations with depth

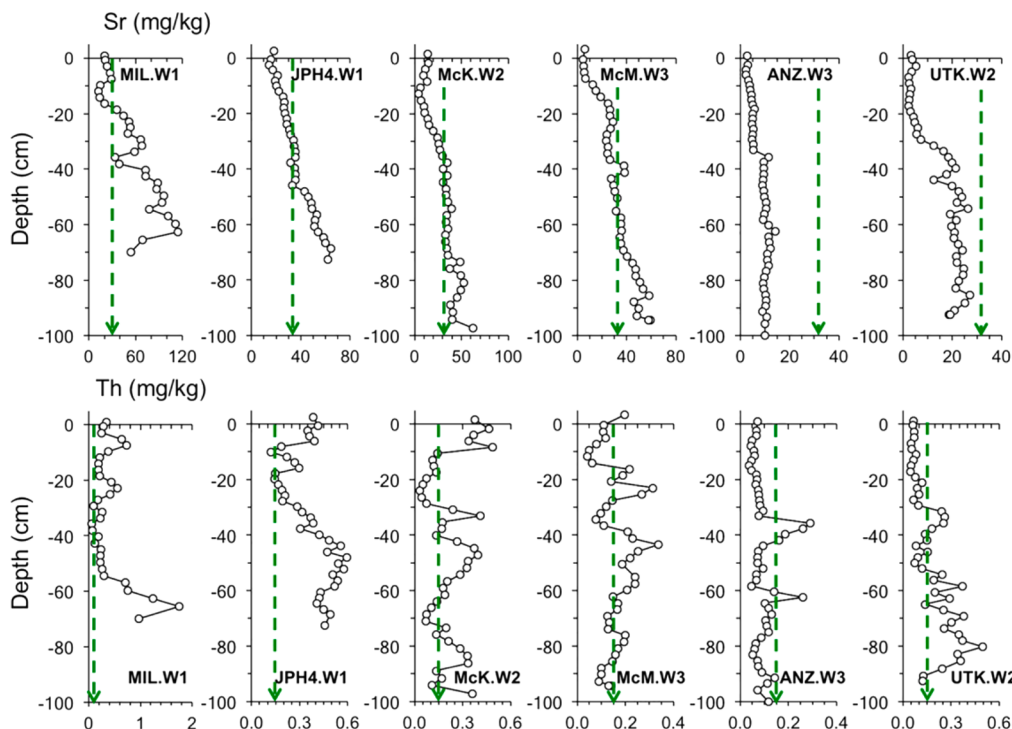


Figure 2. Sr and Th concentration profiles (mg/kg) for the six peat cores. Vertical dashed lines correspond to the average concentrations of Sr (31.7 ± 3.1 mg/kg) and Th (0.15 ± 0.03 mg/kg) in the peat from 69 to 98 cm at SEBA ($n = 19$).

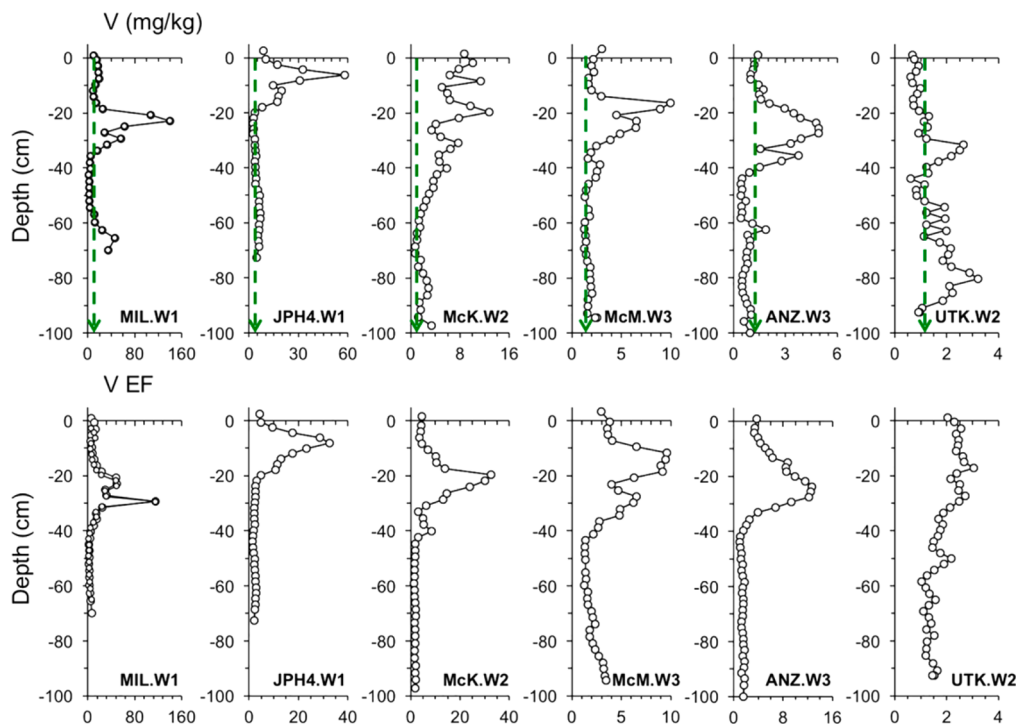


Figure 3. Vanadium concentrations and EF versus depth for the five peat cores of the ABS region as well as the background site (UTK). The EF is calculated as the V/Th ratio of each sample, normalized to the corresponding ratio of the Upper Continental Crust.⁷⁸ Vertical dashed lines correspond to the average concentrations of V (1.3 ± 0.4 mg/kg) in the peat from 69 to 98 cm at SEBA ($n = 19$).

(Figure 2), but the surface peat layers of all cores contain less Sr than the ombrotrophic peat bog at SEBA. Specifically, the Sr concentration profiles suggest that the ombrotrophic zone is restricted to the top 20 cm at MIL, top 30 cm at JPH4, and top 40 cm at McK and McM; in contrast, the peat cores from ANZ and UTK are ombrotrophic throughout (Figure 2).

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^{66,67} as well as peat.⁶⁸ 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 194

Table 1. Comparison of Contemporary and Past Enrichment Factors for Trace Metals^a

element	Mildred (MIL)	JPH4	McKay (McK)	McMurray (McM)	Anzac (ANZ)	Utikuma (UTK)
	[11.0 km]	[12.4 km]	[24.9 km]	[48.7 km]	[68.4 km]	[263.8 km]
V EF (contemporary)	6	4	4	3	4	2
V EF (maximum)	49	33	33	10	13	3
ratio, max/contemporary	8	8	8	3	3	2
Ni EF (contemporary)	7	6	5	3	7	12
Ni EF (maximum)	69	48	91	16	17	26
ratio, max/contemporary	10	8	18	5	2	2
Mo EF (contemporary)	21	10	12	7	18	11
Mo EF (maximum)	246	69	98	32	24	23
ratio, max/contemporary	12	7	8	5	1	2
Ag EF (contemporary)	17	17	9	4	13	28
Ag EF (maximum)	93	40	134	26	46	305
ratio, max/contemporary	5	2	15	7	4	11
Cd EF (contemporary)	13	9	10	31	20	65
Cd EF (maximum)	210	169	554	267	548	304
ratio, max/contemporary	16	19	55	9	27	5
Sb EF (contemporary)	8	4	6	5	8	11
Sb EF (maximum)	33	21	34	21	25	22
ratio, max/contemporary	4	5	6	4	3	2
Tl EF (contemporary)	1	1	1	1	1	2
Tl EF (maximum)	3	6	8	5	5	2
ratio, max/contemporary	3	6	8	5	5	1
Pb EF (contemporary) ⁶⁸	3	2	2	2	3	2
Pb EF (maximum) ⁶⁸	18	17	48	26	66	23
ratio, max/contemporary	6	9	24	13	22	12

^aValues for Pb taken from Shoty et al.⁶⁸.

195 70 cm (SEBA 63) dates from 765 ± 15 ¹⁴C yr BP (AD 1242–
 196 1279) which predates the arrival of the first European in
 197 Alberta (Anthony Henday, 1754) by several centuries. These
 198 Th concentrations are within a factor of 2 of the values for the
 199 “cleanest” peat layers from the Swiss bog “EGR” (0.07 ± 0.02
 200 mg/kg, $n = 19$). The Swiss peat samples, dating from 5320 and
 201 8030 ¹⁴C yr BP and corresponding to the Holocene Climate
 202 Optimum, represent the lowest rates of dust deposition seen
 203 since the Late Glacial.^{25,26} Thus, the average Th concentration
 204 in preindustrial peat from SEBA provides a useful reference
 205 level for understanding soil-derived dust inputs to the bogs
 206 from the ABS region. Thorium concentrations in the top slice
 207 of the peat cores (corresponding to the living vegetation)
 208 decline with distance (Figure 2) from industry as follows (mg/
 209 kg): 0.34 (MIL), 0.39 (JPH4), 0.38 (McK), 0.20 (McM), 0.07
 210 (ANZ), and 0.07 (UTK). Assuming similar rates of plant
 211 growth in each bog, the declining Th concentrations with
 212 distance from industry reflects elevated rates of dust deposition
 213 from anthropogenic activities near the mines and upgraders: the
 214 consequences of these elevated dust fluxes for trace metal
 215 deposition is considered below. However, it is very important
 216 to note that the Th concentrations at the top of the bogs from
 217 the ABS region do not differ by more than a factor of 6, and are
 218 all within a factor of 3 of the values for the deeper peat layers
 219 from the SEBA site (0.15 mg/kg). Thorium concentrations,
 220 therefore provide an upper limit on the significance of dust
 221 deposition for the trace metal inputs.

222 **3.3. V, Ni, Mo.** Vanadium concentrations in the top layers of
 223 the peat cores (corresponding to the living vegetation) decline
 224 with distance from industry (Figure 3) as follows (mg/kg): 10.5
 225 (MIL), 8.8 (JPH4), 8.6 (McK), 3.0 (McM), 1.4 (ANZ), and 0.8
 226 (UTK). For perspective, the abundance of V at the top of the
 227 ANZ bog (1.4 mg/kg) is comparable to preindustrial peat from

SEBA (1.3 ± 0.4 mg/kg), even though the core at ANZ was 228
 collected within 10 km of the nearest upgrader (Nexen). We 229
 note that the ratio of maximum to minimum V concentrations 230
 (13.1:1) in the surface layers of these peat cores exceeds the 231
 corresponding ratio in Th concentrations (5.6:1) by little more 232
 than a factor of 2. Moreover the greatest V concentrations in 233
 each core are found below the surface which suggests that 234
 atmospheric V deposition was greater in the past and has 235
 declined over time. Some part of the V concentrations seen in 236
 these cores will be due to gas phase emissions from upgraders 237
 because of the volatility of V-containing porphyrins,⁷¹ the 238
 dominant chemical form of V in bitumen.^{72–74} However, some 239
 fraction of the V inputs to the bogs is in the form of dust 240
 particles.^{66,67} open pit mines, unpaved roads, coke piles and 241
 tailings ponds are all important sources of dusts to the air in 242
 this region.⁷⁵ To correct the metal concentrations for dust 243
 inputs, the enrichment factor^{76,77} was calculated using the V/ 244
 Th ratio of the peat samples and normalizing to the V/Th ratio 245
 of the Upper Continental Crust.⁷⁸ These calculations reveal 246
 modest EF values for V in the living layer of these bogs: 6 247
 (MIL), 4 (JPH4), 4 (McK), 3 (McM), 4 (ANZ), and 2 (UTK) 248
 which are consistent with previous work on V in moss from 249
 these locations.^{66,67} Most importantly, the peat cores show 250
 considerable declines in V enrichments over time in all of the 251
 bogs from the ABS region, with maximum EF values of 49 252
 (MIL), 33 (JPH4), 33 (McK), 10 (McM), and 13 (ANZ). 253
 Notice that both the V concentrations as well as the V EF, have 254
 strongly declined with depth in the uppermost section of the 255
 cores from MIL and JPH4 (Figure 3), the two peat bogs which 256
 are closest to the midpoint between the two central upgraders 257
 (Figure 1). Vanadium concentrations in these two cores 258
 increased since the mid-19th century, reached their zenith by 259
 ~1970, and have since declined (SI Figure S2). 260

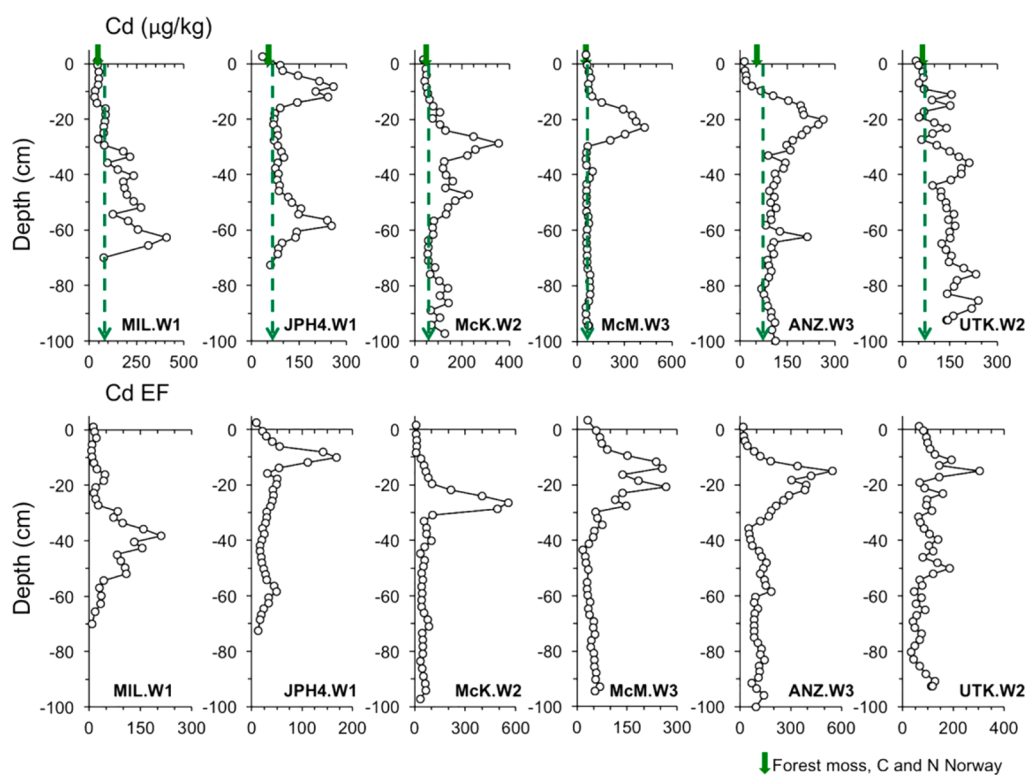


Figure 4. Cadmium concentrations and EF versus depth for the five peat cores of the ABS region as well as the background site (UTK). Vertical dashed lines correspond to the average concentrations of Cd ($67 \pm 13 \mu\text{g}/\text{kg}$) in the peat from 69 to 98 cm at SEBA ($n = 19$). Other details as per Figure 3. The small green vertical arrow at the top of the concentration profiles indicates the “background” concentrations of Cd in forest moss from central and northern Norway.⁶⁷

261 Like V, Ni, and Mo are also enriched in bitumen.⁷⁹ However,
 262 Ni and Mo also show declines in concentrations and EF with
 263 depth in each peat core (SI Figures S3 and S4). Nickel is the
 264 second most abundant trace metal in bitumen, after V, and yet
 265 both the Ni concentrations as well as the Ni EF have strongly
 266 declined at MIL and JPH4 (SI Figure S3), the two bogs nearest
 267 the central upgraders (Figure 1). The declines in atmospheric
 268 contamination by trace metals are summarized in Table 1
 269 which provides the EF for contemporary samples (living
 270 vegetation layer), the maximum EF found in the peat cores as
 271 well as the ratio of maximum to contemporary values. In the
 272 peat profile from MIL which is nearest to industry, the
 273 enrichments of Ni and Mo have declined by a factor of 10 or
 274 more, since their zenith in the past. Nickel and Mo
 275 concentrations and EFs versus time since AD 1800 are
 276 shown in SI Figures S5 and S6, respectively.

277 **3.4. Ag, Cd, Sb, Tl.** The concentration profiles for Cd show
 278 remarkable declines over time in all of the peat cores (Figure
 279 4). To help put these Cd concentrations into perspective, it is
 280 important to note that, in each of the peat cores from northern
 281 AB (Figure 4), the Cd concentrations in the surface layers are
 282 actually lower than the values ($67 \pm 13 \mu\text{g}/\text{kg}$, $n = 19$) found in
 283 the deeper, preindustrial peat layers at SEBA (SI Table S7)
 284 which are more than 700 years old. It is also worth noting that
 285 the Cd concentrations in the top slice of the peat core from
 286 MIL ($43 \mu\text{g}/\text{kg}$), the peat deposit closest to industrial
 287 development, is much lower than the Cd concentrations
 288 reported for the living layer of peat cores collected across
 289 Canada⁶⁷ which range from $106 \mu\text{g}/\text{kg}$ in northern Quebec to
 290 $362 \mu\text{g}/\text{kg}$ in southern Ontario. The EF values in the
 291 contemporary samples are much less than the maximum values

292 seen in the past, in some cases (McK) up to 55 times less. 292
 293 Graphs illustrating the chronology of Cd accumulation show 293
 294 that all of the bogs sampled within the ABS region have 294
 295 witnessed declining concentrations and enrichments of Cd in 295
 296 recent decades (SI Figure S7). 296

297 Like Cd, the concentrations of Ag and Sb are greater in 297
 298 deeper, older peat layers, revealing declining inputs to the bogs 298
 299 (SI Figures S8, S9). Thallium is slightly more complicated, as it 299
 300 is more abundant in the upper layers at MIL, JPH4 and McK, 300
 301 but not McM or ANZ (SI Figure S10). Silver, Sb and Tl all 301
 302 show declining enrichments as well (SI Figure S8–10). There 302
 303 is no significant enrichment of Tl at the surface of any of the 303
 304 peat cores from the ABS region of northern Alberta (SI Figure 304
 305 S10). The chronology of atmospheric deposition of Ag, Sb and 305
 306 Tl, as reflected in their concentrations and EFs since AD 1800, 306
 307 is shown in SI Figures S11–13. 307

4. DISCUSSION

Based on snowpack sampling,⁶² it was claimed that “the oil 308
 309 sands industry releases the 13 elements considered priority 309
 310 pollutants (PPE) under the Environmental Protection Agency’s 310
 311 Clean Water Act, via air, soil, and water, to the Athabasca River 311
 312 and its watershed” and that “all PPE except Se were greater 312
 313 near oil sands developments than at more remote sites”. Our 313
 314 work on moss and peat collected in the ABS region is part of an 314
 315 effort to provide an independent assessment of metal emissions 315
 316 from industry, with the composition of moss a reflection of 316
 317 contemporary inputs, and peat providing insight into 317
 318 atmospheric deposition in the past. If the priority pollutants 318
 319 listed by Kelly et al.,⁶² namely Ag, As, Be, Cd, Cr, Cu, Hg, Ni, 319
 320 Pb, Sb, Se, Tl, and Zn, are emitted to the atmosphere in 320

321 significant amounts from mining and upgrading of bitumen,
322 then the peat cores taken from surrounding bogs should show
323 increasing concentrations of these elements over time. The peat
324 cores from bogs of this area, however, tell a very different story
325 from the expected one, namely that concentrations of Ag, Cd,
326 Sb, and Tl as well as enrichments, relative to crustal abundance,
327 have been in decline for decades. This finding is all the more
328 remarkable, given that synthetic oil production from mining
329 began in 1967 and increased to more than 50 million m³/yr by
330 2015.⁸⁰ It is especially noteworthy that the concentrations of V
331 and Ni in the peat profiles also have declined during recent
332 decades, even though these are the two most abundant trace
333 metals found in bitumen.⁷⁹ While the peat bog records
334 presented here and elsewhere⁶⁸ contradict the claims by Kelly
335 et al.,⁶² we show below that our findings are consistent with
336 many other reports of trace elements in the ABS region
337 undertaken during the past four decades, including studies of
338 moss, lichens, snow, and sediment.⁸¹

339 **4.1. Surface Peat Versus *Sphagnum* Moss.** The trace
340 metal concentrations reported here for the top (living) layer of
341 these bogs are consistent with the published data for trace
342 metals in *Sphagnum* moss from bogs in this region, even though
343 the living layer is a complex mixture of many plant species
344 including both moss as well as herbs and ericaceous shrubs;
345 some of these materials may represent multiple growing
346 seasons. In contrast, the *Sphagnum* moss data^{66,67} corresponds
347 to samples that were hand-picked to isolate a single moss
348 species (mainly *Sphagnum fuscum*) by removing foreign plant
349 matter, and they were sectioned to ensure that only the living
350 portion corresponding to that growing season was selected for
351 analysis. In our study of *Sphagnum* moss from 21 bogs
352 surrounding the ABS region, we found that (1) the
353 concentrations of Ag, Cd, Pb, Sb, and Tl (determined in the
354 metal-free, ultraclean SWAMP lab) were considerably lower
355 than the values found in the same species of moss from four
356 bogs in southern Germany (determined in the metal-free,
357 ultraclean lab at the University of Heidelberg), (2) the
358 concentrations of these metals in moss from the ABS region
359 showed strong linear correlations with Th, a conservative
360 lithophile element indicative of the abundance of mineral
361 particles in the plants, and (3) that none of these elements was
362 enriched in the plants from the ABS region, relative to the M/
363 Th ratio of ancient peat samples ca. 6000 to 9000 years old,
364 from Switzerland.⁶⁶ In a subsequent study, we showed that the
365 concentrations of Ag, As, Bi, Cd, Cu, Mo, Ni, Pb, Sb, Tl, and
366 Zn in the same set of moss from the ABS region, but
367 determined at a commercial lab, were comparable to the
368 concentrations reported for forest moss from remote areas of
369 central and northern Norway.⁶⁷ Thus, by any measure that we
370 know of, the concentrations of trace elements in the *Sphagnum*
371 *fuscum* moss of the bogs surrounding the ABS region,^{66,67} and
372 the surface layers of the peat profiles shown here, are low.

373 **4.2. Lichens and Forest Moss.** Early work by Addison and
374 Puckett⁸² employing lichens as biomonitors showed decreasing
375 V concentrations with distance from the Suncor operations.
376 The map showing V concentrations at 69 sites (Figure 2)⁸² is
377 reproduced here (SI Figure S14) and shows that samples
378 nearest the upgrading operation at that time contained
379 hundreds of mg/kg V. Their V concentration data for selected
380 sites versus distance (Addison and Puckett, Table 1) is
381 reproduced here and shows V concentrations reaching values
382 of 3 mg/kg at a distance of 85 km (SI Figure S14); at the time,
383 3 mg/kg was considered the “background” abundance of V in

the lichens but today, this is the average concentration of V 384
found in *Sphagnum* moss from the ABS region.⁶⁷ It should be 385
noted that the V concentration data of Addison and Puckett⁸² 386
was obtained at that time using instrumental neutron activation 387
analysis (INAA), a sensitive, accurate, and precise method for 388
the determination of V in solid samples⁸³ which is still in use 389
today.^{66,67} In a separate study by the Alberta Research Council, 390
forest moss (*Pleurozium schreberi*) was collected from 391
numerous sites in the ABS region during 1976, 1983, and 392
1990, and in addition, the lichen *Usnea* spp. sampled during 393
1983 and 1990.⁸⁴ The V and Ni concentrations given in the 394
summary of elemental concentrations in that report (Table 395
4.4)⁸⁴ is reproduced here (SI Figure S15) and dramatic declines 396
over time are seen for both metals. In respect to the quality of 397
the analytical data, the lichens had been digested in acid 398
(HNO₃, HClO₄, and HF) and total concentrations of trace 399
metals determined using ICP-AES; however, the authors also 400
analyzed the 1976 and 1983 samples using INAA of solid 401
samples, and the V concentration data obtained by the two 402
independent methods was in excellent agreement (Figure 403
4.1).⁸⁴ 404

Lichen samples (*Hypogymia physodes*) recently collected 405
around the ABS region by the Wood Buffalo Environmental 406
Monitoring Association (WBEA) and measured for a broad 407
range of trace metals⁸⁵ reveal V concentrations more than ten 408
times lower than those reported decades earlier by Addison and 409
Puckett⁸² and Pauls et al.⁸⁴ For convenience, we have plotted 410
the average values presented by Edgerton et al. (Table 14.5)⁸⁵ 411
for proximal ($n = 60$) and distal ($n = 61$) samples for V, Ni, 412
Mo, Cd, Pb, Sb, and Th (SI Figure S16). For elements enriched 413
in bitumen (V, Ni, and Mo), the range in concentrations seen 414
in the contemporary lichens is similar to the range seen in the 415
top layers of the peat cores presented here, and comparable to 416
the concentrations found in *Sphagnum* moss.^{66,67} The differ- 417
ence between proximal versus distal sites, on average, is 418
approximately 3X for each of these elements, but also for Th 419
which suggests the differences in V, Ni, and Mo are mainly the 420
result of differences in dust loadings, even though all three are 421
enriched in bitumen. Linear regression analyses of this lichen 422
data⁸⁵ showed strong correlations between V and Al as well as 423
between Ni and Al ($R^2 = 0.830$ and 0.851 , respectively, $n =$ 424
121). According to these authors, road dusts, and overburden 425
contain much greater concentrations of V and Ni than do the 426
tailings sands themselves, leading to the conclusion that the 427
greatest impact on element concentrations in lichen tissues of 428
this region is related to fugitive dust.^{85,86} 429

430 **4.3. Trace Metals Data in Precipitation.** During the late 431
1970s, fly ash samples from coke combustion at the Great 432
Canadian Oil Sands upgrader (today Suncor) yielded ca. 2.5% 433
V, 1% Ni, and 0.25% Mo with the metals being almost entirely 434
in the stable oxide form.⁸⁷ In a subsequent study employing 435
snowpack sampling it was found that the soluble fraction of Al 436
and V was generally less than 1% and 10%, respectively and that 437
their insoluble fraction essentially represents total deposition.⁸⁸ 438
In a follow up study also using snowpack sampling, it was found 439
that loadings had decreased substantially because “electrostatic 440
precipitators had been installed in the Suncor power plant in 441
November of 1979 to reduce the emissions of particulate 442
matter.”⁸⁹ The relevant maps showing V loadings in snow 443
collected in January of 1978 versus January and February of 444
1981, are reproduced here (SI Figure S17). Between these two 445
snow sampling campaigns, V loadings had declined by a factor 446
of 10 (SI Figure S17).

Contemporary snow data from Bari et al.,⁹⁰ 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, 5×; Cd, 2×, Pb, 3×; Sb, 7×, Tl, 7×.⁹⁰ However, comparing these same two sites shows that there are similar concentration differences in Al (6.9×), Ba (6.6×), and Sr (7.4×). Taking Al (or Ba or Sr) as an indicator of the abundance of dust particles, a factor of 7 difference in trace metal concentrations would anyway be expected between these two sites. In other words, the concentration differences seen in Ag, 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.^{75,85,86,91,92} 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:⁹³ 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),⁷⁸ but far removed from the corresponding ratios in bitumen (174 and 70, respectively, according to Hitchon and Filby, 1983).⁹⁴

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 is 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,⁷⁹ 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,⁶⁵ 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 mg/kg, respectively.⁷⁹ Compare these values with their abundance in the Upper Continental Crust,⁷⁸ namely 53 and 19 mg/kg, respectively.⁷⁸ 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 silts 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.,⁷⁶ and applied to tropospheric aerosols worldwide by Rahn,⁷⁷ 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.⁹⁵ Is it 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)⁸⁵ 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.⁶⁷ 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.^{96,97} Here, we have presented both the metal concentration profiles as well as the metal EF profiles, 571

572 to provide a more complete picture of the history of
573 atmospheric metal deposition in this region.

574 **4.6. Decades of Declining Atmospheric Deposition of**
575 **Trace Metals.** The maximum enrichment by Ag, Cd, Sb and
576 Tl, as well as V, Ni and Mo, is found in deeper, older peat layers
577 from these bogs (Table 1): clearly, the extent of atmospheric
578 metal contamination was greater in the past. In fact, the EF
579 values for Ag, Cd, and Sb in the top layers of the bogs in the
580 ABS region (Table 1) are less than the values reported for the
581 control site (UTK). In respect to Tl, there is no significant
582 enrichment of this metal in the top sample of any of these peat
583 cores. Atmospheric deposition of all these metals, as well as
584 Pb,⁶⁸ has been in decline for decades (SI). Taking V as a tracer
585 of atmospheric metal emissions from the industrial develop-
586 ment of the ABS, the declining enrichments over time of trace
587 elements in these peat cores is entirely consistent with the
588 results presented in many previous studies.^{82,84,87–89} The data
589 provided by these peat cores is consistent with the findings
590 obtained from sediment cores taken in the Peace-Athabasca
591 Delta, downstream of industry, which yielded a chronology of
592 As, Pb and Sb accumulation which was inversely related to oil
593 production in the ABS region.⁹⁸

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

612 Compared with the retrospective, peat bog studies of
613 environmental contamination by trace metals cited in the
614 Introduction, the concentrations found in these peat cores,
615 especially in recent layers, are low. For example, the maximum
616 concentration of Sb found in this study (SI Figure S9) is 75
617 times less than the maximum reported for some Swiss
618 peatlands,⁵² 21 times less than that reported for Scottish peat
619 bogs,³⁶ and 8 times less than the maximum reported for the
620 Myrarnar peatland on the remote Faroe Islands.³¹ In fact, the
621 maximum Sb concentration found in the ABS bogs is similar to
622 peat from Myrarnar dating from the Roman Period. In these
623 other studies, however, Sb was supplied by long-range,
624 atmospheric transport of submicrometer aerosols from high
625 temperature industrial operations such as pyrometallurgical
626 processing of base metal ores (sintering, roasting, smelting, and
627 refining), coal combustion and other emissions from heavy
628 industry. Lead ores are rich in Sb, with lead minerals commonly
629 ranging from 12 to 56 wt % Sb.⁵² In contrast, existing data
630 suggests that the Sb content of the ABS is approximately 30
631 $\mu\text{g}/\text{kg}$ ⁹⁴ which is an order of magnitude less than its abundance
632 in the Upper Continental Crust.⁷⁸ There is surprisingly little
633 modern data for trace elements in the ABS, and a detailed
634 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.⁹⁹

4.7. Analytical Challenges Presented by Ag and Tl.
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 \times ,
71 \times , and 83 \times , 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 Tl (2). Despite the use of the metal-free,
ultraclean lab facilities, related infrastructure, and state-of-the-
art quadrupole ICP-MS, Ag and Tl still present a challenge. In
the current study of 251 peat samples, Ag and Tl were below
the MDL in 15 and 7 samples, respectively. Seventy-five
percent of the peat samples contained <30 $\mu\text{g}/\text{kg}$ of Ag and Tl.
But this is largely to be expected, given that the natural
abundances of these elements is also very low: Ag and Tl in the
Upper Continental Crust, for example, are only 55 and 75 $\mu\text{g}/$
kg, respectively.⁷⁸ 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 Tl 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 Tl 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

📄 Supporting Information

The Supporting Information is available free of charge on the
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Description of age dating, ¹⁴C age dates for samples and
standards and ²¹⁰Pb 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 Tl; metal concentrations and EF profiles (V, Ni,
Mo, Ag, Cd, Sb and Tl) versus calendar year since AD
1800; V concentrations in lichens, from Addison and
Puckett;⁸² V and Ni concentrations in moss and lichens
from Pauls et al.⁸⁴ and *Sphagnum* moss from Shotytk et
al.;⁶⁶ metal concentrations in lichens from Edgerton et
al.;⁸⁵ V in snow from Barrie and Kovalick⁸⁸ and
Murray;⁸⁹ GPS coordinates of peat bogs sampled; QA/
QC data for trace metal determinations using ICP-MS;
average concentrations of trace metals in peat from
deeper layers at Seba Beach (PDF)

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