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Environmental significance of trace elements in the Athabasca Bituminous Sands: facts and misconceptions†

William Shotyk 

The bituminous sands of Alberta, Canada, represent the second largest reserves of hydrocarbons on earth. Open pit bitumen mining and upgrading of the Athabasca Bituminous Sands (ABS), the largest of the deposits, began in 1967. Concerns about fugitive release of trace elements (TEs) to the environment began with studies of V, as this is the most abundant trace metal in bitumen. Recent studies, however, have extended to Ag, As, Be, Cd, Cr, Cu, Pb, Sb, and Tl, and this has led to considerable confusion about which TEs are relevant to ecosystem health. While V along with Ni, Mo, Se and Re are enriched in bitumen, Ag, As, Be, Cd, Cr, Cu, Pb, Sb and Tl are found almost exclusively in the mineral (*i.e.* sand) fraction of the ABS, with limited opportunity to become bioaccessible, much less bioavailable. Here, a summary is given of ten misunderstandings that have arisen regarding TEs in the environment of the ABS region. To help illustrate the significance of the misconceptions that have arisen regarding (a) air and (b) water resources, published and unpublished TE data obtained from the metal-free, ultraclean SWAMP lab is presented for: (a) snow, moss, and peat cores from bogs, and (b) the dissolved, particulate, and colloidal fractions of water from the Athabasca River (AR), as well as pristine groundwater. Natural enrichments of Ni in plants such as Rat Root (*Acorus calamus*) and pine (*Pinus banksiana*), Tl in fish (*Percopsis omiscomaycus*) and Cd in cranberries (*Vaccinium oxycoccus*), Labrador Tea (*Rhododendron groenlandicum*) and beaver (*Castor canadensis*), are also presented.

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Environmental significance

In the Athabasca Bituminous Sands, Ag, As, Be, Cr, Cd, Pb, Sb and Tl are all depleted, relative to the Upper Continental Crust, and found almost exclusively in the mineral fraction. This helps to explain why atmospheric deposition of trace elements (TEs) in the region has been in decline for decades, why dust particles in the area have such low concentrations of TEs, and why TE concentrations in the dissolved fraction of the Athabasca River (AR) are at natural, background levels.

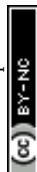
Introduction

The bituminous sands of Alberta cover an area of approximately 140 000 km² and are estimated to contain hydrocarbon reserves equivalent to 27 billion m³: these oil reserves¹ are second only to those of Saudi Arabia. The Athabasca Bituminous Sands (ABS) are by far the largest of the four main deposits, with commercial exploitation having begun in 1967 *via* open pit mining and upgrading. Since that time, there have been many environmental studies of trace elements (TEs) in the vicinity of these open-pit bitumen mines and upgraders.

These include studies of wet² and dry deposition,³ snow,^{4–6} surface waters,^{7–9} fish,^{10,11} mussels,¹² soil,¹³ sediments,^{14–16} lichens,^{17,18} higher plants,^{19,20} and wildlife.^{21–23} Implicit in all of these studies is the assumption that mining and upgrading of bitumen is a significant source of TEs to the environment. From a geochemical perspective, there is no obvious reason why this would be true for elements other than V, Ni and Mo which are well known for their enrichments in bitumen.^{24,25} More recently, it became known that Re is also enriched in bitumen,²⁶ as well as Se.²⁷ In the absence of an understanding of the geochemistry of bitumen, it seems that many, if not most environmental studies simply assume that all of the potentially toxic TEs of environmental concern, *e.g.* Ag, As, Be, Cd, Cr, Cu, Pb, Sb, and Tl, occur in the ABS at elevated concentrations. Mining and upgrading is further assumed to release these elements to the environment at rates and in forms that present threats to the health of aquatic and terrestrial ecosystems. So, from a lack of familiarity with the

Bocock Chair for Agriculture and the Environment, Department of Renewable Resources, University of Alberta, 348B, South Academic Building, Edmonton, Alberta T6G 2H1, Canada. E-mail: shotyk@ualberta.ca; Fax: +1-780-492-4323; Tel: +1-780-492-7155

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Misconception 1. The ABS contain elevated concentrations of potentially toxic TEs including Ag, As, Be, Cd, Cr, Cu, Pb, Sb, Tl, and Zn

Until recently, there was very little quantitative data for TEs in the ABS.³¹ Early work using emission spectrographs was only semi-quantitative.³² Some data was obtained using instrumental neutron activation analysis (INAA) which is an established method providing excellent data for lithophile elements such as Al, Cr, Sc, Th, and V, as well some chalcophile TEs of environmental concern including As and Sb.³³ However, while this method provides excellent sensitivity (*e.g.* $\mu\text{g kg}^{-1}$) for the elements listed above,^{34,35} it cannot be used to determine some of the chalcophile elements of greatest concern such as Cd, Pb or Tl. X-ray fluorescence spectroscopy (XRF) was also used in early work on bitumen,³⁶ but yielded very little data for TEs of environmental relevance because of the relatively high (mg kg^{-1}) limits of detection.³⁷ Both INAA and XRF share the great advantage of providing data for solid materials, thereby eliminating the need for sample digestion. So, for elements such as Ti and Zr which are abundant in the ABS and occur in stable mineral phases which are difficult to dissolve, XRF is the perfect analytical tool for their determination. Hydride-generation atomic fluorescence spectroscopy (HG-AFS) is a very sensitive method for the determination of hydride forming elements including As, Sb, and Se,³⁸ but, until recently,^{27,39} has found little application to bitumen. Despite the introduction in recent decades of far more sensitive methods such as inductively-coupled plasma mass spectrometry (ICP-MS), there have been remarkably few applications of this technique to the study of TEs in bitumen. Recently, however, sector-field ICP-MS was used to determine the abundance of almost all of the TEs of environmental relevance, in both bulk samples (*i.e.* ores) and the bitumen itself.³⁹

Comparing the abundance of TEs in bulk samples (*i.e.* ores) of ABS with the corresponding abundance of TEs in the Upper Continental Crust (UCC) shows that only two elements are more abundant in the ABS, compared to the crust: Mo and Re (Fig. 2). When the concentrations of TEs in ABS are normalized to the corresponding abundance of TEs in the UCC, it becomes clear that only two elements are actually enriched in the ABS, compared to the crust: Mo and Re (Fig. 3). Neither Mo nor Re is of general environmental concern. Molybdenum, for example, is a micro-nutrient, essential for the health of all plants and animals.⁴¹ Rhenium, one of the platinum group elements (PGE), is one of the most rare elements in the Earth's crust, being less abundant than either Pt or Au.⁴⁰ In summary, the concentrations of the potentially toxic, so-called "heavy metals"[‡] of environmental concern, namely Ag, As, Be, Cd, Cr, Cu, Pb, Sb, Tl and Zn, are all less abundant in the bulk ABS than typical rocks at the surface of the earth.

‡ The term “heavy metal” has criticized for many reasons and generated considerable confusion.^{42–49} Although there have been efforts to replace it with more precise descriptions,⁵⁰ the term is still popular. Given that Be is a “light metal”, As and Sb are metalloids (or semi-metals) and Se is a non-metal,⁵¹ we prefer to simply use the term “trace element”.

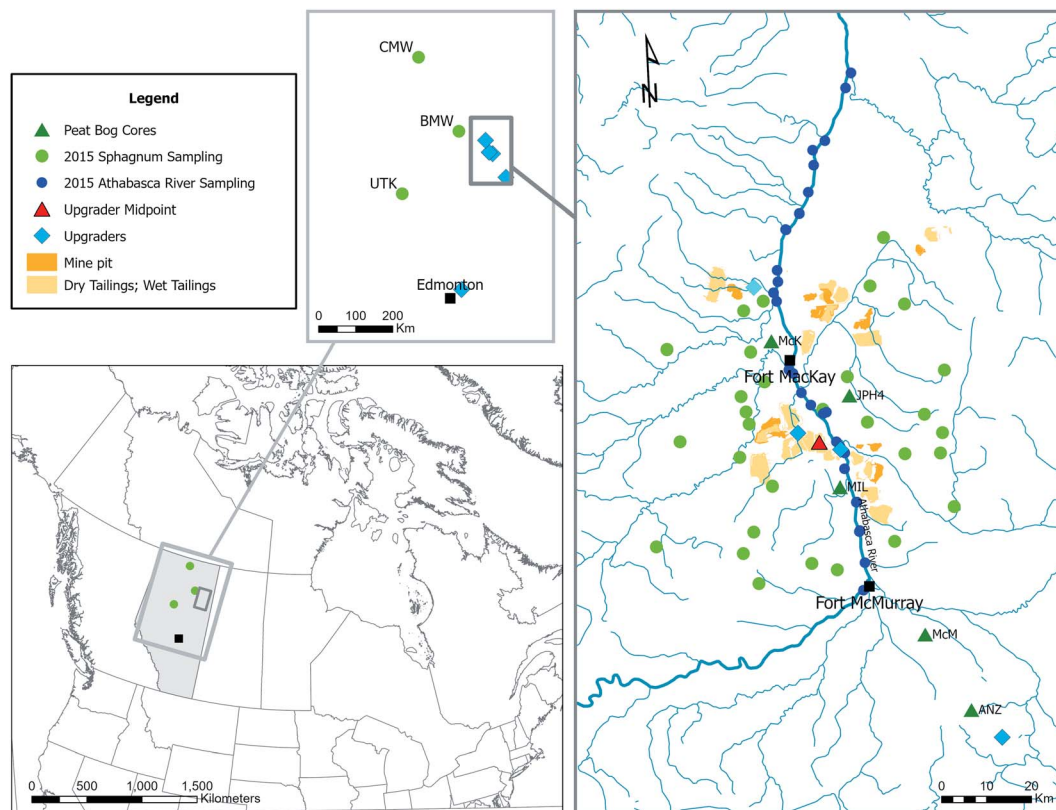


Fig. 1 Locations of some of the sampling sites mentioned in the text: peat cores from bogs (green triangles), *Sphagnum* moss collected in 2015 (green circles), and AR surface waters collected in 2015 (blue circles). The small, inset map shows the approximate locations of moss and peat samples collected at control locations: Birch Mountain Wildlands (BMW), Caribou Mountain Wildlands (CMW), and Utikuma (UTK) which are approximately 103, 320 and 264 km, respectively, from the mid-point between the two central bitumen upgraders. The four bitumen upgraders in the area are indicated by blue diamonds, and the mid-point between the two central upgraders by red triangle.

Misconception 2. Potentially toxic TEs in the ABS are enriched in the bitumen fraction of the ABS

Bitumen was carefully extracted from the ABS using metal-free protocols (*e.g.* employing high purity quartz instead of glassware when using organic solvents), digested, and analyzed for

the full suite of TEs using sector-field ICP-MS.³⁹ However, only five elements are found predominantly in the bitumen fraction. Listed in order of decreasing abundance, they are V, Ni, Mo, Se and Re (Table 1). The extent of enrichment of these elements in bitumen, relative to crustal abundance, increases in the order Ni (1.8 $\times$), V (2.4 $\times$), Se (4.4 $\times$), Mo (9.1 $\times$) and Re (250 $\times$). So, even though V and Ni are the most abundant trace metals in bitumen, their enrichment, relative to crustal abundance, is

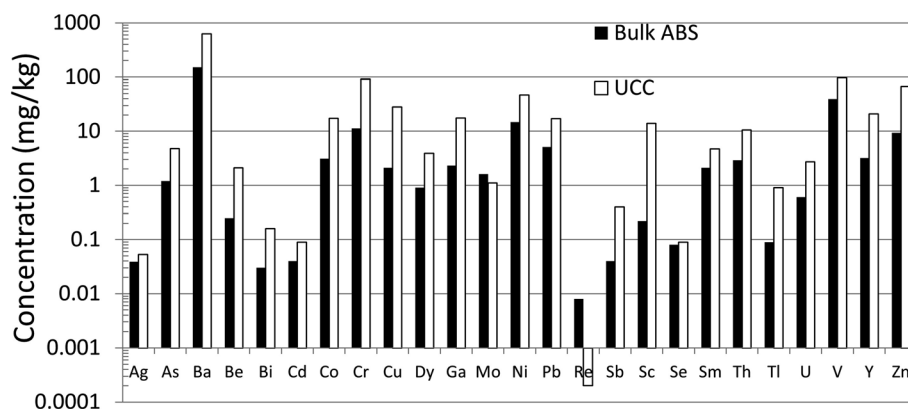


Fig. 2 Abundance of TEs in bulk ABS and UCC. Concentration data for ABS from Bicalho *et al.*³⁹ except for Se.²⁷ Data for the UCC from Rudnick and Gao.⁴⁰



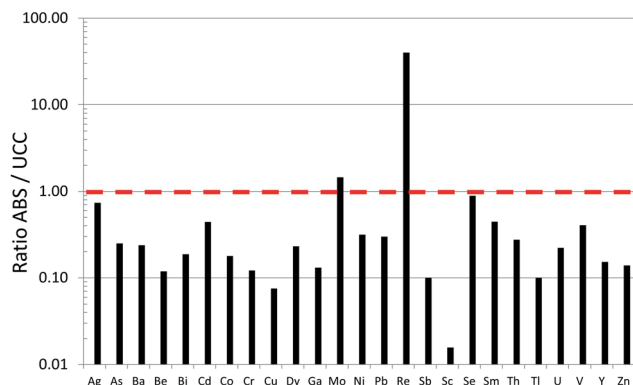


Fig. 3 Ratios of TE concentrations in bulk ABS³⁹ to the UCC.⁴⁰ The horizontal dashed line (ABS/UCC = 1) represents values that are neither enriched nor depleted, in the ABS relative to the UCC. Notice that Mo and Re are the only elements enriched in the ABS, relative to the UCC.

modest *i.e.* within a factor of two of their abundance in the UCC. Rhenium, one of the most rare elements on earth, is by far the most highly enriched TE in bitumen. Of the five TEs enriched in bitumen, one is a lithophile (V), two are siderophiles (Ni and Re), one is chalcophile (Se) and one (Mo) has recently been considered “variably chalcophile”.⁵² Thus, unlike the enrichments of TEs in coal which are almost exclusively restricted to the chalcophile elements,^{53,54} there is no simple relationship between the enrichment of these TEs in bitumen, and their geochemical classification.

The mechanism of enrichment of V and Ni in petroleum has been studied for decades.⁵⁵ The enrichment of V in bitumen was first noted by Kyle in 1891,⁵⁶ the role of marine organisms in its accumulation was discovered by Vernadsky in 1924,⁵⁷ and Treibs in 1935,⁵⁸ recognized that this metal was present in the form of porphyrins. Champlin and Dunning⁵⁹ identified both Ni- and V-containing porphyrin compounds in samples of ABS from Abasand and Bitumount in northern Alberta. With an average of 180 ppm V and 80 ppm Ni, approximately 10% of the V and Ni in the bitumen was found to be in porphyrins. Subsequent studies of V and Ni in crude oils have suggested that the remainder of the V and Ni may also be in the form of porphyrins which cannot be readily extracted, or in the form of metal naphthenates.⁶⁰ Given that V and Ni are by far the most abundant trace metals found in bitumen, and that they are in predominantly organic forms, these are the two elements that

could reasonably be expected to be enriched in environmental media from fugitive atmospheric and aquatic releases by industry.

Regarding the other TEs of environmental interest, namely Ag, As, Be, Cd, Cr, Cu, Pb, Sb, Tl and Zn, these are found predominantly and almost exclusively in the mineral fraction of the ABS.³⁹ On average, the ABS are approximately 85% mineral matter, predominantly dune and beach aeolian sands,⁵⁸ with most particles >100 μm .⁶¹ The mineral composition is dominated by light minerals (99%), mainly quartz (60–90%) and clays (kaolinite and illite), with minor amounts of feldspars (including orthoclase), mica (biotite and muscovite), carbonates, and chalcedony.⁶² Quartz is not a host for TEs⁶³ and its predominance in the mineral fraction of the ABS explains the depletions of nearly all the TEs, relative to the composition of the UCC (Fig. 3). Heavy minerals (density > 2.96 g cm⁻³) account for 1% of the mineral fraction, and includes Ti, Y, and Zr-bearing minerals such as ilmenite, tourmaline and zircon.⁶² As noted in the detailed work by Bichard (1987),⁶² the bulk of the minerals are relatively inert materials similar to clastic sediments that have undergone intensive weathering. The principal mineral hosts of TEs in the mineral fraction of ABS are likely the clays, feldspars, and micas. For example, Pb occurs in the lattice structure of silicates: Pb²⁺ is known to substitute for Ca²⁺ in plagioclase feldspar, and for K⁺ in orthoclase feldspar and mica.⁶⁴ Similarly, Tl occurs in orthoclase feldspars and mica, where Tl⁺ can easily replace K⁺,⁶⁴ given that they have the same ionic radius and charge.⁵¹

In contrast to the “sand” fraction, within the bitumen fraction of the ABS, concentrations of the TEs of concern are generally very low. Zinc is most abundant, at 5 mg kg⁻¹, followed by Cu at 1 mg kg⁻¹. Lead and As in bitumen are <1 mg kg⁻¹, and Ag, Bi, Cd, Sb and Tl are all below 0.05 mg kg⁻¹.³⁹ The abundance of Tl in bitumen, for example, is only 0.005 mg kg⁻¹. Thus, most of the TEs of environmental concern are hosted by relatively stable, predominantly silicate minerals which make up the bulk of the ABS ore. The presence of the low and variable concentrations of these elements in the bitumen itself may simply reflect the abundance of fine grained mineral particles which remain, even after extraction and filtration through a 0.45 µm membrane filter.³⁹ Thus, even within the bitumen fraction, many of the elements of environmental relevance may be hosted by silicate minerals with sub-micron dimensions.

Misconception 3. TEs are released to the atmospheric environment from bitumen mining and upgrading by combustion, generating sub-micron aerosols which are respirable and capable of long-range atmospheric transport

The combustion of fossil fuels is widely recognized as a globally significant source of TEs to the atmosphere.⁶⁵ Again, however, the suite of TEs which are naturally enriched in coal and those

Table 1 Abundance of V, Ni, Mo, Se and Re in bitumen, listed in order abundance. Data for the UCC from Rudnick and Gao (2014)⁴⁰

Element	Bitumen (mg kg ⁻¹)	UCC (mg kg ⁻¹)	Ratio bitumen/UCC
V	237 ^a	97	2.4
Ni	83 ^a	47	1.8
Mo	10 ^a	1.1	9.1
Se	0.4 ^b	0.09	4.4
Re	0.05 ^a	0.0002	250

^a From Bicalho *et al.* (2017).³⁹ ^b From Donner *et al.* (2018).²⁷

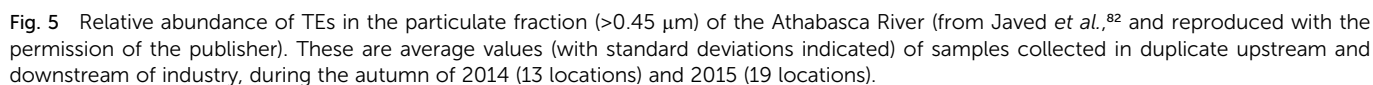
Misconception 4. TEs in the Lower Athabasca River, downstream of industry, occur in elevated concentrations, and occur mainly in the form of soluble, ionic species

In regard to the dissolved fraction of TEs, those of greatest perceived concern (Ag, Cd, Pb, Sb and Tl) may be found at very low concentrations in the main stem of the AR. In consequence, extreme precautions need to be taken in regard to acid cleaning of bottles, filters, and syringes before sampling, and great efforts are needed to minimize the risk of contamination during sample processing and analysis: the absolute necessity for these extreme precautions is described in detail elsewhere.^{30,83–89} As noted by Tölg and Garten (1985):⁹⁰ “since it is primarily the blank value that limits the power of detection, it must be remembered that it is the ratio of the concentration of the element to be determined in the sample to its concentration in the environment of the analytical system which is decisive rather than the sensitivity of the detector system itself. Thus, in present day ultratrace analysis, it is more meaningful to keep the blank concentration as low as possible than to search for new and more sensitive detectors” (p. 489).⁹⁰ In 2014, for

Bar chart showing the ratio of concentrations for various elements in Coke 1 and Coke 2. The y-axis is logarithmic, ranging from 0.01 to 100. The x-axis lists elements: Ag, Al, Ba, Bi, Cd, Co, Cr, Cu, Fe, Ga, Mn, Mo, Ni, Pb, Sb, Sr, Th, Tl, U, V, Y, Zn. Coke 1 is represented by black bars and Coke 2 by grey bars.

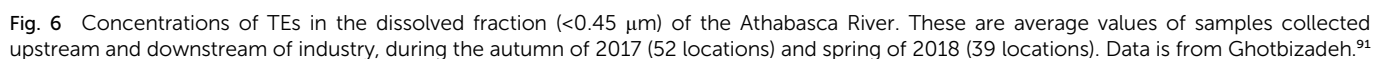
Element	Coke 1 Ratio	Coke 2 Ratio
Ag	1.3	2.2
Al	0.08	0.08
Ba	0.15	0.00
Bi	2.0	2.5
Cd	0.35	0.65
Co	0.65	1.1
Cr	0.45	0.75
Cu	0.75	0.95
Fe	0.25	0.25
Ga	0.35	0.65
Mn	0.6	0.4
Mo	30	65
Ni	20	35
Pb	0.45	0.75
Sb	0.08	0.08
Sr	0.15	0.25
Th	0.3	0.4
Tl	0.08	0.12
U	0.35	0.65
V	22	35
Y	0.45	0.45
Zn	0.7	0.4

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Arsenic and Se require special consideration, as these two elements can be very challenging to determine using ICP-MS employing a single quadrupole mass analyzer, and an independent analytical method is recommended to ensure high

It was suggested that bitumen mining and upgrading results in environmental contamination by Ag, Be, and Tl.⁴ Silver and Tl are rare elements: abundance in the UCC is only 53 and 90 $\mu\text{g kg}^{-1}$, respectively; the abundance of Be in the UCC is only 2.1 mg kg^{-1} .⁴⁰ The reliable determination of Ag at the level found in the AR (at or below 1 ng L^{-1}) is a considerable



challenge. As noted elsewhere, similar Ag concentrations are found in open ocean seawater in the South Pacific and ancient arctic ice.⁸¹ Very few laboratories are capable of reliable measurements at these extremely low levels. Silver is unlikely to have any ecological relevance under these conditions, and for this reason efforts to measure this metal in AR water samples was discontinued by our laboratory soon after the 2015 field campaign. In regard to Be, the average concentration (ng L^{-1}) in the dissolved fraction of the AR was 5.6 ± 1.4 ($n = 13$) and 5.1 ± 2.0 ($n = 15$) in the autumn of 2014 and 2015, respectively.⁸² These values are probably one-half the values for uncontaminated river water globally.⁹⁴ Finally, in respect of Tl, as noted elsewhere, the values for the AR in 2014 were slightly below the reported value for global average uncontaminated river water.⁸¹

Misconception 5. All of the TEs of environmental significance can be easily and reliably measured in environmental samples using modern methods of instrumental analysis

The reliable determination of TEs in the dissolved fraction of surface and groundwaters of the Lower AR watershed, the

filterable fraction of snowpack samples, and in the tissues of biota, remains a considerable analytical challenge. This is true, despite the impressive advances in sensitivity of modern methods of instrumental analysis. But even in regard to soil and sediment samples, where TE concentrations may be orders of magnitude greater, there are issues related to the challenges caused by incomplete digestion of refractory mineral phases.

Aqueous samples

Snowpack samples. Based on snowpack sampling in the vicinity of open pit bitumen mines and upgraders, Kelly *et al.* (2010)⁴ claimed that industry was releasing to the AR 13 elements listed as priority pollutants by the U.S. Environmental Protection Agency (EPA): Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, and Zn. In snow samples collected near development (ND), however, in the dissolved (*i.e.* $<0.45 \mu\text{m}$ or “filterable” fraction), Ag, As, Be, Se were below the limits of detection (LOD) at all sites.⁴ The LODs in that study were comparatively high: in ng L^{-1} , these LODs were 20, 250, 50, and 500. For perspective, the average concentrations of these elements in the dissolved fraction of the AR are well below these LODs: by approximately $50\times$ in the case of Be,⁸² $20\times$ for Ag,⁸¹ $2\times$ regarding As,⁹² and $3\text{--}4\times$ in respect of Se.⁹³

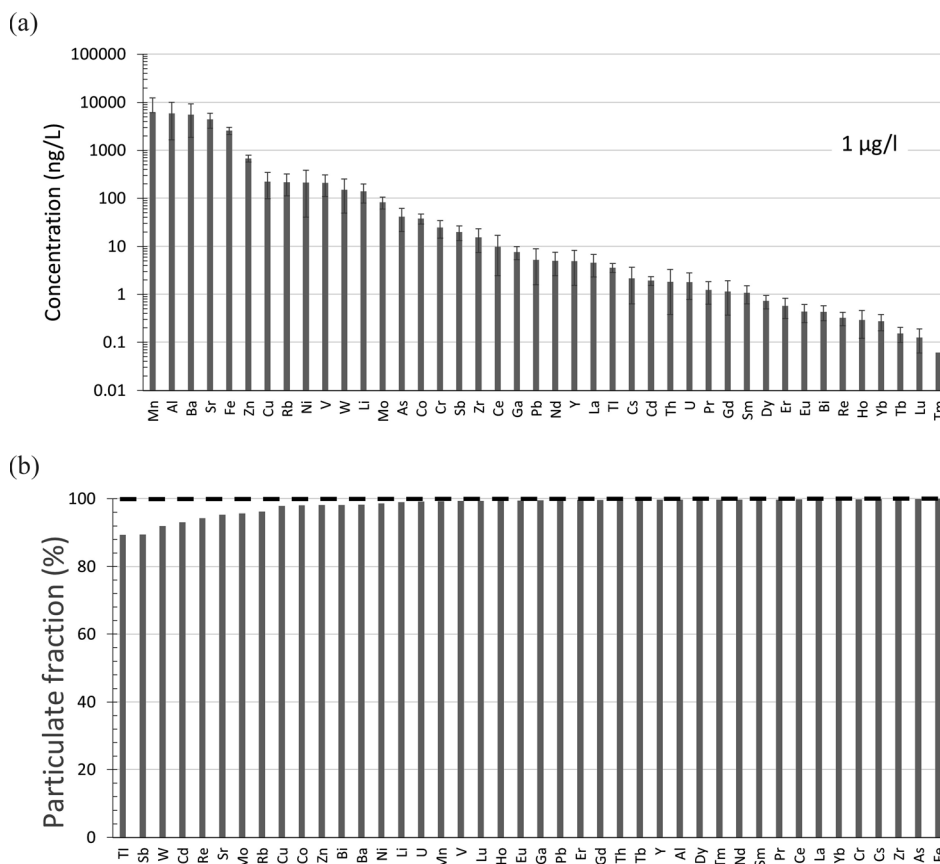


Fig. 7 (a) Average concentrations (with standard deviations indicated) of TEs in the “dissolved” or filterable ($<0.45 \mu\text{m}$ fraction) of snow collected from the same 5 peat bogs where peat cores were collected in the ABS region.^{97,98} The distances (km) from these sites to the mid-point between the two central bitumen upgraders are MIL 11, JPH4 12, McK 25, McM 49, and ANZ 68. (b) Percent of each TE found in the particulate fraction. Data from Javed *et al.*⁹⁶



Trace elements have been measured by our laboratory in snow collected from five peat bogs in the vicinity of bitumen mines and upgraders.^{95,96} Lead is almost entirely found in the particulate fraction, with the concentrations in the filterable fraction on the order of 5 ng L^{-1} .⁹⁵ Within this fraction the average concentrations (ng L^{-1}) of other elements of concern are $\text{Cd } 1.9 \pm 1.5$, $\text{Tl } 3.6 \pm 1.2$, $\text{Sb } 19.8 \pm 9.6$ and $\text{As } 40.8 \pm 23.3$ (Fig. 7a). Again, in an absolute sense, these are very low concentrations. For comparison with the dissolved fraction of the AR upstream of industry, Cd in the filterable fraction of snow is approximately 5 times lower, while Sb and As are approximately one-half of the concentrations found in the river. Thallium in the filterable fraction of snow is similar in concentration to the dissolved fraction of the river. Thus, the filterable fraction of snow near industry is an unlikely source of dissolved TEs to the river, simply because the elements are found almost exclusively in the particulate fraction (Fig. 7b).

Groundwaters. The attempt by Savard *et al.*⁹⁹ to determine TEs in groundwaters in the vicinity of tailings ponds failed, largely because the measured concentrations were either below or near the LODs. However, it should be noted that the LODs in this study were rather high (100 ng L^{-1}) which renders them unsuitable for studies of TEs in groundwater. For perspective, the natural abundance of TEs in pristine groundwater from a carbonate terrain is summarized in Fig. 8. Notice that Cr, Ni and V are in the concentration range of 10 ng L^{-1} which is a factor of 10 below the LOD reported by Savard *et al.*⁹⁹ Moreover Ag, Cd, Pb, Sb and Tl in pristine groundwater are all at or below 1 ng L^{-1} (Fig. 8) which is a factor of 100 below their LODs.⁹⁹ The attempt to use stable Pb isotope ratios to trace the migration of oil sands leachate was poorly conceived, for many reasons. First, as noted above, the abundance of Pb in the ABS is below its abundance in the UCC. Second, Pb in the ABS occurs predominantly in the mineral fraction where it is hosted by comparatively insoluble minerals. Third, it is well known Pb is particle-reactive and readily scavenged in natural waters.¹⁰⁰ Finally, as seen here (Fig. 8), Pb concentrations in groundwaters of carbonate terrains are extremely low: in fact, they may be at or

well below the concentrations found in ancient Arctic ice.¹⁰¹ Thus, the determination of the isotopic composition of Pb in groundwaters would require the extreme “clean” lab methods used to study polar snow and ice,^{102–104} and most likely require sample preconcentration in order to obtain sufficient Pb for accurate measurements.

Solid samples

Acid digests of soils and sediments. A recent paper on TEs in soils of the ABS region illustrates some of the technical challenges that remain in obtaining robust data for source assessments.¹³ The interpretation of their findings was evaluated critically and discussed in detailed elsewhere.¹⁰⁵ Here, it is essential to draw attention to the quality of their analytical data. Based on their analyses of certified, standard reference materials (SRMs), the recoveries of Al were only one-third of the expected values. Arsenic was 245% of the certified value, and Ni 399 to 612% of the certified values. Aluminum is the most abundant metal in soils, and Ni is one of the more abundant TEs.¹⁰⁶ When major and common TEs present analytical challenges, data on rare elements such as Ag, Be, Cd, Sb and Tl, often lacking certified values in SRMs, must be viewed with skepticism. The poor quality of the analytical data noted above may be partly problems associated with the instrumental method of analysis (*e.g.* interferences in the mass spectrum of ICP-MS instruments with a single quadrupole analyzer), but could also be due to the well known challenge associated with the complete dissolution of soil. Nitric acid alone is sufficient to completely liberate Cd, Co, Cr, Fe, Mn, Ni, Pb, V, and Zn in both soil and sediments, with recoveries ranging from 87%–120%.¹⁰⁷ However, the use of HF or HFB₄, in addition to HNO₃, is necessary for nearly all other elements, to destroy the more recalcitrant minerals in soils. However, the blank contributions from HBF₄ for Ag, Cd, and Tl are problematic,¹⁰⁷ making it very challenging to measure these elements when they occur in soils at low concentrations. In the suspended solids from the AR, for example, the concentrations of Ag, Bi, Cd, Sb and Tl could not be determined with acceptable accuracy because of their low

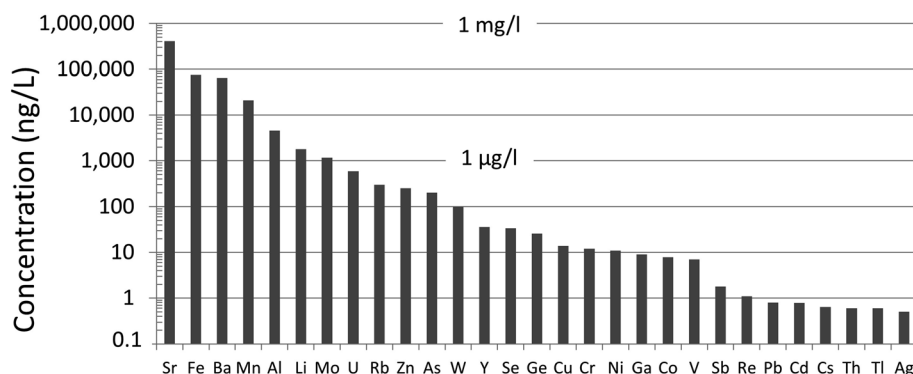


Fig. 8 Abundance of TEs in pristine groundwater from a flowing, artesian well in a carbonate terrain (Elmvalle Groundwater Observatory, Elmvalle, Ontario). The water is sampled from an aquifer at a depth of 60 m, using a purpose-built well which is constructed entirely of surgical (316) stainless steel, and collected within a laminar flow, clean air cabinet. The concentrations are average values obtained from 10 (unfiltered) samples. The waters were collected in acid-cleaned polypropylene (PP) bottles containing 5 mL L^{-1} of HNO₃ to acidify them; the acid had been purified twice by sub-boiling distillation in quartz. Unpublished data.



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concentrations with distance from mining and upgrading activities. Their map shows that samples nearest the upgrading operation at that time contained hundreds of mg kg^{-1} V, compared to 3 mg kg^{-1} at a distance of 85 km. At that time, 3 mg kg^{-1} was considered the “background” abundance of V in the lichens but today, this is the average concentration of V found in lichens¹¹² and *Sphagnum* moss^{113–115} from the ABS region. It should be noted that the V concentration data of Addison and Puckett¹¹¹ was obtained at that time using INAA, a sensitive, accurate, and precise method for the determination of V in solid samples which is still in use today.³⁵ In fact, in the recent paper on TE in *Sphagnum* moss,¹¹³ although V concentrations were obtained using ICP-MS of acid digests, the concentrations were confirmed using INAA of solid samples at an independent laboratory. So, the V concentrations in lichens determined long ago by Addison and Puckett¹¹¹ turn out to be extremely valuable, as they show that atmospheric V deposition rates in the ABS region were much greater in the past than they are today.¹¹²

A study undertaken by the Alberta Research Council of TEs in forest moss (*Pleurozium schreberi*) and the lichen *Usnea* spp. also documented declining rates of atmospheric V deposition.¹¹⁶ Moss samples were collected from many sites in the ABS region during 1976, 1983, and 1990, and lichens sampled during 1983 and 1990. The V concentrations given in the summary of elemental concentrations in that report show dramatic declines over time. In respect of the quality of the analytical data, the lichens had been subjected to a full acid digestion (HNO_3 , HClO_4 and HF) and total concentrations of trace metals determined using ICP – atomic emission spectroscopy (ICP-AES). However, as an independent check, 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 were in excellent agreement.¹¹⁶

Snow

Early work employing snowpack sampling showed that 90% of V being deposited in the ABS region was in particulate form.¹¹⁷ A follow up study using snowpack sampling the following year showed a factor of ten decline in V loadings because of the installation of electrostatic precipitators in 1979 to reduce emissions of particulate matter during bitumen upgrading.¹¹⁸ For the convenience of readers, the relevant maps showing V loadings in snow collected in January of 1978 *versus* January and February of 1981, have been redrawn.⁹⁸ All of this early work on V, in fly ash¹¹⁹ and in snow,^{117,118} employed INAA.

Water

In the State of the Athabasca River Watershed report prepared for the Athabasca Watershed Council,¹²⁰ TE data from provincial and federal water quality monitoring programs were evaluated for the period between 2007 and 2011. Detection limits for parameters of interest were extracted from available sources. Useable TE data is mainly restricted to metals of comparative abundance such as Al, Fe, and Mn, as well as Cu and V. However, these reports contain very little useable data for most of the potentially toxic chalcophile TEs. These government

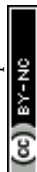
agencies have since been criticized for poor water quality monitoring in the watershed. However, this is not simply an issue of inadequate LODs. In fact, as noted earlier, the TEs of concern are found at extremely low concentrations in the dissolved fraction of the AR,^{81,82,91–93,121} and present a challenge for most laboratories, especially for the ones providing routine analyses.

Misconception 7. The presence of potentially toxic TEs in soils, sediments, plants and waters from northern Alberta is due exclusively to anthropogenic inputs, and mainly from the development of the ABS

It is important to recognize that all of the elements of the periodic table, from H to U, except for technetium (Tc) and promethium (Pm), occur naturally at the surface of the Earth. Eight major elements account for more than 98% of the mass of the Earth's crust: listed in decreasing order, these are O, Si, Al, Fe, Ca, Na, K and Mg; these elements range in abundance from 46.6 to 1.5 weight percent.⁴⁰ These are followed by the minor elements which, in order of decreasing abundance, are Ti, Mn, P, Ba, S, F, Cl, Sr and Zr; these range in abundance from 0.38 (Ti) to 0.02 (Zr) weight percent.⁴⁰ Trace elements are those elements whose abundance in the UCC is below 100 mg kg^{-1} . In this category we find elements of environmental concern, ranging from V (97 mg kg^{-1}) through Cr, Zn, Ni, Cu, Co, Pb, As, Be to Mo (1.1 mg kg^{-1}). The final group of elements, all found in the UCC at levels less than 1 mg kg^{-1} , can be considered ultratrace elements. The abundance of these elements range from Tl ($90 \text{ } \mu\text{g kg}^{-1}$) through Sb, Bi, Se, Cd to Ag ($53 \text{ } \mu\text{g kg}^{-1}$). Thus, the potentially toxic TEs of environmental concern are found throughout the lithosphere, pedosphere, hydrosphere, biosphere and atmosphere. For each element, therefore, there exists a natural “background” concentration which must either be known or become established, before anthropogenic contributions can be quantified.

Soils and sediments

All of the naturally occurring elements are found in soils and sediments, given that these materials are derived from the physical, chemical and biological weathering of crustal rocks. In general, soils and sediments are mainly made up of mineral matter, but TE concentrations become diluted as organic matter is added and incorporated. So, as a rough guide to the natural levels of TE in soils or sediments, we can start with the abundance of the element in the UCC, and apply an appropriate dilution factor, based on the amount of organic matter.¹⁰⁵ For example, the abundance of Pb in the UCC is 17 mg kg^{-1} ;⁴⁰ in a soil containing 5% organic matter, and assuming there are no anthropogenic contributions, a minimum dry weight Pb concentration of 16.2 mg kg^{-1} would be expected. This simplistic calculation is only a rough guide, as it does not take into account geology, mineralogy, texture, topography, age of the soil or



Similarly, all of the elements found in the UCC occur in all natural waters, including rainwater, surface waters, soil and sediment porewaters, and groundwater, because of the complete or partial dissolution of minerals which constitute the rocks of the Earth's crust. The TE concentrations in the dissolved fraction of the AR shown in Fig. 6 are average values

			BMW		CMW	
Element	Units of concentration		Average	std. dev.	Average	std. dev.
Ag	mg kg ⁻¹	μg kg ⁻¹	12.5	2.9	13.1	3.3
Al			259	12	138	31.6
As		μg kg ⁻¹	122.8	40	79.3	37.1
Ba			22.0	9.1	20.5	6.1
Be	mg kg ⁻¹	μg kg ⁻¹	5.82	0.3	3.28	1.5
Cd			23.9	2.3	31.4	9.6
Co		μg kg ⁻¹	109.2	7.4	52.2	5.7
Cr			399	20	231	51.3
Cu	mg kg ⁻¹		1.68	0.1	1.73	0.1
Fe			201	15	109	21.3
Ga	mg kg ⁻¹	μg kg ⁻¹	99.8	7.0	63.3	3.5
Li			464	329	98	6.6
Mn			797	338	528	262
Mo		μg kg ⁻¹	68.3	3.7	51.0	13.6
Ni	mg kg ⁻¹	μg kg ⁻¹	417	93	195	55.9
Pb			177	15	186	53.6
Rb			8.93	0.3	6.13	0.1
Re		ng kg ⁻¹	219	118	44.3	27.7
Sb	mg kg ⁻¹	μg kg ⁻¹	12.6	1.1	12.2	5.6
Sc			46.5	4.0	19.5	2.2
Se		μg kg ⁻¹	161	91	128	87.6
Sr			4.11	0.4	3.06	0.4
Th	mg kg ⁻¹	μg kg ⁻¹	45.8	4.7	25.6	7.0
Tl			5.75	1.5	4.22	1.3
U		μg kg ⁻¹	15.6	0.6	9.1	1.6
V			0.76	0.1	0.37	0.0
Y	mg kg ⁻¹	μg kg ⁻¹	112.8	7.8	55.5	11.4
Zn			17.5	2.8	17.9	4.6

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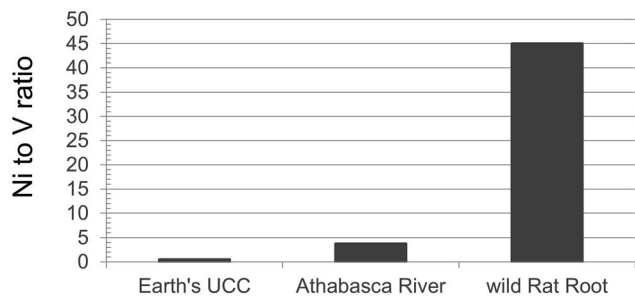


Fig. 9 Ratio of Ni to V in wild Rat Root (*Acorus calamus*) collected in September of 2016 at Chip Lake, Alberta (53°36'35"N 115°18'10"W). Data from Garipey.¹⁴² Values for the Athabasca River refer to average ratios within the dissolved fraction, autumn of 2014.⁸¹ The ratio for the UCC is from Rudnick and Gao.⁴⁰

a factor of 10 greater than the corresponding value for the Athabasca River, and more than 90 times the ratio in the UCC (Fig. 9). Uptake of Ni by plants is also seen in pine trees (*Pinus banksiana*) growing in soils developed from natural bitumen deposits *versus* soils free of bitumen. Trace elements were determined in tree cores, but also soil and soil solutions.¹⁴³ Nickel concentrations in wood from trees growing on shallow bitumen deposits were approximately 3× greater than those growing in bitumen-free soils.

Animals

Thallium and many other TEs (including Ba, Cr, Co, Cu, Fe, Mn, Mo, Ni, Pb, Sr, V and Zn) were determined in otoliths (calcium carbonate ear bones) of Trout-perch (*Percopsis omiscomaycus*), collected along the AR.¹⁴⁴ The ear bones of these small fish are tiny, but quantitative measurements were made possible simply by dissolving individual otoliths (3–15 mg) in a small volume (200 µL) of double-distilled HNO₃ for 30 minutes, before diluting them with ASTM Type I water and analyzing them using ICP-MS. Compared to their average abundance in the dissolved (<0.45 µm) fraction of AR, Tl showed the greatest enrichment in otoliths of any TE.¹⁴⁴ The extent of Tl enrichment was not significantly different downstream of industry compared to upstream. This natural bioaccumulation of Tl in fish most likely reflects the ability of Tl⁺ to pass through the potassium ion channel in cell membranes: it is the only metal to pass as easily K⁺.⁴¹

In an effort to determine the natural abundance of TE in tissue of beaver (*Castor canadensis*), animals were harvested from a small watershed with no point source of environmental contamination by TEs, at a rural location in southern Ontario.¹⁴⁵ Chalcophile (Ag, Cd, Co, Cu, Mo, Ni, Pb, Se, Tl, Zn) and lithophile (Al, Ba, Ce, Cr, Cs, Fe, La, Li, Mn, Nd, Rb, Sr, V, Y) trace elements (TEs) were determined in kidney, liver and muscle. To estimate the relative bioavailability of TEs in the landscape, they were also determined in the dissolved (<0.45 µm) fraction of water from the river where the animals were harvested. By far the greatest concentration ratios (tissue/water) were found for Cd (kidney, 3.6×10^6 ; liver, 1.1×10^6 ; muscle, 3.4×10^5). Despite its potential toxicity, Tl also showed considerable

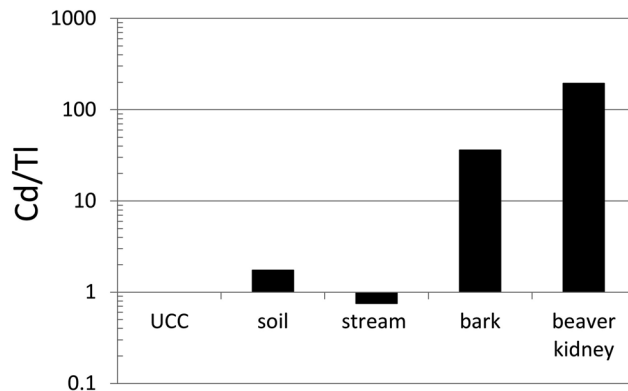


Fig. 10 Ratios of Cd to Tl in beaver kidney,¹⁴⁵ compared to bark (average values for 40 species of trees and shrubs from the farm property in southern Ontario where the beaver were collected), stream (Wye River from the same farm), soil (from the same farm; average of 10 samples taken from 13 m of sediment representing approximately 12 000 years of accumulation; the soil of the farm is derived from these sediments), and the Upper Continental Crust.⁴⁰ The Wye River data is from Shoty et al.,¹⁴⁵ whereas the bark and sediment data are unpublished.

enrichment, with the following concentration ratios: kidney, 1.3×10^4 ; liver 5.5×10^3 ; muscle 8.2×10^4 . When the Cd/Tl ratio of beaver kidney is compared with the corresponding ratio in the UCC and relevant samples from the watershed where the beaver were taken (sediments, stream water and bark from local vegetation), it becomes clear that the main source of Cd is from the vegetation that makes up the diet of these animals (Fig. 10).

In summary, even in remote locations with background rates of atmospheric metal deposition, uptake of Cd by plants has been documented. In fish from control locations, we see that Tl is more enriched in otoliths than any other TE. In beaver from a rural watershed, Cd is enriched in kidney, liver and muscle more than any other TE. *Sphagnum* moss, Labrador Tea, Rat Root, Trout-perch and beaver are all promising biomonitors of environmental contamination by TEs. But these studies show that it is vital to first establish the natural background concentrations and extent of enrichment of TEs, before anthropogenic contributions can be determined.

Misconception 9. Emissions of TEs to the environment in northern Alberta have been increasing over time, due to increasing industrial development

There has been a profound increase in the production of synthetic crude oil in northern Alberta since commercial extraction and upgrading of bitumen began in 1967 (Fig. 11). If open pit bitumen mining and upgrading was contributing significant quantities of TEs to the environment, then one would intuitively expect to see a similar increase in the rates of accumulation of TEs in various archives. However, using age-dated peat cores from ombrotrophic bogs collected near mines and upgraders,⁹⁷ it is clear that atmospheric Pb



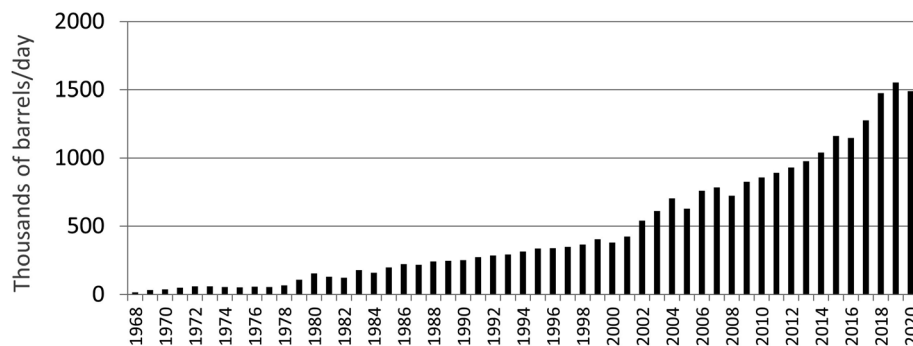


Fig. 11 Bitumen production from mining in Alberta, since 1968. Downloaded from www.oilsandsmagazine.com (November 16, 2021) and used with permission.¹⁴⁶

contamination has been in decline for decades (Fig. 12). Using the same peat cores, it was shown that Ag, Cd, Sb and Tl also had been declining for decades;⁹⁸ the same is true of As and Se.¹⁴⁸ Even the extent of atmospheric contamination by V, Ni and Mo, the three most abundant trace metals in bitumen, show similar declines in the peat profiles.⁹⁸ Independent studies of age-dated sediment cores from the Peace Athabasca Delta also show declines in many of the same TEs, including As, Pb, and Sb.¹⁴⁹ Further, the authors found no increase in concentrations of Be, Cd, Cr, Cu, Ni, V and Zn, relative to pre-industrial levels in the sediments.¹⁵⁰

Open pit bitumen mines generate tremendous volumes of dust, from the mines themselves, from haul roads, gravel roads, aggregate quarries, *etc.*^{151,152} Analyses of the ash contents of *Sphagnum* moss show increasing rates of dust deposition with increasing distance toward industry.¹⁵³ Similarly, wild berries collected near the mines have more dust on their surfaces than berries collected from rural and remote locations.^{154,155} In the vicinity of the bitumen mines, using the same age-dated peat cores from bogs as noted above, increasing rates of dust deposition over time were documented.¹⁵⁶ The declines in atmospheric deposition of TEs over time in the peat cores from bogs appear to contradict the increases in dust deposition over time

at the same locations. However, part of the explanation may lie in the chemical analyses of dust particles extracted from the snow collected at these same bogs: the concentrations of Cd, Pb, Sb and Tl, and even V and Ni, in the dusts, are well below or far below, the corresponding crustal values.⁹⁶

Misconception 10. TEs released to the environment in mineral or particulate forms have the same ecological significance as ionic forms of the same elements

For many TEs, the Guidelines for the Protection of Aquatic Life proscribed by the Canadian Council of Ministers of the Environment (CCME) are based on total concentrations. There are a number of scientific and technical limitations with this approach. In the case of the AR, total concentrations of TEs are dominated by particulate forms (Fig. 5), and particle concentrations can show extreme seasonal variation. Total concentrations of suspended solids (TSS) can be very high in the AR in the spring during snowmelt. For example, at the Town of

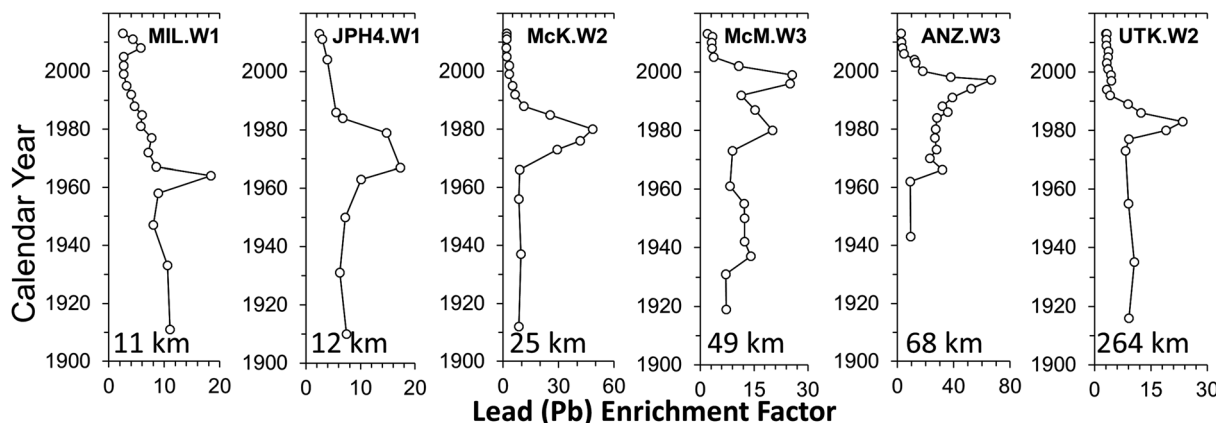


Fig. 12 Crustal enrichment factor, calculated using Th, for Pb in peat cores from 5 bogs in the ABS region (MIL, JPH4, McK, McM, ANZ) and UTK, the control site located 264 km from the mid-point between the two central upgraders.⁹⁷ The peat cores were dated using a combination of ²¹⁰Pb and ¹⁴C, including the atmospheric bomb pulse curve.¹⁴⁷



Athabasca, far upstream from the oil industry, TSS concentrations can reach up to 1200 mg L^{-1} .¹²⁰ Assuming these solids contain TEs in the same proportions as the UCC, a simple calculation shows that 1200 mg L^{-1} of TSS will yield total concentrations of As, Cu and Pb of 5.8, 20.4 and $33.6 \text{ } \mu\text{g L}^{-1}$ which all exceed the corresponding CCME guideline values. Thus, under circumstances governed exclusively by natural processes, in a section of the river where there has been no indication of anthropogenic inputs of TEs, TE concentrations may exceed guideline values for the protection of aquatic life.

What about the chemical reactivity of the particles themselves? Studies of particles suspended in the AR using sequential extraction¹⁵⁷ have shown that As and Cu are found almost exclusively, and Pb (and Tl) predominantly, in the residual, mineral fraction (Fig. 13). Regarding elements such as Ag, Cd and Sb, efforts to fractionate them from suspended solids using sequential extraction have failed thus far, as their concentrations are so low.¹⁵⁷ Within the residual, mineral fraction, TEs are incorporated within the crystalline structures of various silicates, most likely dominated by those of the feldspar group, micas, and clays. In such cases, TEs will not be released to the aquatic environment at a significant rate, given that (a) the pH of the AR¹²⁰ is approximately 8 and (b) the dissolution rate of silicate minerals is at a minimum at this pH:¹⁵⁸ much lower or much higher pH values are needed to hydrolyze the critical Al-O bonds at an appreciable rate.¹⁵⁹ In other words, elements such as Pb contained within silicate minerals will have no direct relevance to biota. Even ingestion by aquatic organisms, despite the extremely low pH of digestive fluids, seems unlikely to have any measurable effect on such stable mineral phases, given how quickly food particles pass through the gut of the animals.

It is well known that “dissolved” concentrations provide a much better indication of potentially toxicity to aquatic

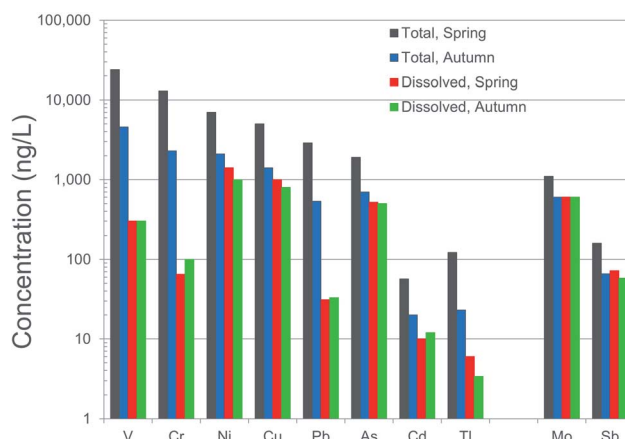


Fig. 14 Comparison of total and dissolved (<0.45 µm) concentrations of trace elements in the Athabasca River. These are average values of samples collected upstream and downstream of industry, during the autumn of 2017 and spring of 2018. Data is from Ghotbizadeh.⁹¹

organisms, compared to “total concentrations”.¹⁶⁰ From an environmental or ecological perspective, the dissolved concentrations are clearly far more important than the totals. For this reason, water quality guidelines in the EU and the USA are based on dissolved concentrations. Referring again to the AR, it is remarkable how different total concentrations are between spring and fall (high flow *versus* low flow conditions) while at the same time, just as remarkable how similar the dissolved concentrations are (Fig. 14). Dissolved concentrations of V and Pb, for example, are effectively identical during spring and autumn, while total concentrations are five times greater in spring compared to autumn (Fig. 14). Ironically, even though particulate forms of V and Pb dominate the inventory of these elements in the river, toxicity testing of these metals to biota employ ionic forms of the elements.^{22,161}

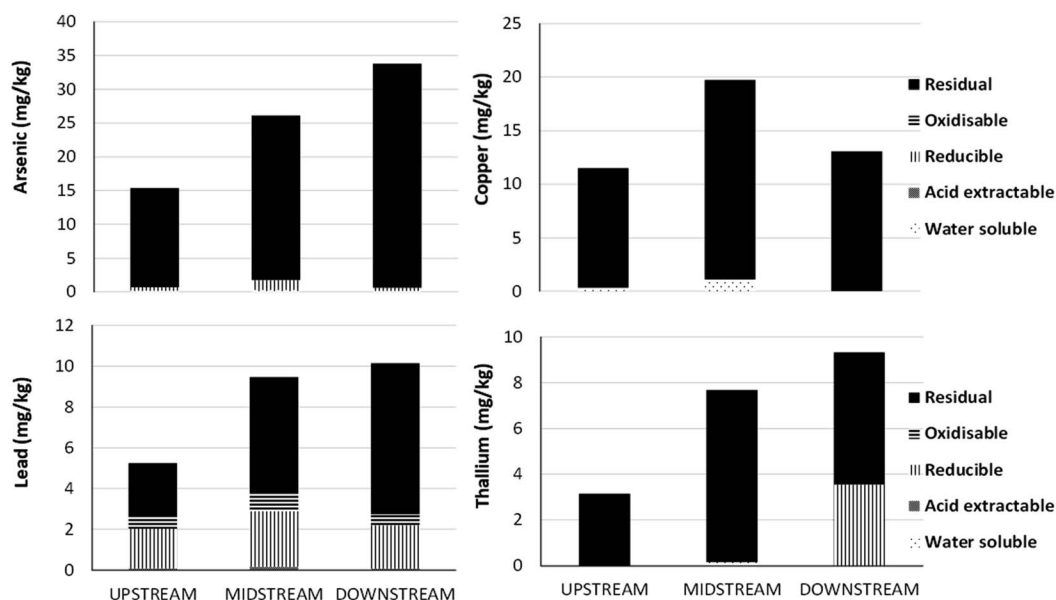


Fig. 13 Sequential extraction of As, Cu, Pb and Tl using suspended solids collected from the Athabasca River. Average values for samples collected within the upstream ($n = 3$), midstream ($n = 2$), and downstream ($n = 2$) sections of the river. From Javed and Shoty¹⁵⁷

In regard to bioavailability of TEs, as noted by the US EPA more than 50 years ago, “toxicity is dependent upon the ionic, salt, or complex forms of the element”.¹⁶² Similarly, in an early study on TEs in precipitation of Ontario, it was noted that “it is becoming increasingly clear that simple determination of total component concentration provides insufficient information to allow evaluation of its environmental impact”.¹⁶³ Further, that “determination of ‘free’ component concentrations should be the ultimate aim of the researcher”.¹⁶³ Within the dissolved fraction, the elements that are directly bioavailable are those in ionic form, or simple complexes with molecular mass below 500 Da, as these can directly pass through cell membranes.¹⁶⁴ Efforts to determine free metal ion concentrations include calculations of the distribution of dissolved species using equilibrium chemical thermodynamics^{165,166} or direct measurements using electrochemical methods.¹⁶⁷ The importance of chemical speciation for understanding the bioavailability of TEs is well established.¹⁶⁸

Today, we have technologies such as flow-field flow-fractionation (AF4) coupled to ICP-MS to measure the concentrations of many TEs in the dissolved (*i.e.* <0.45 μm) fraction as a function of molecular size,¹⁶⁹ and this technique has been applied to surface waters of the AR watershed.¹²¹ Using a 300 Da membrane, these efforts have shown that some TEs in the AR are found primarily or exclusively in the form of ions or simple complexes (*e.g.* Li, Sr) while others are to a large extent associated with organic or inorganic colloids (*e.g.* Cu, Pb). Given that the larger organic and inorganic colloids range in size from approximately 1 to 20 kDa,¹²¹ the TEs they contain are expected to have limited bioavailability. However, TEs associated with these materials may be potentially bioavailable *i.e.* they may be bioaccessible, depending on the lability and stability of the colloids.^{170–172} In summary, we have the technology today to reliably determine total, dissolved, and “truly dissolved” concentrations of TEs in the AR, for most of the potentially toxic TEs of interest. Regarding TEs that cannot be separated into these classes using AF4-ICP-MS *i.e.* Ag, Cd, Sb, and Tl, even with using state-of-the-art metal-free, ultraclean laboratory facilities, their concentrations in the AR are so low that they are very unlikely to have any ecological relevance.

Summary and conclusions

Mining and upgrading of bitumen have given rise to five decades of studies of TEs in the environment of the Lower AR watershed. The underlying assumption in most of these studies is that the ABS contain elevated concentrations of TEs, and that industrial development mobilizes them in quantities and forms that threaten terrestrial and aquatic life. In fact, the ABS ores are depleted in every element we have measured, relative to the UCC, with the exception of Mo and Re. The distribution of TEs in the ABS is dichotomous: V, Ni, Mo, Se and Re are found almost exclusively in the bitumen fraction, with enrichments of approximately 2 (V, Ni), 4 (Se), 9 (Mo) and 250 times (Re), relative to the UCC. All of the other TEs occur in the mineral fraction which is made up mainly of quartz sand.

Pioneering environmental studies focused on V, as this is the most abundant metal in bitumen, but more recent studies have

shifted focus to emphasize the potentially toxic chalcophile elements (Ag, As, Cd, Pb, Sb, Tl) which along with Be and Cr, are found almost exclusively in the mineral fraction. With the number of studies and diversity of sample media being collected in the region, a considerable volume of data is being created, but varying in quality. Modern, multielement methods of instrumental analysis such as ICP-MS are excellent, but certainly not perfect, and cannot be used uncritically. Elements such as As and Se, for example, pose serious challenges because of molecular interferences in the mass spectrum. While these issues can be addressed using collision cell technologies and overcome using medium or high mass resolution using sector-field ICP-MS, there are very few of these larger, more sophisticated instruments being applied in this region. Further, acid digestion of solid samples continue to present challenges, and complete dissolution of certain phases in soil and sediment samples remains difficult. Older, established methods such as INAA do not require samples to be digested, and provide high quality data with excellent sensitivity for some lithophile elements such as Al, Cr, Sc, Th and V, but also some chalcophile elements such as As and Sb. In fact, the early measurements of V in bitumen, fly ash, snow, lichens and moss are excellent, despite their antiquity, and provide useful reference levels, for comparison with modern samples.

In regard to aquatic inputs of TEs to the AR, most of the elements of concern are found predominantly in the particulate fraction. In consequence, total concentrations of TEs in the AR show extreme seasonal variation, with springtime values commonly two to five times greater than those in autumn. Using ultraclean lab procedures and protocols, TE concentrations within the dissolved fraction are found to be extremely low (*e.g.* ng L⁻¹ level for Ag, Be, Cd, Pb, Sb, Se and Tl), very similar in spring and autumn, and are remarkably reproducible, year after year. Measuring TEs as a function of molecular size within the dissolved fraction shows that some of the TEs of greatest concern, are associated to a great degree with, or dominated by, colloidal forms. Therefore, the “truly dissolved” fraction of TEs such as Pb *i.e.* ionic forms and simple inorganic and organic complexes, occur at extremely low concentrations.

Regarding atmospheric deposition, most TEs in *Sphagnum* moss and in snow, are associated with dust particles; concentrations in the filterable fractions are very low. Further, retrospective analyses using peat cores from bogs and sediment cores from the Peace-Athabasca Delta, show that emissions of TE to the environment in this region have been in decline for decades. With respect of TEs in biota, more effort is needed to determine the natural abundance of elements in plants and animals from remote or at least rural regions, for comparison with samples from industrialized areas. Also, the natural enrichment of elements such as Cu, Ni, Zn, Cd and Tl in plants and animals, living far removed from industrial activities, warrants further investigation. Similarly, the natural processes that enrich TEs in soils and sediments, relative to UCC, including physical and chemical weathering, as well as winnowing during wind erosion and sorting during water erosion, must be duly considered.

Environmental monitoring requires clearly defined scientific questions, well planned sampling campaigns which include



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