Natural and anthropogenic inputs of arsenic and selenium to the environment in the Athabasca Bituminous Sands Region

by

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Abstract

Industrial development of the Athabasca Bituminous Sands (ABS) in northern Alberta, Canada, has raised concerns that emissions of arsenic and selenium to the surrounding landscape and waterbodies have been increasing over time. To test this hypothesis, a comprehensive study of arsenic and selenium in a variety of environmental media from the ABS region was conducted. The foci included: i) bituminous ores and the distribution of arsenic and selenium between mineral and bitumen fractions ii) *Sphagnum* moss from ombrotrophic bogs to determine contemporary atmospheric deposition iii) age-dated (^{210}Pb, ^{14}C) peat cores to determine historical trends in arsenic and selenium deposition iv) chemical speciation in Athabasca River water and v) Trout-perch (*Percopsis omiscomaycus*) from the Athabasca River as a biological indictor of selenium inputs.

Similar to other potentially toxic trace elements (Ag, Be, Bi, Cd, Pb, Sb, Tl), analyses of laboratory separated mineral and bitumen components of ABS revealed that As is contained predominantly in the mineral fraction of ABS ores. In contrast, selenium was found predominantly (ca. 80%) in the bitumen fraction. Therefore, due to the high degree of chemical stability of mineral material in ABS, selenium likely exhibits greater mobility than As during the bitumen upgrading process. To examine potential emissions to the aquatic environment, the concentration and chemical speciation of arsenic and selenium were determined along a ~125 km transect of the Athabasca River. Despite nearby bitumen mines and upgraders, as well as natural inputs of salts, humic material, naphthenic acids and suspended solids, dissolved (i.e., < 0.45 µm) concentrations of both elements (arsenic ~0.4 µg/L; selenium ~0.2 µg/L) remained remarkably consistent in time (2014, 2015) and space, with no increasing trend in concentrations observed upstream to downstream of industry. The chemical speciation of both elements also remained consistent upstream to downstream, with As(V) and Se(VI) being the predominant forms determined in surface water. The average concentration of selenium in Trout-Perch muscle (2.2 ± 0.4 mg/kg; n=34) was below U.S. EPA guideline values and concentrations were not significantly different ($p > 0.05$) between upstream and midstream or downstream reaches.

The average concentration of selenium in *Sphagnum* moss collected from peat bogs around the ABS region (57.5 ± 13.1 µg/kg; n = 75) was similar to concentrations in moss collected from other parts of Alberta. Moss from the east and west coasts of Canada were found to contain much greater concentrations (~ 3x) of selenium than moss collected from the ABS region due to natural inputs from the marine biosphere. An age-dated peat core from an ombrotrophic (rain-fed) bog near open-pit mines and upgraders did not reveal an increasing trend in selenium deposition over time. Arsenic concentrations in the same peat core demonstrated an increase with time; however, the apparent increase was attributed to greater mineral dust deposition, which has been increasing in the region due to industrial activities. A peat core collected from the Utikuma Region Study Area (UTK), a remote reference site approximately 250 km upwind from the ABS region, revealed a 2700-year record of atmospheric arsenic and selenium deposition. Accumulation rates of arsenic and selenium in UTK demonstrated a considerable increase beginning in the early 20th century, peaking in ~1970, before going into a steady decline. The timing of these increases implicates coal combustion and base metal smelting and refining, combined with long-range atmospheric transport, as predominant sources of both elements to the bog and provides important perspective on the limited nature of atmospheric arsenic and selenium deposition in the ABS region. Viewed together, these findings suggest that inputs of arsenic and selenium to the environment in northern Alberta due to bitumen mining and upgrading are difficult to distinguish from natural inputs.

Preface

Chapter Two of this thesis has been published as Donner, M.W., Javed, M.B., Shotyk, W., Francesconi, K.A., and Siddique, T., “Arsenic speciation in the lower Athabasca River Watershed: a geochemical investigation of the dissolved and particulate phases,” *Environmental Pollution*, 2017, vol. 224, 265-274. I performed the field work, data interpretation and writing of the manuscript. I also performed all laboratory analyses, excluding particulate/total arsenic data (Dr. Javed) and independent verification analyses for arsenic (Dr. Francesconi). Dr. Shotyk and Dr. Siddique contributed manuscript review and concept formation.

Chapter Three of this thesis has been published as Donner, M.W., Bicalho, B.B., Sinn, C., and Shotyk, W., “Selenium and Sulphur in Athabasca Bituminous Sands Mineral and Bitumen Fractions”, *Fuel*, 2018, vol. 224, 718-725. I performed HG-AFS analyses, data interpretation and manuscript writing. Dr. Bicalho was responsible for lab separations of minerals from bitumen and ICP-SFMS analysis for selenium. Mr. Sinn assisted in bitumen extractions and acid digestion. Dr. Shotyk provided manuscript review and concept formation.

Chapter Four of this thesis has been published as Donner, M.W., and Siddique T., “A rapid and sensitive IC-ICP-MS method for determining selenium speciation in natural waters”, *Canadian Journal of Chemistry*, 2018, Vol. 96, 795-802. I was responsible for concept formation, analyses and manuscript writing. Dr. Siddique aided in concept formation and manuscript review.

Chapter Five of this thesis has been published as Donner, M.W., Cuss, C.W., Poesch, M., Sinnatamby, R.N., Shotyk, W., and Siddique, T. “Selenium in surface waters of the lower Athabasca River: chemical speciation and implications for aquatic life”, *Environmental Pollution*, 2018, Vol. 243, 1343-1351. I was responsible for field work, lab analyses, data interpretation and writing of the manuscript. Dr. Sinnatamby provided dissected Trout-perch samples and related supporting information, Dr. Cuss supported statistical testing and data analysis, Dr. Poesch supervised the study of Trout-perch, Dr. Siddique and Dr. Shotyk provided concept formation and manuscript review.

Chapter Six of this thesis has been prepared as a manuscript for submission to a peer-reviewed journal: Donner, M.W., Bicalho, B., Shotyk, W. “Contemporary and historical atmospheric deposition of arsenic and selenium in the Athabasca Bituminous Sands Region”. I performed Se analyses of peat cores and moss, data interpretation and manuscript writing. Dr. Bicalho provided arsenic analyses in peat and Dr. Shotyk provided manuscript review and concept formation.

This thesis, and all my life's work, is dedicated to my parents, William and Wanda Donner

“Nature uses only the longest threads to weave her patterns, so that each small piece of her fabric reveals the organization of the entire tapestry”

Dr. Richard A. Feynman
Cornell University, 1946

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Mark W. Donner

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1.0 INTRODUCTION

1.1 Arsenic

1.1.1 Historical overview

Few elements on Earth have had greater influence on human history than arsenic (As). Knowledge of arsenic and its chemical properties can be traced back to ancient times, as the transition to the Bronze Age likely resulted in considerable human exposure due to the co-occurrence of arsenic-bearing minerals found in abundance with copper, such as arsenopyrite ($FeAsS$), orpiment (As_2S_3), realgar (As_2S_2), olivenite (Cu_2OHAsO_4), cobaltite ($CoAsS$), and proustite (Ag_3AsS_3) (Nriagu, 2002). Smelting of such minerals would have produced large quantities of arsenious oxide (As_2O_3), which likely impacted the health of millions of people including the Egyptians, Chinese and Greeks (Nriagu, 2002). Due to the co-occurrence of arsenic in minerals with economic value or substantial utility such as copper, lead, silver, and gold, it wasn't long until arsenic minerals were identified and pursued for experimentation (Azcue and Nriagu, 1994). While early attempts by alchemists to produce gold from orpiment were undoubtedly met with spectacular failure, experimentation with arsenic ultimately gave way to two categories of use that continued well into modern times: medicine and warfare. Those topics will not be reviewed further here, as they are not relevant to this thesis. However, a brief acknowledgement of the ancient history of arsenic is a good reminder of how this element grew to become an enormous environmental and public health threat in the modern era, despite a long history of knowledge concerning its toxic properties.

Direct environmental contamination of arsenic began in the mid 1800's with the introduction of its use as a pesticide in the form of copper arsenate, commonly known as "Paris green" (Nriagu, 2002). Over a period of approximately 60 years, more than 450 million kg of arsenic-based pesticide was sprayed over crops in the United States, largely as either lead arsenate or calcium arsenate (Nriagu., 2002). Organoarsenical compounds such as dimethylarsenic acid (DMA) and monomethylarsenous acid (MMA) also became a popular herbicide choice in the 1970's, with millions of kg of arsenic being applied annually (Nriagu, 2002). The use of arsenic in agriculture ushered in an era of environmental pollution that is still measurable today, with much of it still retained in orchard soils of the United States (e.g., Durkee et al., 2017). With so much public awareness and concern for arsenic in society today, it's remarkable to reflect on the amount that was directly applied to our food less than a century ago.

Despite its eventual removal from industries such as agriculture and wood preservation, environmental contamination by arsenic is still an important issue worldwide. Non-ferrous metal production (smelting) is known to be the largest contributor of global anthropogenic atmospheric arsenic emissions, followed by fossil fuel combustion, iron and steel production, cement production and waste disposal (Pacyna and Pacyna, 2001). Natural sources of arsenic are also relevant, such as low-temperature volatilization, volcanic emissions, wind erosion, forest fires and sea-salt spray (Chilvers and Peterson, 1987). Today, arsenic is perhaps most well known as a problematic constituent in groundwater wells. Areas of Argentina, Bangladesh, Chile, China, Hungary, India, Mexico, Romania, Taiwan, Vietnam and the USA are known for elevated concentrations of arsenic in groundwater (Smedley and Kinniburgh, 2002). Greater monitoring efforts, as well as the clear impacts of elevated arsenic concentrations on human health in densely populated countries such as Bangladesh and India, has prompted considerable research efforts into understanding its biogeochemical cycling. An estimated 30 – 50 million people in Bangladesh are exposed to drinking water with As concentrations exceeding the World Health Organization (WHO) standard of 10 $\mu g\ L^{-1}$, with concentrations as high as ca. 3200 $\mu g\ L^{-1}$ (Smedley and Kinniburgh, 2002).

1.1.2 Environmental chemistry

A seemingly endless number of arsenic-containing compounds (arsenicals) are known to exist in nature, with many having drastically different characteristics related to mobility and toxicity. This diversity in speciation places arsenic in a relatively unique category as compared to other potentially toxic, chalcophile "heavy metals" such as Ag, Sb, Pb, Hg and Tl. The oxyanions arsenite (+III oxidation state) and arsenate (+V oxidation state) are typically the most well-known forms of arsenic due to their abundance in aquatic systems and toxicity at relatively low concentrations. Depending on the pH of their environment, these compounds will possess different degrees of protonation [e.g., arsenite is commonly as $As(OH)_3^0$ and arsenate is as $HAsO_4^{-2}$ or AsO_4^{-3}] (Essington, 2015). Oxidation states of +III and +V are also applicable to other forms of arsenic (see below), however the common approach of denoting As(III) and As(V) to represent inorganic forms of arsenite and arsenate, respectively, will be used here. In natural waters, As(III) and As(V) are often the most frequently encountered species, with As(V) being predominant in oxic waters and As(III) in reducing conditions (Smedley and Kinniburgh, 2002; Wang and Mulligan, 2006). When biological productivity is high, those inorganic species have the potential to undergo methylation to form MMA and DMA in either trivalent or pentavalent oxidation states [MMA(V), MMA(III), DMA(V), DMA(III)] (Rahman and Hasegawa, 2012; Challenger, 1945; Cullen and Reimer, 1989; Ferguson and Gavis, 1972; Hasegawa, 1997; Hasegawa et al., 2010). A general consensus on the order of toxicity, from most toxic to least toxic (as defined by potency of DNA damage) for those compounds is: DMA(III) > MMA(III) > As(III), As(V) > MMA(V) > DMA(V) (Dopp et al., 2004; Wang and Mulligan, 2006). In the atmosphere, arsenic is mostly present as inorganic particulates with a minor portion of methylated species produced from biological activity (Wang and Mulligan, 2006). Atmospheric emissions from high temperature combustion reactions (e.g., smelters, volcanoes, coal-fired plants) can also produce substantial amounts of arsenic oxide (Wang and Mulligan, 2006).

There is a remarkably long list of naturally occurring organo-arsenicals found in the environment as a result of biological uptake and metabolism. Many years of curious speculation (e.g., Chapman, 1926) about the form(s) of arsenic present in marine organisms at extremely high concentration (upwards of 100 mg/kg) was finally resolved when Edmonds et al., (1977) determined that arsenic in the western rock lobster (*Panulirus longipes cygnus*) was predominantly as the non-toxic compound arsenobetaine. Unlike As(V) and As(III), arsenobetaine passes through the human body relatively quickly (half-life of ca. 10 hours) and is excreted without modification (Cannon et al., 1981; Stoeppler, 2004; Stoeppler and Vahter, 1994). This is in contrast to inorganic arsenicals such as As(III) and As(V), which are detoxified primarily in the liver through chemical reduction and methylation to MMA, DMA and some other trace metabolites (Stoeppler, 2004). Today, the number of known arsenic compounds (both inorganic and organic) has expanded considerably and continues to grow; this raises obvious challenges associated with interpreting and communicating any potential toxicological implications or dietary restrictions (e.g., Francesconi, 2010; Hinrichsen et al., 2015; Stiboller et al., 2017). Advancements in analytical instrumentation, particularly in areas of molecular characterization and limits of detection, has also allowed researchers to quantify some of these organo-arsenicals (such as arsenobetaine) in ultra-trace amounts as *dissolved* constituents in seawater (Glabonjat et al., 2017) and freshwater environments (Mikutta and Rothwell, 2016).

Having the name “arsenic” be synonymous with “poison” is a problem when communicating to the general population. While cases of hazardous exposure to high arsenic concentrations still exist today (e.g. drinking water wells), there are also considerable misconceptions surrounding the element. A good example of this comes from modern medicine: despite its established toxicity at a relatively low dose, arsenic trioxide has been found to be an effective treatment for acute promyelocytic leukemia and has led to complete remission for relapsed patients (Soignet et al., 1998). Arsenic-based chemotherapy options are also being explored for other cancers as well as a variety of other problematic diseases and medical conditions (Cullen and Reimer, 2016). From an environmental perspective, the challenge in communication comes from the fact that we can now measure (total) arsenic reliably in virtually all substances on Earth, but assessing whether it poses a threat to our environment or health requires knowledge of both its concentration and speciation (Cullen and Reimer, 2016). The analytical chemistry used for determining arsenic and its speciation also plays a critical role in our understanding; this topic has been reviewed extensively elsewhere (e.g., B'Hymer and Caruso, 2004; Gong et al., 2002; Francesconi and Kuehnelt, 2004) and is discussed specifically in Chapters Two and Six of this thesis.

1.2 Selenium

1.2.1 Historical overview

The discovery of selenium is credited to Jöns Jacob Berzelius, a famous Swedish chemist who was intrigued by an unknown red 'mineral body' found in ovens of a sulphuric acid factory following the combustion of sulphide ores from the Fahlun Mine, Sweden (Berzelius, 1817). Due to its similarity with tellurium, an element named from the word *tellus* meaning Earth, Berzelius aptly named the element *selenium*, derived from the Greek word "Sēlenē", meaning Moon (Berzelius, 1817, 1818). Despite its brief history of study compared to other chalcophile elements (e.g., As, Ag, Pb, Sb), our understanding of selenium has evolved at an extremely rapid pace that has been spurred on by important discoveries regarding its toxicity and beneficial properties. Interestingly, most research has only taken place in the last century, as very little was made of selenium's potential and the environmental significance of selenium only became apparent many decades after its discovery. In fact, even the general properties of selenium were not of significant interest until Willoughby Smith, an electrician of the Telegraph Construction Company, discovered its sensitivity to light (D'albe and Fournier, 1924; Smith, 1873). That discovery led to the creation of the first "selenium cell", and shortly after a patent filed by Alexander Graham Bell for the invention of the photophone (D'albe and Fournier, 1924).

Attention to the role of selenium in agriculture and the environment began in the early 1930's following an announcement of its apparent association with a problematic disease in agriculture called "alkali disease" or "blind staggers"; the disease appeared to be caused by forage plants and grains with elevated concentrations of selenium, resulting in the deaths of entire herds of cattle and sheep (Trelease and Beath, 1949). A considerable amount of research was conducted to further understand selenium-plant relationships and prevent any potential health impacts to the general population. The stigma of selenium as a poisonous element in agriculture began to change following the discovery of its physiological need as a micronutrient (Schwarz and Foltz, 1957), setting the stage for other important discoveries such as its role as an antioxidant (Rotruck, 1972) and its presence in proteins as selenoamino acids (Cone et al., 1976). Unfortunately, the importance of selenium as a micronutrient became overshadowed in the early 1980's after it was found that irrigation drainwater in the western United States contained extremely high concentrations of selenium (ca. 300 $\mu g\ L^{-1}$) due to its contact with seleniferous geology and soils (Ohlendorf et al., 1986). As a result, the receiving ecosystems had highly elevated concentrations of selenium in sediments, plants, invertebrates and fish, leading to devastating teratogenic and mutagenic effects on waterfowl (Ohlendorf et al., 1986; Saiki and Lowe, 1987).

In addition to agriculture, there are a number of other industrial activities associated with selenium contamination such as coal combustion, crude oil refining, mine waste rock drainage and sulphide ore smelting (Young et al., 2010). Despite the ubiquitous presence of these industries, on a world-wide basis selenium deficiency in the human diet is considered to be more problematic than risk of its toxic effects – an estimated one billion people worldwide have insufficient selenium intake, a problem that has been predicted to become worse with climate change (Jones et al., 2017). A good example of selenium deficiency comes from Finland, where potential health problems related to selenium deficiency prompted the government to implement a law requiring that selenium (as inorganic sodium selenite) was to be added to all multi-element agricultural fertilizers (Reilly, 2006a). A considerable increase in selenium concentrations was found in crops and meat after only the first growing season, raising concern for over supplementation and eventually leading to a reduction of supplementation (Reilly, 2006a).

1.2.2 Environmental chemistry

Selenium exists in multiple oxidation states (-II, -I, 0, IV, VI) and has six natural isotopes (^{74}Se, ^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se, ^{82}Se) (Winkel et al., 2015). The chemical properties of selenium are similar to that of sulphur, an observation made at the time of its discovery (Berzelius, 1817). Selenium is considered the 63rd most abundant element in the Upper Continental Crust with a concentration of 83 μg kg^{-1} (Wedepohl, 1995). However, there is a considerable amount of variability in its distribution, particularly in areas where soils have been derived from weathering of organic-rich marine sedimentary rocks (Young et al., 2010).

Selenium is emitted to the atmosphere by anthropogenic and natural sources. Natural sources dominate the global selenium inventory and are derived primarily from crustal weathering, sea salt, volcanos, and biogenic emissions from the continents and the oceans (Mosher & Duce, 1987). The greatest flux of selenium to the atmosphere comes from the oceans, where selenium undergoes biomethylation and emission to the atmosphere as gaseous species (mainly dimethylselenide; DMSe); the same processes also occurs in terrestrial environments, which represents the second largest source to the atmosphere (Mosher & Duce, 1987; Wen & Carignan, 2007). Major anthropogenic sources of selenium to the atmosphere are related to combustion processes (coal, oil, fuelwood, etc.), non-ferrous metal production (copper, lead, zinc) and other manufacturing industries (glass/ceramics, electronics, pigments, iron/steel) (Mosher & Duce, 1987). During combustion processes, a portion of selenium is capable of converting to gaseous forms (e.g., selenium dioxide, SeO_2) or extremely fine particles (e.g., elemental selenium) that are capable of passing through basic particulate controls such as baghouse filters (Petrov et al., 2012; Shendrikar et al., 1983).

Selenium in natural waters is commonly present as soluble oxyanions selenite (+IV oxidation state) and selenate (+VI oxidation state), which exhibit varying degrees of protonation (e.g., selenate: SeO_4^{2-}, biselenate:$HSeO_4^-$; selenite =$HSeO_3^-$ SeO_3^{2-}) (Fernández-Martínez and Charlet, 2009). Selenite anions are considerably less mobile and bioaccessible due to their ability to form strong, inner-sphere surface complexes (e.g., binuclear bidentate) with common minerals such as goethite (FeOOH) or organic matter (Bruggeman et al., 2007; Gustafsson and Johnsson, 1994; Hayes et al., 1987; Sposito, 1995). Conversely, Se(VI) in the presence of goethite is only loosely attracted, held either by outer-sphere complexation or as part of the diffuse swarm created by the mineral surface charges (Hayes et al., 1987; Sposito, 1995). Another factor affecting Se(IV) mobility is that it is more readily reduced by a wide array of microorganisms to lower, and less mobile, oxidation states [Se(0), Se(-II)] (Milne, 1998): for these reasons, Se(VI) tends to dominant in oxic waters.

Similar to arsenic, there are many organic biomolecules of selenium produced by organisms during metabolic processes (Wallschläger and Feldman, 2010). Despite their beneficial role in humans and animal physiology, organo-selenium species are important when considering the potential for selenium to act as an environmental toxin in aquatic ecosystems, as the organic forms are considered to be the most bioavailable (Young et al., 2010). Discrete organo-selenium compounds (e.g., selenomethionene) are not typically observed in natural aquatic systems, however, their presence at low concentrations in highly productive waters has been determined (Leblanc et al., 2016; Leblanc and Wallschläger, 2016). Total selenium in water can be an unreliable indicator of toxicity due to its complex speciation and contrasting bioavailability between forms. As reflected in the new 2016 United States Environmental Protection Agency (US EPA) guidelines for selenium in aquatic environments, measurements of selenium in fish muscle or reproductive organs now take precedent over concentrations in water (US EPA, 2016). Separate guideline values have also been established for lentic (e.g., wetland) and lotic systems to reflect differences in the behavior of selenium and its potential bioaccumulation under different hydrological conditions (US EPA, 2016; Simmons and Wallschläger, 2005). An important factor in the decision to prioritize fish tissue as a guideline also comes from the fact that accurate and precise measurements of selenium and its chemical speciation can be a considerable challenge. The analytical chemistry of selenium has been reviewed at length in Chapters 3, 4, 5 and 6 of this thesis.

It is well known that selenium is important for both maintaining important physiological functions in humans and animals such as antioxidant systems, thyroid function and immune system (Reilly, 2006b); selenium may also play an important role in the prevention of Alzheimer's disease (Cardoso et al., 2010, 2017). However, another important and relevant role of selenium in human and animal physiology is its ability to mediate the toxicity of potentially toxic metal(oid)s (Frost and Olson, 1972). For example, part of the toxicity of As(III) and Hg(II) is related to their high affinity for thiol (SH) groups contained in enzymes (Morris, 2015); in the presence of the antioxidant glutathione (GSH), selenium reduces their toxicity by forming extremely strong double bonds (As=Se), which have been suggested to be even stronger than As-S bonding (Gailer et al., 2000; Morris, 2015). That compound, e.g., $[(GS)_2AsSe]^-$, is then transported from the liver as a component of bile and is ultimately removed from the body through the kidneys (Gailer et al., 2000). Similar processes, forming Hg-Se bonds to replace Hg-S bonds, affect the biochemistry of Hg (Morris, 2015). Any assessment of potential health risks associated with toxic metals such as mercury in humans and animals should also consider the protective effects of selenium (Sørmo et al., 2011).

1.3 Research background and rationale

1.3.1 Athabasca Bituminous Sands

The Lower Cretaceous Mannville group in Alberta, Canada, represents the third-largest hydrocarbon reserve on Earth and is comprised of three primary deposits: Athabasca-Wabasca, Peace River and Cold Lake (Garven, 1989). Hydrocarbons in these deposits are present in the form of bituminous sands, a mixture of sand and clay, coated by water and a heavily biodegraded crude oil known as bitumen (Larter and Head, 2014). Combined, they contain an estimated 165.4 x 10^9 barrels of remaining (established) reserves, with the largest of this group being the

Athabasca bituminous sands (ABS) region (32.09 x 10^9 barrels remaining) (Alberta Energy Regulator, 2017). Due to the highly viscous nature of bitumen, its extraction and refining requires unconventional extraction techniques and additional upgrading prior to refining. Bitumen at depths greater than 150 m require *in-situ* extraction techniques, the bulk of which is performed using a technique known as steam-assisted gravity drainage (Gosselin et al., 2010). Bitumen in the ABS region, however, often appears at depths less than 70 m and is able to be surface mined using large open-pit style mines (Gosselin et al., 2010). In addition to occupying a large active-mining area, further landscape disturbance comes from the need to store large volumes of produced tailings. As of 2015, tailings ponds and their associated structures cover an area of 246 km^2 with a total volume of (fine fluid) tailings of 1075 Mm^3 (http://osip.alberta.ca/map/). Details regarding the mining and upgrading of ores from the ABS, as well as relevant chemical and physical properties, are described in Chapter 3 of this thesis.

Although this resource is an important contributor to the economy in Alberta and Canada, the large-scale extraction and refining of bitumen in the ABS has raised concern for human and ecosystem health (Schindler, 2010; Schindler, 2013; Timoney and Lee, 2009). Amidst an array of important environmental concerns (e.g., loss of habitat and ecosystem function, emissions of greenhouse gases, water-use, pace of land reclamation, etc.) (Gosselin et al., 2010), inputs of potentially toxic trace elements to the landscape and waterbodies around surface mines, bitumen upgrading facilities, and large tailings ponds remains a controversial issue (Blais and Donahue, 2015; Boutin and Carpenter, 2017; Kelly et al., 2010; Shotyk et al., 2014; Shotyk, 2018; Timoney, 2012; Wiklund et al., 2014).

1.3.2 Atmospheric deposition of trace metals

Open pit mines and upgraders in the ABS region have been suggested to be a relevant source of potentially toxic metals such as Ag, As, Be, Cd, Pb, Hg, Sb, Se, and Tl by atmospheric deposition (Kelly et al., 2010). This list, however, is at odds with knowledge of the metals known to be enriched in bitumen (V, Ni, Mo, Re) (Goldschmidt, 1937; Selby, 2005) and is an unexpected impact of bitumen mining. Recent studies have contradicted claims that open pit mines and upgraders are a source of trace metal pollution (Javed et al., 2017; Shotyk et al., 2014; Shotyk et al., 2016a; Shotyk et al., 2016b; Shotyk et al., 2017; Shotyk, 2018), indicating that dust serves as the dominant source of metals to the ABS region (Mullan-Boudreau et al., 2017a; Mullan-Boudreau et al., 2017b; Shotyk et al., 2014; Shotyk et al., 2016a). While these preceding studies addressed the majority of metals listed above, claims of As and Se contamination still remain unresolved and are a concern for residents in the area. Moreover, prior to the research presented here, there was very little reliable analytical data on As and Se in bituminous sands. Without having basic geochemical data regarding the host phase (mineral or bitumen) of trace elements, assessing their potential fate and mobility during mining and upgrading is a challenge.

A lack of information on the chronology of atmospheric As and Se deposition to compare with contemporary atmospheric deposition is also important: has atmospheric deposition of As and Se increased with the development and growth of bitumen mining and upgrading? The recent approval for additional mines to be built in the coming years signals an urgent need to establish contemporary, as well as background (pre-industrial), rates of atmospheric As and Se deposition. Without an understanding of the natural, background rates of atmospheric deposition, contemporary rates cannot be viewed in context and industrial impacts are difficult to quantify.

1.3.3 The Lower Athabasca River

With regard to the aquatic environment, the lower Athabasca River is a major priority for assessing contamination from industrial operations. Due to the close proximity of mines and upgraders to the river, some of its tributaries are subject to atmospheric deposition of contaminants and are suspected to be receiving some inputs of process affected (waste) water seeping from large tailings ponds (Frank et al., 2014; Ross et al., 2012). Therefore, the lower Athabasca River and its watershed (tributaries, groundwater) has been the focus of some prominent studies aimed at assessing metal contamination in the ABS region e.g., (Kelly et al., 2010; Wiklund et al., 2014). Concentrations trace elements listed above, including As and Se, have also been described as being greater in the Athabasca River near industry (Kelly et al., 2010). Those claims are supported by a relatively limited data set on the aquatic chemistry of these elements in the river, which does not include information on chemical speciation; as described above, such measurements are critical to consider in the case of As and Se, as their chemical form largely determines toxicity and mobility. Moreover, by virtue of its geological setting, the potential sources of As, Se, and other chemical parameters in Athabasca River water are diverse and therefore complex. The river receives substantial inputs of highly saline groundwater from geological formations such as the prairie evaporites (Gibson et al., 2013) and the erosion of bitumen-laden banks along the Athabasca River, combined with inputs of humic-rich tributary water, further complicates water chemistry by supplying large quantities of diverse natural organic matter (Headley et al., 2011; Ross et al., 2012). This unique aquatic environment has sparked interest and debate amongst scientists, government, and the public — the result of which, has led to general confusion of whether trace elements are natural or anthropogenic in origin. The research described here is part of two large multi-disciplinary studies evaluating both air and water quality in the region.

1.4 Research goals and objectives

1.4.1 Overall goal

The goal of this study is to evaluate natural and anthropogenic inputs of As and Se to the Athabasca River and landscape near industrial development of the ABS. The aquatic chemistry of As and Se in the lower Athabasca River Watershed, viewed together with their contemporary and historic atmospheric deposition, will provide a more clear understanding of whether natural or anthropogenic sources of these elements dominate the ABS region.

1.4.2 Specific Objectives

1. Evaluate the concentrations and chemical speciation of As and Se in the Athabasca River and associated tributaries within the Athabasca bituminous sands region
2. Determine the extent of atmospheric As and Se contamination introduced to the environment by mining and upgrading of the Athabasca bituminous sands

1.4.3 Research Questions

i. Is the industrial development of the Athabasca bituminous sands an important source of As and Se to the lower Athabasca River?
ii. What are the physical (dissolved, particulate) and chemical (redox-state) forms of As and Se in surface waters and groundwaters? Which are the dominant forms/species?
iii. Are atmospheric emissions from industrial development an important source of As and Se in contemporary atmospheric deposition?

iv. Has the atmospheric deposition of As and Se in northern Alberta increased due to mining and upgrading of the Athabasca bituminous sands?

1.4.4 Research Approach

In order to address these research questions, the following investigations were undertaken:

a. Determine dissolved (< 0.45µm) concentrations of As and Se in Athabasca River water, major tributaries and shallow groundwater (saline and fresh).
b. Assess the environmental fate and behavior of As and Se in the watershed based on their chemical speciation.
c. Determine the total concentrations and distribution of As and Se between mineral and bitumen fractions in ABS ores.
d. Determine As and Se in the living layer of *Sphagnum* moss from ombrotrophic bogs as a measure of contemporary As and Se atmospheric deposition. Compare with:
    - Conservative, lithophile elements (e.g, Sc)
    - Moss from other regions (e.g., urban, rural, and remote)
e. Quantify historic As and Se atmospheric deposition using age-dated peat cores from ombrotrophic (i.e., rain-fed) peat bogs as environmental archives.

1.4.5 Thesis outline

This thesis is composed of seven chapters, beginning with the background information summarized above as the Introduction (Chapter One), followed by five chapters presented as individual manuscripts. Each manuscript addresses the research questions outlined above, with a final synthesis chapter (Chapter Seven) to present the main conclusions. Chapter Two examines the total concentrations and chemical speciation of arsenic in surface waters and groundwaters in the Athabasca River, upstream and downstream of bitumen mines and upgraders. Chapter Three explores the concentration and distribution of selenium and sulphur in mineral and bitumen fractions of Athabasca Bituminous Sands ores. Chapter Four describes an analytical method for determining common selenium species present in natural waters using ion chromatography paired with inductively coupled plasma mass spectrometry (IC-ICP-MS). Chapter Five examines the chemical speciation and total dissolved concentration of selenium in water samples from the lower Athabasca River, as well as the concentration of selenium in Trout-perch (*Percopsis omiscomaycus*) muscle. Chapter Six is a study of arsenic and selenium in *Sphagnum* moss and age-dated peat cores to evaluate contemporary and historic atmospheric inputs of arsenic and selenium in the Athabasca Bituminous Sands Region. Chapter Seven summarizes and links conclusions from all chapters and highlights the study findings and limitations. The Appendix consists of six published articles: four articles are published versions of Chapters Two, Three, Four and Five, with two additional articles (Appendix V and VI) on related, collaborative research which support the studies described here. All studies provided in the Appendix were authored or co-authored by Mark Donner.

1.5 References

Alberta Energy Regulator, 2017. ST98: 2017 Alberta's Energy Reserves & Supply/Demand Outlook. http://www1.aer.ca/st98/data/executive_summary/ST98-2017_Executive_Summary.pdf; 2017 [accessed 12.19.2017].

Azcue, J.M., Nriagu, J. O., 1994. Arsenic: historical perspectives, in: Nriagu, J.O. (Eds.), Arsenic in the Environment Part I: Cycling and Characterization. John Wiley and Sons, New

York, NY, pp. 1–15.

Berzelius, J.J., 1817. Lettre de M. Berzelius a M. Berthollet sur deux metaux nouveaux. Annales de Chimie et de Physique, 199–206.

Berzelius, J.J., 1818. Recherches sur un nouveau corps mineral trouve dans le souffre fabrique a Fahlun. Annales de Chimie et de Physique.

B'Hymer, C., Caruso, J.A., 2004. Arsenic and its speciation analysis using high-performance liquid chromatography and inductively coupled plasma mass spectrometry. J. Chromatogr. A. 1045, 1–13.

Bicalho, B., Grant-Weaver, I., Sinn, C., Donner, M.W., Woodland, S., Pearson, G., Larter, S., Duke, J.,Shotyk, W., 2017. Determination of ultratrace (<0.1 mg/kg) elements in Athabasca bituminous sands mineral and bitumen fractions using inductively coupled plasma sector field mass spectrometry (ICP-SFMS). Fuel. 206, 248–257.

Blais, J. M. and Donahue, W.F., 2015. Comment on " sphagnum mosses from 21 ombrotrophic bogs in the Athabasca bituminous sands region show no significant atmospheric contamination of 'heavy metals'". Environ. Sci. Technol. 49, 6352–6353.

Boutin, C., Carpenter, D. J., 2017. Assessment of wetland/upland vegetation communities and evaluation of soil-plant contamination by polycyclic aromatic hydrocarbons and trace metals in regions near oil sands mining in Alberta. Sci. Total Environ. 576, 829–839.

Bruggeman, C., Maes, A., Vancluysen, J., 2007. The interaction of dissolved boom clay and gorleben humic substances with selenium oxyanions (selenite and selenate). Appl. Geochem. 22, 1371–1379.

Cannon, J. R., Edmonds, J.S., Francesconi, K.A., Raston, C.L., Saunders, J.B., Skelton, B.W., White, A.H., 1981. Isolation, crystal structure and synthesis of arsenobetaine, a constituent of the western rock lobster, the duskey shark, and some samples of human urine. Aust. J. Chem. 34, 787–798.

Cardoso, B.R., Hare, D.J., Lind, M., McLean, C.A., Volitakis, I., Laws, S.M., Masters, C.L., Bush, A.I., Roberts, B.R., 2017. The *APOE* ε4 allele is associated with lower selenium levels in the brain: implications for alzheimer's disease. ACS. Chem. Neurosci. 8, 1459–1464.

Cardoso, B.R., Ong, T.P., Jacob-Filho, W., Jaluul, O., Freitas, M.I., Cozzolino, S.M.F., 2010. Nutritional status of selenium in alzheimer's disease patients. Br. J. Nutr. 103, 803–806.

Challenger, F., 1945. Biological methylation. Chem. Rev. 36, 315–361.

Chapman, A.C., 1926. On the presence of compounds of arsenic in marine crustaceans and shell fish. The Analyst. 51, 548–563.

Chilvers, D.C., Peterson, P.J., 1987. Global cycling of arsenic, in: Hutchinson, T.C., Memma, K.M. (Eds.), Lead, Mercury, Cadmium and Arsenic in the Environment. John Wiley & Sons., New York, pp. 279–301.

Cone, J.E., Del Río, R.M., Davis, J.N., Stadtman, T.C., 1976. Chemical characterization of the selenoprotein component of clostridial glycine reductase: identification of selenocysteine as the organoselenium moiety. Proc. Natl. Acad. Sci. USA. 73, 2659–2663.

Cullen, W. R., Reimer, K. J., 1989. Arsenic speciation in the environment. Chem. Rev. 89, 713–764.

Cullen, W.R., Reimer, K.J., 2016. Arsenic is everywhere: cause for concern? Royal Society of Chemistry, Cambridge, United Kingdom, pp. 257.

D'albe, Fournier, E. E., 1924. Data and data concerning selenium and selenium cells, in: The Moon-Element: An Introduction to the Wonders of Selenium. T. Fisher Unwin Ltd. London: Adelphi Terrace, pp. 33–45.

Dopp, E., Hartmann, L.M., Florea, A.M., Von Recklinghausen, U., Pieper, R., Shokouhi, B., Rettenmeier, A.W., Hirner, A.V., Obe, G., 2004. Uptake of inorganic and organic derivatives of arsenic associated with induced cytotoxic and genotoxic effects in Chinese hamster ovary (CHO) cells. Toxicol. Appl. Pharmacol. 201, 156–165.

Durkee, J., Bartrem, C., Möller, G., 2017. Legacy lead arsenate soil contamination at childcare centers in the Yakima valley, central Washington, USA. Chemosphere. 168, 1126–1135.

Edmonds, J. S., Francesconi, K. A., Cannon, J. R., Raston, C. L., Skelton, B. W., White, A. H., 1977. Isolation, crystal structure and synthesis of arsenobetaine, the arsenical constituent of the western rock lobster *panulirus longipes cygnus* George. Tetrahedron Lett. 18, 1543–1546.

Essington, M., 2015. Oxidation-reduction reactions in soils, in: Soil and Water Chemistry An Integrative Approach. CRC Press., Boca Raton, Florida, pp. 349–381.

Ferguson, J. F., Gavis, J., 1972. A review of the arsenic cycle in natural waters. Water Res. 6, 1259–1274.

Fernández-Martínez, A., Charlet, L., 2009. Selenium environmental cycling and bioavailability: a structural chemist point of view. Rev. Environ. Sci. Biotechnol. 8, 81–110.

Francesconi, K.A., 2010. Arsenic species in seafood: origin and human health implications. Pure Appl. Chem. 82, 373–381.

Francesconi, K.A., Kuehnelt, D., 2004. Determination of arsenic species: a critical review of methods and applications, 2000-2003. Analyst. 129, 373–395.

Frank, R.A., Roy, J.W., Bickerton, G., Rowland, S.J., Headley, J.V., Scarlett, A.G., West, C.E., Peru, K.M., Parrott, J.L., Conly, F.M., Hewitt, L.M., 2014. Profiling oil sands mixtures from industrial developments and natural groundwaters for source identification. Environ. Sci. Technol. 48, 2660–2670.

Frost, D.V, Olson, O.E., 1972. The two faces of selenium – can selenophobia be cured? CRC Critical Reviews in Toxicology, 1:4, 467-514.

Gailer, J., George, G.N., Pickering, I.J., Prince, R.C., Ringwald, S.C., Pemberton, J.E., Glass, R.S., Younis, H.S., DeYoung, D.W., Aposhian, H.V., 2000. A metabolic link between arsenite and selenite: the seleno-bis(*S*-glutathionyl) arsinium ion. J. Am. Chem. Soc. 122, 4637–4639.

Garven, G.,1989. A hydrogeologic model for the formation of the giant oil sands deposits of the Western Canada sedimentary basin. Am. J. Sci. 289, 105–166.

Gibson, J.J., Fennell, J., Birks, S.J., Yi, Y., Moncur, M.C., Hansen, B., Jasechko, S., 2013. Evidence of discharging saline formation water to the Athabasca river in the oil sands mining region, northern Alberta, Can. J. Earth Sci. 50, 1244–1257.

Glabonjat, R.A., Raber, G., Van Mooy, B.A.S., Francesconi, K.A., 2017. Arsenobetaine in seawater: depth profiles from selected sites in the north Atlantic. Env. Sci. Technol. 52, 522–

530.

Goldschmidt, V.M., 1937. The principles of distribution of chemical elements in minerals and rocks. J. Chem. Soc. 655–673.

Gong, Z., Lu, X., Ma, M., Watt, C., Le, X.C., 2002. Arsenic speciation analysis. Talanta. 58, 77–96.

Gosselin, P., Hrudey, S.E., Naeth, M.A. Plourde, A., Therrien, R., Van Der Kraak, G., Xu, Z., 2010. Environmental and health impacts of Canada's oil sands industry. The Royal Society of Canada (RSC), Ottawa, Ontario, Canada (414 pp). https://rsc-src.ca/sites/default/files/pdf/RSCreportcompletesecured9Mb_Mar28_11.pdf

Gustafsson, J.P., Johnsson, L., 1994. The association between selenium and humic substances in forested ecosystems–laboratory evidence. Appl. Organomet. Chem. 8, 141–147.

Hasegawa, H., 1997. The behavior of trivalent and pentavalent methylarsenicals in Lake Biwa. Appl. Organometal. Chem. 11, 305–311.

Hasegawa, H., Rahman, M.A., Kitahara, K., Itaya, Y., Maki, T., Ueda, K., 2010. Seasonal changes of arsenic speciation in lake waters in relation to eutrophication. Sci. Total. Environ. 408, 1684–1690.

Hayes, K.F., Roe, A.L., Brown, G. E. Jr., Hodgson, K.O., Leckie, J.O., Parks, G.A., 1987. In situ x-ray absorption study of surface complexes: selenium oxyanions on α-FeOOH. Science. 238, 783–786.

Headley, J.V., Barrow, M.P., Peru, K.M., Fahlman, B., Frank, R.A., Bickerton, G., McMaster, M.E., Parrott, J., Hewitt, L.M., 2011. Preliminary fingerprinting of Athabasca oil sands polar organics in environmental samples using electrospray ionization fourier transform ion cyclotron resonance mass spectrometry. Rapid Commun. Mass Spectrom. 25, 1899–1909.

Hinrichsen, S., Geist, F., Planer-Friedrich, B., 2015. Inorganic and methylated thioarsenates pass the gastrointestinal barrier. Chem. Res. Toxicol. 28, 1678–1680.

Javed, M.B., Cuss, C.W., Grant-Weaver, I., Shotyk, W., 2017. Size-resolved Pb distribution in the Athabasca river shows snowmelt in the bituminous sands region an insignificant source of dissolved Pb. Sci. Rep. 7, 43622–43633

Jones, G.D., Droz, B., Greve, P., Gottschalk, P., Poffet, D., McGrath, S.P., Seneviratne, S.I., Smith, P., Winkel, L.H.E., 2017. Selenium deficiency risk predicted to increase under future climate change. Proc. Natl. Acad. Sci. USA. 114, 2848–2853.

Kelly, E.N., Schindler, D.W., Hodson, P.V., Short, J.W., Radmanovich, R., Nielsen, C. C., 2010. Oil sands development contributes elements toxic at low concentrations to the Athabasca river and its tributaries. Proc. Natl. Acad. Sci. USA. 107, 16178–16183.

Larter, S.R., Head, I.M., 2014. Oil sands and heavy oil: origin and exploitation. Elements. 10, 277–283.

Leblanc, K.L., Ruzicka, J., Wallschläger, D., 2016. Identification of trace levels of selenomethionine and related organic selenium species in high-ionic-strength waters. Anal. Bioanal. Chem. 408, 1033–1042.

Leblanc, K.L., Wallschläger, D., 2016. Production and release of selenomethionine and

Rrlated organic selenium species by microorganisms in natural and industrial waters. Environ. Sci. Technol. 50, 6164-6171.

Mikutta, C., Rothwell, J. J., 2016. Peat bogs as hotspots for organoarsenical formation and persistence. Environ. Sci. Technol. 50, 4314–4323.

Milne, J.B., 1998. The uptake and metabolism of inorganic selenium species, in: Frankenberger, Jr.W.T. (Eds.), Environmental Chemistry of Selenium. Marcel Dekker Inc., New York, pp. 459–477.

Morris, D.L., 2015. Chemistry and activity of selenium dioxide and selenite ions, in: Preedy, V.R. (Eds.), Selenium: chemistry, analysis, function and effects. The Royal Society of Chemistry., Cambridge, UK, pp. 65–80.

Mosher, B.W., Duce, R.A., 1987. A global atmospheric selenium budget. J. Geophys. Res. Atmos. 92, 289–13298.

Mullan-Boudreau, G., Belland, R., Devito, K., Noernberg, T., Pelletier, R., Shotyk, W., 2017. *Sphagnum* moss as an indicator of contemporary rates of atmospheric dust deposition in the Athabasca bituminous sands region. Environ. Sci. Technol. 51, 7422-7431.

Mullan-Boudreau, G., Davies, L., Devito, K., Froese, D., Noernberg, T., Pelletier, R., Shotyk, W., 2017. Reconstructing past rates of atmospheric dust deposition in the Athabasca bituminous sands region using peat cores from bogs. Land Degrad. Dev. 28, 2468–2481.

Nriagu, J. O., 2002. Arsenic poisoning through the ages, in: Frankenberger, Jr. W.T. (Eds.), Environmental Chemistry of Arsenic. Marcel Dekker Inc., New York, pp. 1–26.

Ohlendorf, H.M., Hoffman, D.J., Saiki, M.K., Aldrich, T.W., 1986. Embryonic mortality and abnormalities of aquatic birds: apparent impacts of selenium from irrigation drainwater. Sci. Total Environ. 52, 49–63.

Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environ. Rev. 9, 269–298.

Petrov, P.K., Charters, J.W., Wallschläger, D., 2012. Identification and determination of selenosulfate and selenocyanate in flue gas desulfurization waters. Environ. Sci. Technol. 46, 1716–1723.

Rahman, M.A., Hasegawa, H., 2012. Arsenic in freshwater systems: influence of eutrophication on occurrence, distribution, speciation, and bioaccumulation. Appl. Geochem. 27, 304–314.

Reilly, C., 2006a. Selenium in diets, in: Selenium in Food and Health, second ed. Springer, New York, New York, pp. 173–199.

Reilly, C., 2006b. Selenium in food and health, second ed. Springer, New York, New York.

Ross, M.S., Pereira, A.D.S., Fennell, J., Davies, M., Johnson, J., Sliva, L., Martin, J.W., 2012. Quantitative and qualitative analysis of naphthenic acids in natural waters surrounding the canadian oil sands industry. Environ. Sci. Technol. 46, 12796–12805.

Rotruck, J.T., Pope, A.L., Ganther, H.E., Swanson, A.B. Hafeman, D.G., Hoekstra, W.G., 1972. Selenium: biochemical role as a component of glutathione peroxidase. Science. 179, 588-590.

Saiki, M.K., Lowe, P.T., 1987. Selenium in aquatic organisms from subsurfaec agricultural drainage water, San Joaquin Valley, California. Arch. Environ. Contam. Toxicol. 16, 657–

670.

Schindler, D.W., 2010. Tar sands need solid science. Nature. 468, 499–501.

Schindler, D.W., 2013. Geoscience of climate and energy 12. Water quality issues in the oil sands region of the lower Athabasca river, Alberta. Geosci. Can. 40, 202–214.

Schwarz, K., Foltz, C.M., 1957. Selenium as an integral part of factor 3 against dietary necrotic liver degeneration. J. Am. Chem. Soc. 79, 3292–3293.

Selby, D., 2005. Direct radiometric dating of hydrocarbon deposits using rhenium-osmium isotopes. Science. 308, 1293–1295.

Shendrikar, A.D., Ensor, D.S., Cowent, S.J., Woffindei, G.J., 1983. Size-dependent penetration through a utility of trace elements baghouse. Atmos. Environ. 17, 1411–1421.

Shotyk, W., 2018. Trace metals in soils of the bituminous sands mining region of Alberta: a critical, geochemical perspective on the study by Boutin and Carpenter (2017). Sci. Total. Environ. 618, 866–869.

Shotyk, W., Appleby, P.G., Bicalho, B., Davies, L., Froese, D., Grant-Weaver, I., Krachler, M., Magnan, G., Mullan-Boudreau, G., Noernberg, T., Pelletier, R., Shannon, B., van Bellen, S., Zaccone, C., 2016b. Peat bogs in northern Alberta, Canada reveal decades of declining atmospheric Pb contamination. Geophys. Res. Lett. 43, 1–11.

Shotyk, W., Appleby, P.G., Bicalho, B., Davies, L., Froese, D., Grant-Weaver, I., Magnan, G., Mullan-Boudreau, G., Noernberg, T., Pelletier, R., Shannon, B., van Bellen, S., Zaccone, C., 2017. Peat bogs document decades of declining atmospheric contamination by trace metals in the Athabasca bituminous sands region. Environ. Sci. Technol. 51, 6237-6249.

Shotyk, W., Belland, R., Duke, J., Kempter, H., Krachler, M., Noernberg, T., Pelletier, R., Vile, M.A., Wieder, K., Zaccone, C., Zhang, S., 2014. *Sphagnum* mosses from 21 ombrotrophic bogs in the Athabasca bituminous sands region show no significant atmospheric contamination of "heavy metals". Environ. Sci. Technol. 48, 12603–12611.

Shotyk, W., Bicalho, B., Cuss, C.W., Duke, M.J.M., Noernberg, T., Pelletier, R., Steinnes, E., Zaccone, C., 2016a. Dust is the dominant source of "heavy metals" to peat moss (*Sphagnum fuscum*) in the bogs of the Athabasca bituminous sands region of northern Alberta. Environ. Int. 92–93, 494–506.

Simmons, D.B.D., Wallschläger, D., 2005. A critical review of the biogeochemistry and ecotoxicology in lotic and lentic environments. Environ. Toxicol. Chem. 24, 1331–1343.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517–568.

Smith, W., 1873. Effect of light on selenium during the passage of an electric current. Nature. 303.

Soignet, S.L., Maslak, P., Wang, Z., Jhanwar, S., Calleja, E., Dardashti, L.J., Corso, D., DeBlasio, A., Gabrilove, J., Scheinberg, D.A., Pandolfi, P.P., Warrell, R.P. Jr., 1998. Complete remission after treatment of acute promyelocytic leukemia with arsenic trioxide. N. Engl. J. Med. 339, 1341–1348.

Sørmo, E.G., Ciesielski, T.M., Øverjordet, I.B., Lierhagen, S., Eggen, G.S., Berg, T., Jenssen, B. M., 2011. Selenium moderates mercury toxicity in free-ranging freshwater fish. Environ. Sci. Technol. 45, 6561–6566.

Sposito, G., 1995. Adsorption as a problem in coordination chemistry: the concept of the surface complex, in: Huang, C.P., O'Melia, C.R., Morgan, J.J. (Eds.), Aquatic Chemistry Interfacial and Interspecies Processes. American Chemical Society., Washington, DC, pp. 33–57.

Stiboller, M., Raber, G., Lenters, V., Gjengedal, E.L.F., Eggesbø, M., Francesconi, K.A., 2017. Arsenolipids detected in the milk of nursing mothers. Environ. Sci. Technol. Lett. 4, 273–279.

Stoeppler, M., 2004. Arsenic, in: Merian, E., Anke, M., Ihnat, M., Stoeppler, M. (Eds.), Elements and their compounds in the environent occurrence, analysis and biological relevance, second edition. Wiley-VCH Verlag, GmbH & Co. KGaA, pp. 1321–1364.

Stoeppler, M., Vahter, M., 1994. Arsenic, in: Herber, R.F.M., Stoeppler, M. (Eds.), Trace element analysis in biological specimens. Elsevier., Amsterdam, pp. 291–320.

Timoney, K., 2012. Environmental and health impacts of Canada's bitumen industry: in search of answers. Environ. Sci. Technol. 46, 2496–2497.

Timoney, K., Lee, P., 2009. Does the Alberta tar sands industry pollute? The scientific evidence. The Open Conservation Biology Journal. 3, 65–81.

Trelease, S.F., Beath, O.A., 1949. History, in: Selenium: Its Geological Occurrence and its Biological Effects in Relation to Botany, Chemistry, Agriculture, Nutrition, and Medicine. New York, pp. 1–12.

USEPA, 2016. Aquatic Life Ambient Water Quality Criterion for Selenium – Freshwater, 2016, United States Environmental Protection Agency.

https://www.epa.gov/sites/production/files/2016-07/documents/aquatic_life_awqc_for_selenium_-_freshwater_2016.pdf

Wallschläger, D., Feldmann, J., 2010. Formation, occurrence, significance, and analysis of organoselenium and organotellurium compounds in the environment, in: Sigel, A., Sigel, H., Sigel, R.K.O (Eds.), Organometallics in Environment and Toxicology: Metal Ions in Life Sciences. Royal Society of Chemistry., Cambridge, UK, pp. 319–364.

Wang, S., Mulligan, C.N., 2006. Occurrence of arsenic contamination in Canada: sources, behavior and distribution. Sci. Total. Environ. 366, 701–721.

Wedepohl, K.H., 1995. The composition of the continental crust. Geochim. Cosmochim. Acta. 59, 1217–1232.

Wen, H., Carignan, J., 2007. Reviews on atmospheric selenium: Emissions, speciation and fate. Atmos. Environ. 41, 7151–7165.

Wiklund, J.A., Hall, R.I., Wolfe, B.B., Edwards, T.W.D., Farwell, A.J., Dixon, D.G., 2014. Use of pre-industrial floodplain lake sediments to establish baseline river metal concentrations downstream of Alberta oil sands: A new approach for detecting pollution of rivers. Environ. Res. Lett. 9, 124019–124028.

Winkel, L.H.E., Vriens, B., Jones, G.D., Schneider, L.S., Pilon-Smits, E., Bañuelos, G.S., 2015. Selenium cycling across soil-plant-atmosphere interfaces: a critical review. Nutrients. 7, 4199-4239.

Young, T.G., Finley, K., Adams, W.J., Besser, J., Hopkins, W.D., Jolley, D., McNaughton, E., Presser, T.S., Shaw, P., Unrine, J., 2010. What you need to know about selenium, in:

Chapman, P.M., Adams, W.J., Brooks, M.L., Delos, C.G., Luoma, S.N., Maher, W.A., Ohlendorf, H.M., Presser, T.S., Shaw, D.P. (Eds.), Ecological assessment of selenium in the aquatic environment. CRC Press, Taylor & Francis Group., Boca Raton, pp. 7-46.

2.0 ARSENIC SPECIATION IN THE LOWER ATHABASCA RIVER WATERSHED: A GEOCHEMICAL INVESTIGATION OF THE DISSOLVED AND PARTICULATE PHASES *

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[*] A version of this chapter has been published as: Arsenic speciation in the lower Athabasca River Watershed: a geochemical investigation of the dissolved and particulate phases, *Environmental Pollution*, 2017, vol. 224, 265-274. The published journal article is provided in Appendix I.

2.1 Introduction

Extending over 1300 km across the province of Alberta, Canada, the Athabasca River (AR) and its watershed is an ecologically rich and diverse aquatic system that forms part of the Peace-Athabasca Delta, the largest freshwater boreal delta in the world (Wolfe et al., 2007). While the Athabasca River as a whole faces numerous environmental stresses, the area of the river under the most intense scrutiny is the lower reach where surface mining of the Athabasca Bituminous Sands (ABS) is located. Development of the ABS deposit is one of the largest surface mining operations in the world, generating enormous volumes of waste as fluid fine tailings that now have a total storage volume approaching 1 billion m^3 (http://osip.alberta.ca/map/). Due to the continual growth and development of ABS mining, the current and future status of water quality in the lower Athabasca River and watershed has received significant national and international attention (Gosselin et al., 2010; Schindler, 2010, 2013). Arsenic (As) has been described as a contaminant from ABS industrial operations in reports, peer-reviewed publications (Timoney and Lee, 2009; Kelly et al., 2010) and even an environmental petition to the government of Canada (Government of Canada, 2008). The negative health effects of long-term exposure to elevated concentrations of As are well known, with specific As compounds classified as carcinogens, teratogens, and mutagens (Stoeppler, 2004). Despite these concerns, no study has examined As in-depth and there have been no source assessments or studies of its chemical speciation, in this region. Health concerns for residents and aquatic life downstream of mining operations is a priority, as previous reports have suggested that As concentrations in water and sediments may have increased over time (Timoney and Lee, 2009). In addition, an evaluation of metals in snow around the region of the ABS described As concentrations (along with other potentially toxic elements) as being greater near

ABS industrial development (Kelly et al., 2010). The same study also concluded that As concentrations were greater in the Athabasca River downstream of mining suggesting ABS development as the potential source of As (Kelly et al., 2010). That information generated considerable attention and has recently been disputed by studies that suggest a lack of metal pollution around the region of the ABS (Shotyk et al., 2014; Wiklund et al., 2014). To further examine atmospheric deposition of heavy metals, Sphagnum moss was collected around the region of the ABS and analyzed for a variety of potentially toxic metals (Ag, Cd, Ni, Pb, Sb and Tl); but no evidence of atmospheric contamination of heavy metals was found (Shotyk et al., 2014). Similarly, a study of sediment cores from the Peace- Athabasca Delta provided evidence that the Athabasca River had been depositing metals (Be, Cd, Cr, Cu, Pb, Ni, Zn, V) for many years prior to industrial development of the ABS (Wiklund et al., 2014). However, neither of these two preceding studies addressed the potential contribution of As, an element of concern for people living downstream in the First Nations communities of Fort McKay and Fort Chipewyan. To address this information gap, water samples were collected in October 2014 and 2015 from the lower Athabasca River as well as surrounding tributaries and groundwater as part of a multidisciplinary study to investigate natural and anthropogenic inputs to the river. Because the river is known for its unique natural chemical inputs, primarily as high salinity groundwater intrusions and hydrocarbons from the erosion of bitumen-laden banks, sampling was focused on studying As from areas with suspected influence from these potential sources. While measurements of total As provide important preliminary information, chemical speciation is a crucial component of any study assessing the fate and behavior of As in aquatic systems (Gong et al., 2002). Arsenite [As(III)] and arsenate [As(V)] are known to be carcinogenic to humans (Vahter, 2002) and tend to be the predominant forms in natural waters (Smedley and Kinniburgh, 2002). In surface waters with circumneutral pH, As is thermodynamically stable as As(V) whereas anoxic waters such as ground waters yield As(III) as the stable and more abundant form (Cullen and Reimer, 1989). Methylated As(V) species (monomethylarsonic acid, MMA and dimethylarsinic acid, DMA) are less toxic than the inorganic forms (Dopp et al., 2004) and may also occur in natural waters in significant concentrations as a result of biological activity (Hasegawa, 1997; Hasegawa et al., 2010). Here, we present data for As in the dissolved (<0.45 μm) and suspended particulate phases (>0.45 μm) in the Athabasca River, tributaries and groundwater, as well as common chemical species [As(V), As(III) and DMA] of As.

2.2 Materials and methods

2.2.1 Study area

Water samples were collected from the Athabasca River at 13 locations in October 2014 (Fig. 2.6) and 19 locations in October 2015 (Fig. 2.1). Sampling took place during the autumn when water levels are typically at their lowest and under the greatest influence of groundwater inputs. Sampling sites began upstream of the town of Fort McMurray and extended over 125 km downstream to the confluence of the Firebag River. Additional water samples were collected from a total of 11 tributaries, 5 shallow (0.7 – 3.0 m) groundwater aquifers, 3 saline springs and a saline lake during 2014–2015. Many of the tributaries selected (Steepbank River, Beaver Creek, McLean Creek, Ells River, Tar River) drain areas heavily disturbed by mining operations. The Firebag River, which is relatively far downstream of industrial areas, was sampled for comparison. Water samples were also collected from streams flowing through banks containing large bitumen outcrops (A20e Spring, A9w Creek) and from Pierre River which is known for naturally elevated concentrations of heavy metals due to the occurrence of metalliferous black shales in the Birch Mountains, the source water for the river (Dufresne et al., 2001). Input of saline waters in the Athabasca River has been shown to be extensive in the study area (Gibson et al., 2013), raising questions about the contribution of trace elements such as As from naturally saline groundwater. The area of the Athabasca River under the greatest influence of saline water was identified in a previous study using terrain conductivity mapping (Gibson et al., 2013) which provided insight into potential sampling locations for high salinity (>20 000 $\mu S\ cm^{-1}$) shallow groundwater. Site A5w is located in an area well removed from industrial activity but with a significant amount of saline groundwater seepage (Fig. 2.1). Samples were also collected from artesian saline springs (FMSS, NSS, SLSP) at various locations on the river as well as at Saline Lake, a naturally saline body of water on the shore of the Athabasca River. From each location, samples were collected and analyzed for a variety of chemical and physical parameters (e.g. organic pollutants, trace metals, stable and radiogenic isotopes) to expand on existing water quality knowledge in the region. Here, the focus is exclusively As with select physicochemical properties as complementary information.

2.2.2 Sample collection and handling

Surface water samples from the Athabasca River were collected beneath the surface (~30 cm) from the bow of a small boat anchored approximately 80 m from shore. Water was collected from the mouth of tributaries upstream of the Athabasca River. Samples were collected from the central portion of the stream, upstream from where the person sampling was positioned. For logistical reasons, and in anticipation of a wide variety of water sample compositions, a broad and practical approach comprising field filtration (0.45 μm), acidification using hydrochloric acid (HCl) and dark refrigeration was used to preserve As(III) and As(V) (Kumar and Riyazuddin, 2010; McCleskey et al., 2004; Polya et al., 2003). Hydrochloric acid is the preferred acid for hydride generation atomic fluorescence spectrometry (HG-AFS), the instrument used for analyzing high salinity samples for As. Samples for dissolved As and chemical speciation were filtered in the field using 30 mL plastic syringes (Thermo Scientific™; Cat. #S7510-30) through 0.45 µm polytetrafluoroethylene (PTFE) disk filters (Thermo Scientific™; 30 mm; Cat. # 03-391-1C) into 125 mL low density polyethylene (Thermo Scientific™; Cat. #02-893-4B) or fluorinated high density polyethylene Nalgene™ bottles (Thermo Scientific™; Cat. #0331220); higher volume samples were also collected in 250 mL fluorinated high density polyethylene Nalgene™ bottles (Thermo Scientific™; Cat. # 0331 213). Syringes and filters were pre-cleaned as described in detail elsewhere (Shotyk et al., 2017). Samples were acidified (pH < 2) in the field using Optima™ HCl (Fisher Scientific; Cat. # A466-500; certified test value < 1 ng L^{-1} As) and kept in a cool box until being refrigerated (4 °C) at the end of the day. Samples for As speciation were kept in the dark and analyzed immediately upon arrival at the laboratory. To determine As associated with suspended particulate matter in river water, filters containing the particles >0.45 µm were retained after filtration. Unfiltered and unacidified water samples were also collected in 125 mL polypropylene (PP) bottles to determine the total As (dissolved + particulate As) and major anions. Particulate As was estimated by subtracting the dissolved As (<0.45 µm) from total As. Samples for major cation analysis were filtered in the field into 125 mL PP bottles containing 100 mL of double-distilled nitric acid (HNO_3). Groundwater samples were obtained using a peristaltic pump by inserting a stainless steel drive point well casing into the sediment and pumping water to the surface through acid cleaned PP tubing. A custom PP cap fitting was constructed so that sample bottles could be attached directly to the line minimizing exposure to the atmosphere. Prior to any sampling, the wells were purged and monitored for basic water quality parameters using a portable multimeter (YSI Pro Plus, Yellow Springs, OH, USA). Samples were collected after stable readings were obtained. For the 2015 sampling campaign, custom PP wells were constructed in advance and installed at sites A18, A15 and A5 approximately 6 weeks prior to water sampling. All samples were filtered and acidified immediately after collection, well within a suggested 10 min time frame for inorganic As speciation in Fe-rich waters (Kumar and Riyazuddin, 2010). Due to the disturbance of the aquifer during drive-point well installation, total As concentrations are not representative. Furthermore, the oxidation of dissolved Fe(II) to Fe(III) was manifested as precipitates on the container wall and these may have scavenged As; therefore, total As in groundwater and saline springs will not be presented.

2.2.3 Arsenic quantification

Inorganic As(III) and As(V) were separated using a high performance ion chromatograph (HPIC; Thermo Scientific Dionex ICS-5000$^+$) equipped with a Dionex Ion Pac™ AS7 anion exchange column (4 mm ID x 250 mm length) and a 25 mL sample loop. The method also included use of a Dionex IonPac™ AG7 guard column (4 mm ID x 50 mm length) for greater separation of DMA from As(V). The system mobile phase consisted of dilute HNO_3 operated using a step-wise program with concentrations from 2.5 mM to 50 mM HNO_3 and a constant flow rate of 1 mL min^{-1}. After chromatographic separation, column effluent was pumped to the inductively coupled plasma mass spectrometer (ICP-MS; iCap Q, Thermo Scientific) for As determination and quantification. Owing to the extremely low concentrations of As, sample groups were analyzed in triplicate to evaluate repeatability. Calculated limits of detection (LOD) for As(III), As(V) and DMA were 6.3 ng L^{-1}, 8.9 ng L^{-1} and 5.4 ng L^{-1}, respectively. Limits of quantification (LOQ) for As species were also calculated and assessed experimentally, with the greatest accuracy and precision at concentrations ~ 20 ng L^{-1}. The LODs for dissolved As using ICP-MS and HG-AFS were 10 ng L^{-1} and 55 ng L^{-1}, respectively.

All surface water samples were analyzed undiluted whereas groundwater and highly saline surface water samples were diluted up to ten-fold (1 mL + 9 mL) to reduce potential chromatographic or spectral interferences. Dissolved As was measured using ICP-MS under kinetic energy discrimination mode, with 0.05 s dwell time and 120 sweeps. A multi-element internal standard solution (SPEX CertiPrep) was added at a concentration of 1 mg L^{-1} during analysis using a continuous on-line approach. For an independent confirmation of dissolved As in high salinity water, numerous samples were also measured using HG-AFS (Millennium Excalibur, P S Analytical). This procedure converts As species [As(III), As(V), MMA, DMA] into a gaseous hydride when reduced with $NaBH_4$ under acidic conditions; since other organic forms of As (which do not readily form a hydride) were not of interest, no additional oxidation pre-treatments were performed (Sánchez-Rodas et al., 2010). For HG-AFS analysis, 10 mL of sample was combined with 15 mL HCl (12 M), reduced with 1mL of a potassium iodide and L-ascorbic acid solution (30 min hold time) then diluted and analyzed. The lengthy storage time of saline samples in 2014 precluded reliable chemical speciation data for saline samples and therefore only dissolved As was measured. To determine total As concentration in untreated water samples, 2 mL of sample was digested with 3 mL double-distilled HNO_3 and 0.1 mL tetrafluoroboric (HBF_4) in PTFE digestion vessels inside a high pressure UltraClave (Milestone, Germany). Optimized parameters and full methodology for digestion of samples is described elsewhere (Shotyk et al., 2014). Diluted samples after digestion were analyzed for As and thorium (Th) using quadrupole ICP-MS housed in the metal-free ultraclean SWAMP laboratory at the University of Alberta. Arsenic and Th concentrations were calculated by averaging three main runs (0.03 s dwell time, 30 sweeps) after adjusting instrumental drift using indium (In) as an internal standard. To determine As and Th in the suspended (>0.45 µm) particulate fraction, filter discs used for filtration in the field were vacuum dried to remove excess water and increase adherence of particles to the membrane. A mechanical lathe was used to remove the filter membrane without any loss of particulate matter. Membranes laden with particulate matter were then digested in double-distilled HNO_3 (6 mL) and HBF_4 (0.2 mL) following the same analytical protocol used for untreated water digestion. Description of water analyses conducted on samples collected in 2014 for basic measurements (pH, electrical conductivity, temperature, redox potential, etc.) and other complementary chemical data such as dissolved organic carbon (DOC), major cations (Na, Ca, Mg, K, Fe, and Mn) and anions (Cl^-, SO_4^{2-}, NO_3^-) in AR water and tributaries is published separately (Shotyk et al., 2017); however, groundwater data for 2014 and 2015 is presented here (Tables 2.1 and 2.2). Site coordinates and their distance relative to the city of Fort McMurray are provided in Table 2.5.

2.2.4 Quality control

All analyses followed a strict and detailed quality control protocol that included experimental blanks, certified standard reference materials (SRM; SLRS-5 and NIST 1640a), continuous calibration verification, and matrix spikes to assess the accuracy and precision of measurements. The average value obtained for each SRM was within 5% of the certified value (see full details in Table 2.3). Experimental blanks and triplicate laboratory and field blanks (ultrapure water plus preservative i.e., HNO_3 or HCl) were included to indicate any sources of contamination. Field duplicates were collected at 7 sites to provide insight on sampling reproducibility. Dissolved As was also analyzed in 2 different sample bottles collected from each site at the same time, but for a collaborative study examining trace metals (Shotyk et al., 2017). Aliquots from samples were also sent to an independent lab (University of Graz, Austria) and analyzed blind. Results of independent laboratory measurements confirm the reproducibility of both sampling and analytical measurements (detailed results for analyses of QC solutions and independent laboratory analyses are provided in Table 2.3 and Figs. 2.7, 2.8, 2.9). Written details regarding the acid cleaning procedure are provided in Section 2.9.1, laboratory reagents (Section 2.9.2), calculation of LOD/LOQ (Section 2.9.3), independent laboratory methodology (Section 2.9.4) and upstream water samples (Section 2.9.5) are also provided in the Supplementary Information.

2.3 Results and discussion

2.3.1 Athabasca River water

Arsenic in the dissolved fraction of Athabasca River water averaged 0.37 ± 0.01 μg L^{-1} in 2014 (n = 14, Fig. 2.2A) and 0.34 ± 0.01 μg L^{-1} in 2015 (n = 21, Fig. 2.2B). These concentrations fluctuated very little both spatially and temporally (2014 - 2015) showing no discernable increase in As downstream of ABS mines and upgraders in either year. As an additional control to this study, triplicate water samples were provided by Alberta Environment from 3 locations (Fig. 2.6) upstream of Fort McMurray and were analyzed at the SWAMP laboratory, University of Alberta. Concentrations of dissolved As in water collected near mountain headwaters were extremely low (0.08 μg L^{-1} ± 0.005) whereas the other 2 upstream sites were very similar (0.39 ± 0.01 μg L^{-1} and 0.33 ± 0.01 μg L^{-1}) to water collected in the lower Athabasca River in our study. Dissolved As concentrations in the main stem of the Athabasca River are consistent with the data presented in the Athabasca State of the Watershed Phase III Report from the years 2007 - 2012, for both Fall/Winter and Spring/Summer periods (Fiera Biological Consulting Ltd, 2013). Until now, the chemical speciation of As has not yet been investigated in the Athabasca River but a number of (non-peer reviewed) reports produced by government and environmental consulting groups exist that contain information about total and dissolved As. A complete review and comparison between these data sets and ours is difficult due to differences in the analytical capabilities of the various laboratories, with concomitant variations in the accuracy and precision of previous work: this is a fundamental issue when comparing data with historical measurements of trace elements in water. For accurate and precise measurements of elements in trace concentrations, strict QA/QC is needed and can only be obtained using suitable instruments capable of detecting analytes in very low concentrations (parts per trillion or lower); this is especially important in determining concentrations of individual species. Regarding redox state speciation, concentrations of As(V) and As(III) and their ratio remained consistent in Athabasca River water (Fig. 2.2) with no noticeable change in values downstream of ABS development. The predominant form in Athabasca River surface water was As(V), with an average concentration of 0.18 $\mu g\ L^{-1}$ ± 0.09 in 2014 and 0.18 $\mu g\ L^{-1}$ ± 0.02 in 2015. Arsenite was present in trace amounts, averaging 43 $ng\ L^{-1}$ ± 5 $ng\ L^{-1}$ in 2014 and 60 $ng\ L^{-1}$ ± 17 in 2015. Samples from 2014 were later screened for MMA and DMA by an independent laboratory, but all Athabasca River samples had concentrations below the LOD (50 $ng\ L^{-1}$). River water samples collected in 2015 were analyzed for DMA only, with a slightly lower limit of detection, however no trends or anomalous values were observed and all samples contained < 20 $ng\ L^{-1}$ (data not shown). Seasonal variation might affect As speciation because changes in methylated As has been shown to correspond with water temperature, with greater concentrations of methylated As compounds occurring in biologically productive warm summer months (Rahman and Hasegawa, 2012). In our study, cooler water temperature in the Athabasca River (7-8 °C) at the time of sample collection might have caused low yield of methylated As. The effect of seasonal variation on As speciation was not investigated because the primary focus of our study was to determine

As inputs from water sources such as natural seepages and shallow groundwater to Athabasca River surface water; groundwater-surface water interactions are more pronounced during fall season when sampling was performed because groundwater inputs become relatively more important. Quantitative data for methylated As species (e.g., MMA, DMA) would be an asset in any study determining seasonal changes in As speciation in the lower Athabasca River Watershed; the extremely low As concentrations, however, present a considerable analytical challenge. Total As concentrations averaged 12.7 ± 2.8 $\mu g\ L^{-1}$ (n = 14; Fig. 2.2A) in 2014 and 3.3 ± 0.65 $\mu g\ L^{-1}$ in 2015 (n = 21; Fig. 2.2B). Similar to the dissolved phase, no increasing trend was observed from upstream to downstream in AR water and concentrations were considerably lower in 2015 than 2014. Comparing with dissolved As (0.34 - 0.37 $\mu g\ L^{-1}$), total As reflects the abundance of suspended particulates in water (Fig. 2.3). To further investigate As association with mineral or organic constituents of the particulate fraction, particles on the 0.45 µm filters were digested and measured for both As and Th. Concentrations of As were variable, with an average of 24.8 ± 14 $\mu g\ g^{-1}$ (n = 13) in 2014 and 13.2 ± 9.3 $\mu g\ g^{-1}$ (n = 20) in 2015 (Table 2.4). Thorium, a conservative lithophile element, was used as an indicator of mineral abundance. In 2014, when greater total (i.e. particulate) As concentrations were observed, there was a significant correlation ($p < 0.05$) between Th and As in particles retained on the filter (Fig. 2.3). This is in contrast to 2015, when As concentrations were lower and the correlation with Th was not significant ($p > 0.05$; Fig. 2.3). Therefore, it would seem that mineral material (i.e. > 0.45 µm fraction) was the dominant source of As in 2014, but not 2015. The use of Th offers some preliminary information but additional study is required to examine the exact composition of particulate matter, including the role of organic matter in As cycling. However, the consistent concentrations upstream to downstream within a given year suggests that the considerable difference in total As concentrations between 2014 and 2015 is likely driven by natural processes, and the concentrations fluctuate independently of industrial activities (Fig. 2.3). During spring melt when erosion is greatest, river water contains more particles carrying As and other trace elements (Fiera Biological Consulting Ltd, 2013). On this basis, measuring total suspended solids (TSS) or turbidity can be used to estimate metal loading in river water (Nasrabadi et al., 2016). Permissible levels of As set by the United States Environmental Protection Agency (US EPA) for the protection of aquatic life is 150 μg L^{-1} of dissolved As (U.S EPA, 1995). In contrast, the critical value set by the Canadian Council of Ministers for the Environment (CCME) is much lower, at 5 μg L^{-1} total As (CCME, 1999). Given the discrepancy between two bordering nations with some of the world's largest watersheds in common, the concentrations of As acceptable for aquatic life should perhaps be re-examined. In the case of the Athabasca River, dissolved As concentrations (<0.4 μg L^{-1}) are on the order of 375x below the US EPA guideline value, but during 2014, exceeded the CCME recommended value for total As by a factor of 2x at most locations.

2.3.2 Tributary water

Tributary waters were highly variable in both concentration and ratio of As(III)/As(V) with all waters containing < 1 μg L^{-1} dissolved As (Fig. 2.4). In both 2014 and 2015, Pierre River contained the highest concentration of dissolved As compared to tributaries draining heavily mined areas such as Beaver Creek, Steepbank River, Ells River, Muskeg River and McLean Creek. Arsenic concentrations are considerably higher in Pierre River most likely due to inputs of As and many trace metals from metalliferous black shale (Dufresne et al., 2001). Similar to Athabasca River water, the total As in tributary water was much greater than the dissolved phase and noticeably lower in 2015 (Fig. 2.4). This discrepancy is again an indication that the difference in total As values observed between years is likely due to natural variations, probably related to water flow rates and erosion in each year. It was observed by the field team that water levels in the Athabasca River and tributaries were noticeably higher in 2015 compared to 2014, and this may be the simplest explanation for the much lower concentrations of total As during 2015.

Significant variation in the distribution of As species in tributaries is expected due to the different physical and chemical characteristics of each waterbody. However in general, the chemical speciation is consistent with measured redox conditions (Tables 2.2 and 2.3) with As(V) relatively more important in streams with higher redox potentials, and As(III) relatively more abundant at lower redox values. For example, a small turbulent creek (A20e) with elevated dissolved oxygen (DO,13 mg L^{-1}) and redox potential (Eh, 232 mV) contained almost all As in As(V) form. The notable exception to the tributaries was Beaver Creek which contained mostly As(III). This anomaly may indicate a greater influence of groundwater seepage in the area as the redox potential measurements in 2014 in Beaver Creek were quite low (~29 mV). Based on the incomplete sum of inorganic As species relative to (total) dissolved As in Athabasca River water (Fig. 2.2; 55-70% in 2014 and 63-73% in 2015) and tributaries (Fig. 2.4; 53-76% in 2014 and 28-75% in 2015), there also appears to be a variable portion of unidentified As species present in surface water. However, because the tributaries drain water from the extensive boreal forest with its numerous, vast peatlands, there is also considerable input of DOC (Shotyk et al., 2017). It seems likely, therefore, that there may be important contributions of organo-As species from peatlands surrounding the Athabasca River. Support for this hypothesis comes from the recent report of an abundance of organic (arsenobetaine) and unidentified As species in peatland surface waters, with low proportions of inorganic As species relative to total dissolved As (Mikutta and Rothwell, 2016).

2.3.3 Naturally saline waters

A confounding factor for assessing water quality in the lower Athabasca River has been the input of naturally saline groundwater from Devonian and other geological formations of marine origin. Overall, there is only limited information on As in these types of saline groundwaters. A recent study of saline springs along the Athabasca River and Clearwater River, a major tributary of the Athabasca River, indicated that only 1 spring on the Clearwater River contained a relatively high concentration of total As (9.63 μg L^{-1}) and neither of the saline springs sampled along the Athabasca River was an important source of As (Gue et al., 2015).

As a part of this study, 3 saline springs (SLSP, NSS, and FMSS) and 1 saline groundwater aquifer (site A5w) on the Athabasca River were sampled to further investigate the potential contribution of As by saline waters. SLSP is an artesian spring located in La Saline Natural Area approximately 15 m above Saline Lake (Borneuf, 1983); NSS also comes to surface naturally. Site FMSS, near Fort McKay (Fig. 2.1) is unique as it flows up directly from the saline aquifer through an abandoned well casing suspected to have been drilled decades earlier. As a result, FMSS water is undiluted and extremely saline (see Table 2.1). Groundwater sampled at site A5w was collected with drive point wells at a depth of ~3 m below the sediment on a seasonally dry section of the Athabasca River. Concentrations of dissolved As in A5w groundwater were consistent in both years with an average concentration of ~1.8 μg L^{-1} in both 2014 and 2015 (Fig. 2.5A and B). Chemical speciation by IC-ICP-MS revealed that As is almost entirely As(III) (Fig. 2.5B). Samples collected from NSS, SLSP and FMSS were taken at the surface before these naturally flowing artesian springs reached the Athabasca River. The concentration of dissolved As (measured by HG-AFS) in NSS was 0.37 μg L^{-1}, while values were < LOD (0.05 μg L^{-1}) in FMSS and SLSP spring water (Fig. 2.5). Saline Lake, located in the La Saline Natural Area, is a highly productive, shallow oxbow lake on the shore of the Athabasca River that is naturally saline due to input from underground springs (Borneuf, 1983). In terms of As speciation, this area is anomalous compared to samples from Athabasca River water, tributaries, saline springs and groundwater. Chemical speciation (Fig. 2.4) of surface water from the lake showed that DMA was actually a significant component of dissolved As (1.07 μg L^{-1}). The breakdown of the three species was as follows: 0.18 μg L^{-1} As(III), 0.12 μg L^{-1} As(V) and 0.15 μg L^{-1} DMA. It is likely that many biological processes are responsible for cycling As within this unique ecosystem. Saline Lake was the only site where reliable concentrations of DMA were found, but a more detailed study of the As speciation at this site is beyond the project scope.

2.3.4 The analytical challenges posed by saline waters

The measurement of trace elements such as As in highly saline water poses a significant analytical challenge. Even with dilution, water collected from saline springs clearly strained the operational capabilities of ICP-MS showing severe changes in the peak intensity of internal standard and yielded a positive bias. For an independent method check of As in saline waters, HG-AFS and ICP-QQQ-MS (triple quadrupole) were employed. Measurements of As by HGAFS and ICP-MS (single quadrupole) yielded similar results (<10% difference) for groundwater at site A5w (Table 2.3). However, for FMSS, NSS and SLSP, HG-AFS yielded lower results suggesting a potential positive bias for measurements made using ICP-MS. Also, values for As from FMSS with (single quadrupole) ICP-MS were > 17x higher than measurements by ICP-QQQ-MS (data not shown). This discrepancy in As values is due to the well documented interference on As (m/z = 75) by ${}^{40}Ar^{35}Cl^+$ (m/z = 75) polyatomic ions formed in the Ar plasma gas and in samples containing elevated chloride (B'Hymer and Caruso, 2004). Collision cell technology can reduce this positive bias but it may not completely eliminate this effect in high salinity samples. It is recommended that these types of waters be analyzed with caution when using conventional single quadrupole ICP-MS; spectral interference can be overcome by using HG-AFS (Terlecka, 2005; Wu and Sun, 2016), high resolution sector field ICP-MS (Jackson et al., 2015), or ICP-QQQ-MS (Jackson et al., 2015). Due to the extremely high salinity in comparison with low As concentrations in the saline springs, these samples could not be reliably analyzed for As species. Furthermore because of the high sulfur content and unique chemistry of these springs, comprehensive As speciation analysis should include thio-based As species, which have been shown to be abundant in sulfidic waters (Planer-Friedrich et al., 2007); these As forms also require specialized collection and preservation techniques for representative measurements (Suess et al., 2015). Although chloride concentrations increase with distance downstream of Fort McMurray due to saline groundwater inputs (Gibson et al., 2013; Shotyk et al., 2017) the low, uniform As concentrations in the main stem Athabasca River combined with the low concentrations of As in the saline groundwater suggest that naturally saline groundwater is not a significant source of As to the river.

2.3.5 Groundwater

In contrast to many other potentially toxic trace elements which may be present at ultra-low concentrations in groundwater (Shotyk et al., 2010), As is often found to be naturally enriched relative to meteoric water due to mineral dissolution combined with anoxia, particularly when organic matter is present (Ziegler et al., 2015). More importantly, because it forms anionic species, removal processes in soils and sediments which are so effective for cationic species such as Pb^{2+}, are ineffective for adsorbing $H_3As^{III}O_3^0$ (Shotyk and Krachler, 2009; Shotyk et al., 2010). In shallow groundwater wells sampled on the Athabasca River near the banks (Fig. 2.5), dissolved As concentrations varied substantially (1.8 – 50.4 µg L^{-1}) between the five locations. The predominant form in all groundwater samples was As(III), constituting 63 – 103% of the dissolved As. Given the abundance of DOC (8 – 61 mg L^{-1}) and low redox potentials (Tables 2.1 and 2.2), As(III) was expected to predominate due to biotic/abiotic reduction of As(V) (Cullen and Reimer, 1989). Although a small portion of As(V) was found, this may be attributed to changes which occurred during field sampling or storage. Only by comparing multiple preservation techniques with immediate analysis could the appearance of As(V) in the groundwater thoroughly be assessed. Concentrations of dissolved As in groundwater situated near a bitumen upgrader (A16w) and a tailings pond (A17w) were anomalous. This finding contrasts with a recent survey of shallow riparian groundwater near a tailings pond (site A17w in this study) which found no significant difference between As concentrations in "Pond Site" groundwater versus nearby control sites (Roy et al., 2016); it appears that the groundwater in this area contains variable concentrations of As. While As concentrations at site A16w remained similar in both years, concentrations at A17w were greater in 2015 than 2014 (50 µg L^{-1} versus 20 µg L^{-1}, respectively; Fig. 2.5A and B). In comparison to other groundwater sites (A5w, A15w, and A18w), which showed almost no change in As concentration between 2014 and 2015, a 30 µg L^{-1} difference at site A17w is substantial. Given the close proximity of this sampling location to industrial activity, a more detailed investigation of As in groundwater at this site is warranted. This could be accomplished by focusing on i) long term monitoring ii) biogeochemical processes taking place at the groundwater - surface water interface iii) quantifying the fluxes of groundwater entering the river during different water level (or seasonal) conditions and iv) comparing data with isotopic tracers and other sourcing techniques to determine the source of water. Long term monitoring would be complemented by understanding the precipitation and complexation reactions occurring at the groundwater e surface water interface. These processes are driven by many chemical and physical factors (pH, sediment texture and mineralogy, speciation, redox potential, etc.) and may contribute to natural As removal processes (Mok and Wai, 1994). For example, scavenging of As(V) by Fe and Mn (hydr)oxides formed during the transition of groundwater from anoxic to oxic (groundwater - surface water interface) is a natural removal processes which is known to be a major controlling factor for As in river sediment (Gorny et al., 2015). Elucidating which biogeochemical processes are at work in sediments of the Athabasca River would aid in further understanding the source(s) of As and may help explain the observed variability in concentrations between years; laboratory experiments focused on the host phases of As in sediments and the microorganisms present are underway to determine the source and fate of As in shallow groundwater. It is important to note that when discussing As contamination in relation to bituminous sands in Alberta, the distinction must be made between surface mining (ex-situ) in the Athabasca formation and in-situ extraction in the Cold Lake Region of Alberta (CLRA) as the CLRA is known for naturally high concentrations of As (up to 179 $\mu g\ L^{-1}$) in shallow groundwater (Moncur et al., 2015). Laboratory trials of simulated in-situ bituminous sand mining processes (underground heating via steam injection) has demonstrated the potential for substantial release of As from sediments and its mobilization in groundwater aquifers (Javed and Siddique, 2016).

2.4 Conclusion

The purpose of this study was to determine the form of As in the lower Athabasca River and distinguish between natural and anthropogenic inputs. The lack of change in As concentrations in surface water upstream versus downstream of industry during two intensive water sampling campaigns suggests that natural inputs dominate the As inventory of the river. Total concentrations of As show considerable spatial and temporal variation, but there was no observed increase in concentration downstream of industry. In contrast, “dissolved” As concentrations (ie < 0.45 µm) are remarkably consistent in space and time and again, show no increasing trend downstream of industry. Total concentrations of As reflect physical inputs to the river from erosion within the watershed, and these vary seasonally. Dissolved As, on the other hand, is supplied by chemical processes such as mineral weathering and these inputs are expected to be rather uniform and constant, given the pH buffering of surface and groundwaters in this basin by abundant carbonate alkalinity. High and variable As concentrations in groundwater near an industrial site warrants additional study to determine the source and biogeochemical cycling at the sediment water interface. These findings are important not only for communities living downstream of ABS industrial activity concerned about As contamination, but also for water monitoring agencies tasked with understanding the partitioning of As in the dissolved or particulate phase of water. While the primary focus of this study was groundwater - surface water interactions, additional work is ongoing to evaluate atmospheric inputs to the snowpack and release during spring melt.

2.5 Acknowledgements

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2.6 References

B'Hymer, C., Caruso, J.A., 2004. Arsenic and its speciation analysis using high performance liquid chromatography and inductively coupled plasma mass spectrometry. J. Chromatogr. A 1045, 1–13.

Borneuf, D., 1983. Springs of Alberta. Alberta Research Council; Earth Sciences Report 82–3, Edmonton, Alberta, Canada (280 pp). Accessed at http://ags.aer.ca/document/ESR/ESR_1982_03.PDF.

CCME, 1999. Canadian Environmental Quality Guidelines. Canadian Council of Ministers of the Environment. Environment Canada, Hull, Quebec, 8 Chapters. Accessed at. http://st-ts.ccme.ca/en/index.html?chems¼9&chapters¼1,2.

Cullen, W.R., Reimer, K.J., 1989. Arsenic speciation in the environment. Chem. Rev. 89, 713–764.

Dopp, E., Hartmann, L.M., Florea, A.-M., von Recklinghausen, U., Pieper, R., Shokouhi, B., Rettenmeier, A.W., Hirner, A.V., Obe, G., 2004. Uptake of inorganic and organic derivatives of arsenic associated with induced cytotoxic and genotoxic effects in Chinese hamster ovary (CHO) cells. Toxicol. Appl. Pharmacol. 201, 156–165.

Dufresne, M.B., Eccles, D.R., Leckie, D.A., 2001. The geological and geochemical setting of the mid-cretaceous shaftesbury formation and other Colorado group sedimentary units in northern Alberta. Alberta Energy and Utilities Board and Alberta Geological Survey. Special Report 09 (654 pp). Accessed at http://ags.aer.ca/document/SPE/SPE_009.PDF.

Fiera (Fiera Biological Consulting Ltd), 2013. State of the watershed report e phase 3: water quantity and basic water quality in the Athabasca watershed. Report prepared for the Athabasca Watershed Council, Fiera Biological Consulting report #1234. Accessed at. http://www.awc-wpac.ca/sites/default/files/SOW3complete.pdf.

Gibson, J.J., Fennell, J., Birks, S.J., Yi, Y., Moncur, M.C., Hansen, B., Jasechko, S., 2013. Evidence of discharging saline formation water to the Athabasca River in the oil sands mining region. North. Alta. Can. J. Earth Sci. 50, 1244–1257.

Gong, Z., Lu, X., Ma, M., Watt, C., Le, X.C., 2002. Arsenic speciation analysis. Talanta 58, 77–96.

Gorny, J., Billon, G., Lesven, L., Dumoulin, D., Mad_e, B., Noiriel, C., 2015. Arsenic behavior in river sediments under redox gradient: a review. Sci. Total Environ. 505, 423–434.

Gosselin, P., Hrudey, S.E., Naeth, M.A., Plourde, A., Therrien, R., Van Der Kraak, G., Xu, Z., 2010. Environmental and health impacts of Canada's oil sands industry. Royal Society of Canada (RSC), Ottawa, Ontario, Canada (414 pp). Accessed at. https://rsc-src.ca/sites/default/files/pdf/RSC%20Oil%20Sands%20Panel%20Main%20Report%20Oct%202012.pdf.

Government of Canada, 2008. Environmental Petition: No. 238. Water and sediment contamination of the Athabasca river due to oilsands production. Office of the Auditor General of Canada. Commissioner of the Environment and Sustainable Development, Ottawa, Canada.

Gue, A.E., Mayer, B., Grasby, S.E., 2015. Origin and geochemistry of saline spring waters in the Athabasca oil sands region, Alberta, Canada. Appl. Geochem 61, 132–145.

Hasegawa, H., 1997. The behavior of trivalent and pentavalent methylarsenicals in Lake Biwa. Appl. Organometal. Chem. 11, 305–311.

Hasegawa, H., Rahman, M.A., Kitahara, K., Itaya, Y., Maki, T., Ueda, K., 2010. Seasonal changes of arsenic speciation in lake waters in relation to eutrophication. Sci. Total Environ. 408, 1684–1690.

Jackson, B.P., Liba, A., Nelson, J., 2015. Advantages of reaction cell ICP-MS on doubly charged interferences for arsenic and selenium analysis in foods. J. Anal. At. Spectrom. 30, 1179–1183.

Javed, M.B., Siddique, T., 2016. Thermally released arsenic in porewater from sediments in the Cold Lake area of Alberta, Canada. Environ. Sci. Technol. 50, 2191–2199.

Kelly, E.N., Schindler, D.W., Hodson, P.V., Short, J.W., Radmanovich, R., Nielsen, C.C., 2010. Oil sands development contributes elements toxic at low concentrations to the Athabasca river and its tributaries. Proc. Natl. Acad. Sci. U. S. A. 107, 16178–16183.

Kumar, A.R., Riyazuddin, P., 2010. Preservation of inorganic arsenic species in environmental water samples for reliable speciation analysis. Trends Anal. Chem. 29, 1212–1223.

McCleskey, R.B., Nordstrom, D.K., Maest, A.S., 2004. Preservation of water samples for arsenic(III/V) determinations: an evaluation of the literature and new analytical results. Appl. Geochem 19, 995–1009.

Mikutta, C., Rothwell, J.J., 2016. Peat bogs as hotspots for organoarsenical formation and persistence. Environ. Sci. Technol. 50, 4314–4323.

Mok, W.M., Wai, C.M., 1994. Mobilization of arsenic in contaminated river waters, in: Nriagu, J.O. (Ed.), Arsenic in the Environment Part I: Cycling and Characterization. John Wiley and Sons, New York, NY, pp. 99–114.

Moncur, M.C., Paktunc, D., Jean Birks, S., Ptacek, C.J., Welsh, B., Thibault, Y., 2015. Source and distribution of naturally occurring arsenic in groundwater from Alberta's Southern Oil Sands Regions. Appl. Geochem 62, 171–185.

Nasrabadi, T., Ruegner, H., Sirdari, Z.Z., Schwientek, M., Grathwohl, P., 2016. Using total suspended solids (TSS) and turbidity as proxies for evaluation of metal transport in river water. Appl. Geochem 68, 1–9.

Planer-Friedrich, B., London, J., Mccleskey, R.B., Nordstrom, D.K., Wallschl€ager, D., 2007. Thioarsenates in geothermal waters of yellowstone national park: determination, preservation, and geochemical importance. Environ. Sci. Technol. 41, 5245–5251.

Polya, D.A., Lythgoe, P.R., Abou-Shakra, F., Gault, A.G., Brydie, J.R., Webster, J.G., Brown, K.L., Nimfopoulos, M.K., Michailidis, K.M., 2003. IC-ICP-MS and IC-ICPHEX-MS determination of arsenic speciation in surface and groundwaters: preservation and analytical issues. Mineral. Mag. 67, 247–261.

Rahman, M.A, Hasegawa, H., 2012. Arsenic in freshwater systems: influence of eutrophication on occurrence, distribution, speciation, and bioaccumulation. Appl. Geochem 27, 304–314.

Roy, J.W., Bickerton, G., Frank, R.A., Grapentine, L., Hewitt, L.M., 2016. Assessing risks of shallow riparian groundwater quality near an oil sands tailings pond. Groundwater 54, 545–558.

Sánchez-Rodas, D., Corns, W.T., Chen, B., Stockwell, P.B., 2010. Atomic fluorescence spectrometry: a suitable detection technique in speciation studies for arsenic, selenium, antimony and mercury. J. Anal. At. Spectrom. 25, 933–946.

Schindler, D.W., 2010. Tar sands need solid science. Nature 468, 499–501.

Schindler, D.W., 2013. Geoscience of climate and energy 12. Water quality issues in the oil sands region of the lower Athabasca River, Alberta. Geosci. Can. 40, 202–214.

Shotyk, W., Belland, R., Duke, J., Kempter, H., Krachler, M., Noernberg, T., Pelletier, R., Vile, M.A., Wieder, K., Zaccone, C., Zhang, S., 2014. *Sphagnum* mosses from 21 ombrotrophic bogs in the Athabasca bituminous sands region show no significant atmospheric contamination of “heavy metals”. Environ. Sci. Technol. 48, 12603–12611.

Shotyk, W., Krachler, M., 2009. Determination of trace element concentrations in natural freshwaters: how low is “low”, and how low do we need to go? J. Environ. Monit. 11, 1747–1753.

Shotyk, W., Krachler, M., Aeschbach-Hertig, W., Hillier, S., Zheng, J., 2010. Trace elements in recent groundwater of an artesian flow system and comparison with snow: enrichments, depletions, and chemical evolution of the water. J. Environ. Monit. 12, 208–217.

Shotyk, W., Bicalho, B., Cuss, C.W., Donner, M.W., Grant-Weaver, I., Haas-Neill, S., Javed, M.B., Krachler, M., Noernberg, T., Pelletier, R. Zaccone, C., 2017. Trace metals in the dissolved fraction (< 0.45 μm) of the lower Athabasca River: Analytical challenges and environmental implications. Sci. Total Environ., 580: 660–669.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem 17, 517–568.

Stoeppler, M., 2004. Arsenic, in: Merian, E., Anke, M., Ihnat, M., Stoeppler, M. (Eds.), Elements and Their Compounds in the Environment. Volume 3: Nonmetals, Particular Aspects. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, pp. 1321–1364.

Suess, E., Mehlhorn, J., Planer-Friedrich, B., 2015. Anoxic, ethanolic, and cool – an improved method for thioarsenate preservation in iron-rich waters. Appl. Geochem 62, 224–233.

Terlecka, E., 2005. Arsenic speciation analysis in water samples: a review of the hyphenated techniques. Environ. Monit. Assess. 107, 259–284.

Timoney, K.P., Lee, P., 2009. Does the Alberta tar sands industry pollute? The scientific evidence. Open Conserv. Biol. J. 3, 65–81.

USEPA, 1995. National recommended water quality criteria aquatic life criteria table. Accessed at. https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table.

Vahter, M., 2002. Mechanisms of arsenic biotransformation. Toxicology 181–182, 211–217.

Wiklund, J.A., Hall, R.I., Wolfe, B.B., Edwards, T.W.D., Farwell, A.J., Dixon, D.G., 2014. Use of pre-industrial floodplain lake sediments to establish baseline river metal concentrations downstream of Alberta oil sands: a new approach for detecting pollution of rivers. Environ. Res. Lett. 9, 124019–124028.

Wolfe, B.B., Karst-Riddoch, T.L., Hall, R.I., Edwards, T.W.D., English, M.C., Palmini, R., McGowan, S., Leavitt, P.R., Vardy, Sheila, R., 2007. Classification of hydrological regimes of northern floodplain basins (Peace-Athabasca Delta, Canada) from analysis of stable isotopes ($\delta^{18}O$, $\delta^{2}H$) and water chemistry. Hydrol. Process 21, 151–168.

Wu, D., Sun, S., 2016. Speciation analysis of As, Sb and Se. Trends Environ. Anal. Chem. 11, 9–22.

Ziegler, B.A., McGuire, J.T., Cozzarelli, I.M., 2015. Rates of as and trace-element mobilization caused by Fe reduction in mixed BTEX-ethanol experimental plumes. Environ. Sci. Technol. 49, 13179e13189.

2.7 Figures

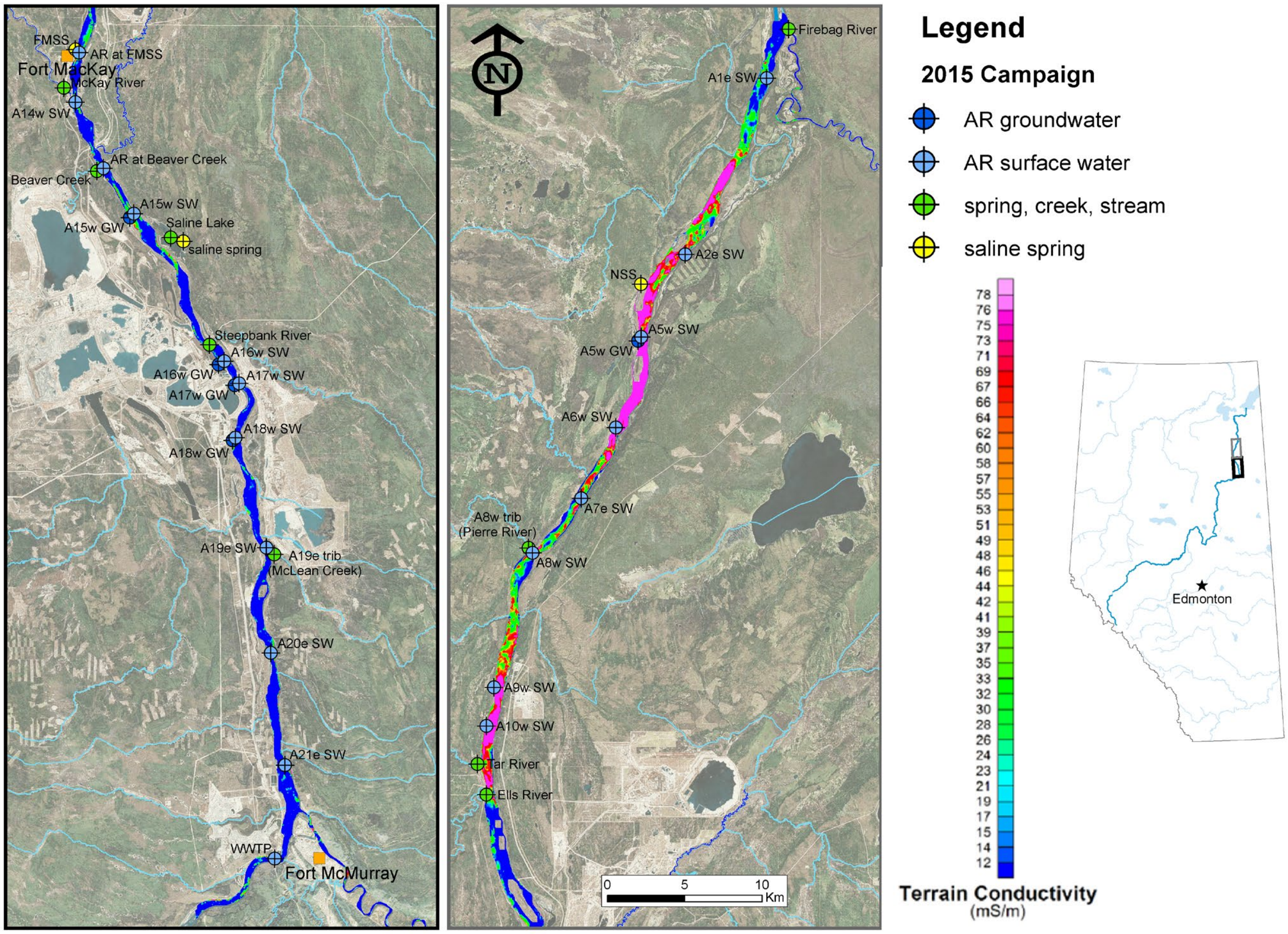

Figure 2.1 Map of study area and sampling locations during the 2015 sampling campaign. Map begins at Fort McMurray (bottom of left panel), moving downstream to Fort MacKay, then from Ells River (bottom of right panel) downstream to the Firebag River. Sampling locations were selected for their proximity to ABS industrial development or to assess areas of known saline groundwater influence. Lower terrain conductivity data were provided by Gibson et al. [2013]. Letters “e” or “w” indicate whether sampling took place on the East or West portion of the Athabasca River (AR).

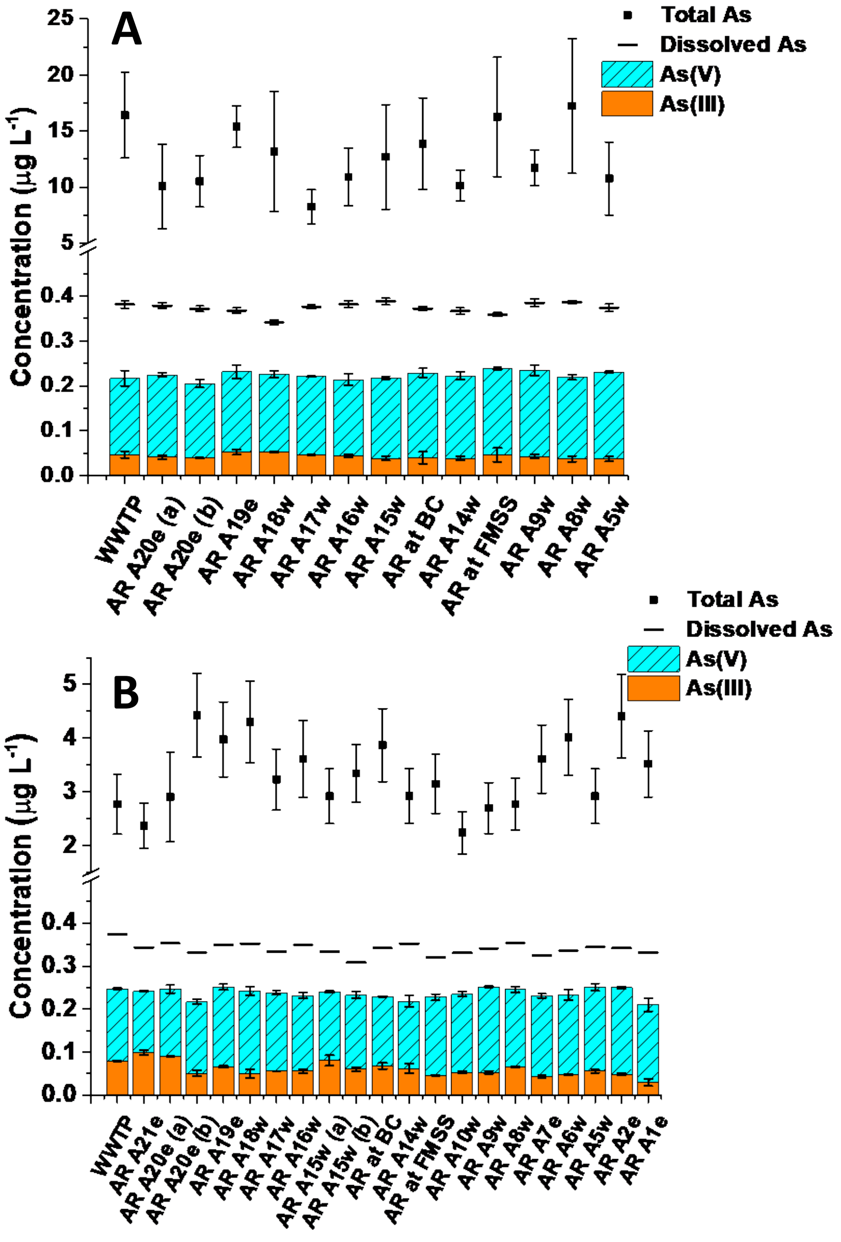

Figure 2.2 Total (particulate plus dissolved), dissolved and chemical speciation of As (III, V) in surface water of the Athabasca River (AR) during autumn 2014 (A) and 2015 (B). Site WWTP is located upstream of the town of Fort McMurray and far upstream of ABS industrial activities. The area of greatest industrial activity is located between sites A18w and A9w. Error bars represent the standard deviation of triplicate measurements of an individual sample. Site duplicates are denoted with (a) or (b). Duplicates in 2014 (panel A) were collected 3 days apart; duplicates in 2015 (panel B) were collected 8 and 3 days apart for sites A20e and A15, respectively.

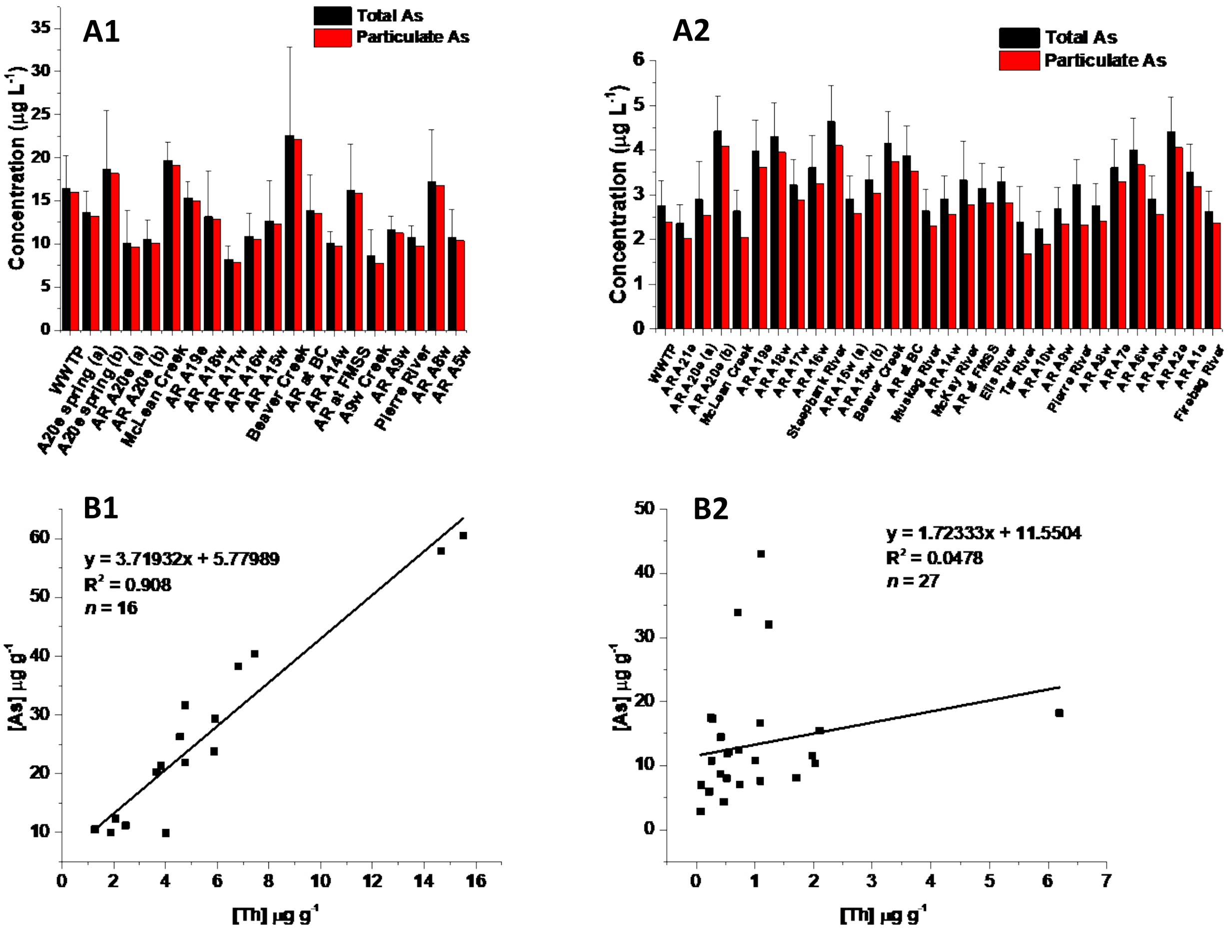

Figure 2.3 Total and particulate As in surface water of the Athabasca River (AR) and tributaries during autumn 2014 (A1) and 2015 (A2). A significant ($p < 0.05$) correlation between As and Th was observed for the particulate phase (> 0.45μm) in 2014 (B1), but no significant ($p > 0.05$) correlation was observed for 2015.

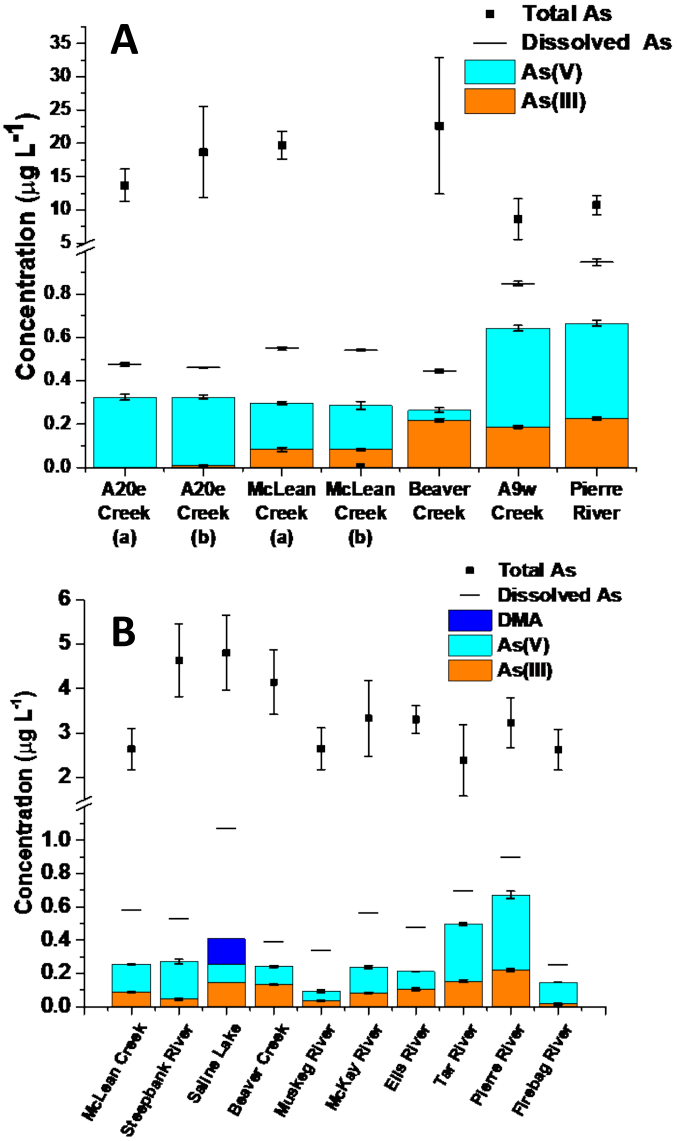

Figure 2.4 Total (particulate + dissolved), dissolved and chemical speciation of As [As(III), As(V) and DMA] in Saline Lake and selected tributaries along the Athabasca River during autumn 2014 (A) and 2015 (B). Tributaries were selected based on their proximity to ABS industrial development (Beaver Creek, McLean Creek, Steepbank River, Tar River, Muskeg River, McKay River), drainage of an area with little to no ABS industrial disturbance (Firebag River) or to assess low volume, high flow rate creeks (A20e and A9w) in areas of natural bitumen outcrops. Error bars represent the standard deviation of triplicate measurements of an individual sample. Site duplicate bottles are denoted with (a) and (b) and were collected approximately 1 hour apart. Sample McLean Creek (b) was not analyzed for total As.

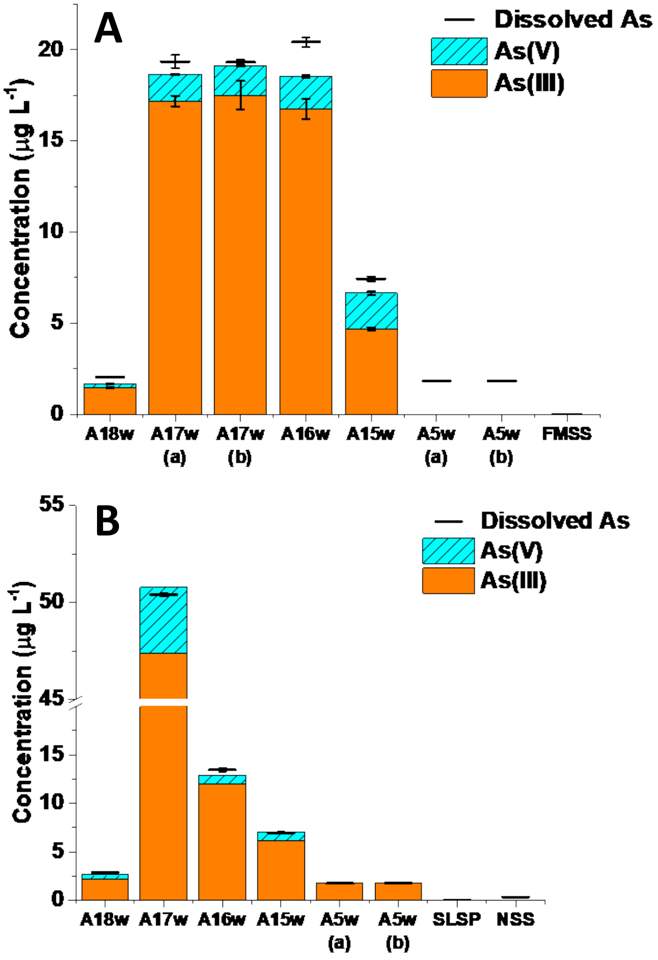

Figure 2.5 Dissolved As and inorganic As(III) and As(V) in shallow groundwater and saline springs (FMSS, NSS, SLSP) of the Athabasca River during autumn 2014 (A) and 2015 (B). Sites A18w, A17w, A16w and A15w are located in areas of industrial activity, whereas A5w is well removed from industry but naturally high in salinity. Samples from saline springs were analyzed for total As using HG-AFS, while groundwater samples were measured with ICP-MS and IC-ICP-MS for speciation. Samples A5w (a) and A5w (b) in 2014 were not analyzed for speciation. Error bars represent the standard deviation of triplicate measurements of an individual sample. Site duplicate bottles are denoted with (a) and (b) and were collected approximately 1 hour apart.

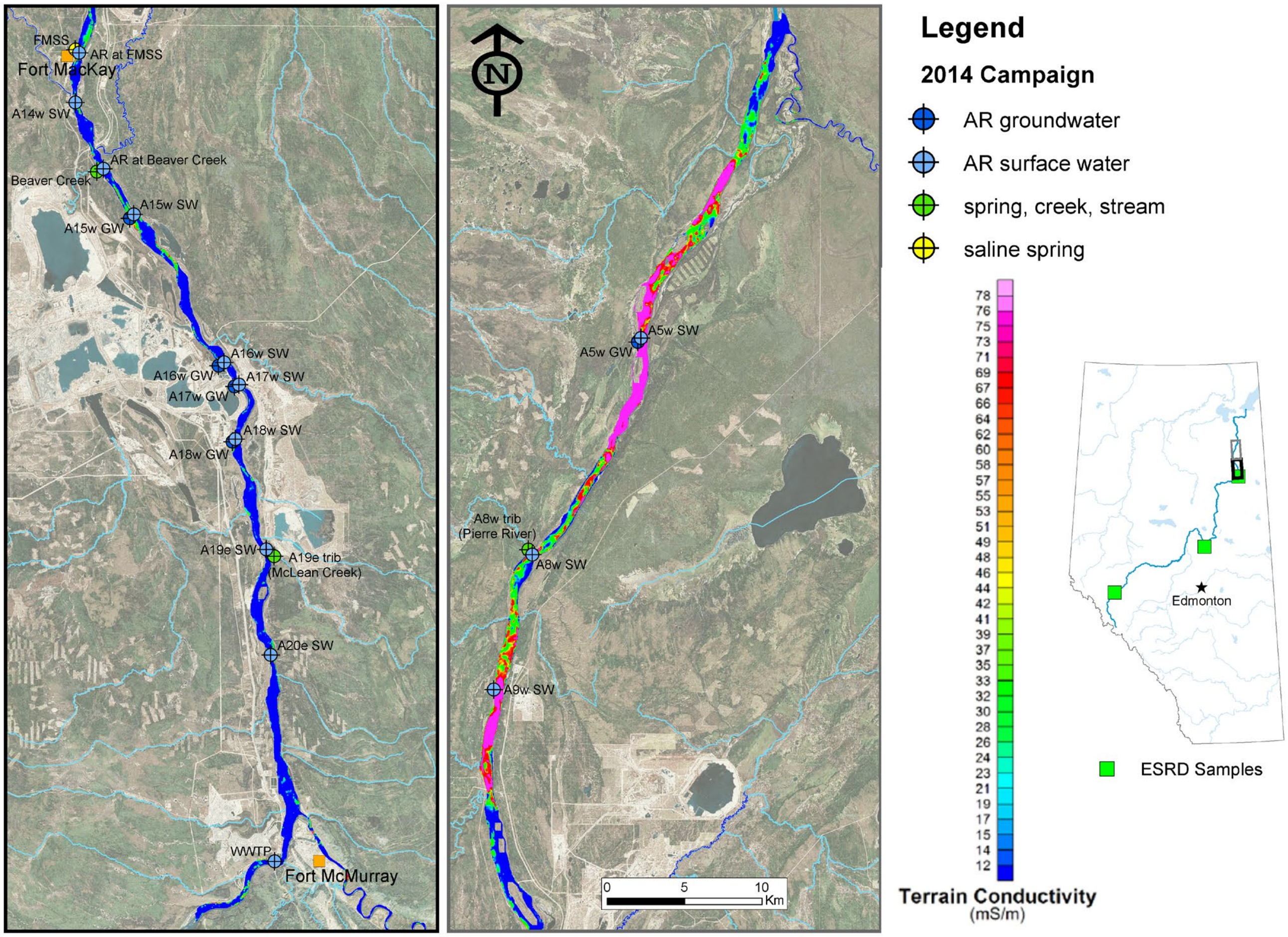

Figure 2.6 Map of study area for sampling locations during 2014 campaign. Sampling locations were selected for their proximity to ABS development or to assess areas of known saline groundwater influence. Lower terrain conductivity data was provided by Gibson et al. [2013]. Letters "e" or "w" indicate whether sampling took place on the East or West portion of the Athabasca River.

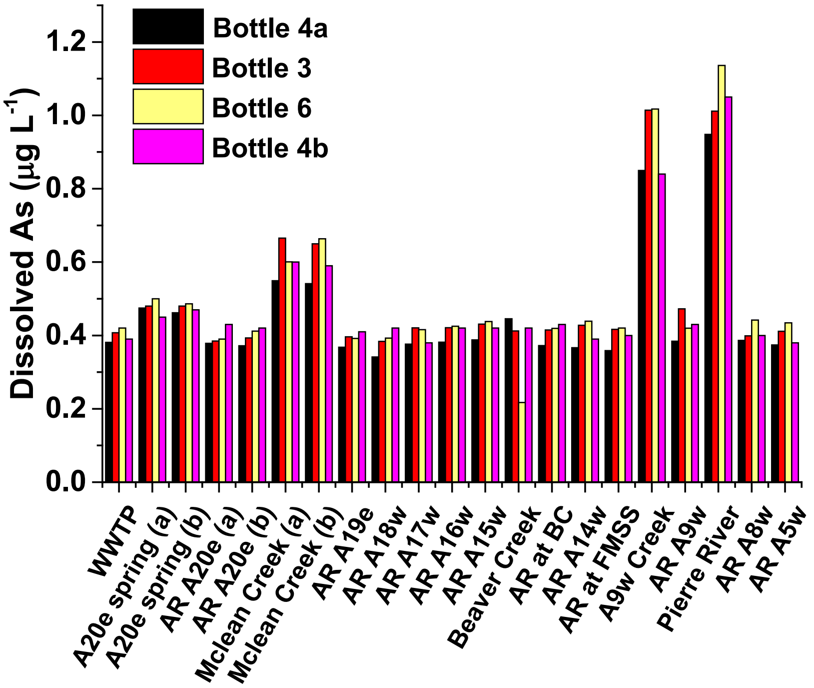

Figure 2.7 Independent laboratory verification of dissolved As in surface water (autumn 2014). 'Bottle 4' represents the samples collected for this study, with '4a' representing data presented in this manuscript and '4b' representing measurements made from the same bottle at the University of Graz using ICP-QQQ-MS. Bottles 3 and 6 were collected at the same time as Bottle 4 but analyzed using single quadrupole ICP-MS in the metal-free, ultraclean SWAMP lab at the University of Alberta.

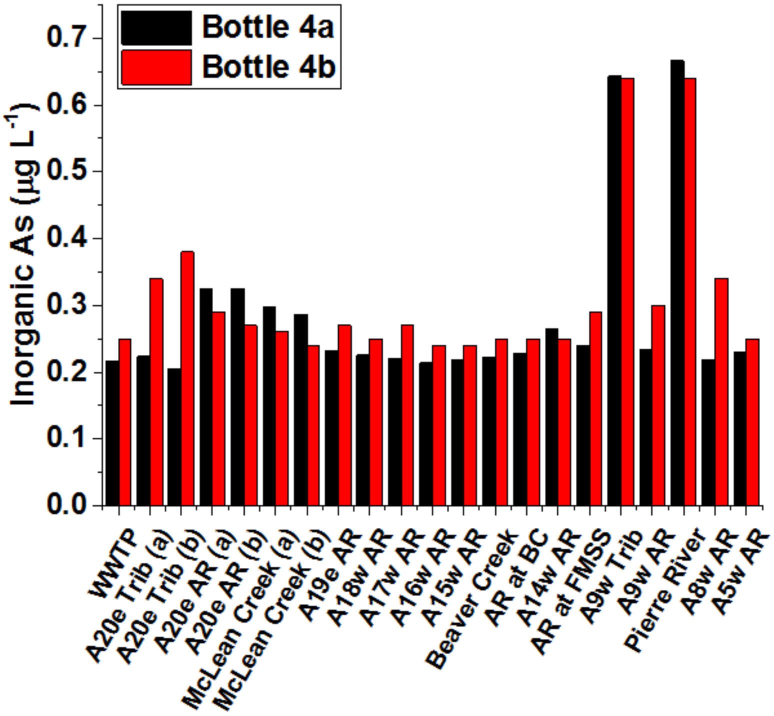

Figure 2.8 Independent laboratory verification of inorganic As (III plus V) speciation in surface water (autumn 2014). 'Bottle 4' represents the samples collected for this study, with '4a' representing data presented in this manuscript and '4b' representing measurements made using HPLC-ICP-MS at the University of Graz from aliquots of the same bottle during an independent check of results.

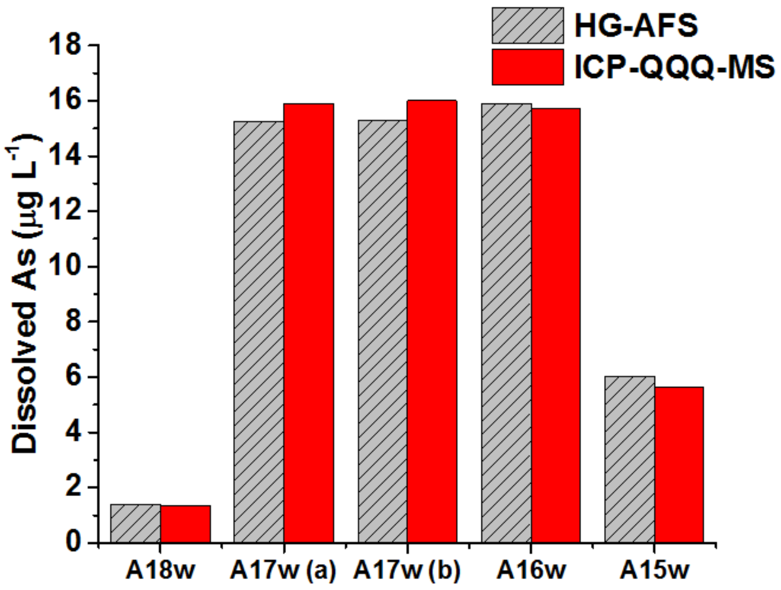

Figure 2.9 Independent method verification (HG-AFS and ICP-QQQ-MS) of dissolved As in non-saline groundwater (autumn 2014).

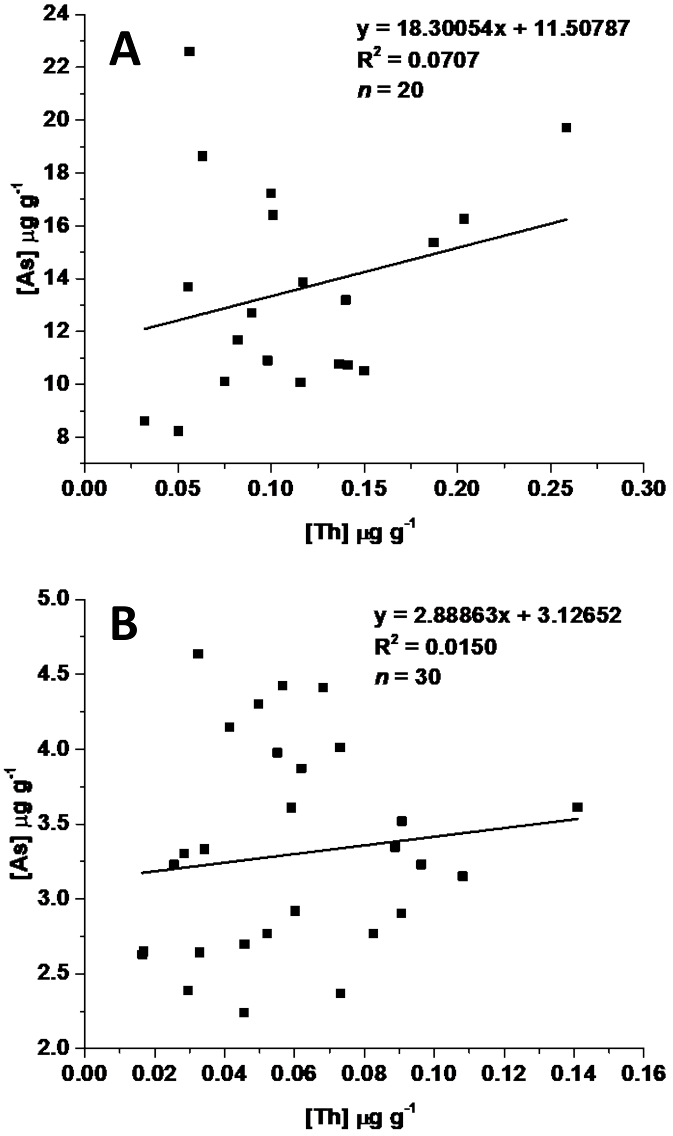

Figure 2.10 Arsenic and Th in unfiltered, unacidified bottles collected from surface water (AR and tributaries) in 2014 (A) and 2015 (B). No significant correlation ($p > 0.05$) was observed in either year.

2.8 Tables

Table 2.1 Chemical characterization (field and laboratory measurements) of groundwater samples collected from A18w, A17w, A16w, A15w and FMSS sites in 2014 (see detailed description in Materials and methods section). Measurements below the limit of detection are denoted with '< LOD' and field measurements are denoted with an asterisk (*). Where applicable, values for duplicate bottles are provided in parentheses.

	A18w	**A17w**	**A16w**	**A15w**	**A5w**	**FMSS**
Latitude (deg. N)	56.963681	56.996550	57.008167	57.093672	57.570489	57.189728
Longitude (deg. W)	-111.457939	-111.454500	-111.471756	-111.568056	-111.514139	-111.627478
Depth (meter)	0.47	0.7	0.7	3.0	3.1	-
Water temperature (°C)*	10	10	9	10	10	-
pH*	6.8	7.2	7.2	7.3	7.5	-
EC (lab) (dS m^{-1})	4.5	1.4 (1.8)	2.3	1.6	52.6 (54.3)	318.2
E_h (mV)*	-18	-142	-134	-134	-114	-
Dissolved oxygen (mg L^{-1})*	1	1	1	2	1	-
Alkalinity (mg L^{-1} as $CaCO_3$)	692	1005 (1013)	1280	469	755 (749)	458
DOC (mg L^{-1})	33	21 (23)	23	8	12 (11)	2
Cl^- (mg L^{-1})	655.1	13.2	24.2	190.6	17323.5 (20290.2)	119024.8
SO_4^{2-} (mg L^{-1})	317.7	10.8	< LOD	186.4	2520.8 (2479.3)	13713.3
NO_3^- (mg L^{-1})	< LOD	12.0	24.0	16.1	< LOD	9763.5
Ca^{2+} (mg L^{-1})	411.9	238.1 (263.4)	292.0	135.4	627.0 (703.0)	1772.7
Mg^{2+} (mg L^{-1})	119.7	73.3 (74.0)	97.7	32.0	91.5 (97.5)	264.1
K^+ (mg L^{-1})	9.5	8.1 (7.8)	8.8	3.7	17.4 (18.7)	70.3
Na^+ (mg L^{-1})	345.3	25.0 (25.4)	39.1	149.6	11156.7 (11946.4)	62977.5
S (dissolved) (mg L^{-1})	167.5	6.7 (5.9)	9.2	70.5	714.2 (760.5)	2286.3
Fe (dissolved) (mg L^{-1})	2.1	64.6 (64.7)	87.6	40.5	14.2 (20.3)	0.2
Mn (dissolved) (mg L^{-1})	8.8	2.8 (3.6)	5.0	1.5	0.3 (0.4)	0.1
Al (dissolved) (μg L^{-1})	263.1	150.0 (226.9)	167.9	331.0	1264.2 (1211.0)	1245.1

Table 2.2 Chemical characterization (field and laboratory measurements) of groundwater samples collected from A18w, A17w, A16w, A15w, NSS and SLSP sites in 2015 (see detailed description in Materials and methods section). Measurements below the limit of detection are denoted with '< LOD', and field measurements are denoted with an asterisk (*).Where applicable, values for duplicate bottles are provided in parentheses.

	A18w	**A17w**	**A16w**	**A15w**	**A5w**	**SLSP**	**NSS**
Latitude (deg. N)	56.963681	56.996550	57.008167	57.093672	57.570489	57.072989	57.603317
Longitude (deg. W)	-111.457939	-111.454500	-111.471756	-111.568056	-111.514139	-111.511361	-111.512117
Depth (meter)	0.47	0.7	0.7	3.0	3.1	-	-
Water temp. (°C)*	8.8	10.6	9.8	12.3	8.7	9.0	6.7
pH*	6.8	7.0	7.0	7.2	7.0	7.2	7.0
EC (lab) (dS m^{-1})	2.0	1.5	2.7	1.2	37.0 (36.3)	54.8	12.5
E$_h$ (mV)*	-41	-160	-151	-172	-116	-57	-
Dissolved oxygen (mg L^{-1})*	<LOD	<LOD	1	<LOD	1	5	-
Alkalinity (mg L^{-1} CaCO$_3$)	423	1159	866	458	689 (546)	327	278
DOC (mg L^{-1})	32.4	60.8	58.4	11.6	14.2 (13.2)	4.0	6.8
Cl$^-$ (mg L^{-1})	540.2	16.9	843.2	167.8	19637.5 (19740.2)	39758.9	5928.1
SO$_4^{2-}$ (mg L^{-1})	484.5	<LOD	<LOD	250.8	2415.8 (2404.7)	3956.2	1660.2
NO$_3^-$ (mg L^{-1})	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ca^{2+} (mg L^{-1})	286.9	291.1	260.4	186.7	722.0 (726.7)	1460.2	398.4
Mg^{2+} (mg L^{-1})	59.8	72.2	55.6	31.9	104.5 (105.3)	320.0	86.9
K$^+$ (mg L^{-1})	7.3	11.5	16.2	4.3	18.5 (18.7)	58.9	12.2
Na$^+$ (mg L^{-1})	350.3	74.7	449.2	141.9	13561.1 (13932.6)	25189.6	81727.5
S (dissolved) (mg L^{-1})	165.5	5.7	5.1	72.1	690.5 (695.1)	664.6	486.5
Fe (dissolved) (mg L^{-1})	4.2	61.7	78.9	31.7	11.8 (12.2)	5.1	0.1
Mn (dissolved) (mg L^{-1})	9.7	0.8	2.0	4.0	0.6 (0.6)	1.3	0.1
Al (dissolved) (µg L^{-1})	27.8	30	66.5	20.4	30.4 (30.2)	44.8	29.6

Table 2.3 Summary table of As QA/QC included in IC-ICP-MS, ICP-MS and HG-AFS analyses.

Year	Analysis	QC type	Accuracy (%)	Relative Standard Deviation (%)	measurements (*n*)
2014	Total As (ICP-MS)	NIST 1640a	100	2.2	22
2014	Total As (ICP-MS)	SLRS-5	95	2.3	16
2014	As speciation (IC-ICP-MS)	NIST 1640a[1]	94	4.1	16
2015	Total As (ICP-MS)	NIST 1640a	100	3.9	7
2015	Total As (ICP-MS)	SLRS-5	99	4.0	7
2015	As speciation (IC-ICP-MS)	NIST 1640a[1]	101	4.2	24
2015	Muskeg River spiked with 0.5 µg L^{-1} As	Matrix spike	97	N/A	1
2015	A5 GW spiked with 0.5 µg L^{-1} As(III) and As(V)	Matrix spike	100 As(III) 99 As(V)	N/A	1
2015	Muskeg River sample spiked with 0.5 µg L^{-1} As(III) and As(V)	Matrix spike	105 As(III) 108 As(V)	N/A	1
2015	A20 AR spiked with 0.5 µg L^{-1} As(III) and As(V)	Matrix spike	106 As(III) 116 As(V)	N/A	1
2015	A18 AR spiked with 0.05 µg L^{-1} As(III)	Matrix spike	110 As(III) 99 As(V)	N/A	1
2015	Total As CCV (ICP-MS)	As(III) FLUKA: 01969	99	3.2	8
2015	Total As (HG-AFS)	NIST 1640a	98	N/A	1
2015	Total As (HG-AFS) A5 GW	Independent method	93	N/A	1
2015	Total As (HG-AFS) A5 GW duplicate	Independent method	95	N/A	1

[1] Value obtained for As(V) was compared with value certified for total As in NIST 1640a. Spiked samples were diluted by 5% with a concentrated solution containing the indicated amount of As and recalculated to adjust for the dilution.

Table 2.4 Concentration of As and Th in suspended particles contained on 0.45 µm filter membranes collected from AR and tributary (indicated in bold) sites in 2014 and 2015. Some samples could not be measured reliably due to the low mass of sediment on filters and are excluded (indicated by 'IN'). The abbreviation 'NA' is used where no sample was collected.

Site	2014		2015	
	As (µg g^{-1})	Th (µg g^{-1})	As (µg g^{-1})	Th (µg g^{-1})
WWTP	12.3	2.1	18.2	6.2
AR A21w	NA	NA	7.1	0.7
AR A20e (a)	10.0	1.9	8.0	0.5
AR A20e (b)	NA	NA	11.5	2.0
AR A19e	23.8	5.9	10.4	2.0
AR A18w	9.9	4.0	32.0	1.2
AR A17w	26.3	4.6	16.6	1.1
AR A16w	20.2	3.7	7.6	1.1
AR A15w (a)	40.3	7.4	10.8	1.0
AR A15w (b)	NA	NA	6.0	0.2
AR @ BC	57.9	14.7	15.5	2.1
AR A14w	21.3	3.8	5.9	0.2
AR @ FMSS	21.9	4.7	8.1	1.7
AR A10w	NA	NA	43.0	1.1
AR A9w	11.2	2.5	12.4	0.7
AR A8w	29.3	5.9	4.4	0.5
AR A7e	NA	NA	8.7	0.4
AR A6e	NA	NA	11.9	0.5
AR A5w	38.3	6.8	14.5	0.4
AR A2e	NA	NA	12.2	0.6
AR A1e	NA	NA	IN	IN
A20e Creek (a)	NA	NA	NA	NA
A20e Creek (b)	NA	NA	NA	NA
McLean Creek (a)	60.5	15.5	IN	IN
McLean Creek (b)	NA	NA	IN	IN
Steepbank River	NA	NA	10.7	0.26
Beaver Creek	10.5	1.3	33.9	0.71
Muskeg River	NA	NA	17.5	0.25
McKay River	NA	NA	2.8	0.07
Ells River	NA	NA	17.3	0.28
Tar River	NA	NA	IN	IN
A9w Creek	NA	NA	NA	NA
Pierre River	31.6	4.8	2.8	0.08
Firebag River	NA	NA	7.0	0.08

Table 2.5 Coordinates of sampling locations (global reference system WGS84) and their distance from the confluence of the Clearwater River and the Athabasca River (city of Fort McMurray). All Athabasca River samples (excluding WWTP) were collected offshore ~80m by boat. Where no sample was collected, the abbreviation 'NA' is used.

Site	2014		2015		Site distance (km)
	Longitude	Latitude	Longitude	Latitude	
WWTP	-111.4096	56.7203	-111.4096	56.7203	3.8
AR A21w	NA	NA	-111.3991	56.7751	3.1
AR A20e (a)	-111.4114	56.8403	-111.4131	56.8381	10.4
AR A20e (b)	-111.4114	56.8403	-111.4131	56.8381	10.4
AR A19e	-111.4164	56.8975	-111.4191	56.8972	17.5
AR A18w	-111.4578	56.9641	-111.4552	56.9647	25.4
AR A17w	-111.4537	56.9957	-111.4511	56.9960	29.4
AR A16w	-111.4717	57.0082	-111.4679	57.0090	31.2
AR A15w (a)	-111.5691	57.0944	-111.5672	57.0954	43.0
AR A15w (b)	-111.5691	57.0944	-111.5672	57.0954	43.0
AR @ BC	-111.5993	57.1204	-111.5977	57.1225	46.6
AR A14w	-111.6316	57.1592	-111.6270	57.1603	51.2
AR @ FMSS	-111.6270	57.1896	-111.6247	57.1891	54.5
AR A10w	NA	NA	-111.6654	57.3443	73.2
AR A9w	-111.6667	57.3673	-111.6667	57.3674	75.8
AR A8w	-111.6281	57.4480	-111.6257	57.4472	85.1
AR A7e	NA	NA	-111.5738	57.4783	89.8
AR A6e	NA	NA	-111.5365	57.5198	95.0
AR A5w	-111.5137	57.5722	-111.5116	57.5732	101.4
AR A2e	NA	NA	-111.4653	57.621	107.5
AR A1e	NA	NA	-111.3772	57.7240	120.4
A20e Creek (a)	-111.4114	56.8403	NA	NA	10.4
A20e Creek (b)	-111.4114	56.8403	NA	NA	10.4
McLean Creek (a)	-111.4164	56.8977	-111.4167	56.8976	17.5
McLean Creek (b)	-111.4164	56.8977	-111.4167	56.8976	17.5
Steepbank River	NA	NA	-111.4805	57.0194	32.6
Beaver Creek	-111.5997	57.1206	-111.5997	57.1206	46.4
Muskeg River	NA	NA	-111.6047	57.1332	47.9
McKay River	NA	NA	-111.6407	57.1679	52.0
Ells River	NA	NA	-111.6737	57.3052	68.6
Tar River	NA	NA	-111.6833	57.3226	70.7
A9w Creek	-111.6667	57.3673	NA	NA	75.8
Pierre River	-111.6281	57.4480	-111.6282	57.4480	85.0
Firebag River	NA	NA	-111.3544	57.7531	123.7

2.9 Supplementary Information

2.9.1 Acid cleaning procedure

To decontaminate bottles for dissolved As and speciation, they were filled with 10% (v/v) trace metal grade HNO_3 and leached at room temperature (~20°C) for 3 days; bottles were then placed in a water bath and heated to 70 ˚C for 6 hours. The dilute acid was poured out and bottles were thoroughly rinsed, filled with ultrapure water, and leached for as long as possible (minimum of 2 days). Bottles were then emptied, rinsed again with ultrapure water and dried inside a HEPA filtered laminar clean air cabinet. Sampling syringes and filters were acid-cleaned in the University of Alberta's SWAMP metal-free ultraclean lab using in-house developed protocols [Shotyk et al., 2017]. All bottles, syringes and filters were acid cleaned, dried in HEPA filtered clean air cabinets and individually packaged in polyethylene bags in the lab prior to field sampling.

2.9.2 Laboratory reagents

Nanopure (18.2 MΩ cm; Barnstead, Thermo Scientific™) or Millipore water (18.2 MΩ cm) was used in all steps of sample dilutions and reagent preparation. Trace metal grade HCl (Sigma Aldrich; Cat. # 72787) and HNO_3 were used when necessary during reagent preparation. Inorganic As(III) and As(V) standards were prepared using individual 100 mg L^{-1} stock solutions (VHG Labs; Cat. # SPAS3-50 and SPAS5W-50), while DMA standard was prepared with sodium cacodylate trihydrate salt (Sigma Aldrich; ≥98%; Cat. # C0250) using ultrapure water. Mass calibration solution for total As and internal standard solution were prepared using SPEX CertiPrep Instrument Calibration Standard 2 and Multi-element Internal Standard 1, respectively. Powder reagents of potassium iodide, (KI, ≥ 99%; Cat. # 221945) and L-ascorbic acid, (≥ 99%;

Cat. # 255564), and caplets of sodium borohydride ($NaBH_4$, 98%; Cat. # 452890) were purchased from Sigma-Aldrich for HG-AFS analysis.

2.9.3 Calculating limits of detection

Limit of detection (LOD) for ICP-MS was determined by the mean of the blank (cps) plus 3 x the standard deviation ($n = 7$ blanks). Limit of quantification (LOQ) were determined by the mean of the blank (cps) plus 10 x the standard deviation ($n = 7$ blanks). These values were confirmed experimentally by analyzing standard samples (5, 10, 50, 100, 200 ng L^{-1}) containing all 3 species. LOD for HG-AFS also used the same calculations, but with peak height instead of peak area.

2.9.4 Independent laboratory analyses

Two bottles (No. 3 and 6) were collected at the same time but for a collaborative study examining trace metals [Shotyk et al., 2017]. Bottles were syringe filtered using the same protocols described above but collected in acid-cleaned polypropylene containers with 100 µL of double-distilled HNO_3 as preservative. Samples were analyzed for As using ICP-MS (iCap Q, Thermo-Scientific) in the University of Alberta's metal-free ultra clean SWAMP lab. Full methodology of the analysis is presented elsewhere [Shotyk et al., 2017].

For additional quality control, aliquots from sample bottles used for As speciation were analyzed for As(V), As(III), MMA, DMA, and total As at the University of Graz, Austria. Total As was determined in aqueous solutions by ICP-MS (Agilent 7900, Agilent, Waldbronn, Germany) using helium as collision cell gas for removing interferences from chloride (polyatomic interference of $^{40}Ar^{35}Cl$ on ^{75}As). A second analysis was performed by ICP-QQQ-MS (Agilent 8800) (*m/z* 75 ➔ *m/z* 91). HPLC–ICPMS measurements were performed with an Agilent 1100 series HPLC (Agilent, Waldbronn, Germany) equipped with a binary pump, a vacuum degasser, column oven, and an autosampler with a variable 100 µL injection loop connected with 0.125 mm PEEK (polyetheretherketone) tubing (Upchurch Scientific, Oak Harbour, USA) to an Agilent 7500ce ICP-MS equipped with a Burgener Ari Mist HP nebulizer (Burgener Research Inc, Mississauga, Canada) and a cyclonic spray chamber. The signals at *m/z* 75 (^{75}As), were monitored using a dwell time of 300 ms. An optional gas (1% CO_2 in argon) was introduced through a T-piece connecting the spray chamber and the torch to achieve the best signal to noise ratio for As. The data evaluation was carried out with chromatographic software G1824C Version C.01.00 (Agilent, Waldbronn, Germany). The quantification was done by external calibration based on peak areas. Determinations of As species were performed at 40°C with a Hamilton PRP-X100 column (4.6 x 150 mm, 5 µm particle size).The mobile phase was 20 $\text{mmol}\cdot\text{L}^{-1}$ malonic acid buffer (pH 9.5, adjusted with aqueous ammonia, flow rate was 1 mL min^{-1}, and injection volume was 20 µL).

2.9.5 Upstream water samples

Water samples collected upstream of Fort McMurray at provincial long term monitoring locations were contained in high density polyethylene (HDPE) bottles and sent to the lab within 3-4 days for filtration (0.45 µm) and acid preservation.

3.0 SELENIUM AND SULPHUR IN ATHABASCA BITUMINOUS SANDS MINERAL AND BITUMEN FRACTIONS[†]

[†] A version of this chapter has been published as: Selenium and Sulphur in Athabasca Bituminous Sands Mineral and Bitumen Fractions, *Fuel*, 2018, vol. 224, 718-725. The published journal article is provided in Appendix II.

3.1 Introduction

Bituminous sands are hydrocarbon reserves consisting of mixtures of sand, clay, water and bitumen – a heavily biodegraded crude oil (Larter and Head, 2014). The largest known group of bitumen deposits is the Lower Cretaceous Mannville group (Athabasca-Wabasca, Peace River, Cold Lake) in Alberta, Canada (Garven, 1989), which together contains an estimated 165.4×10^9 barrels of (remaining) established reserves (Alberta Energy Regulator, 2017). Of this group, the Athabasca bituminous sands (ABS) region is the largest deposit (Garven, 1989), (initial established reserve=6.16×109 m^3) and contains an estimated 32.09×10^9 barrels remaining established reserves (Alberta Energy Regulator, 2017). The Athabasca deposit is also well known for its shallow (average) pay-zone (~30m deep) accessible by surface mining (Mossop, 1980). Geochemical characterization of bitumen from the ABS region was a priority during the early stages of development (ca. 1950–1985). This included determining the trace element content to provide information on the type of petroleum (i.e., origin, geological formation, maturation, etc.) as well as the abundance of elements known to be problematic during the bitumen upgrading processes (Hitchon and Filby, 1984). Much of the trace element research at that time was focused on vanadium (V) and nickel (Ni) due to their enrichment in bitumen as metal porphyrin complexes and ability to cause significant corrosion of equipment and impair the catalytic cracking process (Beach and Shewmaker, 1957; Champlin and Dunning, 1960). Atmospheric emissions of trace elements to the environment were also of interest, with monitoring efforts concentrated on V as an indicator of ABS mining and upgrading emissions (Addison and Puckett, 1980; Hargesheimer et al., 1980).

Aside from V and Ni, there have been very few published studies examining the trace element content of bitumen in the ABS region since the pioneering work over 30 years ago (Hitchon et al., 1975; Hitchon and Filby, 1983, 1984; Jacobs and Filby, 1983; Scott et al., 1954). This is despite: i) considerable improvements in relevant analytical techniques ii) extremely rapid industrial growth and iii) growing concerns in regard to contamination of potentially toxic trace elements such as Ag, As, Be, Cd, Cr, Cu, Ni, Hg, Pb, Sb, Se, Tl and Zn (Hitchon, 1984; Schindler, 2010, 2013); for these reasons, a contemporary investigation of the trace element content in bitumen from the ABS was undertaken (Bicalho et al., 2017). In that study (Bicalho et al., 2017), bitumen and mineral phases were separated under ultra-clean lab conditions using toluene, then digested and analyzed using inductively coupled plasma sector-field mass spectrometry (ICP-SFMS). The results confirmed the enrichment of V, Ni and Mo in bitumen, which is consistent with the historical work by Goldschmidt (Goldschmidt, 1937). Rhenium (Re) was also found to be hosted predominantly in the bitumen fraction, in agreement with the more recent work on Re-Os dating by Creaser and Selby (Selby, 2005). In contrast to V, Ni, Mo and Re, potentially toxic trace elements such as Ag, As, Be, Bi, Cd, Cu, Pb, Sb, Tl and Zn were found almost exclusively in the mineral fraction (Bicalho et al., 2017). Unfortunately, the work by Bicalho et al. (2017) provided no information about selenium (Se), a non-metallic trace element with properties chemically analogous to sulphur (S) (White and Dubrovsky, 1994).

Depending on its concentration and chemical form, Se may act either as an essential micro-nutrient (Navarro-Alarcon and Cabrera-Vique, 2008; Rayman, 2000) or environmental toxin (Hamilton, 2004). The concentration range between toxic and beneficial can be relatively narrow, particularly for aquatic organisms such as fish (Hamilton, 2002, 2003; Lemly, 1998) and waterfowl (Ohlendorf et al., 1990). This highlights the importance of understanding human activities that could mobilize Se or change its speciation, thereby increasing the potential for bioaccumulation within the food chain (Outridge et al.,1999). Industrial combustion and roasting processes involving crude oil, coal and metal sulphide ores dominate anthropogenic Se emissions to the atmosphere (Cutter and San Diego-McGlone, 1990; Mosher and Duce, 1987; Nriagu and Wong, 1983; Nriagu and Pacyna, 1988; Pacyna and Pacyna, 2001). Selenium emissions can be especially problematic during industrial processing of fossil fuels (particularly coal) due to its ability to form sub-micron or gaseous species which by-pass many engineered air pollution controls such as electrostatic precipitators and baghouse filters (Andren et al., 1975; Rahn, 1976; Shendrikar et al., 1983). However, due to its chemical similarity to S, the use of modern wet-scrubber technologies (e.g., flue gas desulphurization; FGD) can be effective in reducing atmospheric Se emissions (Petrov et al., 2012; Senior et al., 2015). The impacts of atmospheric emissions can be assessed by determining Se concentrations in various environmental compartments (soil, water, plants, etc.), but even in polluted areas this can still be a challenge due to its low abundance and complexity of chemical transformations. The most common method of analysis currently used for Se determination is ICP-MS, however, accurate and precise measurements of Se are often hindered by its high ionization potential and a large number of molecular interferences for an array of stable isotopes (^{74}Se, ^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se) (B'Hymer and Caruso, 2006; Jackson et al., 2015; Lum and Leung, 2016; Pettine et al., 2015).

Early work on bitumen from the ABS region that examined a wide spectrum of trace elements either did not include Se in the list of elements studied (Jervis et al.,1982), or reported inadequate limits of detection (Hosterman et al.,1990). Previous studies were also limited to only one or two samples and therefore provided no information about possible relations between Se concentrations and ore quality. The analytical challenges and paucity of information on the abundance and forms of Se in ABS makes it difficult to fully evaluate the potential environmental impacts of resource development, from open pit mining to upgrading and eventually refining. Here we provide an accurate assessment of the distribution of Se between the mineral and bitumen fractions of the ABS. Due to the chemical similarities between Se and S, we also examined the abundance of S in the two fractions, with a view toward using it as a proxy for estimating the abundance of Se in bitumen.

3.2 Materials and methods

3.2.1 General

All experimental procedures were carried out within class 100, metal-free clean air cabinets. High-purity water (18MΩ·cm, Q-Pod Element, Millipore) was used throughout the study. Laboratory soap (Versa-Clean, Fisherbrand) and trace grade acids (Fisherbrand HNO_3 and HCl) were used in material cleaning routines. Trace metal grade HNO_3 used for sample digestion and preparation of working solutions was purified twice by sub-boiling distillation and stored in cleaned polytetrafluoroethylene (PTFE) bottles. ACS certified toluene (> 99.5%, Fisher Scientific) was used for the bitumen extractions. Polypropylene (PP) syringes and filters (30mm PTFE membrane, 0.45 µm, PP housing, Target-2, ThermoFisher) were cleaned by filtering 20 mL of 2% double-distilled HNO_3, water, toluene and methanol (LCMS grade, Fisher Scientific). Chemical reductant solution for HG-AFS analysis consisted of NaOH (BioXtra, ≥98%) and NaBH4 (98%) purchased from Sigma Aldrich; HCl used for sample acidification and preparing the reagent blank was trace metal grade (Fisherbrand).

3.2.2 Athabasca bituminous sands

Seven samples from the McMurray Formation of the ABS region were obtained for analysis. The bitumen content of the samples ranged from 8.0 to 15.6 wt%. This range is ideal for study, as ores are typically graded into three categories based on their bitumen content: rich (> 10 wt% bitumen), moderate (6–10 wt% bitumen), and lean (< 6 wt%) (Takamura, 1982); an ore containing less than 8 wt% bitumen is generally considered uneconomical and is not desirable for mining (Innes and Fear, 1967). Depending on the amount of mineral material, a typical ore also contains ∼3–5wt% connate water present as an ultra-thin film (estimated ∼10 nm) between mineral particles and the bitumen (Gosselin et al., 2010; Takamura, 1982).

Each ore sample was separated into its bitumen and mineral fractions by extraction with toluene three times then twice using methanol (Bicalho et al., 2017). Bulk ore samples and the extracted bitumen and minerals were digested in a mixture of HNO_3 and HBF_4 using a high pressure microwave (ULTRAclave, MLS, Leutkirch, Germany). The mineral phases were also digested using an HF-HNO_3 procedure. The extraction and digestion procedures are described in detail elsewhere (Bicalho et al., 2017). We assume that any connate water present would end up in the organic fraction (bitumen) following the methanol wash. The potential significance of connate water is discussed in greater detail in the Results and Discussion. To calculate the mass balance for Se and S, the concentrations determined using ICP-SFMS and hydride generation atomic fluorescence spectroscopy (HG AFS), for Se, and ICP-SFMS and inductively coupled plasma optical emission spectroscopy (ICP-OES), for S, were combined to produce an average value for each of the following samples: 1) bulk ABS, 2) extracted bitumen and 3) remaining mineral fraction. Then, by assuming that the bulk sample represents the total (100%), the mass fractions of an element associated to the organic and mineral matters were calculated using Eqs. (1) and (2):

$$[E]ABS\ (b) = [E]of\ .\ (Mof\ /\ MABS)\quad (1)$$

[E]ABS (m) = [E]mf . (Mmf / MABS) (2)

where

[E]ABS(b)=concentration of element associated with bitumen in bulk ABS.

[E]ABS(m)=concentration of element associated with minerals in bulk ABS.

[E]of=concentration of element in the organic fraction separated from bulk ABS.

[E]mf=concentration of element in the mineral fraction separated from bulk ABS.

Mof=mass of organic fraction separated from bulk ABS.

Mmf=mass of mineral fraction separated from bulk ABS.

MABS=mass of bulk ABS.

3.2.3 Selenium and S determination using ICP-SFMS

An ICP-SFMS (Element XR, Thermo-Finnigan, Bremen, Germany) was used to determine the concentrations of Se and S in the acid digests of bulk ABS and its mineral and bitumen fractions. Relevant data acquisition parameters specific to Se and S are provided in Table 3.1, and all other general instrument features and operating parameters related to ICP-SFMS are provided elsewhere (Bicalho et al., 2017). For calibration, the external standards were diluted from a 10 mg/L stock solution (Spex CertiPrep; Metuchen, NJ) with 2% HNO_3 to make solutions ranging in concentration from 0.01 to 10 µg/L. To correct for any minor instrument drift over time, indium (In) was spiked into each sample as an internal standard (IS) for a final concentration of 0.5 µg/L. Due to the substantial difference between Se and S concentrations, digestate stocks were diluted 10x and 1000x for Se and S analysis, respectively. Samples were analyzed following the measurement of 5 method blank solutions (2% HNO_3+IS) and instrument calibration; a trio of additional quality control solutions (0.1, 1, and 10 μg/L) was analyzed periodically throughout the analysis.

3.2.4 Selenium determination using HG-AFS

For pre-reduction of Se in the digestates from Se(VI) to Se(IV), aliquots of digestate (1–3 mL) were combined with Milli-Q water and HCl in PTFE digestion vessels to obtain a final acid concentration of 60% (v/v). Solutions were heated to 90 °C using a microwave digestion unit (MARS, CEM Corporation, USA) and held for 60 min. After cooling, the full volume of solution was transferred to graduated 50 mL polypropylene vessels (certified for low background metal analysis). The digestion vessels were rinsed a minimum of 3 times with Milli-Q water, which was added to the beaker until a final volume of 25 mL was achieved. Diluted, pre-reduced, samples were analyzed using a Millennium Excalibur 10.055 HG-AFS system (PS Analytical, Orpington, UK) operated with a continuous flow of sample/reagent (30% HCl v/v) and chemical reductant (7 g/L $NaBH_4$ stabilized in 4 g/L NaOH; prepared fresh daily). Gaseous Se produced in the reaction with $NaBH_4$ was swept from the gas-liquid separator by argon (Ar) gas and passed through a hygroscopic membrane to remove moisture. The gas stream was then atomized by a hydrogen diffusion flame, fueled by the production of excess hydrogen during hydride generation. Selenium atoms were radiated by a boosted discharge hollow cathode lamp with primary and boost settings of 20 mA and 25 mA, respectively. A photomultiplier tube served to detect atomic fluorescence and the electronic signals were recorded as peak areas. Signals were quantified by a 6-point calibration curve (0.05, 0.1, 0.2, 0.4, 0.8, 2 μg/L) with R2 values always>0.999. Instrument calibration solutions were prepared fresh daily by serially diluting a 1000 mg/L stock solution of Se (Fluka Analytical; TraceCERT®). The reagent blank, samples, and calibration standards were prepared using the same source of HCl to ensure consistency.

3.2.5 Quality control

Procedural blanks for the toluene extraction and digestion blanks for non-extract samples were prepared in triplicate and included in the analysis. Certified Standard Reference Materials (SRMs) were analyzed to assess the performance of the analytical procedure. These included two materials developed by the National Institute of Standards and Technology: NIST 1635 (sub-bituminous coal) and NIST 2711 (Montana soil). Both materials are certified for Se and S, but differ in respect to their mineral matter contents. For additional quality control, an inhouse peat reference material (OGS-1878P) was also analyzed. Reference values for Se in OGS-1878P are based on past measurements performed using hydride generation atomic absorption spectroscopy (HG-AAS) at the Environmental Specimen Bank (Jülich, Germany). Details on the development and analysis of OGS-1878 can be found elsewhere (Riley, 1986). For an independent verification of S concentrations, aliquots of the HNO_3-HBF_4 digests (bulk ore, bitumen, minerals) were diluted 10x with 2% HNO_3 and submitted to the Natural Resources Analytical Laboratory, University of Alberta, for ICP-OES analysis (Thermo iCAP 6300Duo, Cambridge, UK). To confirm the pre-reduction of Se(VI) required for HG-AFS analysis, selected samples were spiked with a representative concentration of Se(VI) prepared from a sodium selenate salt (Sigma Aldrich; 99.999%) and diluted appropriately (final concentration of 0.8 μg/L in the sample).

3.3 Results

3.3.1 Method performance

The use of certified SRMs (NIST 2711, NIST 1635) in this study served two purposes: i) to evaluate the performance of each analytical method based on the element recoveries and ii) to determine the suitability of the digestion techniques (HF-HNO_3 and HBF_4-HNO_3). Both instruments yielded good recoveries (100 ± 10%) for Se in NIST 1635 (subbituminous coal), regardless of which acid digestion procedure was applied (Table 3.2). However, similar to the findings of Bicalho et al. (2017), the application of HNO_3-HBF_4 for digesting NIST 2711 (Montana Soil) resulted in a slightly lower recovery (70 ± 10%) than HF-HNO_3 (80 ± 10%; Table 3.2). This is due to the abundance of mineral material in NIST 2711 (presumably>95 wt% mineral matter) compared to NIST 1635 (ash content=4.6%): the mineral soil requires more HF than that generated by HBF_4 in the HNO_3-HBF_4 digestion procedure. For S determination by ICP-SFMS, SRM recoveries were in excellent agreement with the certified values and showed no indication of being influenced by the acid digestion procedure. Sulphur concentrations obtained using ICP-OES were in good agreement with ICP-SFMS (Table 3.3).

As mentioned in the Introduction (Section 3.1), the use of ICP-MS for determining Se concentrations can be challenging due to a plethora of polyatomic interferences. Evidence of a common interference is depicted in Fig. 3.1, where the resolving power of sector-field mass spectrometry is required to distinguish ^{77}Se from $^{37}Cl^{40}Ar$. Despite its abundance, S also requires the high mass resolution offered by ICP-SFMS due to the $^{16}O^{16}O$ interference on ^{32}S (Fig. 3.1). Clearly, both Se and S require high mass resolution to eliminate interferences. Moreover, the data in Fig. 3.1 suggest that determination of Se and S using ICP-MS with a single quadrupole mass analyzer is potentially problematic. In the case of HGAFS for Se measurements, polyatomic interferences are mostly eliminated by the hydride generation step – as only the hydride forming elements are reduced to a gaseous state for measurement by atomic fluorescence. Analysis by HG-AFS is an ideal way to complement the data produced by ICP-SFMS because it operates on completely different physical principles. Both instruments yielded sufficiently low limits of detection for the reliable determination of Se in bitumen. However, because ion transmission is reduced at the high mass resolution required for baseline separation of Se, the ICP-SFMS was less sensitive (0.04 ng/ml) than HG-AFS (0.003 ng/ml). On the other hand, the prereduction step required by HG-AFS introduces an additional dilution of the sample by up to 25 times. Thus, when the method detection limit is expressed on a dry weight basis (Table 3.2), the two techniques provide comparable MDLs, namely 0.02 mg/kg (ICP-SFMS) and 0.04 mg/kg (HG-AFS).

3.3.2 Concentration and distribution of S and Se

The concentrations of Se and S in the studied samples for each analytical technique are presented in Table 3.3. Overall, there was good agreement for all the sample types (bulk ore, minerals, bitumen), with the differences in the data between the methods for determining Se concentrations being in the range of 30 ± 15% and the differences in the methods for determining S in the range of 20 ± 15% (Table 3.3). Not surprisingly, sample type influenced analytical performance, with the bitumen samples resulting in the greatest differences in Se and S between instruments; for bitumen samples alone, the average differences for Se and S were 42 ± 13% and 36 ± 16%, respectively. With these differences assessed, the two sets of results for each element were combined to give an average concentration per sample, to better represent the concentration values obtained (Fig. 3.2). Determination of Se in extracted bitumen and mineral fractions revealed elevated concentrations in the bitumen fraction (390 ± 45 μg/kg) relative to the mineral fraction (15 ± 7 μg/kg), with an average Se concentration in the native ore of 75 ± 15 μg/kg (Fig. 3.2). Sulphur concentrations in bitumen averaged 6 ± 1 wt% versus 0.1 ± 0.04 wt% in the extracted minerals; the average concentration in the ore was 0.9 ± 0.3 wt% (Fig. 3.2). Not only are Se and S both enriched in bitumen, relative to the ore, but there is a positive correlation between the two elements (Fig. 3.3). In contrast, there is a negative correlation between the two elements in the mineral fraction (Fig. 3.3). Using the mass balance equations previously described (Bicalho et al., 2017), the relative abundances of Se and S in the ore compartments are illustrated in Fig. 3.4. There is a positive correlation between the concentrations of Se and S, and the bitumen content (i.e. grade) of the ores (Fig. 3.5). Similar trends were reported earlier (Bicalho et al., 2017) for four other elements (V, Ni, Mo, Re) which are found primarily in the bitumen fraction of ABS. Despite the limited number of samples available for this study, the data obtained thus far certainly suggests that the abundances of Se and S increase with ore grade.

Two potentially relevant artefacts of the extraction are worth noting: i) the presence of Se and S in connate water and ii) the retention of ultra-fine mineral particles<0.45 µm in the bitumen extract. While it was not evaluated experimentally, the presence of Se or S in connate water did not appear to influence the results. This is suggested from the fact that the proportion of connate water content in ABS is known to increase with greater mineral (fines) content (Innes and Fear, 1967; Jia, 2010). Therefore, assuming that a greater proportion of connate water was present in ores with a greater mineral content, we would have expected to see greater concentrations of Se in the analysis of low quality (high mineral) ores than high quality (low mineral); this however is contrary to our results, further indicating that Se is predominantly in the bitumen. Lastly, a very small amount of ultra-fine mineral material is predicted to have been present in the bitumen extract, even after additional syringe filtration (0.45 µm). Evidence of this comes from the analysis of ultratrace concentrations of lithophile elements (Sc, Y, Dy, Sm, Th), which behave conservatively during chemical weathering and serve as indicators of the presence of mineral material (Goldschmidt, 1937); this analysis was performed on the same digests, with details presented in Bicalho et al. (2017). The low concentrations of lithophile elements (Sc, Y, Dy, Sm, Th) suggest that the contribution of Se and S from any such mineral material remaining in the bitumen extract is negligible. Further study of trace elements in both connate water and ultra-fine clays would be of value but would require lab techniques and methods beyond the scope of this study.

3.4 Discussion

3.4.1 Selenium in bitumen from the ABS region compared to other geological materials

The abundance of Se in soils, rocks, sediments, and other materials can vary considerably. For perspective, a brief compilation of Se concentrations in some relevant geological materials is provided in Table 3.4. The average Se concentration in bulk ABS ore (75 ±15µg/kg) is comparable to its abundance provided by Rudnick and Gao (2003) for the Upper Continental Crust (UCC; 90 µg/kg). However, Se in bitumen from oil sands is enriched relative to the UCC, with concentrations comparable to the global average for crude oil, but lower than averages for coal and oil shale (Table 3.4). For a more local perspective on Se abundance, the average concentration of Se in soils from across Alberta (129 sites) and coal from the Genesee coal mine (~70 km from Edmonton, Alberta) are also presented in Table 3.4. The concentrations of Se in coal, soil, and other geological materials vary considerably depending on the environment of formation, accumulation, or deposition. For example, in the case of coal from the Genesee mine, the average Se content for coal samples (No. 2 seam) is relatively consistent; however, higher concentrations are observed for samples collected from rheotrophic (groundwater influenced) zones, while lower concentrations were found in coal formed under ombrotrophic (rain-fed) conditions (Pollock et al., 2000). For one sample, there was also evidence of a volcanic event which in turn greatly increased the concentration of Se in the coal (13 mg/kg) (Pollock et al., 2000). Although consistent Se concentrations were found in the limited number of ABS samples measured in this study, it would be beneficial to conduct a survey of bitumen from the ABS region using a suitable number of samples to evaluate the geochemical heterogeneity of the deposits.

3.4.2 Comparing Se abundance with S

The behavior and fate of Se and S during endogenic (bio) geochemical processes are extremely similar and often leads to the concomitant occurrence of these elements in both minerals and organic materials (Berrow and Ure, 1989). The similar ionic radii of Se(-II) (1.91 Å) and S(-II) (1.84 Å) allows Se to readily substitute for S in sulfide minerals under reducing conditions (Berrow and Ure, 1989). The uptake and transformation of Se and S by organisms is also extremely similar, leading to analogous biomolecules such as amino acids (Young et al., 2010). Owing to the fact that S is found primarily in the form of organic compounds in crude oil (Orr, 1978) as well as ABS (Liu et al., 2010), it is reasonable to assume, given the positive correlation reported here between concentrations of Se and S in bitumen (Fig. 3.3), that most of the Se in the ABS is also in the form of organic compounds.

In a previous survey of Alberta crude oils, 86 conventional and two unconventional (ABS region) crude oil samples were analyzed for 22 trace elements, including S and Se (Hitchon and Filby,1983). Using factor analysis, their results indicated that more than 25% of the cumulative variance between elements could largely be accounted for by V, Ni, S and Se (Hitchon et al., 1975; Hitchon and Filby, 1984). Hitchon and Filby (1983) suggested that, since V, Ni and S are all known to be present mainly in the form of organic compounds, it is likely that Se also exists in an organic form in conventional crude oil. As convincing as their data is for conventional crude oil (n=86), the results were less conclusive for the ABS samples (n=2); also, the authors experienced challenges in separating entrained fine mineral material from the bitumen in the ore. Combining earlier analyses and arguments (Hitchon and Filby,1983) with the results obtained from the current study, the data available to date supports the hypothesis that Se is also part of the organic fraction of the ABS, and is not due to entrained mineral particles. Some additional support for this claim is also found in an independent study of bitumen (Hosterman et al., 1990) that included 1 sample from the ABS region (see Table 3.4 for comparison).

3.4.3 Relevance to the environment in northern Alberta

Mining and upgrading of bitumen in northern Alberta releases S to the environment in both the gaseous as well as particulate phases (Mullan-Boudreau et al., 2017; Wieder et al., 2016), but emissions of Se have received far less attention. To understand the potential for Se to be released to the environment during bitumen mining, upgrading and refining, whether the concerns are emissions to the air, soil, or water, requires an understanding of the abundance and distribution Se in the bitumen versus mineral fractions of the ABS. It is evident from the results presented here that unlike other potentially toxic chalcophile trace elements (Ag, As, Bi, Cd, Cu, Pb, Sb, Tl and Zn), which are found almost exclusively in the mineral fraction (Bicalho et al., 2017), Se is hosted predominantly in the bitumen fraction of the ABS. These other trace elements are expected to be bound within stable mineral structures and should experience limited mobility during industrial processing of the ABS. In contrast, there are several possible sources of Se release to the environment in northern Alberta.

Generally, most of the Se should be in bitumen separated from the ABS during the initial recovery and froth clean-up stages. When the collected bitumen is eventually heated during primary upgrading (430–550 °C for coking,<460 °C for hydroconversion), or further treated to reduce levels of S, nitrogen and oxygen in secondary upgrading, there is then potential for Se partition into the gas phase or be collected as a waste by-product (Gosselin et al., 2010). Selenium may become residually enriched in the produced petroleum coke (petcoke), which is currently being stored primarily as massive stockpiles or added to tailings ponds; some operators also use petcoke as a source of fuel or as a material in land reclamation (Gosselin et al., 2010). Petcoke has recently generated interest when it was determined to be the predominant source of polycyclic aromatic hydrocarbons (PAHs) in the ABS region (Zhang et al., 2016). Due to the high S content of bitumen, there are also engineered technologies in-place to lower the S content of upgraded bitumen and reduce airborne emission of SO_2 and related compounds. The reduction of S in recovered oil is achieved by the Claus process, where reduced S compounds (H_2S) are oxidized and elemental S is produced. The dry S material is stored in large stockpiles and could be a repository of Se. Unlike natural deposits of elemental S, which are commonly enriched in Se (up to 682 mg/kg), the Se contents of diverse examples of elemental sulphur obtained from industrial processing were below the limit of detection (Steudel et al., 1986). The limit of detection in that study employing neutron activation analysis was 1mg/kg (Steudel et al., 1986), which is well above the average value of Se in bitumen reported here (Fig. 3.2). The second S-related removal process is flue-gas desulphurization (FGD), which takes place in stacks and removes SO_2 with $Ca(OH)_2$ to produce gypsum ($CaSO_4 \cdot 2H_2O$) as an end product (Gosselin et al., 2010). The majority of gypsum is landfilled, thereby limiting its relevance as a potential source of Se to the environment in the ABS region; however, some is used as an amendment to increase the rate of tailings densification (composite/consolidated tailings) (Gosselin et al., 2010). Of the two S removal processes, the latter seems likely to be more relevant for Se because the FGD systems are in-place to remove gaseous by-products of combustion. The applications of

FGD systems in coal combustion are known for their potential to also remove Se (e.g., SeO_2) simultaneously (Senior, 2015). Given the potential effectiveness of FGD systems to also capture Se from stack gases, the Se content (and speciation) in both produced gypsum and petcoke should be considered before its widespread use as an amendment in reclamation. Clearly, more work is required to fully understand the sources and sinks of Se during the industrial processing of bitumen, the chemical forms in which Se is emitted and their potential impact to environmental receptors.

3.5 Conclusions

The extraction and analysis of bitumen and mineral fractions of ores from the ABS region has revealed that Se is located predominantly in the bitumen fraction. Selenium abundance in bitumen correlates positively with S, but further study is required to determine if it exhibits similar behavior during industrial processing, especially upgrading and refining. Despite its low abundance in bitumen relative to other fossil fuels, it should be given specific attention in environmental monitoring programs and reclamation projects due to the scale and increasing rate of oil production in the ABS region. Those measurements will require strict attention to the unique analytical challenges posed by Se, including the need for the low limits of detection necessary to provide meaningful information on its abundance in environmental media.

3.6 References

Addison, P.A., Puckett, K.J., 1980. Deposition of atmospheric pollutants as measured by lichen element content in the Athabasca oil sands area. Can. J. Bot. 58, 2323–2334.

Alberta Energy Regulator, 2017. ST98: 2017 Alberta’s Energy Reserves & Supply/Demand

Outlook. http://www1.aer.ca/st98/data/executive_summary/ST98-2017_Executive_Summary.pdf; 2017 [accessed 12.19.2017].

Andren, A.W., Klein, D.H., Talmi, Y., 1975. Selenium in coal-fired steam plant emissions. Environ. Sci. Technol. 9, 856–858.

Beach, L.K., Shewmaker, J.E., 1957. The nature of vanadium in petroleum. Ind. Eng. Chem. 49, 1157-1164.

Berrow, M., Ure, A., 1989. Geological materials and soils, in: Inhat, M., (Eds.), Occurrence and distribution of selenium. CRC Press., Florida, pp. 213–242.

B'Hymer, C., Caruso, J.A., 2006. Selenium speciation analysis using inductively coupled plasma-mass spectrometry. J. Chromatogr. A. 1114, 1–20.

Bicalho, B., Grant-Weaver, I., Sinn, C., Donner, M. W., Woodland, S., Pearson, G., Larter, S., Duke, John., Shotyk, W., 2017. Determination of ultratrace (< 0.1 mg/kg) elements in Athabasca bituminous sands mineral and bitumen fractions using inductively coupled plasma sector field mass spectrometry (ICP-SFMS). Fuel. 206, 248–257.

Bowen, H.J.M., 1979. Environmental chemistry of the elements. London; New York: Academic Press.

Champlin, J.B.F., Dunning, H.N., 1960. A geochemical investigation of the Athabasca bituminous sands. Econ. Geol. 55, 797–804.

Cutter, G.A., San Diego-McGlone, M. L. C., 1990. Temporal variability of selenium fluxes in San Francisco Bay. Sci. Total. Environ. 97, 235–50.

Garven, G., 1989. A hydrogeological model for the formation of the giant oil sands deposits of the western Canada sedimentary basin. Am. J. Sci. 289, 105–166.

Goldschmidt, V.M., 1937. The principles of distribution of chemical elements in minerals and rocks. J. Chem. Soc. 655–673.

Gosselin, P., Hrudey, S.E., Naeth, M.A. Plourde, A., Therrien, R., Van Der Kraak, G., Xu, Z., 2010. Environmental and health impacts of Canada's oil sands industry. The Royal Society of Canada (RSC), Ottawa, Ontario, Canada (414 pp). https://rsc-src.ca/sites/default/files/pdf/RSCreportcompletesecured9Mb_Mar28_11.pdf

Government of Alberta, 2004. The micronutrient and trace element status of forty-three soil quality benchmark sites in Alberta: results and summary. http://www1.agric.gov.ab.ca/$department/deptdocs.nsf/all/aesa8885 (accessed 9 December 2017).

Hamilton, S.J., 2002. Rationale for a tissue-based selenium criterion for aquatic life. Aquat. Toxicol. 57, 85–100.

Hamilton, S.J., 2003. Review of residue-based selenium toxicity thresholds for freshwater fish. Ecotoxicol. Environ. Saf. 56, 201–210.

Hamilton ,S.J., 2004. Review of selenium toxicity in the aquatic food chain. Sci. Total. Environ. 326, 1–31.

Hargesheimer, E.E., Apps, M.J., Malhotra, S.S., 1980. Determination of vanadium in jack pine needles using neutron activation analysis. Environ. Technol. Lett. 1, 273–282.

Hitchon, B., Filby, R., Shah, K., 1975. Geochemistry of trace elements in crude oils, Alberta, Canada, in: Yen, T., (Eds.), The role of trace metals in petroleum. Ann Arbor Science., MI, pp. 111–121.

Hitchon, B., Filby, R.H., 1983. Geochemical studies – 1: trace elements in Alberta crude oils. Alberta. Research. Council. Open. File. Report. 1983-02. p. 38.

Hitchon, B., Filby, R.H., 1984. Use of trace elements for classification of crude oils into families– example from Alberta, Canada. Am. Assoc. Pet. Geologists. Bull. 68, 838–849.

Hosterman, J.W., Meyer, R.F., Palmer, C.A., Doughten, M.W., Anders, D.E., 1990. Chemistry and mineralogy of natural bitumens and heavy oils and their reservoir rocks from the United States, Canada, Trinidad and Tobago, and Venezuela. U.S. Geological. Survey. Circular. 1047. p. 28.

Innes, E.D., Fear, J.V.D., 1967. Canada's first commercial tar sands development. 7th. World. Petrol. Congr. Proc. 3, 633–643.

Jackson, B.P., Liba, A., Nelson, J., 2015. Advantages of reaction cell ICP-MS on doubly charged interferences for arsenic and selenium analysis in foods. J. Anal. At. Spectrom. 30, 1179–1183.

Jacobs, F.S., Filby, R.H., 1983. Solvent extraction of oil-sand components for determination of trace elements by neutron activation analysis. Anal. Chem. 55, 74–77.

Jervis, R.E., Richard Ho, K.L,, Tiefenbach, B., 1982. Trace impurities in Canadian oil-sands, coals and petroleum products and their fate during extraction, up-grading and combustion. J. Radioanal. Chem. 71, 225–241.

Jia, B., 2010. Distribution of oil sands formation water in bitumen froth. Thesis Edmonton: University of Alberta; 2010.

Kelly, E.N., Schindler, D.W., Hodson, P.V., Short, J.W., Radmanovich, R., Nielsen, C.C., 2010. Oil sands development contributes elements toxic at low concentrations to the Athabasca river and its tributaries. Proc. Natl. Acad. Sci. USA. 107, 16178–16183.

Larter, S.R., Head, I.M., 2014. Oil sands and heavy oil: origin and exploitation. Elements. 10, 277–283.

Lemly, D.A., 1998. Pathology of selenium poisoning in fish, in Frankenberger, W.T. Jr., Engberg, R.A. (Eds.) Environmental chemistry of selenium. Marcel Dekker, Inc. New York, NY, pp. 281–296.

Lemly, D.A., 1998. Pathology of selenium poisoning in fish, in Frankenberger, W.T. Jr., Engberg, R.A. (Eds.) Environmental chemistry of selenium. Marcel Dekker, Inc. New York, NY, pp. 281–296.

Liu, P., Shi, Q., Chung, K.H., Zhang, Y., Pan, N., Zhao, S., Xu, C., 2010. Molecular characterization of sulfur compounds in Venezuela crude oil and its SARA fractions by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. Energy. Fuels. 24, 5089–5096.

Lum, T., Leung, K.S., 2016. Strategies to overcome spectral interference in ICP-MS detection. J. Anal. At. Spectrom. 3, 1078–1088.

Mosher, B.W., Duce, R.A., 1987. A global atmospheric selenium budget. J. Geophys. Res. Atmos. 92, 13289–13298.

Mossop, G.D., 1980. Geology of the Athabasca oil sands. Science. 207, 145–152.

Mullan-Boudreau, G., Belland, R., Devito, K., Noernberg, T., Pelletier, R., Shotyk, W., 2017.

Sphagnum moss as an indicator of contemporary rates of atmospheric dust deposition in the Athabasca bituminous sands region. Environ. Sci. Technol. 51, 7422–7431.

Navarro-Alarcon, M., Cabrera-Vique, C., 2008. Selenium in food and the human body: a review. Sci. Total. Environ. 400, 115–141.

Nriagu, J.O., Wong, H.K., 1983. Selenium pollution of lakes near the smelters at Sudbury, Ontario. Nature. 301, 55–57.

Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature. 333, 134–139.

Nriagu, J.O., 1989. Global cycling of selenium, in: Inhat, M., (Eds.), Occurrence and distribution of selenium. Boca Raton. CRC Press., Florida, pp. 327–340.

Ohlendorf , H.M., Hothem, R.L., Bunck, C.M., Marois, K.C., 1990. Bioaccumulation of selenium in birds at Kesterson Reservoir, California. Arch. Environ. Contam. Toxicol. 19, 495–507.

Orr, W.L., 1978. Sulfur in heavy oils, oil sands and oil shales. Oil Sand Oil Shale Chem New York, Verlag Chemie 223–243.

Outridge, P.M., Scheuhammer, A.M., Fox, G.A., Braune, B.M., White, L.M., Gregorich, L.J., Keddy, C., 1999. An assessment of the potential hazards of environmental selenium for Canadian water birds. Environ. Rev. 7, 81–96.

Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environ. Rev. 9, 269–298.

Petrov, P.K., Charters, J.W., Wallschläger, D., 2012. Identification and determination of selenosulfate and selenocyanate in flue gas desulfurization waters. Environ. Sci. Technol. 46, 1716–1723.

Pettine, M., McDonald, T.J., Sohn, M., Anquandah, G.A.K., Zboril, R., Sharma, V.K., 2015. A critical review of selenium analysis in natural water samples. Trends. Environ. Anal. Chem. 5, 1–7.

Pollock, S.M., Goodarzi, F., Riediger, C.L., 2000. Mineralogical and elemental variation of coal from Alberta, Canada: an example from the no. 2 seam, genesee mine. Int. J. Coal. Geol. 43, 259–286.

Rahn, K.A., 1976. The chemical composition of the atmospheric aerosol: technical report. Graduate School of Oceanography, University of Rhode Island, Kinston, R.I., USA.

Rayman, M.P., 2000. The importance of selenium to human health. Lancet. 356, 233–241.

Riley, J.L., 1986. Laboratory methods for testing peat: Ontario peatland inventory project. Open File Report 5572. Ontario Geological Survey, Toronto. http://www.geologyontario.mndm.gov.on.ca/mndmfiles/pub/data/imaging/OFR5572/OFR5572.pdf; 1986 [accessed 27 December 2017].

Rudnick, R.L., Gao, S., 2003. The composition of the continental crust, in: Holland, H., Turekian, K., (Eds.), Treatise on geochemistry. Oxford: Elsevier-Pergamon., pp. 1-64.

Schindler, D., 2010. Tar sands need solid science. Nature. 468, 499–501.

Schindler, D.W., 2013. Water quality issues in the oil sands region of the lower Athabasca river, Alberta. Geosci. Canada. 40, 202–14.

Scott, J., Collins, G.A., Hodgson, G., 1954. Trace metals in the McMurray oil sands and other cretaceous reservoirs of Alberta. Can. Min. Metall. 57, 34–40.

Selby, D., 2005. Direct radiometric dating of hydrocarbon deposits using rhenium-osmium isotopes. Science. 308, 1293–1295.

Senior, C.L., Tyree, C.A., Meeks, N.D., Acharya, C., McCain, J.D., Cushing, K.M., 2015. Selenium partitioning and removal across a wet FGD scrubber at a coal-fired power plant. Envrion. Sci. Technol. 49, 14376–14382.

Shendrikar, A.D., Ensor, D.S., Cowent, S.J., Woffindei, G.J., 1983. Size-dependent penetration of trace elements through a utility baghouse. Atmos. Environ. 17, 1411–1421.

Steudel, R., Strauss, E.M., Papavassiliou, M., Brätter, P., Gatschke, W., 1986. Selenium content of naturally occurring elemental sulfur, of industrially produced sulfur and of the mineral selensulfur. Phosphorus. Sulfur. 29, 17–21.

Takamura, K., 1982. Microscopic structure of Athabasca oil sand. Can. J. Chem. Eng. 60, 538–545.

White, A.F., Dubrovsky, N.M., 1994. Chemical oxidation–reduction controls on selenium mobility in groundwater systems, in: Frankenberger, W.T., Benson, S., (Eds.), Selenium in the environment. Marcel Dekker Inc., New York, pp. 185–221.

Wieder, R.K., Vile, M.A., Scott, K.D., Albright, C.M., McMillen, K.J., Vitt, D.H., Fenn, M. E., 2016. Differential effects of high atmospheric N and S deposition on bog plant/lichen tissue and porewater chemistry across the Athabasca oil sands region. Environ. Sci. Technol. 50, 12630–12640.

Young, T.G., Finley, K., Adams, W.J., Besser, J., Hopkins, W.D., Jolley, D., McNaughton, E., Presser, T.S., Shaw, P., Unrine, J., 2010. What you need to know about selenium, in: Chapman, P.M., Adams, W.J., Brooks, M.L., Delos, C.G., Luoma, S.N., Maher, W.A., Ohlendorf, H.M., Presser, T.S., Shaw, D.P. (Eds.), Ecological assessment of selenium in the aquatic environment. CRC Press, Taylor & Francis Group., Boca Raton, pp. 7-46.

Zhang, Y., Shotyk, W., Zaccone, C., Noernberg, T., Pelletier, R., Bicalho, B., Froese, D.G., Davies, L., Martin, J.W. 2016. Airborne petcoke dust is a major source of polycyclic aromatic hydrocarbons in the Athabasca oil sands region. Environ. Sci. Technol. 50, 1711–1720.

3.7 Figures

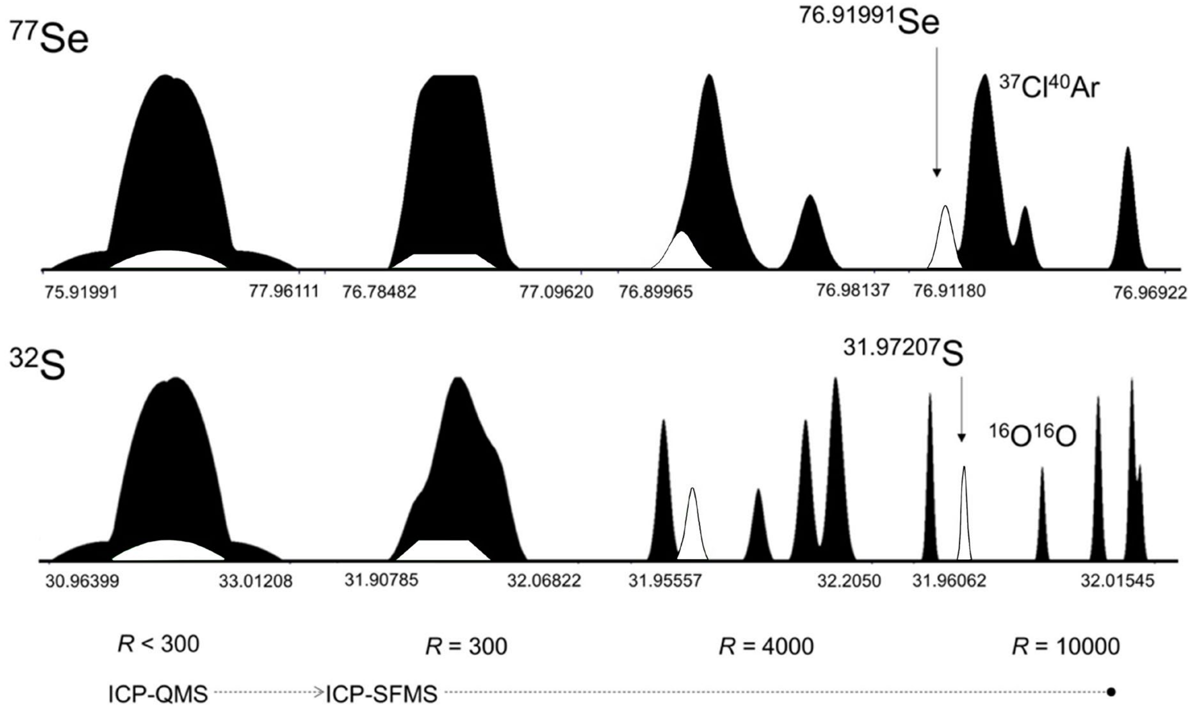

Figure 3.1 Mass spectrometric determination of Se and S (white peaks) as a function of the mass analyzer resolution (R = m/Δm) power. Multiple near isobaric interferences (black peaks) need to be investigated and resolved before Se and S can be determined accurately using ICP-MS. From left to right: the detection of Se and S enabled by a single quadrupole mass spectrometer (QMS) next to the detection of Se and S enabled by a sector field mass spectrometer (SFMS) in low (R = 300), medium (R = 4000) and high (R = 10000) mass resolution modes. Adapted from Element2 Tour and Interferences (Demo Version 3.2), Thermo Electron, Bremen, Germany.

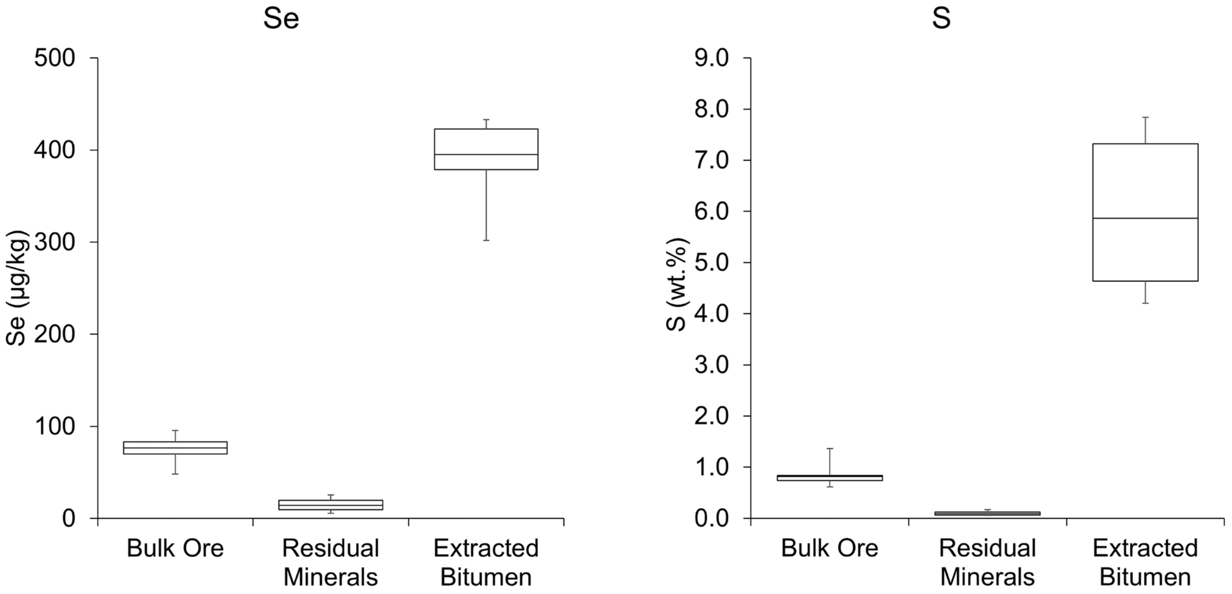

Figure 3.2 Box-and-whisker plots of absolute concentrations of Se and S in the studied ABS samples and subsamples (each n = 7). Plot whiskers denote concentration range, box length represents the upper and lower quartiles, and the horizontal line within the box represents the median. From left to right: native samples (bulk ore), the mineral fraction left over after bitumen removal using toluene (residual minerals) and the separated bitumen (extracted bitumen). Bulk ores consisted of 86 ± 4 wt.% mineral matter and 12 ± 3 wt.% bitumen.

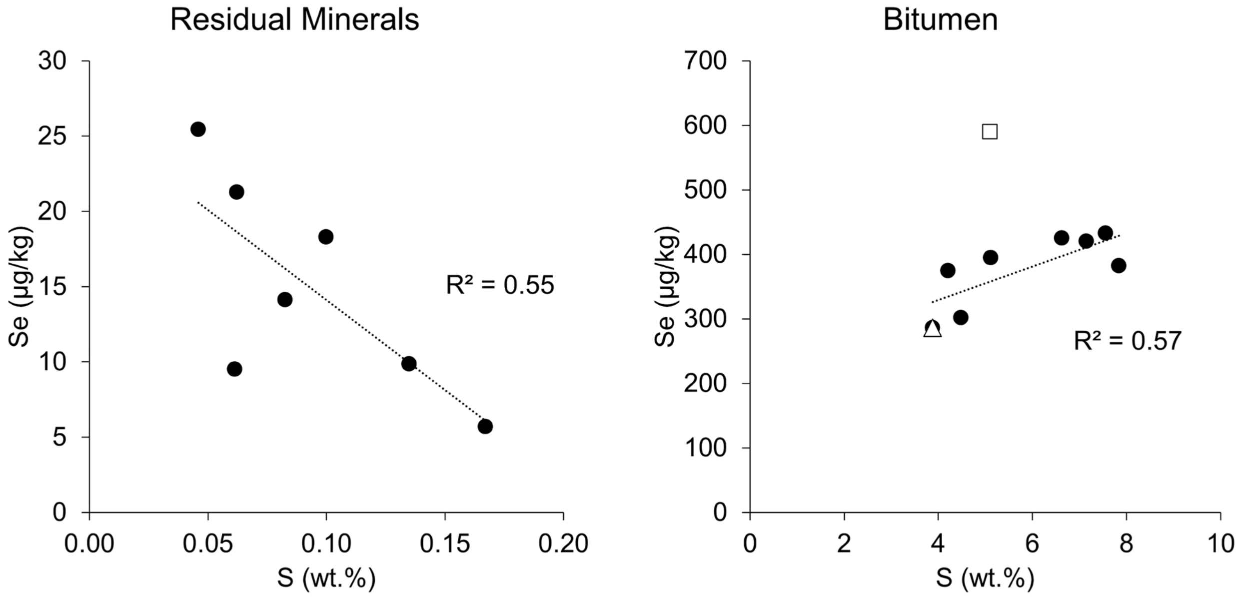

Figure 3.3 Correlations of Se and S concentrations in ABS ore mineral and bitumen subsamples. Apparent trends illustrate a negative correlation for Se and S in the mineral matter and a positive correlation for these elements in the bitumen. In addition to current results (●), previous results by Hitchon and Filby 1983 (Δ) and by Hosterman et al.1990 (□) for Se and S in the ABS bitumen are shown for comparison.

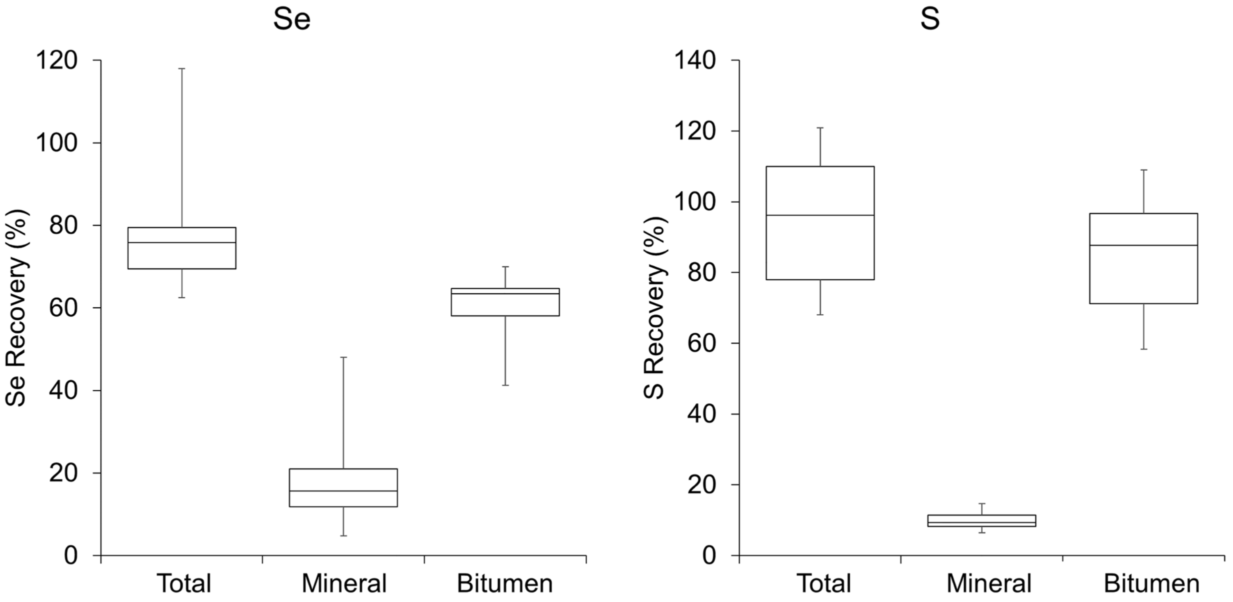

Figure 3.4 Box-and-whisker plots showing relative abundance of Se and S in the studied ABS samples (n = 7). Plot whiskers denote concentration range, box length represents the upper and lower quartiles, and the horizontal line within the box represents the median. From left to right: relative abundance of the element content recovered from bulk ore, mineral fraction, and bitumen fraction.

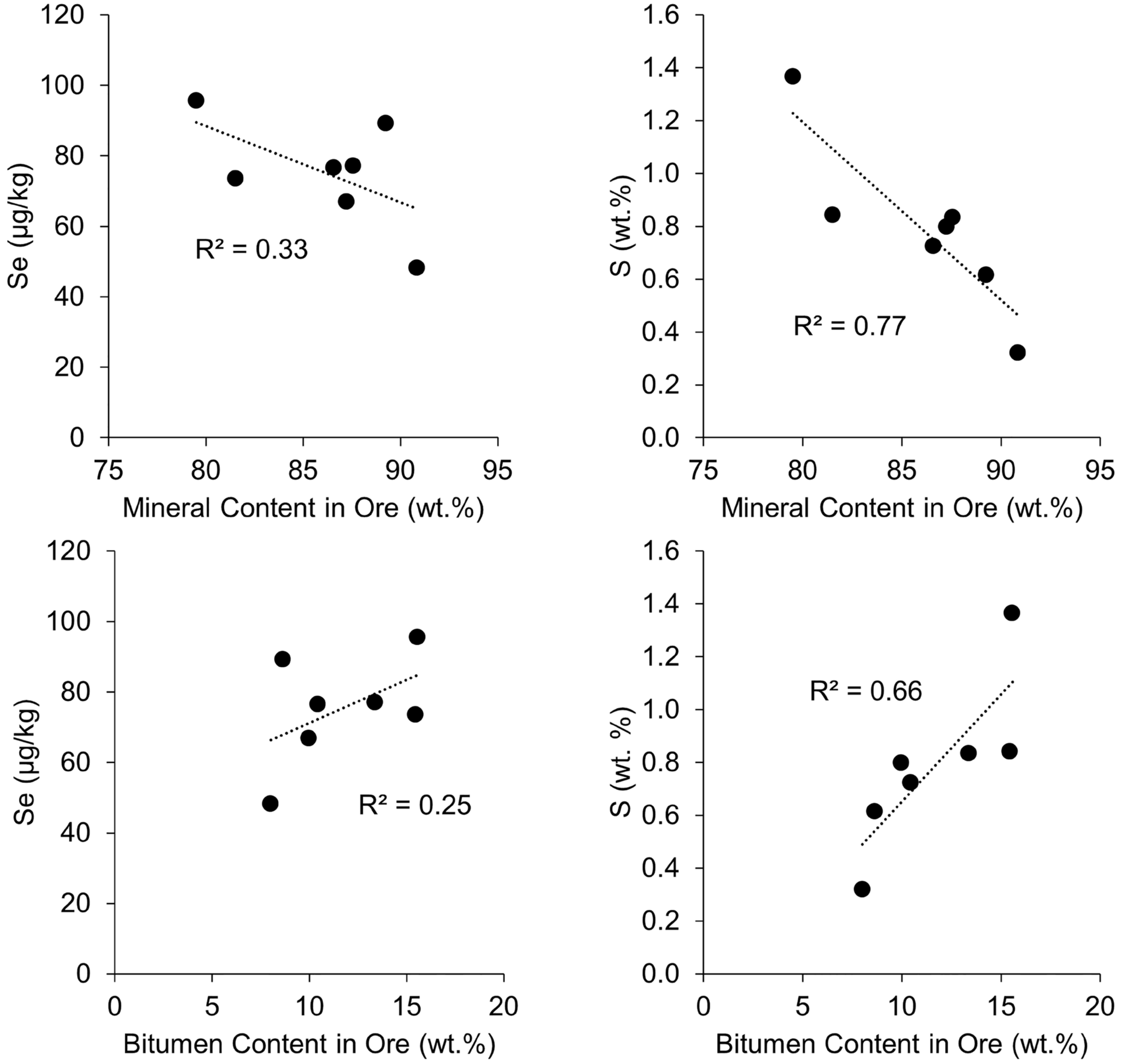

Figure 3.5 Variation in Se and S concentrations versus ore grade (expressed both in terms of bitumen and mineral matter abundance). Although the number of samples is small (n = 7), the concentrations of Se and S tend to increase with the ore grade.

3.9 Tables

Table 3.1 ICP-SFMS data acquisition parameters

Parameter	Settings	
Forward power	1100 W	
Argon flow rates	Coolant gas: 16.0 l/min; Auxiliary gas: 1.0 l/min; Sample gas: 1.1 l/min	
Sample uptake rate	30 µL/min	
Take up time	120 s	
Wash time	120 s	
Acquisition mode	High resolution (10,000)	
Isotope (samples)	^{32}S (100)	^{77}Se (200)
Sample time (ms)	5	5
Mass window (%)	200	125
Integration window (%)	70	50
Run x Passes	3 x 10	3 x 10

Table 3.2 Determination of Se and S in Standard Reference Materials (SRM) using ICP-SFMS and HG-AFS.

Element	Analytical Technique	IDL[a] (ng/ml)	MDL[b] (mg/kg)	SRM[c]	Nominal value	Digestion method	Recovery (%)	(n)[d]
Se	ICP-SFMS	0.04	0.02	OGS 1878P	0.6 ± 0.2 mg/kg	HNO_3-HBF_4	106 ± 2	2
				NIST 1635	0.9 ± 0.3 mg/kg	”	107 ± 13	4
				NIST 2711	1.5 ± 0.1 mg/kg	”	62 ± 4	3
				”	”	HF-HNO_3	71	1
Se	HG-AFS	0.003	0.04	OGS 1878P	0.6 ± 0.2 mg/kg	HNO_3-HBF_4	117	1
				NIST 1635	0.9 ± 0.3 mg/kg	”	95	1
				NIST 2711	1.5 ± 0.1 mg/kg	”	78	1
				”	”	HF-HNO_3	90 ± 3	2
S	ICP-SFMS	5.8	58	NIST 1635	0.4 ± 0.002 %	HNO_3-HBF_4	107 ± 13	4
				NIST 2711	0.04 ± 0.01 %	”	111 ± 10	4
				”	”	HF-HNO_3	91 ± 5	3

[a] Instrument detection limit calculated as follows: (BLK cps AVG + 3*BLK cps SD)*[STD]/(STD cps – BLK cps AVG), where BLK = blank (2% HNO_3); cps = counts per second; AVG = average; SD = standard deviation; [STD] = nominal concentration of the element in a primary standard;(STD cps – BLK cps AVG) = intensity difference between STD and BLK. Method detection limit calculated as follows: IDL (m/v)*sample dilution factor, as per method. [c] Ontario Geological Survey Peat (1878); NIST 1635 Coal Subbituminous; NIST 2711 Montana Soil. [d] n = number of replicates analyzed along current ABS samples and subsamples.

Table 3.3 Concentrations of Se and S in ABS ore samples[a] and subsamples[b] (separated bitumen and minerals), as determined using HG-AFS, ICP-OES and ICP-SFMS.

	Min	Med	Max	Min	Med	Max
Se		HG-AFS			ICP-SFMS	
	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
Bulk	48.9	83.4	108.5	47.5	66.7	82.6
Bitumen	345.9	463.2	504.7	257.4	326.6	425.2
Mineral	4.4	13.4	26.8	5.6	15.0	24.1
Mineral-HF	na	na	na	9.8	22.1	41.9
S		ICP-OES			ICP-SFMS	
	%	%	%	%	%	%
Bulk	0.3	0.7	1.4	0.3	0.8	1.3
Bitumen	3.4	4.9	5.3	4.0	8.2	10.4
Mineral	0.04	0.08	0.15	0.05	0.09	0.18
Mineral-HF	0.02	0.06	0.31	na	na	na

[a]Experimental set = 7 sample units representing different ore locations. [b]Each n = 7. Mineral-HF refers to the digestion method using HF and HNO_3 instead of HBF_4 and HNO_3 (Minerals). "na" denotes samples with concentrations below the MDL.

Table 3.4 Average Se concentrations in some relevant geological materials. Where necessary and available, the range is provided in parenthesis next to the average concentration.

Material type	**Concentration (mg/kg)**	**Source**
Upper Continental Crust	0.09	Rudnick and Gao, 2003
Soil	0.4	Bowen, 1979
Soil organic matter	0.2	Nriagu, 1989
Coal	3.4	Nriagu, 1989
Oil shale	2.3	Nriagu, 1989
Crude oil	0.2	Nriagu, 1989
Alberta soil (0-15 cm)	0.48 (0.1-1.6)	Government of Alberta, 2004
Alberta soil (15-30 cm)	0.47 (0.001-2.3	Government of Alberta, 2004
[a]Genesee Coal	0.77 (0.64-1.24)	Pollock et al., 2000
[b]Bitumen (ABS) #43	0.29	Hitchon and Filby, 1983
[b]Bitumen (ABS) #94	0.52	Hitchon and Filby, 1983
[b]Bitumen (ABS)	0.59	Hosterman, 1990
[b]Bitumen (ABS)	0.4	This study

[a]Se value refers to an average of blends (1-5) for the No. 2 seam. [b]Bitumen refers to samples where mineral particles have been extracted.

4.0 A RAPID AND SENSITIVE IC-ICP-MS METHOD FOR DETERMINING SELENIUM SPECIATION IN NATURAL WATERS‡

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‡ A version of this chapter has been published as: A rapid and sensitive IC-ICP-MS method for determining selenium speciation in natural waters", *Canadian Journal of Chemistry*, 2018, Vol. 96, 795-802. The published journal article is provided in Appendix III.

4.1 Introduction

The chemistry of selenium (Se) in the environment has long captured the interest of researchers from a variety of disciplines. Given that it is an essential trace element for humans and animals (Rayman, 2000) and is also sometimes an environmental toxin (Hamilton, 2004), understanding the complex behavior of Se in environmental systems is of great importance. Depending on biogeochemical processes and redox conditions, Se can exist in a variety of oxidation states (-II, -I, 0, IV, VI) with greater mobility at higher redox potentials (Winkel et al., 2015). Owing to its ability to bio-accumulate in the food chain, Se concentrations in water deemed harmful to aquatic life are low relative to other elements (e.g., Fe, Mo, Zn, Cu) essential to life (Hamilton, 2002, 2004). Surface water (oxic to suboxic environments) where Se concentrations exceed guideline values (typically $\geq 1\ \mu g\ L^{-1}$) are generally attributed to a direct geologic or anthropogenic Se source, with the resulting predominant forms being the oxyanions selenite (SeO_3^{2-} or Se^{IV}), and selenate (SeO_4^{2-} or Se^{VI}) (Maher et al., 2009; Wallschläger and Feldmann, 2010). Reports of other inorganic and organic forms, in addition to the ubiquitous Se^{IV} and Se^{VI}, have been described in aquatic systems that are biologically productive or impacted by industrial effluents (e.g., natural organic matter containing Se, Se-NOM; selenocyanate, $SeCN^-$) (Fernández-Martínez and Charlet, 2009;Wallschläger and Feldmann, 2010). Selenium species are also known to differ with respect to bioavailability (Riedel et al., 1991). Therefore, the fundamental challenge to understand Se in the aquatic environment is the low concentration combined with the need to understand its chemical speciation.

Numerous methods have been developed to determine Se species, (Conde and Sanz Alaejos, 1997; Pettine et al., 2015) with the bulk of conventional methods utilizing the hydride forming ability of Se^{IV}. Following the pioneering work of Cutter (1978, 1982), a large portion of Se speciation analyses of water are based on a selective sequential hydride generation (SSHG) approach (Wallschläger and Feldmann, 2010). That technique takes advantage of the fact that only Se^{IV} forms a hydride; therefore, samples can be analyzed directly for Se^{IV} and then chemically altered through online or offline oxidation and reduction reactions to obtain Se^{VI} and reduced Se species by difference. The SSHG method is a first step towards the chemical speciation and has some advantages. (*i*) It can be used to incorporate colloidal and particulate Se (Cutter, 1985), (*ii*) it is effective for saline waters (e.g., seawater) to bypass chromatographic interferences, and (*iii*) when coupled with appropriate detection technique such as atomic fluorescence, it has excellent sensitivity, even at low concentrations (limit of detection (LOD), typically <10 ng L^{-1}). Modifications to this method have also been made to limit bias resulting from the decomposition of organo-Se molecules during heat-acid reflux (Chen et al., 2005) but there is still considerable potential for large errors to be made when determining speciation by difference (Wallschläger and Feldmann, 2010). SSHG procedures also call for large quantities of sample with considerable time and effort to perform the necessary redox reactions, with each step and sample type requiring detailed quality control. Fundamentally, the greatest disadvantage of any version of the SSHG approach is the inability to identify species within the “reduced Se” (primarily organic) fraction.

Ion chromatography (IC) coupled with inductively coupled plasma mass spectrometry (ICP-MS) is a powerful analytical tool that has been used successfully for identifying a wide variety of Se containing compounds based on their retention times (Bird et al., 1997; Kölbl et al., 1993; Pedersen and Larsen, 1997). For Se analyses, however, conventional quadrupole ICP-MS operation suffers from inadequate sensitivity for concentrations typical of natural waters. This is due to the high ionization potential of Se in the plasma, as well as isobaric and polyatomic interferences (Lum and Leung, 2016; Pettine et al., 2015). Selenium has six stable isotopes (^{74}Se, 0.87%; ^{76}Se, 9.02%; ^{77}Se, 0.58%; ^{78}Se, 23.52%; ^{80}Se, 49.82%; ^{82}Se, 9.19%), which adds complexity to the analysis (Haygarth, 1994). The greatest sensitivity is achieved by monitoring the most abundant isotope (^{80}Se); however, the use of argon (Ar) gas in ICP-MS operation results in the dimer $^{40}Ar^{2+}$ ($m/z = 80$) interference (B'Hymer and Caruso, 2006; Pettine et al., 2015). Using a reaction gas such as hydrogen (H_2) or methane (CH_4) eliminates the interference by $^{40}Ar^{2+}$ and greatly increases sensitivity by reliably quantifying ^{80}Se (B'Hymer and Caruso, 2006).

Although using a chromatographic approach offers greater detail to identify the species that are present, methods for coupling these instruments and achieving the necessary detection limits (parts per trillion or lower) for natural waters are still limited in the literature and may not be practical for routine monitoring due to long run times. Adequate sensitivity is achievable with ICP-MS, but appropriate mobile and stationary phases must also be considered. To provide analysts with a rapid and sensitive method for Se speciation in freshwater, we tested the use of dilute nitric acid (HNO_3) as a mobile phase. This offers some advantages to other mobile phases with basic or near-neutral pH, as follows: (*i*) it prevents precipitation of iron (Fe) and aluminum (Al) (hydr)-oxides in samples taken from acidic (Floor et al., 2011) or anoxic waters (Gorny et al., 2015), (*ii*) it eliminates the need for salt or organic solvent-based eluents that can also be undesirable for interfacing IC with ICP-MS, thus improving detection limits, as well as reducing maintenance costs (Wang et al., 2010), and (*iii*) HNO_3 is already commonly used for ICP-MS analyses and can be distilled and purified to the extent necessary to achieve the desired background concentrations (blank values).

4.2 Experimental

4.2.1 Chemicals and reagents

To prepare standard solutions for selenium speciation, Se compounds were purchased from Sigma-Aldrich and dissolved in high purity (18.2 cm) water (Barnstead Nanopure, Thermo Scientific). Individual stock solutions had concentrations of 2000 mg L^{-1} for sodium selenite (Se^{IV}; 99%; Cat. #S3876) and sodium selenate decahydrate (Se^{VI}; 99.999% — trace metal basis; Cat. #450294), whereas organic Se species were prepared with a concentration of 500 mg L^{-1} using seleno-DL-methionine (SeMet; ≥99%; Cat. #S3876) and Se-(methyl)selenocysteine hydrochloride (MeSeCys; ≥95%; Cat. #M6680). Working standards (20 to 400 ng L^{-1}) were prepared daily from the stock solutions by diluting with high purity water inside a HEPA filtered clean air cabinet. Mass calibration standard solutions for total Se analysis were prepared by diluting SPEX CertiPrep Instrument Calibration Standard 2 (100 mg Se L^{-1} stock) with high purity water and acidifying final calibration solutions (0.1 to 2 g L^{-1}) to 1% HNO_3. A multi-element Internal Standard 1 was also diluted from its original concentration (10 mg L^{-1}) to 2 g L^{-1} with high purity water and acidified to 1% HNO_3.

TraceMetal grade HNO_3 purchased from Fisher Scientific (Cat. #A509P212) was used to prepare the mobile phase and acidify solutions analyzed for total concentration of Se. Hydrochloric acid (HCl) used for preserving samples and determining blank values was either TraceSELECT (Sigma-Aldrich, Cat. #72787) or Optima (Fisher Scientific, Cat. #A466-500) HCl.

4.2.2 Instrument setup for Se speciation and total Se analysis

A high performance ion chromatograph (HPIC; Thermo Scientific Dionex ICS-5000^{+}) equipped with a Dionex IonPac AS7 anion exchange column (inner diameter, 4 mm; length, 250 mm) and AG7 guard column (inner diameter, 4 mm; length, 50 mm) was used to separate different Se species. The system included a single gradient pump, temperature-controlled oven module, degasser, and AS-AP auto-sampler equipped with a 25 L sample loop. The mobile phase was prepared in a stepwise concentration gradient as follows: 0–2 min (50 mmol L^{-1} HNO_3), 2–4 min (400 mmol L^{-1} HNO_3), and 4–5 min (50 mmol L^{-1} HNO_3). It is important to note that the potential corrosion of metallic parts by a dilute HNO_3 mobile phase is not problematic in this system due to the use of PEEK (polyetheretherketone) instead of steel, thus allowing for a "metal-free" flow path. This IC system was connected to a single quadrupole ICP-MS (iCap Q, Thermo Scientific) operated in CRC (chemical reaction cell) mode. After passing through the column, the mobile phase was introduced to the ICP-MS at a fixed flow rate (1.0 mL min^{-1}) through a MicroFlow PFA-LC zero dead volume nebulizer into a quartz cyclonic spray chamber cooled to 3 °C. Peak areas of Se species were integrated using Dionex Chromeleon 7 software.

Preliminary work for the chromatographic conditions presented above is also described by Javed (2015). Two important modifications were made to that method and are as follows: (i) the flow rate of the mobile phase was kept constant (1 mL min^{-1}) to keep the optimized aerosol size and introduction rate consistent with tuned parameters and (ii) H_2 gas was used as a reaction gas in place of He (collision gas) in the pressurized cell to enable the accurate quantification of ^{80}Se. The flow rate of H_2 was adjusted until low background signals were achieved for ^{80}Se, without any substantial loss of sensitivity. The isotopes ^{77}Se and ^{78}Se were monitored during analysis to compare differences in the accuracy and precision and to assess the role of relevant polyatomic interferences such as $^{79}Br^{1}H^{+}$ (see Results and Discussion).

The same ICP-MS was used for total Se analyses; however in this case, the instrument was equipped with a CETAC ASX-520 autosampler and PFA-ST MicroFlow Nebulizer. Total Se in water samples (described below) was determined under kinetic energy discrimination (KED) mode with He as a collision gas. Quantification was based on the average of three main runs with 25 sweeps using ^{78}Se. The internal standard solution was introduced continuously online through a PEEK T-mixing piece. Scandium (Sc), indium (In), and holmium (Ho) from the internal standard solution were monitored and used to account for any instrumental drift on the basis of interpolation. Corrections made by software to account instrument drift were minor, with no substantial changes in the internal standard observed during analyses (±10%). Gases (Ar, He, H_2) used for (IC)-ICP-MS analysis were of ultra-high purity (Praxair, purity 5.0). A summary of relevant operating information for both total Se and Se speciation is provided in Table 4.1.

4.2.3 Quality control and method validation

Method accuracy for Se speciation and total Se concentrations was evaluated by analyzing certified standard reference material (SRM; NIST 1640a: Trace Elements in Natural Water; Se = 20.13 ± 0.17 g L^{-1}), whereas precision was assessed by analyzing samples in triplicate. For routine ICP-MS quality control, instrument blanks (1% HNO_3) and check standards were used. Multiple blanks containing either high purity water only or a dilute mixture of HCl and high purity water (0.8% HCl) were also included to identify any possible contamination and evaluate spectral interference related to the increased chloride concentration from HCl. To further study any interconversion of Se species during separation in the IC or potential chromatographic interferences (e.g., competition from competing ions), an acidified river water sample was also chosen and spiked with Se^{IV} and Se^{VI}.

As an additional method for verification of Se^{IV} and Se^{VI}, acidified blank (0.8% HCl) samples (n = 3) were spiked with Se^{IV} and analyzed using both IC-ICP-MS and HG-AFS. Details for HG-AFS analysis are provided in the Supplementary data. Briefly, samples spiked at 200 ng Se^{IV} L^{-1} were acidified with HCl to 3.6 mol L^{-1}, diluted (5× dilution), and analyzed directly with a PS Analytical 10.055 (Millennium Excalibur) HG-AFS system. During the online chemical reduction with sodium borohydride, only Se^{IV} is capable of forming a gaseous hydride, and therefore, any Se signal is the result of Se^{IV} in the sample.

4.2.4 Method application: river and rainwater sampling

The method was applied to natural water samples collected from three different rivers and one sample of urban rainwater. The purpose was to demonstrate the applicability of the method on chemically diverse natural waters containing low concentrations of Se. The determined chemical speciation is compared with the total concentrations and with the results available in the literature where different Se speciation methods have been applied to similar water types (e.g., snow, rain, river water) (Conde and Sanz Alaejos, 1997). For river water, samples from the shore of the North Saskatchewan River in the city of Edmonton (Alberta, Canada) were collected in June 2016. Four samples were syringe filtered into polypropylene (PP) centrifuge tubes (15 mL) on-site using 30 mL all plastic syringes (Thermo Scientific, Cat. #S7510) and 0.22 µm polytetrafluoroethylene (PTFE) disk filters (Thermo Scientific; 30 mm; Cat. #033911E). Samples were analyzed on the same day; samples for chemical speciation of Se (n = 3) were analyzed directly (i.e., filtered only) without any further treatment, whereas the sample (n = 1) for total Se was acidified with HNO_3 (1% v/v) before analysis. A water sample was also collected from the shore of Maligne River, Jasper National Park, Alberta, Canada, and was immediately syringe filtered using 30 mL plastic syringes (see above) and 0.45 µm PTFE disk filters (Thermo Scientific™; 30 mm; Cat. #03-391-1C) into 125 mL acid-cleaned fluorinated polyethylene (FLPE) bottle containing 1 mL of HCl as preservative. The sample was stored at 4 °C until analysis was performed. The Athabasca River in northern Alberta, Canada was also sampled in October 2015. Water sample collection and handling used the same materials and procedure as described above for Maligne River but were collected from the bow of a small boat anchored in the middle of the river. This sample is unique in that it was collected relatively close to the large surface mines of the Athabasca bituminous (oil) sands. Urban rainwater was collected in an acid-cleaned 125 mL borosilicate glass bottle (Wheaton; 219815) with Teflon lined lid during a rain event at the University of Alberta, Edmonton, on 30 June 2016. The sample was immediately filtered (0.22 μm) using a 30 mL plastic syringe (see above) and PTFE disk filters into three separate vials for analysis on the same day (< 30 min from collection). Only a small portion of the original sample was saved for Se speciation analysis and total Se was not analyzed.

4.3 Results and discussion

4.3.1 Peak resolution of Se species and differences in isotopic sensitivity with corresponding detection limits

Inorganic Se species (Se^{IV} and Se^{VI}) maintained excellent peak shape and resolution at low concentrations when a standard solution containing inorganic Se species (200 ng L^{-1}) was injected into the IC-ICP-MS (Fig. 4.1A). Similar to the behavior of arsenite (As^{III}) in a method using a HNO_3 mobile phase and AS7 column for arsenic speciation (Gorny et al., 2015), the low mobile phase pH and acid dissociation constant of Se^{IV} ($pKa^1 = 2.46$) (Li et al., 2008) explains its quick movement through the column with little retention. Selenate required a stronger HNO_3 eluent concentration (400 mmol L^{-1}) to elute in a suitable amount of time. An additional 60 s of run time using 50 mmol L^{-1} HNO_3 mobile phase was added following the elution of Se^{VI} to re-condition the column and prepare for the next sample. After adequate separation and sensitivity was achieved for the inorganic Se species, the method was thoroughly tested for potential interferences (see below). Because the predominant species in aquatic systems tend to be Se^{IV} and Se^{VI}, the method was optimized for those species. However, to evaluate its performance in samples that contain organo-Se species, two selenoamino acids (SeMet and MeSeCys) were also tested. This is important because Se^{IV} is passing through the column with little interaction with the stationary phase (presumably in the void volume) and an analytical artefact is plausible if there are other Se species that do not interact with the stationary phase. With recent evidence of organo-Se species in ultra-trace quantities in biologically productive waters (Leblanc et al., 2016; Leblanc and Wallschläger, 2016), two selenoamino acids (SeMet and MeSeCys) were also tested using the same instrumental conditions. Although effective for the oxyanions Se^{IV} and Se^{VI}, the analysis of selenoamino acids by ion exchange chromatography is significantly more challenging; this is in part due to the zwitterionic nature of amino acids. For example, at the low pH (<2) of mobile phase used here, SeMet would be present as positively charged cation (Pedersen and Larsen, 1997; Potin-Gautier et al., 1993) and may not be suitable for analysis with an anionic exchange column. However, despite being developed as a strong anion exchange column for polyvalent species (Weiss, 2004), the IonPac AG7 and AS7 are known for both cation and anion exchange capability due to a sulfonic surface coating and an outer layer of submicron anion exchange MicroBeads with alkyl quaternary ammonium functional groups (Xing and Beauchemin, 2010); this is in addition to other retention mechanisms such as molecule and stationary phase polarity, as the stationary phase is hydrophobic. With these processes in mind, simultaneous determination of cationic and anionic Se species using this setup was deemed possible. The results showed that SeMet and MeSeCys had a relatively high affinity for the stationary phase and eluted in a short time (<5 min) with consistent peak shapes and good separation (Fig. 4.1B); however, baseline separation between Se^{VI} and SeMet was not obtained. In an attempt to gain additional resolution between Se^{VI} and SeMet, the eluent strength was decreased to 300 mmol L^{-1} and then to 100 mmol L^{-1}. These manipulations did not yield greater peak resolution and instead showed increased retention times and produced an undesirable peak shape compared with the desired Gaussian peak shape (data not shown). Analysis of calibration standards with different concentrations yielded consistent but considerable differences in sensitivity for all species among the three measured isotopes, with the ranking of most sensitive to least sensitive being $^{80}Se > ^{78}Se > ^{77}Se$ (see Fig. 4.1 for example). The difference in signal intensity of ^{80}Se from ^{77}Se and ^{78}Se was approximately two and five times, respectively (Table 4.2). As mentioned above, this sensitivity was directly related to the natural abundance of each isotope. The LOD and limit of quantification (LOQ) were also calculated based on 3 and 10 times the standard deviation of eight blanks (n = 8), respectively. These values were assessed experimentally by analyzing a 20 ng L^{-1} and a 50 ng L^{-1} standard five times each. Overall, the accuracy and precision of the measured standards were representative of the calculated LODs and LOQs (Table 4.2). Between the three isotopes, ^{80}Se had the lowest overall LODs and produced excellent accuracy and precision at 20 and 50 ng L^{-1} concentrations. Isotope ^{78}Se also produced good overall results and is beneficial to include in the Se analysis for critically evaluating the data for potential interferences (see below). Due to the relatively poor results of ^{77}Se, this isotope will not be discussed in detail; however, it is still useful in the data evaluation stages to distinguish Se from interferences. The importance of using a reaction cell gas (H_2) is further highlighted by an observed increase in sensitivity compared with the previous method that utilized He collision cell performed on the same IC-ICP-MS (Javed, 2015). Using reaction gas and the method described here, the sensitivity was approximately 28 000 and 24 000 cps ppb^{-1} for Se^{IV} and Se^{VI}, respectively. Using He as a collision gas (and ^{78}Se for quantification), the sensitivity was approximately 1400 and 800 cps ppb^{-1} for Se^{IV} and Se^{VI}, respectively (Javed, 2015).

4.3.2 Bromine interference and influence of HCl preservation on Se species determination

Arguably one of the most critical challenges to overcome when using H_2 in a reaction cell of ICP-MS for Se measurements is the polyatomic interferences created by samples containing bromine (Br). Hydrogen gas reacts to form $^{79}Br^{1}H^{+}$ (m/z = 80) and $^{81}Br^{1}H^{+}$ (m/z = 82), and these polyatomic ions overlap with the commonly measured ^{80}Se and ^{82}Se isotopes. In this study, we observed the interference caused by $^{79}Br^{1}H^{+}$ on ^{80}Se; however, because Br (presumably as ionic bromide; Br^{-}) was effectively separated from three of the species in question, there was no influence on the results (Fig. 4.2). SeMet quantified using ^{80}Se was an exception to this, as it was observed to elute at approximately the same time as Br^{-}; therefore, ^{78}Se must be used for accurate quantification of SeMet. If the extremely high sensitivity offered by ^{80}Se is critical for the application, the use of deuterium (D_2) in place of H_2 as the reaction gas has been successful in overcoming the Br interference (Ogra et al., 2005) and might be a suitable alternative in this method as well. Silver cartridges are commonly used for removing unwanted Cl^{-}, Br^{-}, and I^{-} from samples but should not be used in this particular scenario, as it has been reported that these cartridges remove SeMet along with other halogen ions (Leblanc et al., 2016). The potential influence of HCl on this method was also evaluated for two main reasons: (i) it has been described as a preservative (in addition to refrigerated storage) used to stabilize Se^{IV} and Se^{VI} in water samples (Cutter, 1989) and (ii) it is known to contain trace amounts of Br. To test the potential influence from Br contamination, a solution of high purity water and HCl (TraceMetal grade) was analyzed (final HCl concentration 0.8%). This concentration was chosen because it maintains a pH < 2 required for preserving a wide variety of samples and is also appropriate for reliable ICP-MS analysis. Even with the high purity acid, Br contamination was evident from Br^{-} peaks (Supplementary Fig. 4.2A) and is enough to affect quantification of SeMet using ^{80}Se. The effect of HCl used to acidify water containing Se^{IV} and Se^{VI} speciation was assessed by adding the same proportion of HCl (0.8%). The change in sample pH did not affect retention times of either species and Br^{-} eluted after Se^{VI}, without interfering with Se^{VI} (Supplementary Fig. 4.2B). Based on these results, it is confirmed that HCl does not impact the analysis of Se^{IV} or Se^{VI}, and samples preserved with ≤0.8% HCl can be analyzed reliably using this method for Se^{IV} or Se^{VI} determination.

4.3.3 Method validation

The accuracy of measurements was partially determined by measuring certified standard reference material NIST 1640a (Trace Elements in Natural Water; Se = 20.13 ± 0.17 g L^{-1}) because there are currently no certified standard reference water samples for Se species. The SRM was diluted 50 times prior to analysis to bring the concentration into the range of the calibration standards. It was found that all measurable Se was present as Se^{IV} and the recovery for every measurement was within 10% of the certified total Se value. An independent method check of triplicate samples containing 200 ng L^{-1} of Se^{IV} measured by IC-ICP-MS and HG-AFS also yielded no observable difference (Fig. 4.5). To evaluate the recovery of spiked Se species from a natural water sample, an aliquot of the Athabasca River water (deemed to be the most chemically complex of the river samples) was spiked with 100 ng L^{-1} of Se^{IV} and Se^{VI}. Full recovery (>96%) was obtained for both species and repeatability of triplicate measurements had <3%RSD (Table 4.3). Accuracy of total Se measurements was assessed using NIST 1640a (diluted 50 times). Full details for all quality assurance and quality control are provided in Table 4.3.

4.3.4 Se speciation in natural waters

Water samples from three rivers and one rain event were used to evaluate the method. Figure 4.3 displays the Se speciation in those water samples, with each river having slightly different proportions of Se^{IV} and Se^{VI} relative to the total Se. Compared with the North Saskatchewan River (261 ng L^{-1}) and the Athabasca River (187 ng L^{-1}; Table 4), Maligne River contained the highest concentration of total Se (314 ng L^{-1}) and the most Se^{VI}. This observation is most likely a reflection of the local geology, as well as input from snow melt, which has been found to contain predominantly Se^{VI} (Alfthan et al., 1995; Papoff et al., 1998; Wang et al., 1994). The sum of inorganic species (Se^{IV} and Se^{VI}) accounted for most of the Se dissolved in North Saskatchewan River water (77%) and the Maligne River water (88%), but in the Athabasca River water, there was no detectable Se^{IV} and Se^{VI} was only 43% of the total Se (Table 4.4). The differences in proportion of inorganic Se could be related to the natural organic matter (NOM) content of the waters and the known ability of complex organic structures to incorporate Se (Wallschläger and Feldmann, 2010). Dominated by snow melt, the Maligne River likely contains low concentrations of NOM, whereas the Athabasca River is well known for its complex dissolved organic matter consisting of humic material, as well as bitumen derived compounds from bituminous sand outcrops (Headley et al., 2011; Ross et al., 2012). Rainwater was selected for analysis using this method because concentrations are usually low, and therefore, it requires the level of sensitivity demonstrated here. Moreover, because Se speciation in rainwater has been documented using various analytical techniques, it offers some additional insight into performance relative to other methods using a similar matrix. Unlike snow, Se^{IV} is commonly the predominant oxidation state in rainwater (Alfthan et al., 1995; Cutter, 1978; Wallschläger and London, 2004; Wang et al., 1994). The results for rainwater from Edmonton (Table 4.4) yielded similar chemical speciation results as those obtained by others that also employed a chromatography based Se speciation approach (Wallschläger and London, 2004). Rainwater (n = 3) from Edmonton contained 72 ± 5 ng L^{-1} Se^{IV} and 24 ± 5 ng L^{-1} Se^{VI}, whereas Seattle rain (n = 3) contained 59.4 ± 2.6 ng L^{-1} Se^{IV} and 16 ± 0.4 ng L^{-1} Se^{VI} (Wallschläger and London, 2004).

4.3.5 Method limitations

The method was found to be effective for water samples with a very simple matrix (low salinity and NOM concentrations), but its performance with more complex matrices was not critically evaluated. A comprehensive study is necessary to fully evaluate the effect of competing ions (e.g., sulfate) and any necessary sample clean-up steps. This would help expand its application toward samples with greater ionic strength such as seawater or industrial effluents. There is also an inherent disadvantage associated with using a low pH mobile phase on water samples containing abundant colloidal (i.e., <0.45 μm) organic and mineral particles. A more representative determination of the chemical speciation of Se (or other elements) requires methods of collection and analyses, including selection of the mobile phase, to mimic as closely as possible the environmental conditions at the time of sampling. Mobile phases used in chromatography typically are not tuned for site-specific parameters (e.g., pH, ionic strength), so there are risks of potential changes to the colloids such as partial dissolution, desorption, or dissociation. Therefore, a combination of other techniques for Se speciation such as asymmetrical flow-field flow fractionation (Cuss et al., 2017) would be worth investigating. To this point, we offer an example from some preliminary work on Se speciation in surface water of a peat bog in northern Saskatchewan, situated near a flooded uranium mine (Fig. 4.4). The total concentration of Se was 140 ng L^{-1}, with 40 ng L^{-1} Se^{VI} and no detectable Se^{IV}. As in the case of the Athabasca River, the form(s) of the unidentified Se fraction in these waters remains unknown; however, given the complex chemistry and array of organic compounds present in peat bog water, it may be possible that a significant portion of the Se was incorporated into NOM.

4.4 Conclusions

The purpose of this study was to develop a method that can quickly analyze Se species in natural water samples with high sensitivity using a dilute HNO_3 acid mobile phase. Although originally intended for Se^{IV} and Se^{VI}, it was also found to be effective for at least two organic species and, therefore, may also have applications for studying biological (e.g., plant or animal tissue) samples. The use of an acidic mobile phase may also be useful for anoxic groundwater or sediment pore water samples that require acid preservation to prevent the precipitation of Fe (hydr)-oxides. When coupled with single quadrupole ICP-MS using hydrogen in the reaction cell, the method has excellent sensitivity and allows for accurate and precise measurements below 50 ng Se L^{-1}. Given the simple mobile phase, low cost of consumables and rapid elution and detection of species of interest, this method will be a useful analytical option for monitoring agencies tasked with routinely determining Se speciation in freshwater environments.

4.5 Acknowledgements

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4.6 References

Alfthan, G., Wang, D., Aro, A., Soveri, J., 1995. The geochemistry of selenium in groundwaters in Finland. Sci. Total Environ. 162, 93-103.

B'Hymer, C., Caruso, J. A., 2006. Selenium speciation analysis using inductively coupled plasma-mass spectrometry. J. Chromatogr. A. 1114, 1-20.

Bird, S. M., Ge, H., Uden, P. C., Tyson, J. F., Block, E., Denoyer, E. J., 1997. High performance liquid chromatography of selenoamino acids and organo selenium compounds: speciation by inductively coupled plasma mass spectrometry. Chromatogr. A. 789, 349-359.

Chen, Y-W., Zhou, X-L., Tong, J., Truong, Y., Belzile, N., 2005. Photochemical behavior of inorganic and organic selenium compounds in various aqueous solutions. Anal. Chim. Acta, 545 (2): 149–157.

Conde, J. E., Sanz Alaejos, M., 1997. Selenium concentrations in natural and environmental water. Chem. Rev. 97, 1979-2004.

Cuss, C. W., Grant-Weaver, I., Shotyk, W., 2017. AF4-ICPMS with the 300 Da Membrane To

Resolve Metal-Bearing “Colloids” < 1 kDa: Optimization, Fractogram Deconvolution, and Advanced Quality Control. Anal. Chem. 89, 8027-8035.

Cutter, G. A., 1978. Species determination of selenium in natural waters. Anal. Chim. Acta. 98, 59-66.

Cutter, G. A., 1982. Selenium in reducing waters. Science. 217, 829-831.

Cutter, G. A., 1985. Determination of selenium speciation in biogenic particles and sediments. Anal. Chem. 57, 2951-2955.

Cutter, G. A. 1989. Fresh water systems, in: Ihnat. M, (Eds.), Occurrence and Distribution of Selenium. CRC Press., Boca Raton, Fla, pp. 243–262.

Fernández-Martínez, A., Charlet, L., 2009. Selenium environmental cycling and bioavailability: a structural chemist point of view. Rev. Environ. Sci. Biotechnol. 8, 81-110.

Floor, G. H.;, Iglesías, M., Román-Ross, G., Corvini, P. F., Lenz, M., 2011. Selenium speciation in acidic environmental samples: application to acid rain-soil interaction at Mount Etna volcano. Chemosphere. 84, 1664-1670.

Gorny, J., Dumoulin, D., Lesven, L., Noiriel, C., Madé, B., Billon. G., 2015. Development and application of HPIC-ICP-MS method for the redox arsenic speciation in river sediment pore waters. J. Anal. At. Spectrom. 30, 1562-1570.

Hamilton, S. J., 2002. Rationale for a tissue-based selenium criterion for aquatic life. Aquat. Toxicol. 57, 85-100.

Hamilton, S. J., 2004. Review of selenium toxicity in the aquatic food chain. Sci. Total. Environ.

326, 1-31.

Haygarth, P. M., 1994. Global importance and global cycling of selenium, in: Frankenberger, W. T., Jr., Benson, S, (Eds.), Selenium in the Environment. Marcel Dekker., New York, pp. 1–27.

Headley, J. V., Barrow, M. P., Peru, K. M., Fahlman, B., Frank, R. A., Bickerton, G., McMaster, M. E., Parrott, J., Hewitt, L. M., 2011. Preliminary fingerprinting of Athabasca oil sands polar organics in environmental samples using electrospray ionization fourier transform ion cyclotron resonance mass spectrometry. Rapid Commun. Mass. Spectrom. 25, 1899-1909.

Javed, M. B., 2015. Distribution of arsenic in surficial deposits in the Cold Lake area of Alberta, Canda. Ph.D Thesis, University of Alberta, Edmonton, Alberta.

Kölbl, G., Kalcher, K., Irgolic, K. J., Magee, R. J., 1993. Identification and quantification of inorganic and organic selenium compounds with high performance liquid chromatography. Appl. Organomet. Chem. 7, 443–466.

Leblanc, K. L., Ruzicka, J., Wallschläger, D., 2016. Identification of trace levels of selenomothionine and related organic selenium species in high-ionic strength waters. Anal. Bioanal. Chem. 408, 1033-1042.

Leblanc, K. L., Wallschläger, D., 2016. Production and release of selenomethionine and related organic selnium species by microorganisms in natural and industrial waters. Environ. Sci. Technol. 50, 6164-6171.

Li, H.-F., McGrath, S. P., Zhao, F.-J., 2008. Selenium uptake, translocation and speciation in wheat supplied with selenate or selenite. New. Phytol. 178, 92-102.

Lum, T., Leung, K. S., 2016. Strategies to overcome spectral interference in ICP-MS detection.

J. Anal. At. Spectrom. 31, 1078-1088.

Maher, W., Roach, A., Doblin, M., Fan, T., Foster, S., Garrett, R., Möller, G., Oram, L., Wallschläger, D., 2009. Environmental sources, speciation, and partitioning of selenium, in: Ecological assessment of selenium in the aquatic environment; in: Chapman, P. M., Adams, W. J., Brooks, M. L., Delos, C. G., Luoma, S. N., Maher, W. A., Ohlendorf, H. M., Presser, T. S., Shaw, D. P, (Eds.), CRC Press., Boca Raton, Fla, pp. 47–91.

Ogra, Y., Ishiwata, K., Suzuki, K. T., 2005. Effects of deuterium in octopole reaction and collision cell ICP-MS on detection of selenium in extracellular fluids. Anal. Chim. Acta. 554, 123-129.

Papoff, P., Bocci, F., Lanza, F., 1998. Speciation in natural waters and snow by DPCSV at the hanging mercury drop electrode. Microchem. J. 59, 50-76.

Pedersen, G. A., Larsen, E. H., 1997. Speciation of four selenium compounds using high performance liquid chromatography with on-line detection by inductively coupled plasma mass spectrometry or flame atomic absorption spectometry. Fresenius' J. Anal. Chem. 358, 591-598.

Pettine, M., McDonald, T. J., Sohn, M., Anquandah, G. A. K., Zboril, R., Sharma, V. K., 2015. A critical review of selenium analysis in natural water samples. Trends. Environ. Anal. Chem. 5, 1-7.

Potin-Gautier, M., Boucharat, C., Astruc, A., Astruc, M., 1993. Speciation of selenoamino acids by on-line HPLC ETAA. Appl. Organomet. Chem. 7, 593-598.

Rayman, M. P., 2000. The importance of selenium to human health. The Lancet. 356, 233-41.

Riedel, G. F., Ferrier, D. P., Sanders, J. G., 1991. Uptake of selenium by freshwater phtoplankton. Water, Air, and Soil Pollut. 57–58, 23-30.

Ross, M. S., Pereira, A. S., Fennell, J., Davies, M., Johnson, J., Sliva, L., Martin, J. W., 2012. Quantitative and qualitative analysis of naphthenic acids in natural waters surrounding the Canadian oil sands industry. Environ. Sci. Technol. 46, 12796-12805.

Wallschläger, D., Feldmann, J., 2010.Formation, occurrence, significance, and analysis of organoselenium and organotellurium compounds in environment, in: Sigel, A., Sigel, H., Sigel, R. K. O, (Eds.), Organometallics in Environment and Toxicology: Metal Ions in Life Sciences. RSC Publishing., Cambridge, UK, pp. 319–364.

Wallschläger, D., London, J., 2004. Determination of inorganic selenium species in rain and sea waters by anion exchange chromatography-hydride generation-inductively-coupled plasma-dynamic reaction cell-mass spectrometry (AEC-HG-ICP-DRC-MS). J. Anal. At. Spectrom. 19, 1119-1127.

Wang, D., Alfthan, G., Aro, A., 1994. Determination of total selenium and dissolved selenium species in natural waters by fluorometry. Environ. Sci. Technol. 28, 383-387.

Wang, W., Chen, Z., Davey, D. E., Naidu, R., 2010. Speciation of selenium in biological samples by ion chromatography with inductively coupled plasma mass spectrometry. J. Liq. Chromatogr. Relat. Technol. 33, 1151-1173.

Weiss, J., 2004. Handbook of Ion Chromatography. Wiley-VCH: Weinheim, Germany, Vol. 1, pp. 63, 182, and 528.

Winkel, L.H.E, Vriens, B., Jones, G. D., Schneider, L. S., Pilon-Smits, E., Bañuelos, G. S., 2015. Selenium cycling across soil-plant-atmosphere interfaces: a critical review. Nutrients. 7, 4199-

239.

Xing, L., Beauchemin, D. J., 2010. Chromium speciation at trace level in potable water using hyphenated ion exchange chromatography and inductively coupled plasma mass spectrometry with collision/reaction interface. J. Anal. At. Spectrom. 25, 1046-1055.

4.7 Figures

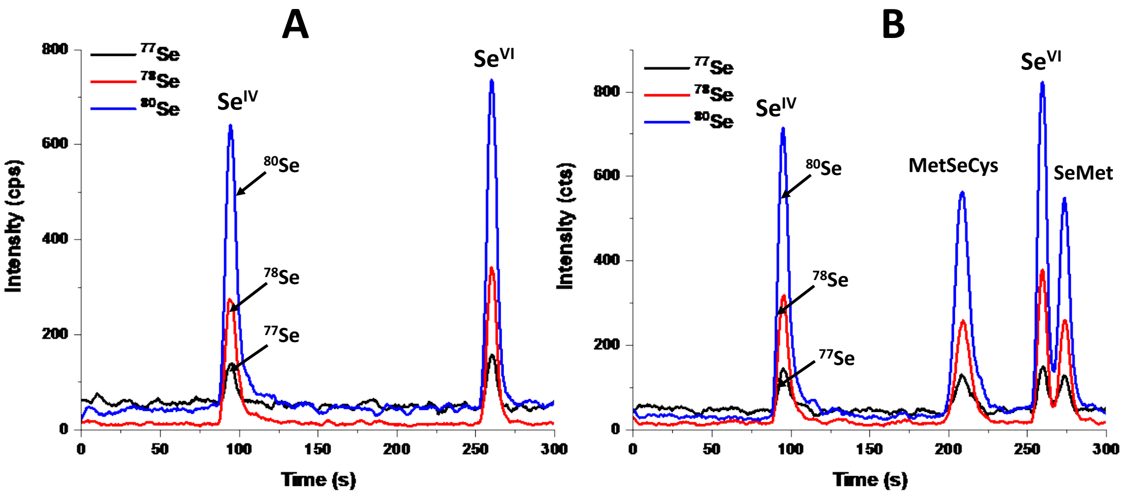

Figure 4.1 Peak resolution of Se species and the sensitivity difference of measured isotopes. Chromatogram A represents a standard solution containing 200 ng L^{-1} each of Se^{IV} and Se^{VI}; Chromatogram B represents a standard solution containing 200 ng L^{-1} of each Se species. Both standards were prepared using high purity water without any acidification of solutions. Chromatography method uses a Dionex IonPac™ AS7 anion exchange column (4 mm ID, 250 mm length, 10µm particles size), AG7 guard column (4 mm ID x 50 mm length) at 30ºC, with 1 mL min^{-1} flow rate and 25µL sample injection.

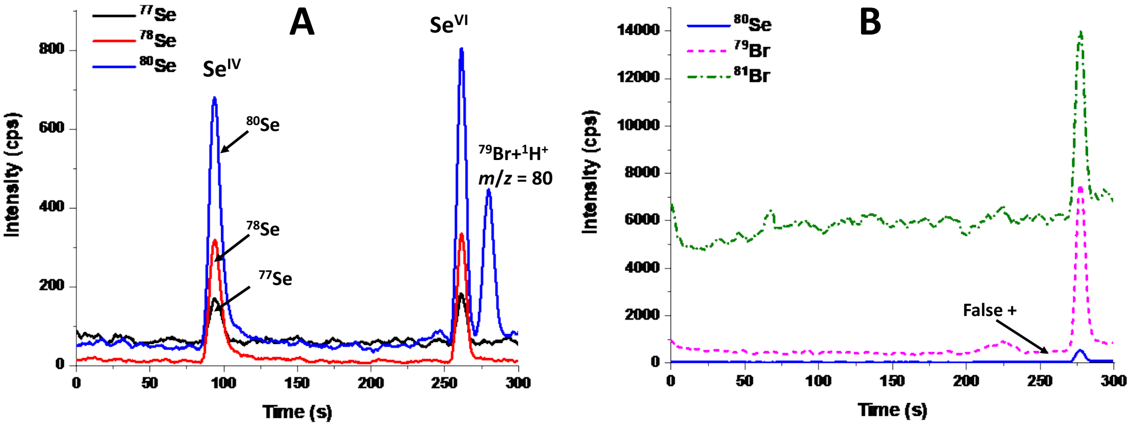

Figure 4.2 The potential influence of bromine (Br) and HCl on Se quantification. Chromatogram A represents a solution of high purity water and HCl (acidified to ~0.8%). Two isotopes of Br were monitored to confirm that Br (presumably as ionic Br^-) was present in HCl, and due to H_2 reaction with ^{79}Br, the resulting $^{79}Br^1H^+$ is responsible for the observed artefact of ^{80}Se. Chromatogram B represents a standard solution (200 ng L^{-1} each of Se^{IV} and Se^{VI}) prepared using high purity water and acidified with HCl. The results indicate that the Br^- peak does not interfere with Se^{VI} and the acidification of the solution has no influence on Se^{IV} and Se^{VI} retention times.

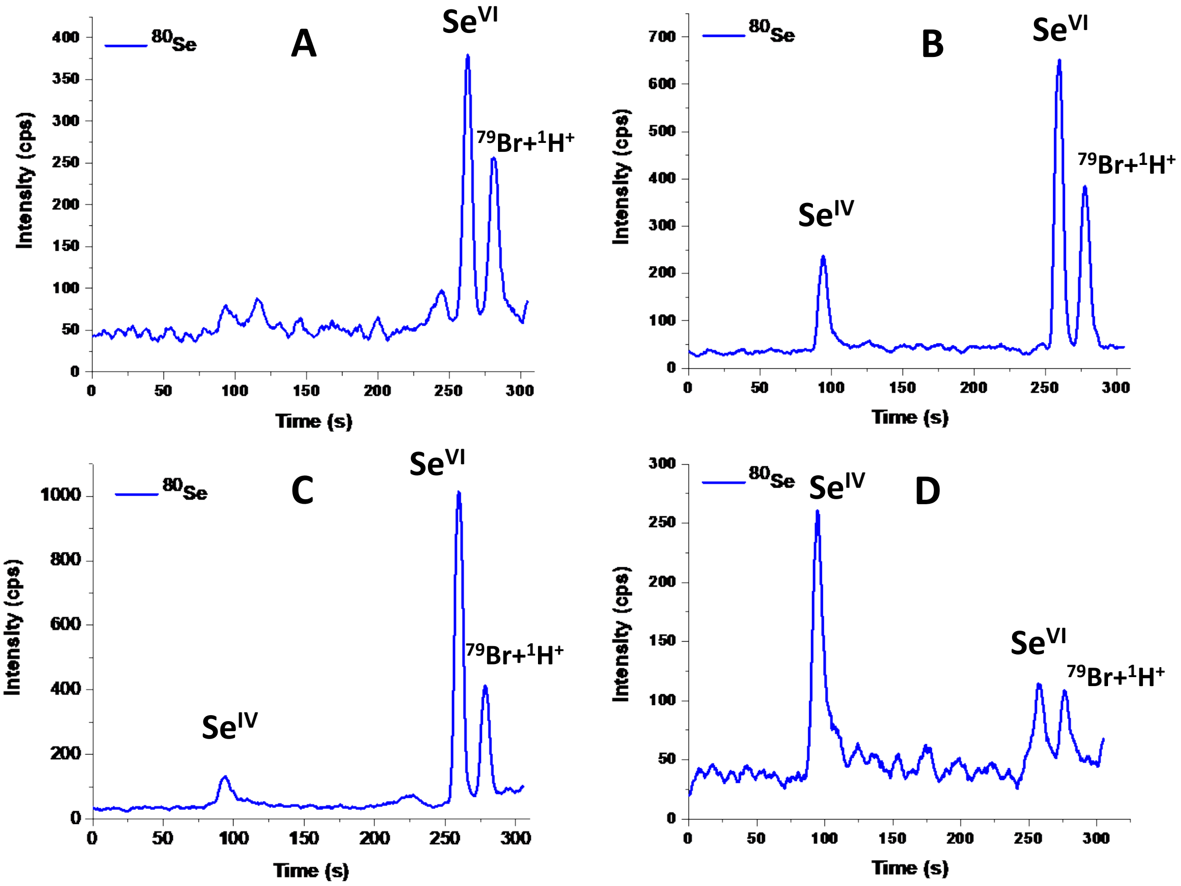

Figure 4.3 General depiction of Se speciation in river and rain water samples obtained using the developed method. Chromatograms represent (A) Athabasca River, (B) North Saskatchewan River, (C) Maligne River and (D) urban rain water. A false Se peak was expected in chromatograms A and C due to preservation with HCl, but trace Br was still detected in un-acidified samples (B, D). See Table 4 for the corresponding concentrations.

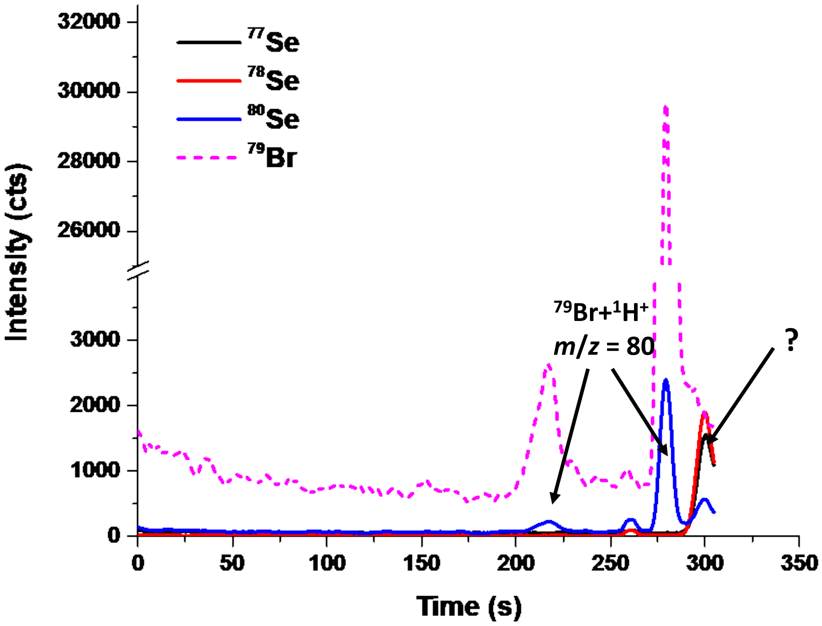

Figure 4.4 Selenium speciation of chemically complex peatbog surface water. A signal response from all three Se isotopes appear at 300s, which suggests that it is Se being detected, but ^{80}Se signal had the lowest response and therefore it's likely that a different spectral interference is at play here. A second Br peak was also observed (~225s), possibly indicating the presence of another form or column artifact due to the very high concentration of Br$^-$.

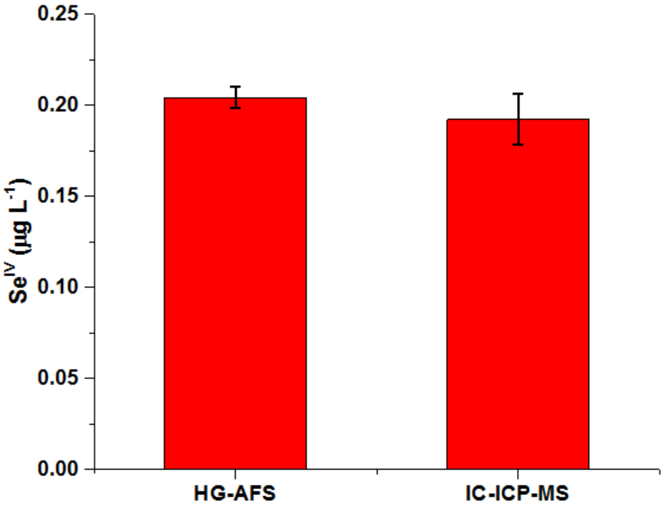

Figure 4.5 Independent method validation of Se speciation. Triplicate samples containing 0.2 µg L^{-1} of Se^{IV} were analyzed by HG-AFS and IC-ICP-MS. Both analyses yielded similar concentrations of Se^{IV}, supporting the speciation method developed for IC-ICP-MS.

4.8 Tables

Table 4.1 Instrumental parameters and conditions for IC-ICP-MS and ICP-MS operations

Instrument	Parameter	Optimized Setting
IC-ICP-MS	Radio frequency power (W)	1548
	Ar flow rate (L min^{-1})	0.8
	H_2 flow rate (mL min^{-1})	9
	Dwell time (s)	0.1 (Se)
	Eluent flow rate (mL min^{-1})	1.0
	Mobile phase A	50 mM HNO_3
	Mobile phase B	400 mM HNO_3
	Gradient program	0-2 min 100% A 2-4 min 100% B 4-5min 100% A
	Wash volume	250 (µL)
	Column temperature	30 (°C)
ICP-MS	Skimmer cone	Ni
	Sample cone	Ni/Cu
	Dwell time (s)	0.2 (Se) 0.02 (Sc) 0.01 (In) 0.01 (Ho)
	Auxiliary gas flow rate	0.8 (L min^{-1})
	He flow rate	5.0 (mL min^{-1})

Table 4.2 Comparison of method accuracy, precision and sensitivity between isotopes for each of the studied species.

Isotope	**Speciation**	**Calibration Linear Coefficient**	**LOD (ng L^{-1})**	**LOQ (ng L^{-1})**	**Recovery of 20 ng L^{-1} standard (*n*=5)**	**Recovery of 50 ng L^{-1} standard (*n*=5)**	**Instrument sensitivity (cts) at 200 ng L^{-1}**
^{77}Se	Se^{IV}	0.961	24	110	**11 (±8)**	**33 (±12)**	1056
	MetSeCys	0.967	41	100	**2 (±5)**	**11 (±16)**	1050
	Se^{VI}	0.984	10	149	**ND**	**28 (±12)**	620
	SeMet	0.970	38	147	**6 (±8)**	**20 (±16)**	498
^{78}Se	Se^{IV}	1.000	9	28	18 (±3)	52 (±7)	2462
	MetSeCys	0.996	20	64	**6 (±4)**	39 (±6)	2697
	Se^{VI}	0.999	3	23	18 (±2)	54 (±5)	2192
	SeMet	0.996	12	36	**20 (±8)**	44 (±3)	1586
^{80}Se	Se^{IV}	0.997	4	14	21 (±3)	49 (±7)	5354
	MetSeCys	0.999	5	12	21 (±3)	51 (±2)	5868
	Se^{VI}	0.999	4	15	20 (±3)	49 (±4)	4673
	SeMet	0.998	9	38	18 (±4)	46 (±4)	3154

Note: LOD, limit of detection; LOQ, limit of quantification; ND, not detected. Standard deviations for measurements are shown in parentheses. Bold values indicate analyses with > 20% RSD.

Table 4.3 Method validation using standard reference water and spiked river water.

Water Type	**Analysis**	**Number of measurements (*n*)**	**Certified or expected value (µg L^{-1})**	**Measured value**	**Recovery (%)**	**Relative standard deviation (%)**
NIST 1640a*	Speciation	4	20.13 (±0.17)	20.35	101	5.7
Se(IV) spike**	Speciation	3	0.100	0.099	99	2.5
Se(VI) spike**	Speciation	3	0.177	0.170	96	2.6
NIST 1640a	Total	1	20.13 (±0.17)	20.20	100	NA

Note: Results are based on quantification of ^{80}Se. Athabasca River water was spiked with Se^{IV} and Se^{VI}. NIST 1640a is used as an indicator of method accuracy for speciation by comparing sum of species with certified total concentration. Spiked solutions diluted the original sample by 5%. NA, not available.

Table 4.4 Total Se and its chemical species in natural water samples.

Water Type	**GPS Location**	**Sample number (*n*)**	**Se^{IV} (ng L^{-1})**	**SeMetCys (ng L^{-1})**	**Se^{VI} (ng L^{-1})**	**SeMet (ng L^{-1})**	**Total Se (ng L^{-1})**	**Sum of species relative to total (%)**
Maligne River	52.921591 - 118.016796	1	24	ND	252	ND	314	88
Athabasca River	56.8971667 - 111.419116	1	<LOD	ND	77	ND	187	43
North Sask. River	53.529857 - 113.517937	3	45 (±6)	ND	155 (±55)	ND	261	77
Edmonton Rain	53.526103 - 113.523896	3	72 (±5)	ND	24 (±5)	ND	NA	NA

Note: Results for chemical speciation were quantified using ^{80}Se and total Se analysis was ^{78}Se. ND: not detected; NA: not available; LOD, limit of detection. Standard deviations for measurements are shown in parentheses.

4.9 Supplementary Information

4.9.1 Chemicals and reagents

All chemicals and reagents were purchased from Sigma-Aldrich. Samples and reagent blanks for HG-AFS analysis were acidified with 3.6M HCl (TraceSELECT®; Cat. #72787) while the instrument reductant solution was prepared fresh by dissolving caplets of sodium tetrahydroborate (NaBH4, 98%; Cat. # 452890) in a 0.1 mol L^{-1} sodium hydroxide (NaOH; BioXtra, ≥98%; Cat. #S8045) solution. External calibration standards were prepared from a 1000 mg L^{-1} stock solution of Se (FLUKA Analytical; TraceCERT®; Cat. #89498)

4.9.2 Instrument and relevant operating conditions

Analyses for HG-AFS analysis were performed on a PS Analytical 10.055 (Millennium Excalibur) unit with a continuous flow of sample/reagent (9.5 mL min^{-1}) and reductant (5 mL min^{-1}). Argon was used as a drying gas and carrier for sweeping the generated hydride to a quartz chimney where an argon-hydrogen flame atomized the gas stream. Atomic fluorescence was achieved by radiation of Se atoms using a boosted discharge hollow cathode lamp with primary and boost settings at 20 and 25mA, respectively.

5.0 SELENIUM IN SURFACE WATERS OF THE LOWER ATHABASCA RIVER WATERSHED: CHEMICAL SPECIATION AND IMPLICATIONS FOR AQUATIC LIFE[§]

[§] A version of this chapter has been published as: Selenium in surface waters of the lower Athabasca River: chemical speciation and implications for aquatic life", *Environmental Pollution*, 2018, Vol. 243, 1343-1351. The published journal article is provided in Appendix IV.

5.1 Introduction

Selenium (Se) is often referred to paradoxically as an “essential toxin” because of its role as either a critical micronutrient, or as a harmful contaminant (Lenz and Lens, 2009). The distinction between toxic or beneficial depends on the form of selenium (chemical speciation) and its concentration (Young et al., 2010). The environmental chemistry of selenium is similar to that of sulphur, as they share similar oxidation states (-II, 0, IV, VI) and form analogous biomolecules. Selenium in the aquatic environment requires special attention due to its ability to bioaccumulate and promote teratogenic effects on organisms at higher trophic levels such as waterfowl and fish (Ohlendorf et al., 1986, 1990). Selenium in oxic surface water is often present as selenite [SeO_3^{2-}; Se(IV)] and selenate [SeO_4^{2-}; Se(VI)]. However, many other forms of Se exist in aquatic environments due to chemical and biological processes, such as reduced selenides [Se(-II)], discrete biomolecules (e.g., amino acids), non-discrete organo-Se compounds (e.g., bound with natural organic matter) as well as volatile gaseous species (e.g., dimethyl selenide) (Wallschläger and Feldmann, 2010). The environmental cycling of Se has some unique and important considerations compared to other potentially toxic trace metals and metalloids (e.g., As, Ag, Cd, Pb, Tl). One critical difference is that the organic forms of Se are the most bioavailable, with diet being the primary route of exposure (Young et al., 2010).

Predicting whether Se is a problem or could become a threat to aquatic organisms in the future, requires knowledge of the local and regional environmental setting, particularly as it relates to hydrology and geology (Outridge et al., 1999). For example, Se bioaccumulation is typically lower in lotic systems (flowing water) than lentic systems (stagnant water), where there is greater biological cycling and production of organo-Se (Hillwalker et al., 2006; Simmons and

Wallschläger, 2005). The unique and complex behavior of Se in the aquatic environment is further reflected by inconsistent environmental guidelines around the world (Luoma, 2009). It is widely accepted that the concentration of Se in fish tissue is a more reliable measure of exposure and potential ecological effects than the concentration in water, however concentration thresholds have also been the focus of considerable research and debate (e.g., Chapman, 2007; Deforest et al., 1999; Hamilton, 2002). In 2016, the United States Environmental Protection Agency (US EPA) issued a new aquatic guideline for Se that prioritizes a fish tissue-based criterion (muscle or gonads) over water-based criteria (US EPA, 2016). If data for fish tissue is not available then guideline values for dissolved Se concentrations in water take precedence, and differ for lotic (3.1 $\mu g L^{-1}$) and lentic systems (1.5 $\mu g L^{-1}$) (US EPA, 2016).

The surface mining and upgrading of bituminous sands along the lower Athabasca River in northeastern Alberta, Canada, have provoked concerns about environmental contamination by potentially toxic trace elements such as Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl and Zn (Kelly et al., 2010). The inclusion of Se on this list requires extra attention given the importance of fish in the diet of local First Nations communities, and the toxic effects observed in fish exposed to high concentrations (Lemly, 1998). A study of historical water quality data (1972 – 2010) in rivers near bitumen mining indicated that 'dissolved' (presumably < 0.45 μm by filtration) Se concentrations were elevated due to construction and other activities related to early bitumen production (Alexander and Chambers , 2016). A similar data analysis based on a 25-year record (1989 – 2014) of water quality in rivers near mining and upgraders found that concentrations of Se and 11 other potentially toxic trace elements were elevated during snow melt due to greater acid deposition (Alexander et al., 2017). Other contemporary studies of trace element concentrations in the Athabasca River either did not include Se (Conly et al., 2007;

Donner et al., 2017; Guéguen et al., 2011; Javed et al., 2017; Shotyk et al., 2017; Zhu and Guéguen, 2016), or did not label it an element of concern (Pilote et al., 2018). Moreover, there have been no studies of the chemical speciation of Se in the Athabasca River, and there is no published data for Se in fish from this river.

An inherent challenge in assessing water quality in the lower Athabasca River is distinguishing natural and anthropogenic inputs (e.g., Shotyk et al., 2017; Sun et al., 2017). Although there is considerable industrial activity related to surface mining and bitumen upgrading, quantifying the contribution of trace elements from industrial activities is complicated by large inputs of dissolved organic matter (DOM), iron oxyhydroxides and associated trace elements from the surrounding boreal forest and peatlands (Cuss et al., 2018), high salinity groundwater (Ellis and Jasechko, 2018; Gibson et al., 2013) and bitumen-derived compounds from the weathering of bituminous sands (Ross et al., 2012; Sun et al., 2017). A recent study of trace metals in the dissolved (< 0.45 μm) fraction of Athabasca River water found that the concentrations of four trace metals increased significantly from upstream to downstream of bitumen mines and upgraders: V, Ni, Mo and Re (Shotyk et al., 2017). These elements are enriched in bitumen (Bicalho et al., 2017; Goldschmidt, 1937; Selby, 2005), whereas many other potentially toxic elements are contained almost exclusively within the mineral fraction (e.g., As, Ag, Pb, Sb, Tl, etc.). Recently, however, determination of Se in mineral and bitumen fractions of Athabasca bituminous sands (ABS) showed that Se was predominantly (ca. 80%) contained in the bitumen fraction (Donner et al., 2018). Therefore, aquatic organisms in the Athabasca River may be exposed to naturally elevated concentrations of Se due to the weathering of bitumen-laden banks, with potentially greater exposure downstream from open-pit bitumen mines and upgrading facilities.

The two objectives of this study were to: i) Measure the concentration and chemical speciation of Se in Athabasca River surface water, upstream, alongside and downstream of bitumen mining and upgrading, and ii) Evaluate the potential impact of Se on aquatic life based on concentrations in the muscle tissue of Trout-perch (*Percopsis omiscomaycus*). Trout-perch are small fish that do not migrate far from a single area (Gibbons et al., 1998), and have been promoted as a valuable sentinel species for the Athabasca River watershed (Spafford, 1999). Water samples from the Athabasca River and tributaries were also collected to determine concentrations in the dissolved (< 0.45 µm) phase and the major chemical species.

5.2 Methods

5.2.1 Water sampling from lower Athabasca River watershed

Water sampling was conducted in October 2014 and 2015 as part of a large multi-disciplinary study of groundwater-surface water interactions in the lower Athabasca River watershed. Samples were collected in the autumn when water levels are typically at their lowest and the contribution of groundwater is greatest. In 2014, samples were collected from 13 sites on the Athabasca River and five associated tributaries. In 2015, 19 sites were sampled along the Athabasca River and nine in tributaries. Field duplicates were collected at various locations in both years to assess sampling reproducibility. As an independent check, dissolved Se concentrations were also determined in two additional bottles collected at the same time, but designated for a suite of trace metal analyses (Shotyk et al., 2017). A comparison of data for additional bottles is provided in Figure 5.6. A map denoting all sampling locations for water samples (2014, 2015) and Trout-perch (see below) is provided in Figure 5.1. Detailed information about the GPS coordinates for all surface water sampling locations can be found elsewhere (Donner et al., 2017; Shotyk et al., 2017). Water samples were collected from the

Athabasca River (main-stem) at a depth of approximately 30 cm, off the bow of a small boat anchored approximately 80 m from shore. Tributary samples were collected midway from each bank in an area of ample flow, near to their confluence with the Athabasca River but upstream of the mixing zone. A detailed description of materials and methods for bottle cleaning and sampling is provided elsewhere (Donner et al., 2017). All sample bottles (low-density polyethylene or fluorinated high-density polyethylene), syringes (polypropylene), and filters (polytetrafluoroethylene) were pre-cleaned in acid and individually packaged in two re-sealable plastic bags. Water was immediately filtered (0.45 μm) into a bottle containing HCl as preservative (OptimaGrade™; 0.8% v/v) and transported in a cooler containing ice packs. Analyses for dissolved (< 0.45 μm) Se and its speciation were conducted using the same water samples as for As published previously (Donner et al., 2017).

A large suite of samples were collected at each site to analyze a variety of parameters, including: dissolved (< 0.45 μm) trace metals (Shotyk et al., 2017), Pb speciation (Javed et al., 2017), naphthenic acids (Sun et al., 2017), speciation of colloidal forms of trace elements (Cuss et al., 2018), dissolved organic matter (DOM) quality and quantity (Cuss et al., in review) and As speciation (Donner et al., 2017). The concentrations of major cations, anions, dissolved organic carbon (DOC) and other water quality parameters are also presented in Shotyk et al. (2017) for the 2014 sampling campaign. Methods and data for DOC determined in 2015 samples is available elsewhere (Cuss et al., in review) and unpublished data for Cl^- in 2015 samples is presented here.

5.2.2 Fish collection and handling

Trout-perch were collected in October of 2014 from 11 locations on the Athabasca River and two on the Clearwater River, with the furthest site (CWR2) being approximately 30 km upstream of its confluence with the Athabasca River. The GPS coordinates for Trout-perch collection sites are available in Table 5.1. Sampling was conducted in coordination with the water sampling teams to ensure comparable results between the biological and chemical components. A Smith-Root 7.5 Generator Powered Pulsator electrofisher (designed for low to very high conductivity water) was operated from a 20 ft. boat that travelled along multiple transects (ca. 1 km each) at each site. Transects began at the indicated site location (Fig. 5.1) and were conducted parallel to the bank; the distance from shore was dependent on channel morphology and varied between sites. Fish were removed using handheld nets and euthanized in accordance with animal care protocol AUP00001111. Fish were kept in cooler boxes and transferred to freezers at the end of each day.

The weight and fork length of 56 Trout-perch were measured in the laboratory. Muscle tissue samples were obtained from above the lateral line in the dorsal portion, excluding bone and skin tissues. Samples were then air-dried for at least 48 hours inside an exhausted (class-100) clean-air cabinet, housed in the ultraclean, metal-free SWAMP facility (Soil Water Air Manure Plants) at the University of Alberta. Dried samples were acid-digested in a mixture of double-distilled nitric acid (3mL) and tetrafluoroboric acid (0.1 mL) using a high pressure microwave (ULTRAclave, MLS, Leutkirch, Germany). After cooling, the liquid digestate was diluted to a total volume of 10 mL with MilliQ water (18.2 MΩ·cm; MilliporeSigma, Massachusetts, USA) and stored under refrigeration until analysis.

5.2.3 Determination of dissolved selenium

Concentrations of dissolved Se were determined using a single quadrupole inductively coupled plasma mass spectrometer (ICP-MS; iCAP-Q Thermo Scientific) operating in kinetic energy discrimination mode, with He collision gas (0.05s dwell time; 120 sweeps). External mass calibration solutions were prepared using SPEX CertiPrep Instrument Calibration Standard 2. Minor instrument drift was accounted for using a multi-element internal standard (Multi-element Internal Standard 1; 1 µg L^{-1}) added continuously on-line through a mixing tee. Concentrations were quantified using ^{78}Se and presented as the average value of three main runs. A blank sample was analyzed after approximately every 10 samples, in addition to a standard reference material (SRM), NIST 1640a Trace Elements in Natural Water; [Se] = 20.13 ± 0.17 µg L^{-1}. The average recoveries of NIST 1640a for analyses in 2014 and 2015 were 94.9 and 98.2%, respectively.

Dissolved Se was also determined in water samples using hydride generation atomic fluorescence spectroscopy (HG-AFS). Selenium analysis by HG-AFS first requires a pre-reduction step to reduce any Se(VI) to Se(IV), as only Se(IV) will form a hydride when reduced by sodium tetraborate under acidic conditions (Sánchez-Rodas et al., 2010). To accomplish this, 10 mL of sample was combined with 15 mL of HCl, heated at 90°C for 60 min. in a microwave digestion unit (MARS, CEM Corporation, USA), and diluted with MilliQ water. Owing to the presence of undissolved or reduced Se forms in water samples, an additional 1mL of HNO_3 was added to enhance oxidizing power and the program was extended to 90 min. The use of high purity HNO_3 (Optima™ HNO_3 or double-distilled TraceGrade HNO_3) was necessary to obtain suitable blank values.

5.2.4 Determination of selenium speciation

Unfortunately, the extremely low concentrations of Se in water samples obtained in 2014 precluded reliable speciation using the methods and instruments that were available. Two analytical techniques capable of measuring low concentrations of Se species were established and applied to samples collected in 2015: sequential selenium hydride generation (SSHG) using HG-AFS and ion chromatography paired with ICP-MS (IC-ICP-MS) (Donner and Siddique, 2018). The focus of these methods was to obtain data for the most commonly expected forms, Se(VI) and Se(IV). Sequential selenium hydride generation takes advantage of the ability of Se(IV) to form a hydride, and the inability of other species present to convert into a gaseous state; this can then be used to determine fractions of selenium present in a water sample. There are several variations of the SSHG (e.g., Chen et al., 2005; Cutter, 1978) and the approach herein was based on three treatments for separating total Se into three fractions:

Analysis of samples without pre-reduction = Se(IV)
Microwave heating with HCl = Se(IV) + Se(VI)
Microwave heating with HNO_3 and HCl = $\sum \mathrm{Se}_{\mathrm{dissolved}}$

The concentration of Se(VI) was obtained as the difference between Se(IV)+Se(VI) and Se(IV), and the difference between $\sum \mathrm{Se}_{\mathrm{dissolved}}$ and Se(IV)+Se(VI) was considered the "reduced Se" fraction. The latter is often referred to as "organo-Se", but this term is imprecise as it does not include reduced inorganic Se compounds that have been found in aquatic systems and wastewaters, such as selenocynate ($SeCN^-$) (Wallschläger and Feldmann, 2010). Importantly, SSHG has some limitations that can produce significant artefacts and misleading results. For example, organo-Se compounds can decompose during the heat-acid reflux step applied to reduce Se(VI) to Se(IV), thereby giving an artificially high concentration of Se(VI) in waters rich in organic matter (Chen et al., 2005). Therefore, SSHG provides broader fractions of Se compounds and does not provide positive identification of individual forms. However, there are advantages to using it in a complementary analytical role. In particular it has an excellent limit of detection (typically ~10 ng L^{-1}), includes of Se-bearing colloids and provides an independent confirmation of analyses performed using ICP-MS. In each sequential step, multiple QC samples were included to ensure the complete reduction (or oxidation then subsequent reduction) of Se in samples. This included spiking 100 ng L^{-1} of Se(IV) or Se(VI) into a sample of Athabasca River water or tributary water. The solutions used for spiking were diluted from 2000 mg L^{-1} stock solutions of sodium selenate decahydrate (99.999% trace metal basis; Sigma Aldrich) and sodium selenite (99%; Sigma Aldrich), which were of a different source than that used to prepare the external calibration (Fluka Analytical; TraceCERT®). The average recovery of spiked samples compared to the expected value was 112 ± 5% (n=4). NIST 1640a was also determined during analyses (108 ± 5% recovery; n=2).

To compare with results obtained by SSHG, water samples from 2015 were also analyzed using an IC-ICP-MS method for determining Se(IV) and Se(VI) in natural freshwaters (Donner and Siddique, 2018). Briefly, the system consisted of the same quadrupole ICP-MS as described above, operated in chemical reaction cell mode using H_2 as a reaction gas instead of He as a collision gas. The use of H_2 allowed for the quantification of the more abundant ^{80}Se isotope by eliminating the interfering dimer $^{40}Ar_2^+$ (m/z=80). To separate Se(VI) and Se(IV), a high performance IC (Thermo Scientific Dionex ICS-5000$^+$) with a Dionex IonPac AS7 anion exchange column and guard column was used. The mobile phase was dilute nitric acid delivered in a step-wise concentration gradient: 0–2 min (50 mM HNO_3), 2–4 min (400 mM HNO_3) and 4–5 min (50 mM HNO_3).

5.2.5 Selenium in fish muscle tissue

Acid digests of Trout-perch muscle tissue, SRMs, and digestion blanks were analyzed for total Se using both ICP-MS and HG-AFS. For HG-AFS analysis, 1mL of digestate was combined with 9mL of MilliQ water and 15mL of HCl. Samples were pre-reduced for 60 min using the same heating procedure as described above for Se(VI) reduction and brought to a volume of 50mL using MilliQ water before analysis using HG-AFS. Instrument operating conditions and calibration solutions were the same as those used to measure total Se in acid-digests of bitumen samples (Donner et al., 2018). Concentrations were derived from an 8-point linear calibration (0.02 – 4 µg L^{-1}) and reported as an average of duplicate injections (< 2% RSD). Each digestion batch contained a minimum of three blanks and triplicates of two different SRMs (n = 6): NIST 1566b (Oyster Tissue; [Se] = 2.06 mg kg^{-1}) and NIST 1577c (Bovine Liver; [Se] = 2.031 mg kg^{-1}). The same digests were measured using ICP-MS after a 50x dilution with MilliQ water using the operating conditions described above. Quality control results for SRMs analyzed by HG-AFS and ICP-MS are provided in Figure 5.7.

5.2.6 Data analysis

Selenium data from fish muscle was grouped into three categories based on their location on the Athabasca River relative to industrial activity: upstream, midstream (area of industrial activity) and downstream. Normality was assessed using Lilliefors test, following the removal of outliers (*n*=5), determined as values > 3x the mean absolute deviation. A Student's *t*-test (one-tailed) was applied to test for significant differences ($p < 0.05$) between Se concentrations in the tissue of Trout-perch collected upstream of industrial activity, compared to the midstream and downstream reaches. Data analyses were performed using MatLab R2017a and Origin graphing software. Selenium data generated using ICP-MS yielded slightly better average recoveries of SRMs (NIST 1566b = 116%; NIST 1577c = 109%) and was chosen as the primary data source to be represented in the main text. Raw data from both instruments are provided in Tables 5.2 (Clearwater River) and 5.3 (Athabasca River).

5.3 Results

5.3.1 Dissolved selenium in Athabasca River water and tributaries

The average concentration of dissolved (i.e., < 0.45 μm fraction) Se in the main stem of the Athabasca River in 2014 was 0.11 ± 0.02 μg L^{-1} (n = 14) and 0.16 ± 0.02 μg L^{-1} (n = 21) in 2015 (Fig. 5.2A and 5.3A). Concentrations of Se were relatively consistent upstream to downstream, despite greater concentrations of Cl^- and dissolved organic carbon (DOC) (Fig. 5.2B and C). Higher Cl^- concentrations indicate greater influence from saline groundwater. In 2014, Se concentrations were lower at site A20e (Fig. 2A), whereas concentrations of Cl^- and DOC at this site were elevated relative to other sections of the river (Fig. 5.2B and C, respectively). This pattern is most likely the result of the Athabasca River mixing with the Clearwater River, which enters approximately 1.5 km upstream of site A20e (Fig. 5.1). Due to the low-flow conditions and substantial channelling, samples were collected from the eastern portion of the river and so were likely subject to greater influence by the Clearwater River. In 2015, when water levels were noticeably higher, a similar pattern of Cl^- concentrations was observed (Fig. 5.8B) but Se (Fig 5.3A) and DOC concentrations were more consistent. (Fig. 5.8A).

Concentrations of dissolved Se in tributaries were generally lower than the Athabasca River (0.02–0.27 µg L^{-1}). Of the tributaries studied, two were previously identified as potentially receiving oil sands process affected water (OSPW) from industrial activity: Beaver Creek and McLean Creek (Ross et al., 2012; Sun et al., 2017). The Se concentrations in these two tributaries were similar to the Athabasca River and other tributaries (Fig. 5.4). The extremely low concentrations (< 100 ng L^{-1}) observed in some tributaries (e.g., Steepbank River, Ells River, McKay River and Beaver Creek) are remarkable given the significant amount of exposure to surrounding industrial activity and natural erosion of bitumen outcrops. The concentration of Se in the Athabasca River and tributaries were also well below the US EPA guideline value for lotic systems (3.1 µg L^{-1}; US EPA, 2016) and are comparable to estimates of background dissolved Se concentrations for undisturbed surface waters (0.07–0.19 µg L^{-1}; Luoma and Rainbow, 2008) and global rivers (0.060 µg L^{-1}; Nriagu, 1989). Unfortunately, dissolved concentrations cannot be compared to guidelines described by the Canadian Council of Ministers of the Environment (CCME) for the protection of aquatic life, as the Se guideline value (1 µg L^{-1}) is based on total concentrations (i.e., bulk, unfiltered water; CCME, 1987).

5.3.2 Selenium speciation in Athabasca River water and tributaries

The average concentration of Se(VI) in the Athabasca River determined using SSHG was 0.11 ± 0.015 µg L^{-1}. Concentrations of Se(IV) were close to, or below the LOD for HG-AFS (0.012 µg L^{-1}) and could not be quantified reliably (Fig. 5.3A). Only after samples were oxidized using HNO_3, full recovery of Se was obtained, as compared to analysis with ICP-MS (Fig. 5.3A), suggesting that a portion of the Se was neither Se(VI) nor Se(IV). Similar to dissolved concentrations, no increasing trend was observed upstream to downstream, failing to indicate inputs from oil sands mining or natural saline groundwater. Analysis using IC-ICP-MS revealed a very similar concentration profile (Fig. 5.3B), but suggested an even lower proportion of Se(IV) and Se(VI), as concentrations of Se(IV) were below the limit of quantification (LOQ; 14 ng L^{-1}) and the average concentration of Se(VI) was only 0.058 ± 0.009 µg L^{-1}. This discrepancy is likely a reflection of the differences between analytical methods, as the strong acid and heat required by SSHG may have promoted decomposition of Se-bearing molecules/colloids that were neither Se(VI) nor Se(IV). This was further revealed by the analysis of water from tributaries, where dissolved concentrations were extremely low (~100 – 300 ng L^{-1}), and Se speciation analysis by IC-ICP-MS did not yield concentrations above the LOQ. The results for tributary waters analyzed using SSHG were considered unreliable given that the waters contained extremely low concentrations of Se but abundant colloidal material (Cuss et al., 2018). To further study this issue, tributary waters were analyzed twice using SSHG: once with the microwave temperature programmed for 90°C (as described above), and again with the temperature at 110°C. Even this slight change in temperature promoted the generation of higher concentrations of Se during HG-AFS analysis, highlighting the uncertainty associated with analyzing low concentrations of Se in colloid-rich water (Fig. 5.9). Clearly, more work is required to understand both the chemical form and behavior of Se in the < 0.45 µm fraction.

5.3.3 Selenium concentrations in Trout-perch muscle

The average concentration of Se in muscle of Trout-perch harvested from the Athabasca River was 2.2 ± 0.4 mg kg^{-1} ($n = 34$) and the concentration in upstream fish was not significantly higher ($p > 0.05$) than those from the midstream or downstream reaches (Fig. 5.5). The results for Se measurements in acid-digests by ICP-MS and HG-AFS were in good agreement (Table 5.3) and the outcome of the statistical analysis was the same. Greater variability in the concentrations of Se in the muscle tissue of Trout-perch from the Clearwater River, together with the low number of samples (n=5), prevented a detailed assessment (Table 5.2); however, Se concentrations in Trout-perch from the Clearwater River were comparable to those collected from Athabasca River (1.1 ± 0.96 mg kg^{-1}; 0.08 – 2.2 mg kg^{-1}). To assess the potential influence of fish size or age as a factor controlling Se concentrations in muscle tissue, Trout-perch fork length and total weights were compared to Se concentrations. However, no significant correlation was observed between Se concentrations and either parameter ($p > 0.05$; Fig. 5.10 and 5.11). Selenium concentrations in Trout-perch muscle were also below guidelines issued by the US EPA (11.3 mg kg^{-1}; US EPA) and the British Columbia Ministry of Environment (interim value of 4 mg kg^{-1}; BC MoE, 2014); Canadian Federal (CCME) tissue guidelines for Se have not been established. Although Se uptake by fish and other aquatic organisms involves a number of interrelated and site specific factors (see Discussion), the enrichment of Se in fish muscle relative to Athabasca River water (~2000 µg/kg versus ~0.2 µg/kg) speaks to the ability of aquatic organisms to accumulate Se. The natural enrichment of Se in fish relative to water is a reminder that measuring the concentration of Se in water is inadequate for determining its ecological implications.

5.4 Discussion

5.4.1 Se in the lower Athabasca River watershed

Previous assertions that Se is more abundant in Athabasca River water downstream of bitumen mining and upgrading (Kelly et al., 2010) have led to considerable public concern regarding fish and human health. However, that conclusion was based on limited data, with all values for the dissolved phase below detection limits and only one sample (downstream) containing a quantifiable amount of total Se (Kelly et al., 2010). The instrumentation and methods applied here yielded much lower limits of detection and failed to reveal evidence of increased Se concentrations in the Athabasca River due to bitumen mining and upgrading. Moreover, Se inputs to the Athabasca River from natural bitumen erosion and saline groundwater did not appear to pose an ecological threat. As the purpose of this study was to distinguish between these different sources and assess their relevance, sampling was purposely conducted under base-flow conditions. Additional studies are underway to assess the atmospheric deposition of Se from ABS mining and upgrading, as well as seasonal changes in trace element concentrations in the Athabasca River.

As a cautionary remark, the potential for Se contamination from bitumen processing still requires careful monitoring due to its enrichment in bitumen (Donner et al., 2018) and a general lack of knowledge regarding its fate in upgrading and refining processes. For example, in 2006, a major bitumen upgrading and refining facility near Edmonton (Alberta) discovered elevated concentrations (up to 600 µg L^{-1}) of Se in their effluent that was being discharged to the North Saskatchewan River (BC MoE, 2014). Since the problem was found, measures were taken to successfully reduce Se loadings by 80%; apparently, however, sediment and biota immediately downstream still showed elevated Se concentrations (BC MoE, 2014).

5.4.2 Colloidal versus truly dissolved Se species

Broadly defined as particles that have a length between 1 nm and 1 µm in at least one dimension, the colloidal phase is often incorrectly equated with the "dissolved" fraction, which is operationally defined as the material that passes through a 0.45 µm membrane (Filella, 2007). Colloids are composed of an array of inorganic (e.g., Fe oxyhydroxides, Mn oxides, carbonate minerals, clays) and organic (e.g., humic substances and fulvic acids) particles, and are known for their considerable influence on trace element speciation, transport and bioavailability (Lead and Wilkinson, 2007). Selenium can be transported as part of the colloidal fraction by way of reversible surface adsorption, incorporation during mineral formation or through biological uptake into tissue. The uptake rates and strength of bonding can differ greatly depending on the speciation of dissolved Se, as selenate and selenite display remarkably different behavior. With respect to adsorption, selenate anions are highly mobile under oxidizing conditions and retained primarily through weak bonding mechanisms such as outer-sphere complexation or attraction in the diffuse swarm (Fernández-Martínez, 2009; Hayes et al., 1987; Zhang and Sparks, 1990; Sposito, 1995). Conversely, selenite mobility is strongly influenced by adsorption phenomena and displays a much higher affinity for reactive sites on particle surfaces (Fernández-Martínez, 2009), particularly –OH bonds on common Fe minerals (Hayes et al., 1987; Zhang and Sparks, 1990), functional groups in DOM (Bruggeman, 2007), or ternary complexes of Fe-DOM constituents (Gustafsson and Johnsson, 1994; Martin et al., 2017; Peel et al., 2017). Selenite is also considerably more bioavailable than Se(VI) and is rapidly sequestered by phytoplankton and other base-level consumers, as well as being used for dissimilatory reduction by sediment dwelling microorganisms (Luoma and Rainbow, 2008). Therefore, unless a major anthropogenic source exists, Se(VI) tends to predominate in oxic surface waters and a larger proportion of "organo-Se" (either incorporated, surface-bound, or as a true biomolecule) is observed in organic-rich waters (Zhang and Moore, 1996).

This general description of biogeochemical behavior is consistent with the results of Se speciation observed in the Athabasca River. Tributaries drain massive areas of boreal forest and peatlands, and deliver large amounts of DOM and Fe to the Athabasca River. A recent study of trace element speciation using asymmetrical flow field-flow fraction coupled to ICP-MS determined that both the concentration and proportion of trace elements (As, Co, Fe, Mn, Pb, U, Zn) bound to natural colloids increased due to inputs from these tributaries, and the concentrations of small, mainly ionic, forms of As, Ba, Mo, and U decreased upstream-downstream, suggesting binding and removal from the dissolved phase (Cuss et al., 2018). The input of DOM and Fe rich material to the Athabasca River could therefore be a primary factor governing the low concentrations of Se(IV). While Se was not included in the list of elements studied by Cuss et al. (2018), dissolved As (also present in water as oxyanions) had the strongest correlation with DOC, which was consistent with observations of its redox-state speciation in a companion study (Donner et al., 2017).

With large fluctuations in suspended particles and wetland material combined with considerable inputs of Fe and organic matter from tributaries, understanding the bioavailability and bioaccessibility of Se as it relates to natural or anthropogenic inputs is challenging and illustrates the need for biological indicators. Indeed, measuring the total (particulate + dissolved) Se concentrations provides additional detail, but Se must be present in the dissolved phase to enter the food chain via uptake by microflora – the transfer rates of Se associated with particulates to higher-level organisms are not well defined and vary depending on their composition (Hodson et al., 2010). In other words, assessing whether suspended particulate matter is a relevant dietary source of Se requires knowledge of its composition (ranging from algae to clay minerals), which cannot be obtained by digesting a bulk water sample and measuring total Se. The same issue exists for the colloidal phase; despite knowing that a significant portion of Se < 0.45 μm is likely colloidal, little information can be inferred regarding its bioaccessibility.

5.4.3 Selenium in Trout-perch

The concentration and bioaccumulation of Se in fish tissue varies with a number of site specific factors, making it difficult to compare with other species of fish or the same species in different habitats (Stewart et al., 2010). Even within the same watershed, fish have seasonal migration routes or are capable of foraging over long distances. Therefore, comparisons of Se concentrations in fish collected from different areas in a river may not be reliable. For that reason, a comparison of Trout-perch in the same water body is a valuable and more reliable indicator of Se exposure, as their lack of migration increases the chances of identifying specific inputs. Unlike elements such as Hg, Cs, and Tl, fish age (excluding juveniles) and trophic position are not considered highly relevant factors for the bioaccumulation of Se (Gantner et al., 2009). Fish size has been linked to Se concentrations, but due to dietary changes at specific times in the life-cycle and not simply due to age or size alone (Stewart et al., 2010). This is consistent with the lack of relationship observed here between Se concentrations in Trout-perch muscle and fork length. Due to these important differences between species and habitat, it is challenging to compare the present results with data for fish from other areas. A study of the biological impacts of bitumen derived contaminants found that the average concentration of Se in the liver of white sucker (*Catostomus commersonii*) in the Muskeg River was 0.87 mg kg^{-1} (n = 6; Arens et al., 2017). Unfortunately, the Se data in that study was compared only to white sucker sampled from a nearby reference lake (lentic system), wherein the processes governing the biogeochemical cycling and hence exposure to and uptake of Se likely differ compared to fish from the lotic system in the Muskeg River. For perspective, the results of a nationwide study (541 sites) of river and stream health in the United States of America conducted in 2008 and 2009 revealed that fish species commonly consumed by humans had a median Se concentration of 1.90 mg kg^{-1} (wet-weight; US EPA, 2016).

The presence of Se in aquatic systems is of interest both due to its potential toxicity, and its role as an essential micronutrient. However, what has not yet been discussed with respect to its presence in the Athabasca River is its potential role in mitigating the toxicity of other potentially toxic metals (Ikemoto et al., 2004; Levander and Argrett, 1969; Magos et al., 2008; Morris, 2015; Sørmo et al., 2011). Selenium is well known for its antagonistic relationship with Hg in animal tissue, limiting toxic effects through the formation of highly stable mercury selenides (Hg-S) (Khan and Wang, 2009; Sørmo et al., 2011). Given concern regarding Hg emissions from the mining and upgrading of ABS (Kirk et al., 2014; Willis et al., 2018), an assessment of the biological relevance of Hg in aquatic organisms in the lower Athabasca River should include information about Se. A good example of this comes from a study of Se contaminated lakes near the metal smelters in Sudbury, Canada, where fish (walleye, *Sander vitreus* and yellow perch, *Perca flavescens*) were harvested from a series of lakes varying in distance from the smelters (Chen et al., 2001). It was found that the concentrations of Se and Hg in fish muscle tissue had a significant, inverse correlation, suggesting that the high input of Se to lakes from smelting had an antagonistic effect on Hg concentrations (Chen et al., 2001).

5.5 Conclusions

Surface water samples collected from the Athabasca River and tributaries in 2014 and 2015 failed to reveal elevated concentrations of Se either due to naturally saline groundwater inputs or emissions from bitumen surface mining and upgrading in the ABS region. Similarly, no significant increase ($p < 0.05$) in the Se concentration of muscle tissue in Trout-perch was observed for regions near-industry or downstream of industry compared to upstream. Despite the enrichment of Se in the bitumen (organic) fraction of ABS, concentrations in the Athabasca River and Trout-perch muscle were consistently low and do not suggest Se contamination by ABS mining and upgrading activities.

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5.7 References

Alexander, A.C., Chambers, P.A., Jeffries, D. S., 2017. Episodic acidification of 5 rivers in Canada's oil sands during snowmelt: A 25-year record. Sci. Total Environ. 599–600: 739–749.

Alexander, D.A., Chambers, D.P., 2016. Assessment of seven Canadian Rivers in relation to stages in oil sands industrial development, 1972 to 2010. Environ. Rev. 24 (4): 484–494.

Aren, C.J., Arens, J.C., Hogan, N.S., Kavanagh, R.J., Berrue, F., Van Der Kraak, G.J., van den Heuvel, M.R., 2017. Population impacts in white sucker (*Catostomus commersonii*) exposed to oil sands-derived contaminants in the Athabasca River. Environ. Toxicol. Chem. 36 (8): 2058–2067.

BC MOE, 2014. British Columbia Ministry of the Environment. Water Quality Guidelines. Accssed at https://www2.gov.bc.ca/gov/content/environment/air-land-water/water/water-quality/water-quality-guidelines/approved-water-quality-guidelines

Bicalho, B., Grant-Weaver, I., Sinn, C., Donner, M.W., Woodland, S., Pearson, G., Larter, S., Duke, J.,Shotyk, W., 2017. Determination of ultratrace (<0.1 mg/kg) elements in Athabasca Bituminous Sands mineral and bitumen fractions using inductively coupled plasma sector field mass spectrometry (ICP-SFMS). Fuel 206: 248–57.

Bruggeman, C., Maes, A., Vancluysen, J., 2007. The interaction of dissolved Boom Clay and Gorleben humic substances with selenium oxyanions (selenite and selenate). Appl. Geochem. 22: 1371–1379.

CCME, 1999. Canadian Environmental Quality Guidelines. Canadian Council of Ministers of the Environment. Environment Canada, Hull, Quebec 1999. Accessed at http://st-ts.ccme.ca/en/index.html?lang=en&factsheet=197#aql_fresh_date.

Chapman, P.M., 2007. Selenium thresholds for fish from cold freshwaters. Hum. Ecol. Risk Assess. 13: 20–24.

Chen, Y-W., Belzile, N., Gunn, J.M., 2001. Antagonistic effect of selenium on mercury assimilation by fish populations near Sudbury metal smelters ? Limnol. Oceanogr. 46 (7): 1814–1818.

Chen, Y-W., Zhou, X-L., Tong, J., Truong, Y., Belzile, N., 2005. Photochemical behavior of inorganic and organic selenium compounds in various aqueous solutions. Anal. Chim. Acta, 545 (2): 149–157.

Conly, F.M., Crosley, R.W., Headley, J.V.; Quagraine, E.K., 2007. Assessment of metals in bed and suspended sediments in tributaries of the lower Athabasca River. J. Environ. Sci. Health, 42:8, 1021–1028.

Cuss, C.W., Donner, M.W., Grant-Weaver, I., Noernberg, T., Pelletier, R., Sinnatamby, R.N., Shotyk, W., 2018. Fingerprinting sources of trace elements in aquatic systems by measuring their distribution amongst colloidal species. Sci. Total Environ., 642: 1242–1251.

Cuss, C.W., Donner, M.W., Noernberg, T., Pellletier, R., Shotyk, W. Disentangling the seasonal and source-based variation of dissolved organic matter quality in a large river and its source waters using EEM-PARAFAC-SOM. J. Geophys. Res. Biogeosci. (In review).

Cutter, G.A., 1978. Species determination of selenium in natural waters. Anal. Chim. Acta, *98*(1): 59–66.

Deforest, D.K., Brix, K.V, Adams, W.J., 1999. Critical review of proposed residue-based selenium toxicity thresholds for freshwater. Hum. Ecol. Risk Assess, 5(6): 1187–1228.

Donner, M.W., Bicalho, B., Sinn, C., Shotyk, W., 2018. Selenium and sulphur in Athabasca bituminous sands mineral and bitumen fractions. Fuel 224: 718–725.

Donner, M.W., Javed, M.B., Shotyk, W., Francesconi, K.A., Siddique, T., 2017. Arsenic speciation in the lower Athabasca River watershed: A geochemical investigation of the dissolved and particulate phases. Environ. Pollut. 224: 265–274

Donner, M.W., Siddique, T., 2018. A rapid and sensitive IC-ICP-MS method for determining selenium speciation in natural waters. Can. J. Chem. In Press. dx.doi.org/10.1139/cjc-2017-0637.

Ellis, J., Jasechko, S., 2018. Formation waters discharge to rivers near oil sands projects. Hydrol. Processes 32(4): 533–549.

Fernández-Martínez, A., Charlet, L., 2009. Selenium environmental cycling and bioavailability: A structural chemist point of view. Rev. Environ. Sci. Biotechnol., 8 (1): 81–110.

Filella, M., 2007. Colloidal properties of submicron particles in natural waters, in Wilkinson, K.J., Lead, J.R. (Eds.) Environmental colloids and particles behaviour, separation and characterisation. John Wiley & Sons, Ltd, England, pp. 17–93.

Gantner, N., Power, M., Babaluk, J.A., Reist, J.D., Köck, G., Lockhart, L.W., Solomon, K.R., Muir, D.C.G., 2009. Temporal trends of mercury, cesium, potassium, selenium, and thallium in Arctic Char (*Salvelinus alpinus*) from Lake Hazen, Nunavut, Canada: Effects of trophic position, size, and age. Environ. Toxicol. Chem., 28(2): 254–263.

Gibbons, W.N., Munkittrick, K.R., McMaster, M.E., Taylor, W.D., 1998. Monitoring aquatic environments receiving industrial effluents using small fish species 2: comparison between responses of trout-perch (*percopsis omiscomaycus*) and white sucker (*catostomus commersoni*) downstream of a pulp mill. Environ. Toxicol. Chem. 17(11): 2238–2245.

Gibson, J.J., Fennell, J., Birks, S.J., Yi, Y., Moncur, M.C., Hansen, B., Jasechko, S, 2013. Evidence of discharging saline formation water to the Athabasca River in the oil sands mining region, Northern Alberta. Can. J. Earth Sci. 50(12): 1244–1257.

Goldschmidt, V.M., 1937. The principles of distribution of chemical elements in minerals and rocks. J. Chem. Soc. 655–673.

Guéguen, C., Clarisse, O., Perroud, A., McDonald, A., 2011. Chemical speciation and partitioning of trace metals (Cd, Co, Cu, Ni, Pb) in the lower Athabasca river and its tributaries (Alberta, Canada). J. Environ. Monit. 13(10): 2865-2872.

Gustafsson, J.P., Johnsson, L., 1994. The association between selenium and humic substances in forested ecosystems–Laboratory Evidence. Appl. Organomet. Chem., 8: 141–147.

Hamilton, S.J., 2002. Rationale for a tissue-based selenium criterion for aquatic life. Aquat. Toxicol., 57: 85–100.

Hayes, K.F., Roe, A.L., Brown, G. E. Jr., Hodgson, K.O., Leckie, J.O., Parks, G.A., 1987. In situ x-ray absorption study of surface complexes: selenium oxyanions on α-FeOOH. Science, 238 (4828): 783–786.

Hillwalker, W.E., Jepson, P.C., Anderson, K.A., 2006. Selenium accumulation patterns in lotic and lentic aquatic systems. Sci. Total Environ. 366: 367–379.

Hodson, P.V., Reash, R.J., Canton, S.P., Campbell, P.V., Delos, C.G., Faribrother, A., Hitt, N.P., Miller, L.L., Ohlendorf, H.M. Selenium risk characterization, in: Chapman, P.M., Adam s, W.J., Brooks, M.L., Delos, C.G., Luoma, S.N., Maher, W.A., Ohlendorf, H.M., Presser, T.S., Shaw, D.P. (Eds.), Ecological assessment of selenium in the aquatic environment, 2010, CRC Press, Taylor & Francis Group, Boca Raton, pp. 233–256.

Ikemoto, T., Kunito, T., Tanaka, H., Baba, N., Miyazaki, N., Tanabe, S., 2004. Detoxification mechanism of heavy metals in marine mammals and seabirds: Interaction of selenium with mercury, silver, copper, zinc, and cadmium in liver. Arch. Environ. Contam. Toxicol. 47: 402–413.

Javed, M.B., Cuss, C.W., Grant-Weaver, I., Shotyk, W., 2017. Size-resolved Pb distribution in the Athabasca River shows snowmelt in the bituminous sands region an insignificant source of dissolved Pb. Sci. Rep., 7: 43622.

Kelly, E.N., Schindler, D.W., Hodson, P.V., Short, J.W., Radmanovich, R., Nielsen, C. C., 2010. Oil sands development contributes elements toxic at low concentrations to the Athabasca River and its tributaries. Proc. Natl. Acad. Sci. USA, 107 (37): 16178–16183.

Khan, M.A.K., Wang F., 2009. Mercury–selenium compounds and their toxicological significance: toward a molecular understanding of the mercury–selenium antagonism. Environ. Toxicol. Chem., 28(8): 1567–1577.

Kirk, J.L., Muir, D.C.G., Gleason, A., Wang, X., Lawson, G., Frank, R.A., Lehnherr, I., Wrona, F., 2014. Atmospheric deposition of mercury and methylmercury to landscapes and waterbodies of the Athabasca Oil Sands Region. Environ. Sci. Technol. 48: 7374–7383.

Lead, J.R., Wilkinson, K.J., 2007. Environmental colloids and particles: Current knowledge and future developments, in Wilkinson, K.J., Lead, J.R. (Eds.) Environmental colloids and particles behaviour, separation and characterisation. John Wiley & Sons, Ltd, England, pp. 1–15.

Lemly, D.A., 1998. Pathology of selenium poisoning in fish, in Frankenberger, W.T. Jr., Engberg, R.A. (Eds.) Environmental chemistry of selenium. Marcel Dekker, Inc. New York, NY, pp. 281–296.

Lenz, M., Lens, P.N.L., 2009. The essential toxin: The changing perception of selenium in environmental sciences. Sci. Total Environ. 407(12): 3620–3633.

Levander, O.A., Argrett, L.C., 1969. Effects of arsenic, mercury, thallium, and lead on selenium metabolism in rats. Toxicol. Appl. Pharmacol. 14: 308–314.

Luoma, S.N., Rainbow, P.S., 2008. Selenium: Dietary exposure, trophic transfer and food web effects, in: Metal contamination in aquatic environments: Science and lateral management. Cambridge University Press, New York, NY, 573p.

Luoma, S.N., 2009. Emerging opportunities in management of selenium contamination. Environ. Sci. Technol. 43: 8483–8487.

Magos, L., Webb, M., Clarkson, T.W., 2008. The interactions of selenium with cadmium and mercury. Crit. Rev. Toxicol. 8 (1): 1–42.

Martin, D.P., Seiter, J.M., Lafferty, B.J., Bednar, A.J., 2017. Exploring the ability of cations to facilitate binding between inorganic oxyanions and humic acid. Chemosphere 166: 192–196.

Morris, D.L., 2015. Chemistry and activity of selenium dioxide and selenite ions, in: Preedy, V.R. (Ed.) Selenium: chemistry, analysis, function and effects. The Royal Society of Chemistry, Cambridge, UK, pp. 65–80.

Nriagu, J.O., 1989. Global cycling of selenium, in: Inhat, M. (Ed.) Occurrence and distribution of selenium. CRC Press, Boca Raton, Florida, pp. 327–340.

Ohlendorf, H.M., Hoffman, D.J., Saiki, M.K., Aldrich, T.W., 1986. Embryonic mortality and abnormalities of aquatic birds: Apparent impacts of selenium from irrigation drainwater. Sci. Total Environ., 52 (1–2): 49–63.

Ohlendorf, H.M., Hothem, R.L., Bunck, C.M., Marois, K.C., 1990. Bioaccumulation of selenium in birds at Kesterson Reservoir, California. Arch. Environ. Contam. Toxicol. 19(4): 495–507.

Outridge, P.M., Scheuhammer, A.M., Fox, G.A., Braune, B.M., White, L.M., Gregorich, L.J., Keddy, C., 1999. An assessment of the potential hazards of environmental selenium for Canadian water birds. Environ. Rev. 7 (2): 81–96.

Peel, H.R., Martin, D.P., Bednar, A.J., 2017. Extraction and characterization of ternary complexes between natural organic matter, cations, and oxyanions from a natural soil. Chemosphere 176: 125–130.

Pilote, M., Turcotte, A.C., Gagné, F., Gagnon, C., 2018. Metal bioaccumulation and biomarkers of effects in caged mussles exposed in the Athabasca oil sands area. Sci. Total Environ. 610–611: 377–390.

Ross, M.S., Pereira, A.D.S., Fennell, J., Davies, M., Johnson, J., Sliva, L., Martin, J.W., 2012. Quantitative and qualitative analysis of naphthenic acids in natural waters surrounding the canadian oil sands industry. Environ. Sci. Technol. 46 (23): 12796–12805.

Sánchez-Rodas, D., Corns, W.T., Chen, B., Stockwell, P.B., 2010. Atomic fluorsecence spectrometry: a suitable detection technique in speciation studies for arsenic, selenium, antiomony and mercury. J. Anal. At. Spectrom. 25: 933–946.

Selby, D., 2005. Direct radiometric dating of hydrocarbon deposits using rhenium-osmium isotopes. Science, 308 (5726): 1293–1295.

Shotyk, W., Bicalho, B., Cuss, C.W., Donner, M.W., Grant-Weaver, I., Haas-Neill, S., Javed, M.B., Krachler, M., Noernberg, T., Pelletier, R. Zaccone, C., 2017. Trace metals in the dissolved fraction (< 0.45 µm) of the lower Athabasca River: Analytical challenges and environmental implications. Sci. Total Environ., 580: 660–669.

Simmons, D.B.D., Wallschläger, D., 2005. A critical review of the biogeochemistry and ecotoxicology in lotic and lentic environments. Environ. Toxicol. Chem. 24 (6): 1331–1343.

Sørmo, E.G., Ciesielski, T.M., Øverjordet, I.B., Lierhagen, S., Eggen, G.S., Berg, T., Jenssen, B. M., 2011. Selenium Moderates Mercury Toxicity in Free-Ranging Freshwater Fish. Environ. Sci. Technol., 45 (15): 6561–6566.

Spafford, M.D., 1999. Trout-perch *Percopsis omiscomaycus* (Walbaum) and lake chub Couesius plumbeus (Agassiz), as sentinel monitoring species in the Athabasca River, Alberta. Thesis. University of Alberta. Edmonton, Alberta.

Sposito, G., 1995. Adsorption as a problem in coordination chemistry: The concept of the surface complex, in: Huang, C.P., O'Melia, C.R., Morgan, J.J. (Eds.), Aquatic chemistry interfacial and interspecies processes. American Chemical Society, Washington, DC, pp. 33–57.

Stewart, R., Grosell, M., Buchwalter, D., Fisher, N., Luoma, S., Mathews, T., Orr, P., Wang, W-X., 2010. Bioaccumulation and trophic transfer of selenium, in: Chapman, P.M., Adam s, W.J., Brooks, M.L., Delos, C.G., Luoma, S.N., Maher, W.A., Ohlendorf, H.M., Presser, T.S., Shaw, D.P. (Eds.), Ecological assessment of selenium in the aquatic environment. CRC Press, Taylor & Francis Group, Boca Raton, pp. 93–139.

Sun, C., Shotyk, W., Cuss, C.W., Donner, M.W., Fennell, J., Javed, M., Noernberg, T., Poesch, M., Pelletier, R., Sinnatamby, N., Siddique, T., Martin, J.W, 2017. Characterization of naphthenic acids and other dissolved organics in natural water from the Athabasca Oil Sands Region, Canada. Environ. Sci. Technol., 51 (17): 9524–9532.

USEPA, 2016. Aquatic Life Ambient Water Quality Criterion for Selenium – Freshwater, 2016, United States Environmental Protection Agency. https://www.epa.gov/sites/production/files/2016-07/documents/aquatic_life_awqc_for_selenium_-_freshwater_2016.pdf

Wallschläger, D., Feldmann, J., 2010. Formation, occurrence, significance, and analysis of organoselenium and organotellurium compounds in the environment, in: Sigel, A., Sigel, H., Sigel, R.K.O (Eds.). Organometallics in Environment and Toxicology: Metal Ions in Life Sciences. Royal Society of Chemistry, Cambridge, UK, pp. 319–364.

Willis, C.E., Kirk, J.L., Louis, V.L.S., Lehnherr, I., Ariya, P.A., Rangel-Alvarado, R.B., 2018. Sources of methylmercury to snowpacks of the Alberta Oil Sands Region: A study of in situ methylation and particulates. Environ. Sci. Technol., 52: 531–540.

Young, T.G., Finley, K., Adams, W.J., Besser, J., Hopkins, W.D., Jolley, D., McNaughton, E., Presser, T.S., Shaw, P., Unrine, J., 2010. What you need to know about selenium, in: Chapman, P.M., Adam s, W.J., Brooks, M.L., Delos, C.G., Luoma, S.N., Maher, W.A., Ohlendorf, H.M., Presser, T.S., Shaw, D.P. (Eds.), Ecological assessment of selenium in the aquatic environment. CRC Press, Taylor & Francis Group, Boca Raton, pp. 7–46.

Zhang, P., Sparks, D.L., 1990. Kinetics of selenate and selenite adsorption/desorption at the goethite/water Interface. Environ. Sci. Technol., 24(12): 1848–1856.

Zhang, Y. and Moore, J.N., 1996. Selenium fractionation and speciation in a wetland system. Environ. Sci. Technol., 30: 2613–2619.

Zhu, Y. and Guéguen, C., 2016. Evaluation of free/labile concentrations of trace metals in Athabasca oil sands region streams (Alberta, Canada) using diffusive gradient in thin films and a thermodynamic equilibrium model. Environ. Pollut., 219: 1140–1147.

5.8 Figures

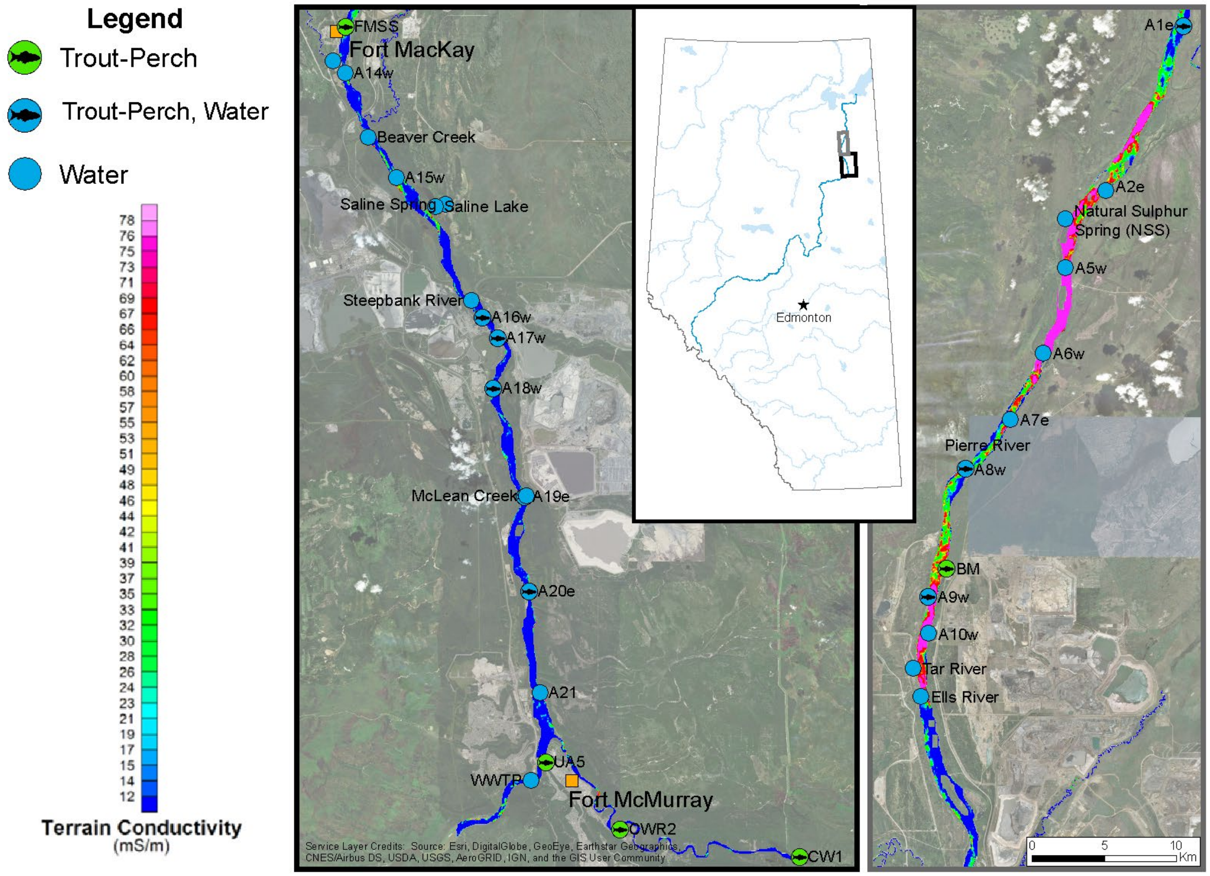

Figure 5.1 Map of the study area and sampling locations during the 2014 (water samples and Trout-perch) and 2015 (water samples only) sampling campaigns. Map begins at the bottom of the left panel and continues from the bottom of the right panel. Water sampling locations for Pierre River and McKay River are hidden from view and some minor adjustments of site labels were applied for greater clarity (see Supplementary Info for exact coordinates). Data for lower terrain conductivity mapping were taken from Gibson et al., (2013).

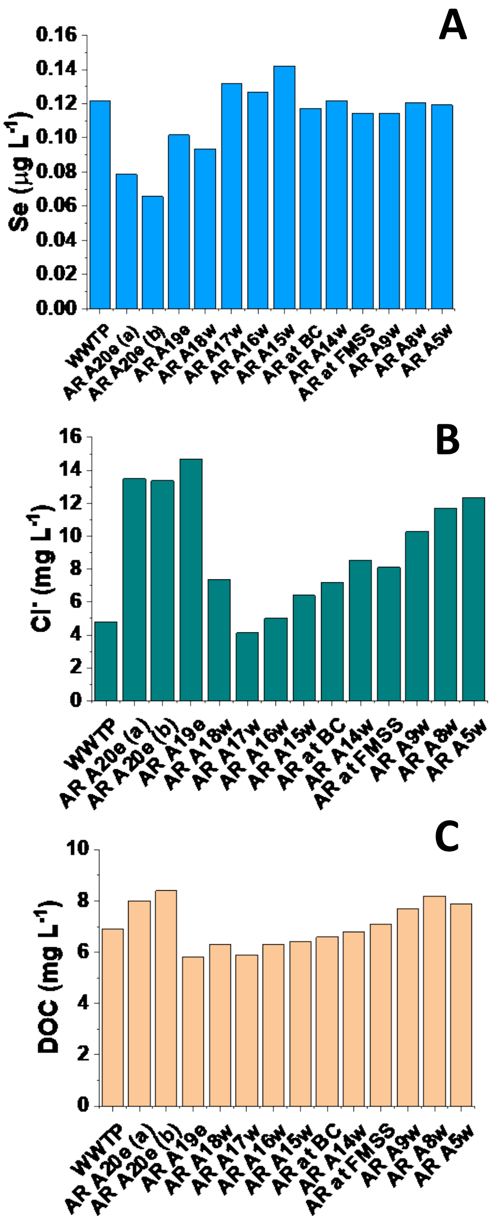

Figure 5.2 Concentrations of dissolved (< 0.45μm) Se (Panel A), Cl^- (Panel B) and DOC (Panel C) in the main-stem of the Athabasca River during 2014. Sites are listed from left to right in order from upstream to downstream, with the area of greatest industrial activity located between sites A18w and A9w. Site duplicates are denoted with (a) or (b) and were collected 3 days apart.

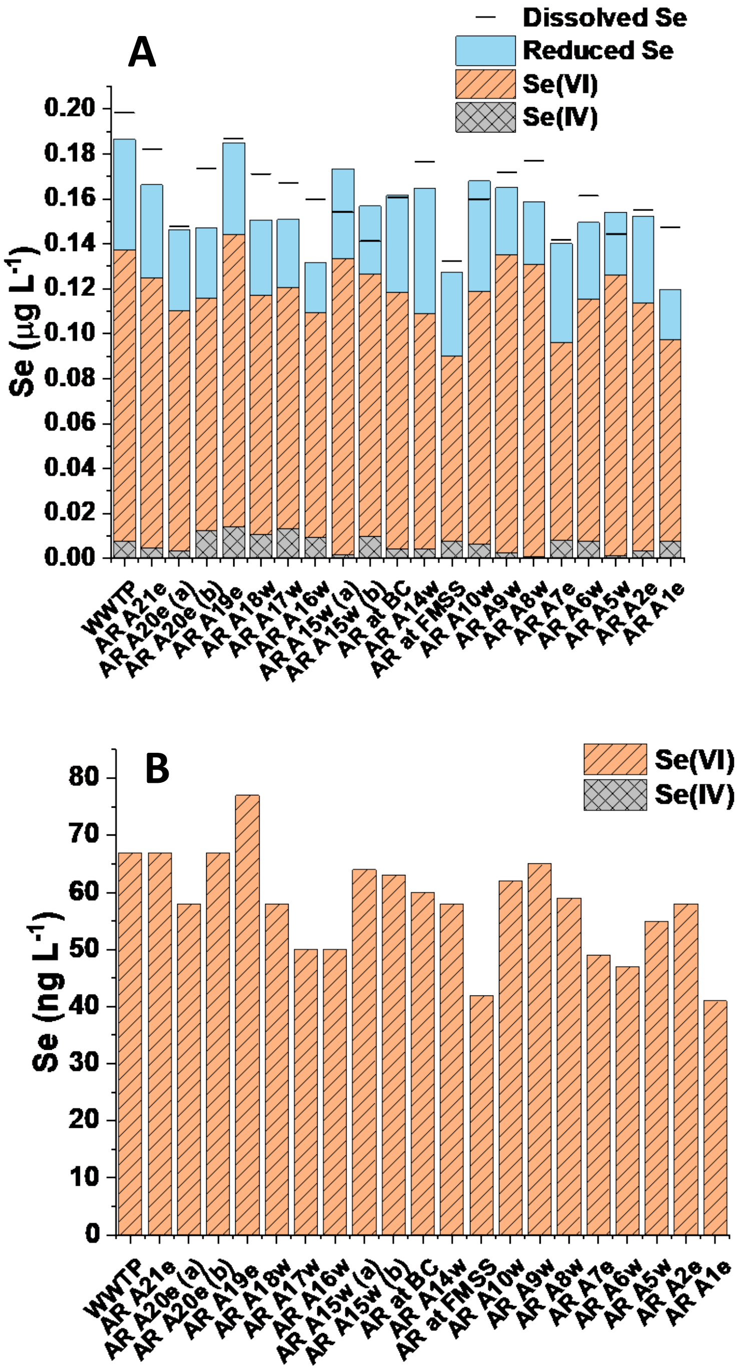

Figure 5.3 Selenium speciation in Athabasca River water (2015) using SSHG (Panel A) and IC-ICP-MS (Panel B). Sites are listed from left to right in order from upstream to downstream, with the area of greatest industrial activity located between sites A18w and A9w. Site duplicates were collected 8 and 3 days apart for A20e and A15, respectively.

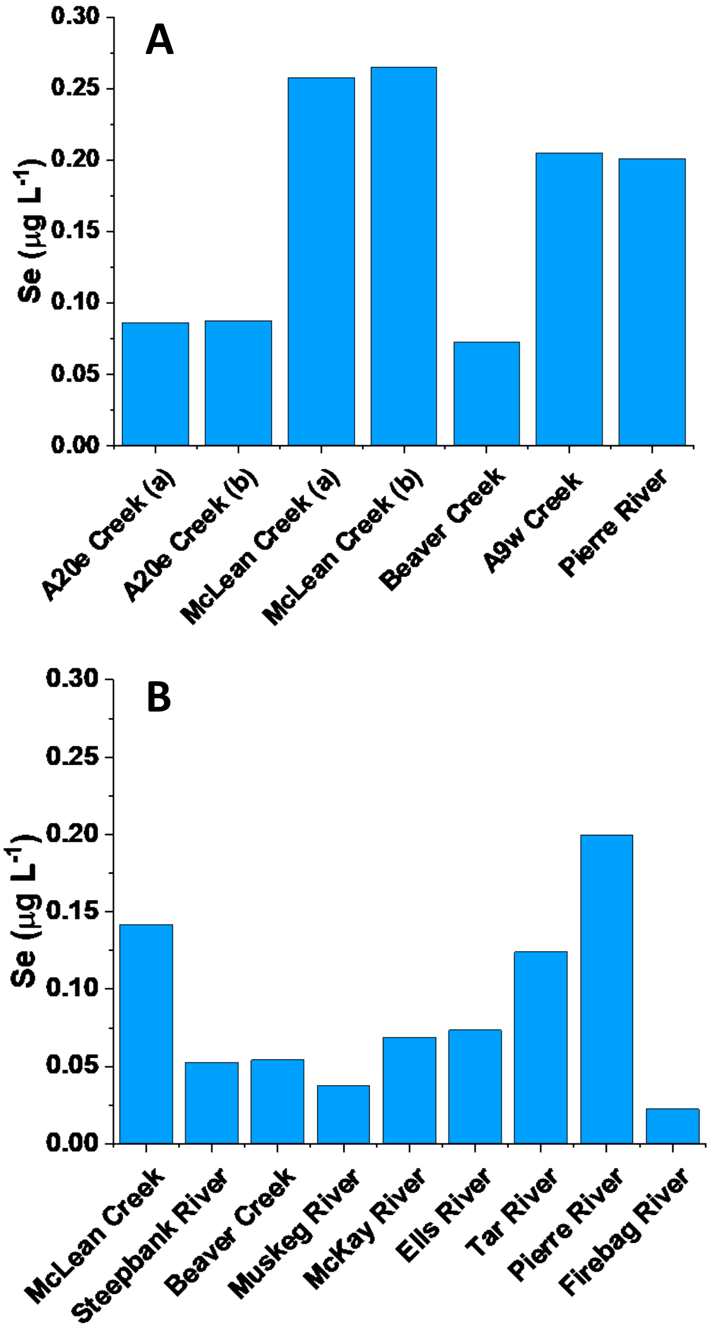

Figure 5.4 Concentrations of dissolved (< 0.45µm) Se in selected tributaries along the Athabasca River in 2014 (Panel A) and 2015 (Panel B). Site duplicates are denoted with (a) or (b) and were collected approximately 1 h apart.

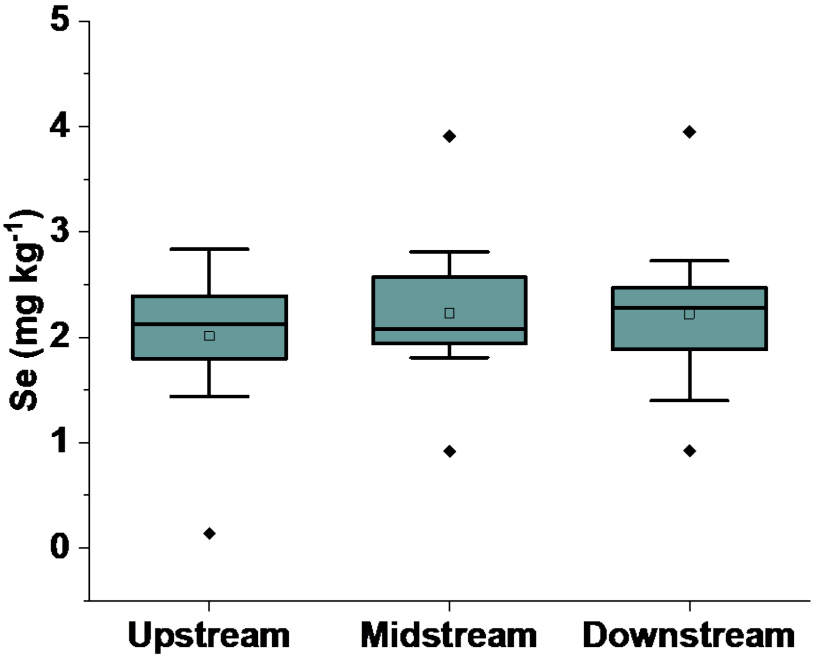

Figure 5.5 Selenium concentration (dry-weight) in muscle tissue of Trout-perch collected from the lower Athabasca River (n=34). No significant difference ($p > 0.05$) was observed in Se concentration from fish collected upstream (reference), midstream (industrial) or downstream (saline groundwater).

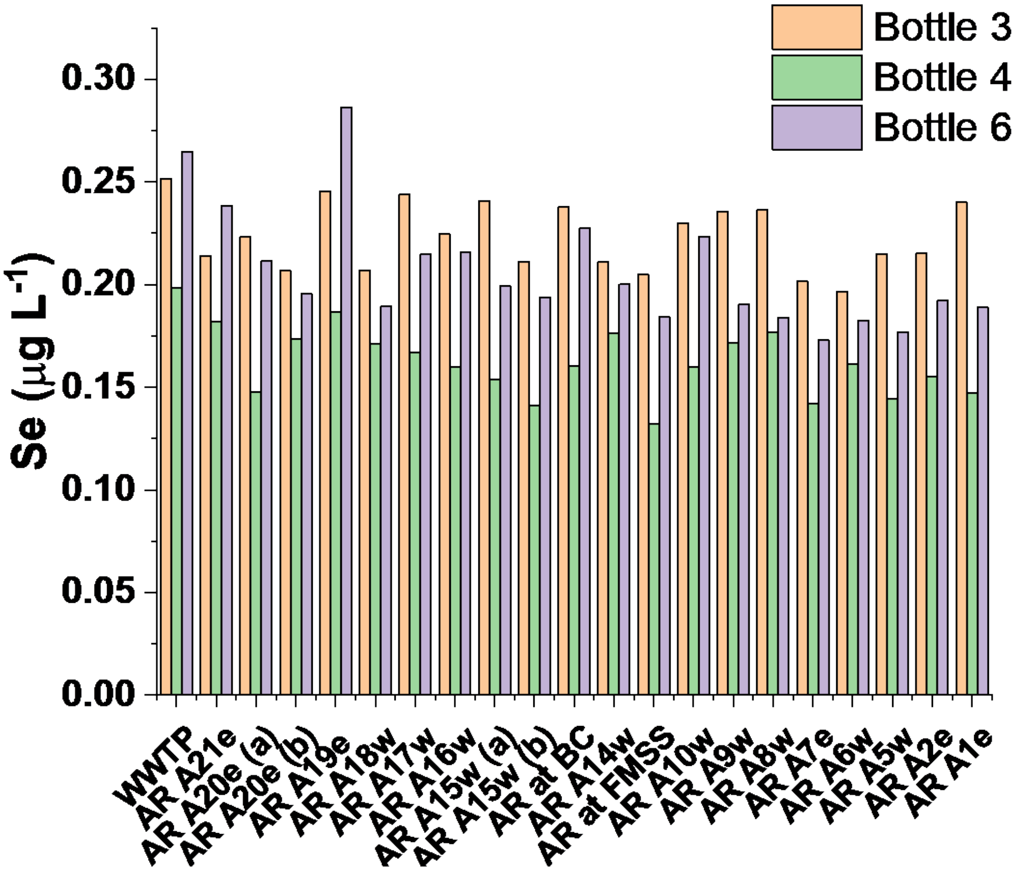

Figure 5.6 Intercalibration study of dissolved (<0.45 µm) Se in Athabasca River water collected in 2015. Bars represent Se concentrations in samples collected minutes apart. Bottles 3 and 6 were filtered (0.45 um) the same way as Bottle 4 (used in this study), but acidified with double-distilled HNO_3 instead of HCl.

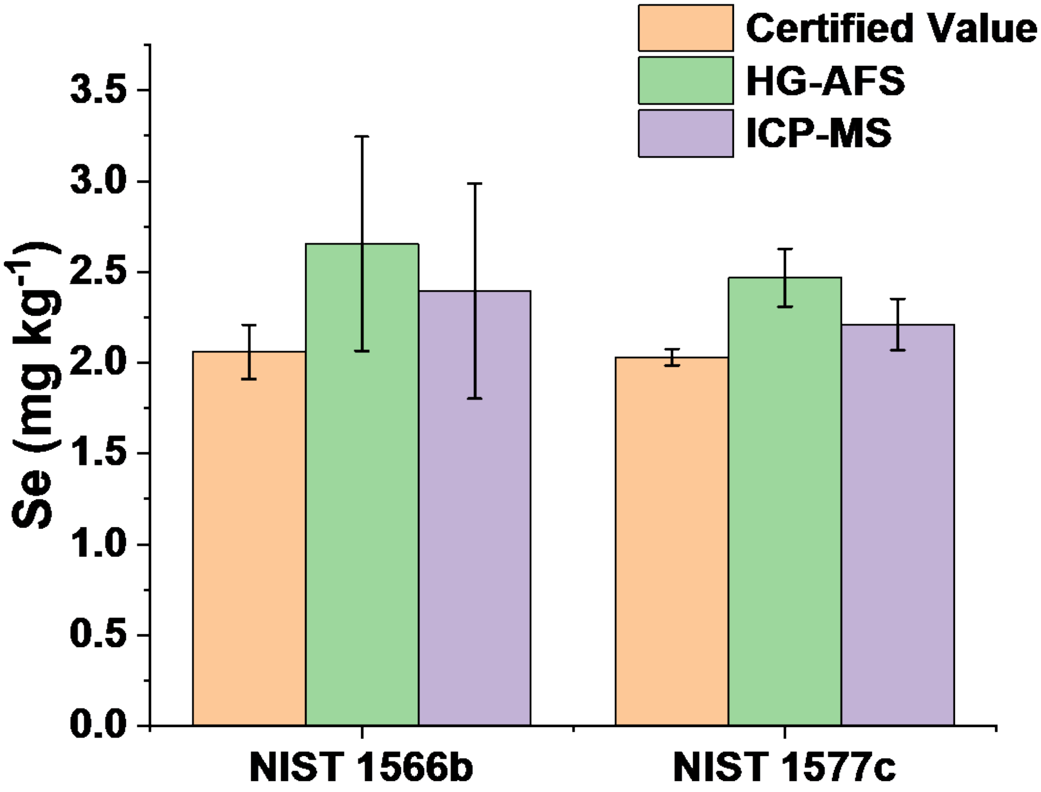

Figure 5.7 Comparison of HG-AFS and ICP-MS recoveries of Se in certified SRM measured during Trout-perch muscle tissue analysis. Error bars for measurements by HG-AFS and ICP-MS represent the standard deviation (n = 6), error bars for the certified values represent a coverage factor (approximately 95% confidence interval) as determined by the National Institute of Standards and Technology (NIST).

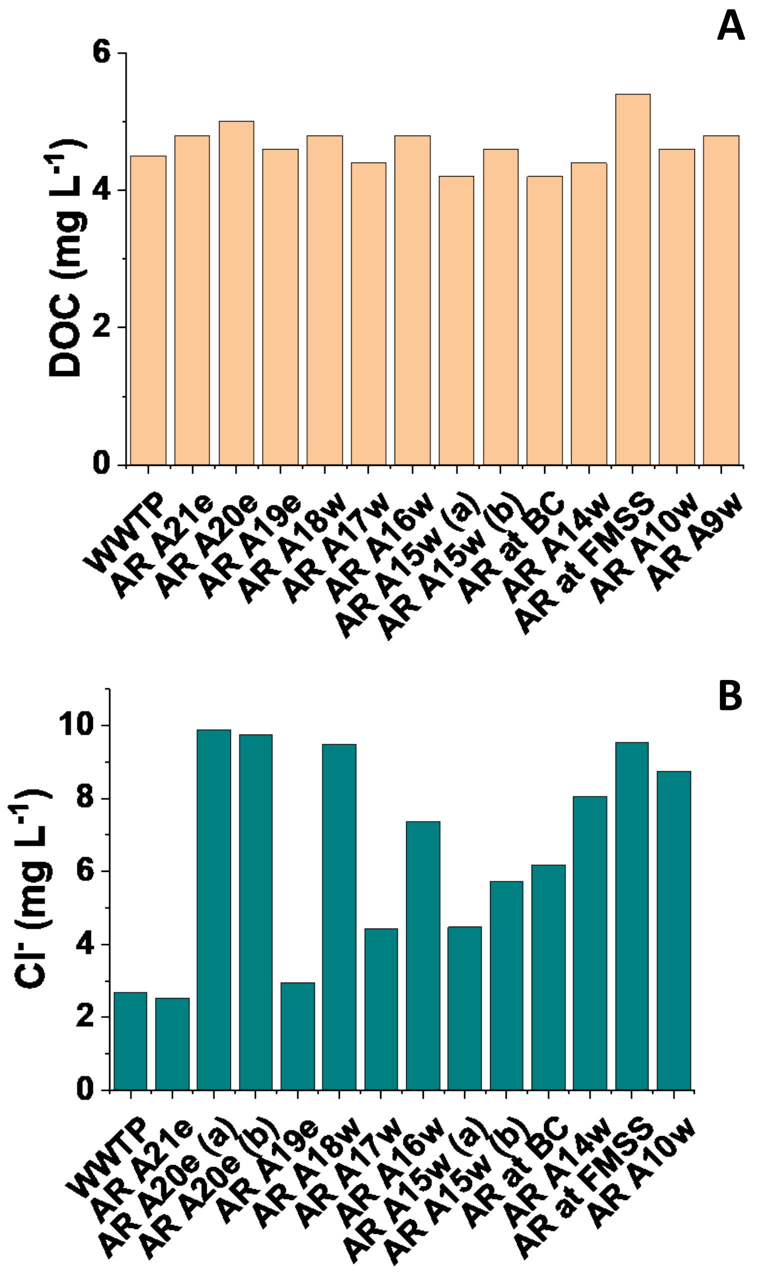

Figure 5.8 Concentrations of DOC (Panel A) and Cl^- (Panel B) in the main-stem of the Athabasca River during 2015.

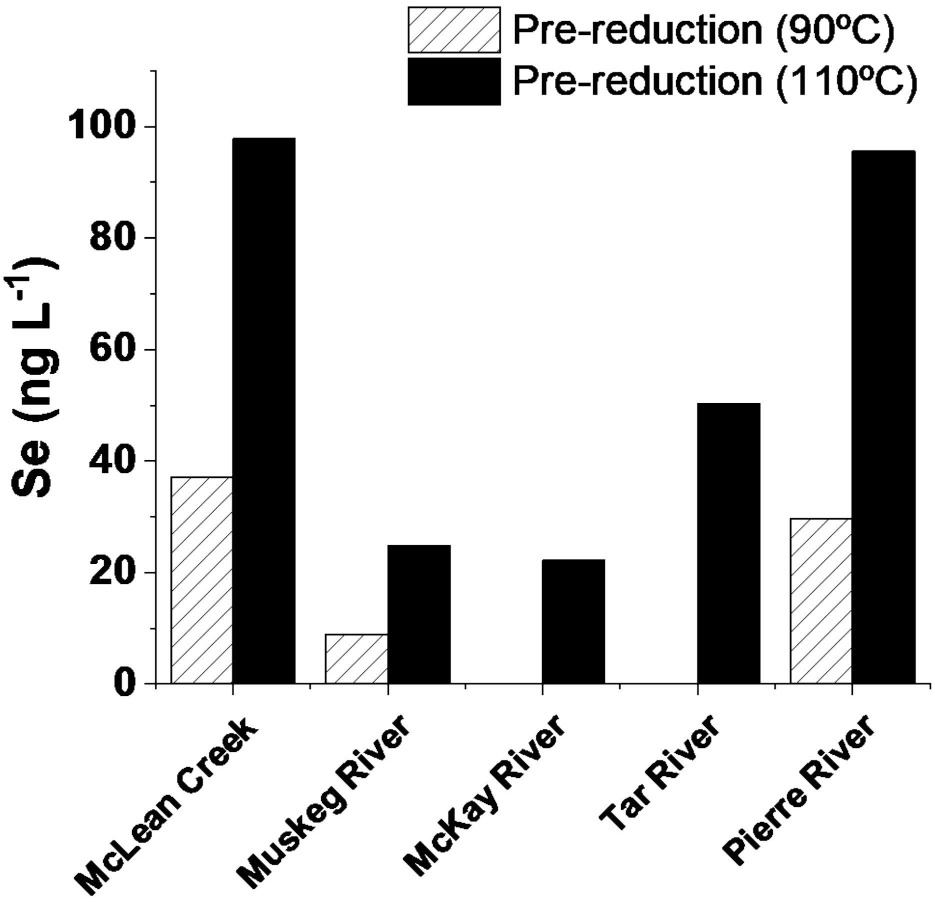

Figure 5.9 Differences in Se concentration of samples pre-reduced at two different temperatures for determining reducible Se [Se(VI) + Se(IV)] during SSHG analysis.

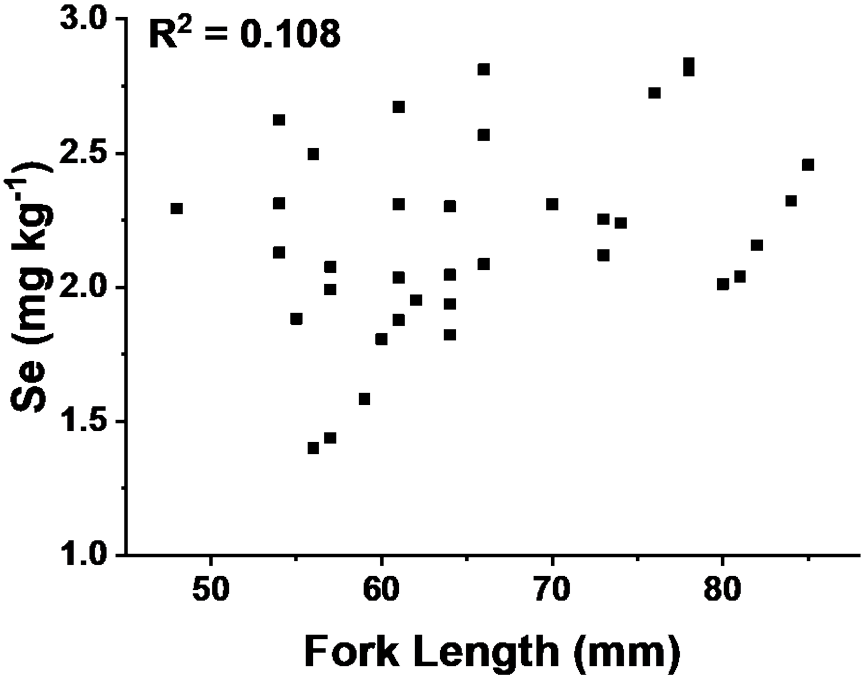

Figure 5.10 Scatter plot and linear regression analysis of Trout-perch fork length and Se concentration in muscle tissue. A significant correlation was not observed (p = 0.050). Raw data is provided in Tables 5.3 and 5.4.

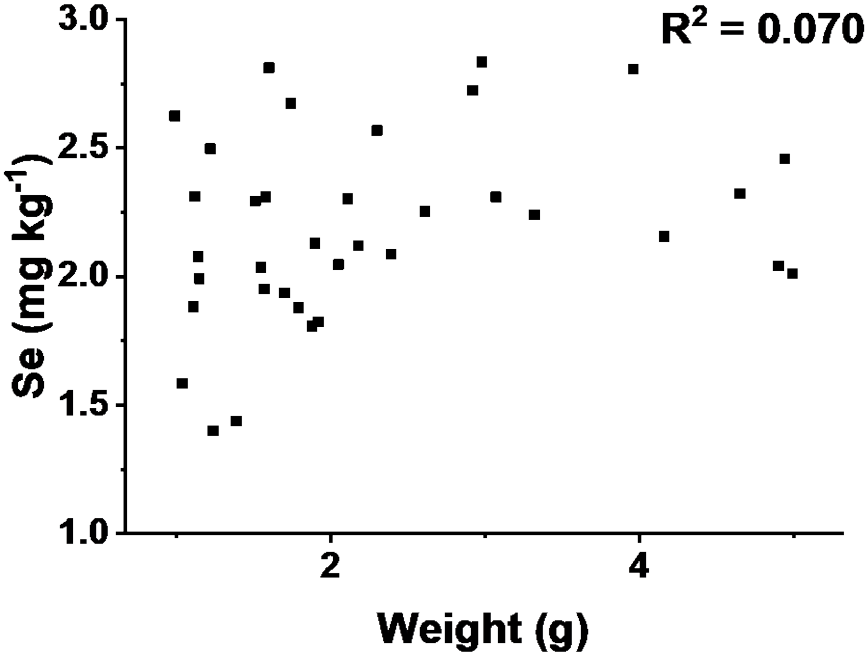

Figure 5.11 Scatter plot and linear regression analysis of Trout-perch weight and Se concentration in muscle tissue. A significant correlation was not observed (p = 0.119). Raw data is provided in Tables 5.3 and 5.4.

5.9 Tables

Table 5.1 Trout-perch collection sites and GPS locations sampled from the Athabasca River and Clearwater River in 2014.

Site Name	Latitude (°N)	Longitude (°W)
A1	57.725220	111.374860
A8	57.448000	111.628220
BM	57.385270	111.645990
A9	57.367360	111.666690
FMSS	57.189640	111.627440
A16	57.008210	111.470640
A17	56.994920	111.452370
A18	56.963800	111.457750
A19	56.897480	111.416360
A20	56.840250	111.411460
UA5	56.731721	111.393190
CWR2	56.690169	111.308400
CW1	56.673330	111.105840

Table 5.2 Concentration of Se determined by ICP-MS and HG-AFS in Trout-perch muscle tissue collected in 2014 from the Clearwater River.

Sample label	HG-AFS (mg Se kg^{-1})	ICP-MS (mg Se kg^{-1})
CW1 D10	1.9	1.8
CW1 D11	1.4	1.4
CWR2 D10	0.1	0.1
CWR2 D11	0.1	0.1
CWR2 D12	2.2	2.2

Table 5.3 Concentration of Se in Trout-perch muscle tissue collected in 2014 from the main-stem of the Athabasca River. Outliers are denoted by an asterisk (*) and were not included in the statistical analysis.

River section	Sample label	HG-AFS (mg Se kg^{-1})	ICP-MS (mg Se kg^{-1})
Upstream (n = 12)	UA5 D01	2.56	2.46
	UA5 D03	2.12	2.01
	A20 D01	2.16	2.24
	A20 D02	1.69	1.58
	A20 D03	2.48	2.32
	A20 D05	3.09	2.81
	A20 D07	1.72	1.44
	A19 D02	2.11	2.04
	A19 D04*	0.12*	0.14*
	A19 D05	2.31	2.09
	A19 D07	3.31	2.83
	A19 D08	2.42	2.16
Midstream (n = 15)	A18 D06	2.85	2.57
	A18 D08	2.42	2.04
	A18 D09	2.08	1.81
	A17 D09	2.31	1.99
	A17 D07	2.65	2.31
	A17 D11	2.71	2.50
	A16 D01	3.15	2.81
	A16 D02	2.17	1.95
	A16 D06	2.46	2.08
	FMSS D08	2.11	1.82
	FMSS D11	2.95	2.67
	FMSS D16*	1.01*	0.92*
	A9 D03	2.36	2.12
	A9 D04	2.14	1.94
	A9 D12*	4.39*	3.91*
Downstream (n = 12)	BM D06	2.71	2.31
	BM D07	2.39	2.05
	BM D08	2.67	2.30
	A8 D08	1.54	1.40
	A8 D09	2.25	1.88
	A8 D11	2.92	2.62
	A1 D01	3.09	2.72
	A1 D02*	4.60*	3.95*
	A1 D05	2.57	2.25
	A1 D07	2.19	1.88
	A1 D09*	1.01*	0.92*
	A1 D10	2.49	2.31

Table 5.4 Trout-perch fork length and weight for individual fish collected from the Athabasca River and Clearwater River in 2014.

Site Name	Fork Length (mm)	Weight (g)	River
A1 D01	76	2.92	Athabasca
A1 D02	71	2.72	Athabasca
A1 D05	73	2.61	Athabasca
A1 D07	55	1.11	Athabasca
A1 D09	57	1.00	Athabasca
A1 D10	54	1.12	Athabasca
A8 D08	56	1.24	Athabasca
A8 D09	61	1.79	Athabasca
A8 D11	54	0.99	Athabasca
BM D06	70	3.07	Athabasca
BM D07	64	2.05	Athabasca
BM D08	64	2.11	Athabasca
A9 D03	73	2.18	Athabasca
A9 D04	64	1.70	Athabasca
A9 D12	67	1.63	Athabasca
FMSS D08	64	1.92	Athabasca
FMSS D11	61	1.74	Athabasca
FMSS D16	60	1.51	Athabasca
A16 D01	66	1.60	Athabasca
A16 D02	62	1.57	Athabasca
A16 D06	57	1.14	Athabasca
A17 D07	61	1.58	Athabasca
A17 D09	57	1.15	Athabasca
A17 D11	56	1.22	Athabasca
A18 D06	66	2.30	Athabasca
A18 D08	61	1.55	Athabasca
A18 D09	60	1.88	Athabasca
A19 D02	81	4.90	Athabasca
A19 D04	78	3.68	Athabasca
A19 D05	66	2.39	Athabasca
A19 D07	78	2.98	Athabasca
A19 D08	82	4.16	Athabasca
A20 D01	74	3.32	Athabasca
A20 D02	59	1.04	Athabasca
A20 D03	84	4.65	Athabasca
A20 D05	78	3.96	Athabasca
A20 D07	57	1.39	Athabasca
UA5 D01	85	4.94	Athabasca
UA5 D03	80	4.99	Athabasca
CW1 D10	59	1.32	Clearwater
CW1 D11	53	1.24	Clearwater
CW2 D10	65	2.09	Clearwater
CW2 D11	66	2.36	Clearwater
CW2 D12	60	1.56	Clearwater

6.0 CONTEMPORARY AND HISTORICAL ATMOSPHERIC DEPOSITION OF ARSENIC AND SELENIUM IN THE ATHABASCA BITUMINOUS SANDS REGION [**]

[**] A version of this chapter has been prepared for submission to a peer-reviewed journal

6.1 Introduction

Ombrotrophic (rain-fed) peat bogs are useful biomonitors of atmospheric trace element deposition because they hydrologically disconnected from groundwater and receive inputs solely from the atmosphere (Shotyk, 1996a). Contemporary inputs of trace elements from the atmosphere can be determined using living vegetation (e.g., *Sphagnum* moss) growing on the surface of bogs (Arafat and Glooschenko, 1982; Glooschenko et al., 1986; Harmens et al., 2010) and over time, a stratified record of atmospheric deposition is formed as moss dies and accumulates as peat (Shotyk, 1996a). Due to these features, peat bogs have been used successfully as environmental archives for documenting both contemporary and historical atmospheric deposition of trace elements in many regions of the world (Roos-Barraclough et al., 2002; Shotyk et al., 1996b, 1998). Peat bogs are effective biomonitors of many trace elements with ecological relevance (Shotyk et al., 1996a), including Se, which is chemically unique due to its complex biogeochemical cycling and speciation (Wen and Carignan, 2007). Mosses have been used successfully in monitoring programs to document major sources of Se to the atmosphere, including volcanos (Arndt et al., 2017), the marine biosphere (Harmens et al., 2010; Steinnes et al., 1992) and industrial emissions (Glooschenko and Arafat, 1988). Selenium has also been used as a reference element in ombrotrophic peat in coastal regions to distinguish natural (marine aerosols) from anthropogenic inputs (Givelet et al., 2004a; Roos-Barraclough et al., 2006; Shotyk et al., 2003). However, the preservation of an atmospheric Se deposition record by continental peat bogs far-removed from inputs by the marine biosphere has not been well studied.

A multi-disciplinary study of moss and age-dated peat cores from ombrotrophic bogs in northern Alberta, Canada was conducted to assess the extent of atmospheric metal pollution from surface mining and upgrading of the Athabasca bituminous sands (ABS). Moss samples from peat bogs in the Athabasca Bituminous Sands Region (ABSR) failed to reveal contemporary pollution of potentially toxic metals from bitumen mining and upgrading (Shotyk et al., 2014, 2016a), and peat core profiles indicated that concentrations of Ag, Cd, Pb, Sb, Tl have been in decline for decades (Shotyk et al., 2016b, 2017). The simplest explanation for the lack of metal pollution in the ABSR lies in the distribution of trace metals in bitumen and mineral (sand) fractions of the ABS, as nearly all metals of environmental significance are contained predominantly in the mineral fraction and only a select few (V, Ni, Mo, Re) are predominantly with bitumen (Bicalho et al., 2017). In contrast to metal deposition, the amount of mineral dust deposition in the ABSR has increased over time, which has resulted in greater inputs of soluble carbonate minerals and major plant nutrients such as P (Mullan-Boudreau et al., 2017a, 2017b).

Selenium was not included in the list of elements previously determined in moss and peat from the ABSR due to its unique environmental chemistry and analytical requirements. Atmospheric emissions of Se due to bitumen upgrading may also be more likely given that it is contained predominantly (ca. 80%) in the organic (bitumen) fraction of bituminous sands (Donner et al., 2018). Here, we assessed contemporary Se deposition by analyzing moss collected from the ABSR and compared with moss obtained from peat bogs across Canada. Historical deposition of Se was determined using age dated peat cores collected from an ombrotrophic bog near industry (11 km from the mid-point between two central upgraders) and from a reference area more than 250 km south-west of the ABSR. Concentrations of As, another element of concern from ABS mining and upgrading, were also determined in the same peat cores for comparison. Unlike Se, As is contained predominantly in the mineral fraction of ABS (Bicalho et al., 2017), and has also been described as an element of potential concern from ABS mining and upgrading (Kelly et al., 2010). Scandium, a conservative lithophile element, was determined in peat cores to provide perspective on the contribution of As and Se from mineral dust. Scandium is an ideal reference element for representing mineral dust because it behaves conservatively during chemical weathering (Shotyk, 1996a). The primary objectives of this study were to i) determine whether Se concentrations in moss from the ABSR are elevated relative to mosses from other areas of Canada and ii) determine whether atmospheric deposition of As and Se in the ABSR have increased over time due to bitumen production.

6.2 Materials and methods

6.2.1 Moss sampling locations

Moss samples (primarily *Sphagnum sp.*) were obtained from Canadian peat bogs in different regions of Alberta and Canada. Samples were collected as part of a greater effort to understand and provide perspective on air quality in the ABSR. Most of this work has already been published (Mullan-Boudreau et al., 2017b; Shotyk et al., 2014, 2016a), including details on general site characteristics, GPS coordinates and other supporting information. A summary of sampling locations, with corresponding references containing detailed information, is provided in Table 6.1. Samples of coastal moss (predominantly *Sphagnum sp.*) were obtained from Miscou Island Bog (N 47° 56.579', W 064° 31.368') New Brunswick, and Shorepine Bog Trail (N 49° 00' 45.1" W 125° 39' 33.2") Pacific Rim National Park, British Columbia. Samples were collected in June and August 2017 for Miscou Island Bog and Shorepine Bog Trail, respectively. A map of sampling locations of moss and peat used in this study is provided in Figure 6.1. Arsenic and Sc concentrations in mosses from the ABSR were determined previously using a commercial lab and have been published elsewhere (Shotyk et al., 2016a). Methods for sample collection, handling and preparation for Se analysis are briefly described in the proceeding sections.

6.2.2 Moss collection and handling

Bulk samples of moss were collected using disposable polyethyelene gloves and contained in plastic bags, or cut from the bog surface using a surgical stainless steel knife and contained inside pre-cleaned square polyethylene containers. Bulk samples of moss were typically obtained from at least three separate locations within each bog. Samples were kept cool (~4 °C) until being transferred to a freezer (-20°C) for long-term storage. To prepare samples for acid-digestion, foreign plant material was removed and mosses were trimmed to retain only the green "living" portion. Samples were dried at 105°C and ground to a fine powder using a Retsch agate centrifugal ball mill operated at 300 rpm (alternating between reverse and forward).

6.2.3 Peat core sampling locations

Peat cores from two bogs in Alberta were selected for this study: Mildred (MIL) and Utikuma (UTK). These peat cores were part of a larger set of cores that were investigated for a number of different purposes, including trace element concentrations (Shotyk et al., 2016b, 2017), age-depth modelling (Davies et al., 2018), climate change impacts on vegetation, testate amoeba records (van Bellen et al., 2018) and dust deposition (Mullan-Boudreau et al., 2017a). A long list of physical, chemical and biological parameters were determined as a result of that work, providing a comprehensive understanding of peat formation and the atmospheric deposition of inorganic and organic constituents. The MIL core (collected in 2013) was chosen in this study because it was the closest to ABS mining and upgrading, located only 11 km from the mid-point between two central upgraders (Fig. 6.1). The UTK core (collected in 2014) was chosen as the reference site because it is well removed from ABS mining and upgrading (~264 km south-west from upgrader mid-point) and is located in the Utikuma Region Study Area, a protected natural area for the long-term study of peatland hydrology and other ecosystem functions (Devito et al., 2016).

6.2.4 Peat core sample processing

Peat cores were obtained using a 15 x 15 x 100 cm Wardenaar monolith sampler (Wardenaar, 1987) and wrapped in plastic for transport back to the lab where they were stored at -20°C. Frozen cores were precisely cut into 1 cm slices on a custom-built polypropylene cutting table using a stainless-steel band saw. The edges of each frozen slice were removed and used for pH and electrical conductivity determination. The inner portion of each slice was divided amongst research teams studying a variety of constituents; a schematic of how each slice was divided is available elsewhere (Mullan-Boudreau et al., 2017a). Samples for trace element determination (including As and Se) were transferred to polypropylene containers for drying and milling, following the same procedures as described above for moss. A detailed protocol for peat core sampling and lab preparation is published elsewhere (Givelet et al., 2004b).

6.2.5 Moss and peat acid digestion

Powdered samples of moss and peat were transferred to the SWAMP ultra-clean lab at the University of Alberta – a metal-free facility for the study of trace and ultra-trace elements in the environment. Approximately 0.2 g of dry material was weighed into PTFE digestion vessels and mixed with 0.1 mL of polytetrafluroboric acid and 3mL of trace metal grade nitric acid, which had been further purified twice by sub-distillation. Samples were digested with a Milestone

UltraCLAVE using high heat and pressure; details regarding the ramp and hold times are available elsewhere (Shotyk et al., 2014). After cooling, liquid digests were transferred to 15 mL polypropylene centrifuge tubes (pre-cleaned in acid), diluted with MilliQ water (18.2 MΩ·cm; MilliporeSigma, Massachusetts, USA) and stored under refrigeration until analysis.

6.2.6 Selenium determination by HG-AFS

Selenium concentrations were determined in acid-digests using hydride generation atomic fluorescence spectroscopy (HG-AFS); the complete method is described in detail elsewhere (Donner et al., 2018). Briefly, 5mL of digestate was combined with 5mL of MilliQ water and 15mL of HCl (trace metal grade, Fisher Scientific) in acid-cleaned PTFE digestion vessels and heated to 90°C for 60 min using a microwave digestion unit (MARS, CEM Corporation, USA). After cooling, the mixture was transferred to calibrated polypropylene vessels (certified for trace metal analysis) and diluted to 50 mL with MilliQ water. Samples were analyzed using a Millennium Excalibur 10.055 HG-AFS system (PS Analytical, Orpington, UK) with a 7 g/L solution of sodium borohydride (stabilized with 4 g of sodium hydroxide) as chemical reductant. Argon gas was used as both the drying and carrier gas to sweep the produced hydrogen and gaseous Se to an argon-hydrogen flame for atomization and radiation by a boosted discharge hollow cathode lamp. External calibration solutions were prepared fresh from a stock solution of 2000 mg/L Se(IV) (sodium selenite; 99%; Sigma Aldrich).

All digestion batches included a variety of certified standard reference materials (SRMs) and three digestion blanks. A summary of SRMs and recovered values is provided in Table 6.2. A blank containing the same proportions of acid was also included in every batch of samples that were pre-reduced (HCl plus heat) for HG-AFS analysis. Pre-reduction blanks were used to verify instrument limits of detection for HG-AFS analysis over multiple analyses and were compared to digestion blank values to monitor for any potential contamination. The instrument detection limit (IDL) was ~3 ng/L; assuming a dry mass of 0.2 g, and accounting for the dilution factor for digestion samples used here (10x), the method detection limit (MDL) was determined to be 15 µg/kg (see Donner et al., 2018 for details). Individual samples were injected into the HG-AFS in duplicate and had a relative standard deviation of < 5%.

6.2.7 Arsenic and scandium determination by ICP-SMS

Acid-digests of peat from MIL and UTK were diluted and analyzed for As and Sc using inductively coupled plasma sector-field mass spectrometry (ICP-SMS; Element XR, Thermo-Finnigan, Bremen, Germany). Details on the instrument operating conditions and sample preparation can be found elsewhere (Bicalho et al., 2017). Information on SRMs and their recoveries is provided in Table 6.3. Instrument detection limits were assessed prior to every analysis, with the maximum MDLs determined to be 9.4 and 5.5 µg/kg for As and Sc, respectively.

6.2.8 Age-depth modelling

Detailed age-depth models were developed for MIL and UTK cores by Davies et al. (2018). Ages were established for each core using Bayesian statistical models, which incorporated measurements of ^{14}C, ^{210}Pb (supported by ^{137}Cs and ^{241}Am) and cryptotephra peaks. Details regarding lab and statistical analyses are available elsewhere (Davies et al., 2018).

6.2.9 Ombrotrophic and minerotrophic zones in peat cores

A critical aspect of using peat cores as archives of atmospheric conditions is to accurately distinguish the ombrotrophic and minerotrophic regions for each core. This was determined and confirmed using a variety of different methods by previous studies of the same cores, including measurements of pH, EC and Sr as indicators of groundwater influence (Shotyk et al., 2017). Unlike UTK, which was determined to be entirely ombrotrophic, peat at depths greater than approximately 20 cm for MIL were determined to be minerotrophic (Mullan-Boudreau et al., 2017a; Shotyk et al., 2017).

6.3 Results

6.3.1 Selenium in moss from Canadian bogs

Moss samples collected from Alberta peat bogs contained low concentrations of Se (typically < 100 µg/kg). Mosses from bogs in the ABSR had an average Se concentration of 57.5 ± 13.1 µg/kg (n = 75) and ranged from 33.0 – 91.3 µg/kg (Fig. 6.2). Similar concentrations were observed for moss collected from EINP (47.1 ± 6.0 µg/kg, n = 3), WAG (38.4 ± 5.3 µg/kg, n = 3) and SEB (81.4 ± 5.4 µg/kg, n = 3; Fig. 6.2). Remote reference sites in Alberta contained very low concentrations of Se, with moss from UTK, CMW and BMW containing 28.7 ± 5.4 µg/kg (n = 3), 35.2 ± 3.1 µg/kg (n = 3) and 37.3 ± 6.6 µg/kg (n = 3), respectively (Fig. 6.2). UTK, EINP and WAG were re-sampled in 2015 and were found to have similar concentrations to the previous year: UTK, 54.1 ± 5.4 µg/kg (n = 3); EINP, 65.7 ± 15.4 µg/kg (n = 3); WAG, 55.4 µg/kg ± 8.9 µg/kg (n = 3). Selenium concentrations in Ontario mosses obtained from LUT (212.5 ± 18.4 µg/kg, n = 3), SIFT (230.1 ± 15.5 µg/kg, n = 3) and ALG (141.5 ± 18.9 µg/kg, n = 3) contained greater concentrations than moss from Alberta (Fig. 6.2). However, moss collected from the East and West coasts of Canada contained the greatest concentrations of Se, with moss from MISC containing 281.9 ± 3.9 µg/kg (n = 1) and SBT containing 231.5 ± 3.9 µg/kg (n = 1;

Fig. 6.2). The elevated concentrations of Se in Ontario moss could be related industrial activity (e.g., steel-production, coal burning power plants, etc.) in southern Ontario and the north-eastern United States of America (McLinden et al., 2012).

The growth rate of *Sphagnum fuscum* was determined by Mullan-Boudreau et al. (2017b) using a volumetric sampling technique in 30 bogs in the ABSR (2015 growing season) and three bogs in the URSA (10 samples each, *n* = 30). Using growth rates determined for the ABSR (215 ± 65 g/m^2/yr) and URSA (192 ± 60 g/m^2/yr) in 2015, multiplied by the average concentrations for ABSR and UTK moss (2013, 2014 seasons), the Se accumulation rates were determined to be 12.4 µg/m^2/yr and 5.5 µg/m^2/yr, respectively.

Mineral dust is known to be an important source of trace metals in moss from the ABSR (Shotyk et al., 2014; Shotyk et al., 2016a). To evaluate the potential contribution of Se from mineral dust particles, we also examined the relationship of Sc and Se in moss. Linear regression analysis was applied using Se (this study) and Sc concentrations (Shotyk et al., 2016a) determined in moss samples. A strong linear relationship between Sc and Se (R^2 =0.719; Fig. 6.5) was found, which is consistent with comparisons of Sc in ABSR moss samples with As and a host of other potentially toxic metals (Ag, Cd, Pb, Sb, Tl), including those enriched in bitumen (V, Ni, Mo; Shotyk et al., 2014, 2016a).

6.3.2 Selenium in Alberta peat cores

Peat in the ombrotrophic zone (uppermost 17 cm) of MIL contained relatively low Se concentrations (93–140 µg/kg) and did not demonstrate a clear increasing or decreasing pattern with depth (Fig. 6.3A). The Se accumulation rate in the ombrotrophic zone of MIL (average = 38.5 ± 9.8 µg/m^2/year; n = 9) also yielded a similar profile (Fig. 6.3B). In contrast, a clear increase in Se concentrations was apparent with greater depth in the minerotrophic zone due to inputs from groundwater, reaching a maximum concentration of 4649 µg/kg (Fig. 6.3A). The substantial difference in concentration between ombrotrophic and minerotrophic zones reflects the ability for Se to bind strongly with peat (González et al., 2006) and emphasizes the importance of distinguishing minerotrophic and ombrotrophic conditions. Fortunately, the age of peat in the ombrotrophic zone begins at ~1982, providing an ample period of time for assessing potential changes in Se (and As) deposition due to bitumen mining, which began in 1967.

Selenium concentrations in UTK were more consistent throughout the entire profile (46 – 349 µg/kg) due to the absence of groundwater influence (Fig. 6.3C). A modest increasing trend in Se concentrations at greater depths was apparent due to peat compaction and decomposition (Fig. 6.3C), which was also reflected by its strong correlation ($r^2 = 0.91$; Fig 6.6) with dry bulk density. Using the Se accumulation rate, which takes into account differences in peat growth rates over time, a visible increase in Se concentrations was apparent in peat dated around the early 20th century (Fig. 6.3D). The rate of Se accumulation increases beginning in the early 1900's until reaching its zenith at ~1971–1984, where it steadily decreases (Fig. 6.3D). The Se accumulation rate in the living layer (moss plus bog vegetation) of UTK was determined to be similar to values prior to the start of the 20th century (Fig. 6.3D), indicating that the atmospheric deposition of Se today is similar to background conditions (see Discussion). The Se accumulation rate in the ombrotrophic zone of MIL (Fig. 6.3B) was consistently greater than that of UTK (Fig. 6.3D), however, values were within a factor of ~1–3x and did not demonstrate an increase with time.

6.3.3 Arsenic in Alberta peat cores

Similar to Se, the concentration profile of As in MIL demonstrated a visible increase in concentration with depth due to inputs from groundwater in the minerotrophic zone (Fig. 6.4A). The ability of As to bind strongly with peat is a well-described phenomenon (Langner et al., 2011), with extremely high concentrations often observed under minerotrophic conditions (González et al., 2006; Shotyk, 1994, 1996c). Arsenic concentrations in the ombrotrophic zone of MIL ranged from 0.63 – 1.58 mg/kg (n = 9) and appeared to show a slight increase with time (Fig. 6.4A); a similar trend in As accumulation rate was also apparent for the same time period (Fig. 6.4B). In UTK, increasing trends in As concentration and accumulation rate were apparent beginning in the early 20th century, reaching its zenith in 1959 (± 6) where concentrations decreased steadily to near background concentrations (Fig. 6.4C and 6.4D). The concentration of As and its accumulation rate in the living layer of MIL were ~10x greater than the living layer of UTK. However, the concentration of Sc was ~10x greater at MIL (~0.6 mg/kg) than UTK (~0.07 mg/kg; Fig. 6.7), reflecting the importance of mineral dust contributions (see Discussion). By dividing the As/Sc ratio determined in peat by the ratio of As/Sc for the upper continental crust (Rudnick and Gao, 2003), we can obtain the crustal enrichment factor (EF). The EF profile of peat from MIL does not demonstrate an increase that corresponds to the time period of ABS mining and upgrading (i.e., 1967 onward); instead, the maximum enrichment of As in both MIL and UTK takes place before 1967 (Fig. 6.8).

6.4 Discussion

6.4.1 Contemporary atmospheric deposition of As and Se from bitumen mining and upgrading

Bitumen mining and upgrading has resulted in concern regarding the atmospheric deposition of potentially toxic trace elements to the landscape and waterbodies (Kelly et al., 2010). However, the input of potentially toxic elements (e.g., Ag, Sb, Pb, Tl) has been confounded by the abundance of mineral dust deposition (e.g., Shotyk, 2014, 2016a, 2018b). Despite the scale of industrial activity and the predominance of Se in the bitumen fraction of the ABS, the average concentration of Se in *Sphagnum* moss collected from the ABSR was found to be within a factor of ~2 of moss from an extremely remote region in Canada (e.g., CMW, BMW), and highly similar to moss from suburban areas of Alberta (EINP, WAG, SEB). While the average concentration of Se and its accumulation rate were greater in moss from the ABSR than the control site (UTK), the differences are modest (factor of ~2x), especially when viewed in comparison to coastal moss (Fig. 6.2), which receive natural inputs of Se from the marine environment (Steinnes et al., 1992).

It's important to understand the potential sources when considering differences in As or Se concentrations in moss from the ABSR and reference sites. As described above, concentrations of As and Se for moss collected from the ABSR correlate strongly with Sc (Fig. 6.5; Shotyk et al. 2016a), suggesting that a portion of the total Se concentration determined in moss was present as mineral dust. The concentration of As determined in living layer of MIL was approximately 10x greater than UTK, however, there was approximately 10x more Sc at MIL than UTK, implicating mineral dust as the predominant source. Unlike As, the difference in Se concentration between the living layer of MIL and UTK was only ~2x. One explanation for this difference could simply be the natural abundance of As and Se in common soil minerals. For example, wind-blown dust from soil erosion and bituminous sand is likely an important source of mineral material to the bogs. Taking As and Se values for the upper continental crust (As = 4.8 mg/kg, Se = 0.09 mg/kg) as a reflection of their abundance in mineral soils (Rudnick and Gao, 2003), and the concentration of As (1.1 mg/kg) and Se (0.015 mg/kg) in mineral material extracted from the ABS (Bicalho et al., 2017; Donner et al., 2018), the contribution of As from either source is expected to be approximately 10–50x greater than Se.

6.4.2 Has atmospheric deposition of As and Se increased due to bitumen mining and upgrading?

Oil production from open-pit mining and upgrading of ABS has experienced extremely rapid growth since 1967; an approximate 15-fold increase in oil production was experienced from 1980 to 2010, reaching over 1.5 million barrels of oil per day (Orbach, 2012). If industrial development of the ABS were a significant source of atmospheric Se to the environment, a corresponding increase in Se deposition would be expected in ombrotrophic peat near industry. However, the maximum concentration of Se (140.2 µg/kg) in the ombrotrophic zone of MIL (11 km from mid-point between central upgraders; Fig. 6.1) was determined in the oldest (ombrotrophic) peat layer (AD 1982 ± 2), while the uppermost peat layer (i.e., cm 1) contained 110.8 µg/kg. Similar results were found for V, Ni and Mo, which are also enriched in bitumen, determined in the same core (Shotyk et al., 2017). The apparent lack of contamination by these four elements in the peat cores is remarkable given their enrichment in bitumen and scale of industrial activity. In the case of V, one explanation for the low, decreasing concentrations with time could be related to the installation of electrostatic precipitators to upgrader stacks in 1979. A decrease in fly ash particle abundance was observed in the MIL core with depth (Mullan-Boudreau et al., 2017a), as well as a decrease in V concentrations after its zenith in 1979 ± 2 (Shotyk et al., 2017). A study of a near-field lake sediment cores in the ABSR also found decreasing inputs of V beginning in the early 1980's, attributing the trend to changes emission control technology (electrostatic precipitators) and the transition of conveyer belt ore transport to hauler trucks (Cooke et al., 2017). It seems likely that these improvements in mining technology and air pollution controls may have also helped limit Se inputs to the environment. It's important to note that these inputs would apply to Se in the *particulate* form. Selenium is capable of being emitted as gaseous species (e.g., SeO_2) formed during combustion processes (Wen and Carignan, 2007); in which case, local moss and peat may provide little information on emissions of gaseous Se due to its longer atmospheric residence time. Given the similarity between Se and S, it's possible that some amount of Se may be removed due to the targeted removal S by flue gas desulphurization (Donner et al., 2018); however, this pathway requires greater study.

Mineral dust is most likely the predominant source of As in the upper (~17cm) section of MIL. Support for this hypothesis comes from the similarity in As and Sc trends (see Results for comparison). Arsenic concentrations also followed an extremely similar trend as ash and acid insoluble ash determined in the same peat slices during a companion study of dust deposition in the ABSR (Mullan-Boudreau et al., 2017a). Taken together, contributions of As from surface mining and upgrading of the ABS are effectively indistinguishable from background and are far lower than other industrial sources of the past (see below). This finding emphasizes the importance of distinguishing metals contained in the chemical structure of stable soil minerals, from metals present in a bioaccessible form.

6.4.3 Utikuma: A long-term record of atmospheric As and Se deposition in Alberta

The UTK core represents a record of over 2700 years of atmospheric deposition in north-central Alberta. Comparing the accumulation rates of As and Se, it's clear that atmospheric deposition of both elements increased considerably in the early 1900's until going into decline in the middle of the 20th century (Figs. 6.3 and 6.4). This trend may reflect the history of coal production in the province of Alberta. Arsenic and Se are both enriched in coals (Vejahati et al., 2010) and are emitted in significant quantities to the atmosphere globally as a result of its burning (Pacyna and Pacyna, 2001). Coal mining in Alberta began in the late 19th century, with the first coal-fired power station opening in 1879; production increased to more than 8 million tons by the mid-1900's and was burned for transportation purposes, domestic heating and power generation (Piper and Green, 2017). This historical observation coincides with an increase in the rate of As accumulation by a factor ~7 compared to pre-industrial conditions, as well as an increased enrichment factor during approximately the same time period (Fig 6.8). A similar trend was also apparent for the Se accumulation rate during the same time period, and was a factor of ~3x that of pre-industrial background. Comparing the Se accumulation rate together with the Se/Sc ratio (Fig. 6.3), it's apparent that there was a significant source of atmospheric Se to UTK during this time period.

A similar chronology of As enrichment has been observed in environmental archives from other parts of the world. A peat core from a Swiss bog demonstrated a similar chronology of As deposition (~1850–1920) which corresponded to a time period of increasing coal imports, followed by a decrease during its replacement by other fuels (Shotyk et al., 1996b). A peat core from an ombrotrophic bog in Denmark also revealed a similar profile, with the enrichment of As increasing during the early 20th century (Shotyk, 2003). In that study (Shotyk, 2003), lead isotope data supported the conclusion that the increase was due to coal burning, and As concentrations in peat went into decline in the mid-1950's following the passing of the U.K. Clean Air Act (Shotyk, 2003). Sediment cores from the Peace-Athabasca Delta (north-eastern Alberta) revealed a highly similar As profile to the UTK peat core, with a maximum adjusted excess flux of ~0.14 mg/m^2/yr occurring between ~1950–60; the maximum calculated flux determined in UTK peat was 0.22 mg/m^2/yr and occurred in peat from 1959 (± 6). The similarity in chronology and peak fluxes strongly suggests a common source, while the slight difference in magnitude is likely due the Peace-Athabasca Delta being situated further from central and southern Alberta, where coal-burning industries were located (Piper and Green, 2017). It's worth nothing that coal production in Alberta has increased considerably following its replacement of natural gas for power generation (Piper and Green, 2017). However, this increase occurred during a time of more stringent environmental legislation and improved air pollution control technologies, which may have mitigated As and Se emissions to the atmosphere.

6.5 Conclusions

Atmospheric deposition of As and Se from bitumen mining and upgrading in the ABSR was assessed by determining concentrations in moss and age-dated ombrotrophic peat cores. Concentrations of Se determined in moss collected from the ABSR were comparable to other regions of Alberta (remote and urban) and substantially lower than moss obtained from coastal regions and southern Ontario. Mineral dust appeared to be a relevant source of both elements to moss from the ABSR. After accounting for the abundance of mineral dust particles, concentrations and deposition rates for As and Se in the living layer of MIL (industrial) were comparable to that of UTK, located ~264 km south-west. Arsenic and Se deposition rates determined in the UTK core, which represents over 2700 years of peat accumulation, clearly demonstrated that the greatest anthropogenic atmospheric inputs of As and Se occurred in the middle of the 20th century, and have decreased considerably since.

6.6 Acknowledgements

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6.7 References

Arafat, N.M., Glooschenko, W.A., 1982. The use of bog vegetation as an indicator of atmospheric deposition of arsenic in northern Ontario. Environ. Pollut. B. 4:85–90.

Arndt, J., Calabrese, S., D'Alessandro, W., Planer-Friedrich, B., 2017. Using mosses as biomonitors to study trace element emissions and their distribution in six different volcanic areas. J. Volcanol. Geotherm. Res. 343, 220–232.

Bicalho, B., Grant-Weaver, I., Sinn, C., Donner, M.W., Woodland, S., Pearson, G., Larter, S., Duke, J.,Shotyk, W., 2017. Determination of ultratrace (<0.1 mg/kg) elements in Athabasca Bituminous Sands mineral and bitumen fractions using inductively coupled plasma sector field mass spectrometry (ICP-SFMS). Fuel 206: 248–57.

Cooke, C.A., Kirk, J.L., Muir, D.C.G., Wiklund, J.A., Wang, X., Gleason, A., Evans, M.S., 2017. Spatial and temporal patterns in trace element deposition to lakes in the Athabasca oil sands region (Alberta, Canada). Environ. Res. Lett. 12: 124001.

Davies, L.J., Appleby, P., Jensen, B.J.L., Magnan, G., Mullan-Boudreau, G., Noernberg, T., Shannon, B., Shotyk, W., van Bellen, S., Zaccone, C., Froese, D.G., 2018. High-resolution age modelling of peat bogs from northern Alberta, Canada, using pre- and post-bomb ^{14}C, ^{210}Pb and historical cryptotephra. Quat. Geochronol. 47: 138–162.

Devito, K.J., Mendoza, C., Petrone, R.M., Kettridge, N., Waddington, J.M., 2016. Utikuma Region Study Area (URSA) – Part 1 : Hydrogeological and ecohydrological studies (HEAD). For. Chron. 92: 57–61.

Donner, M.W., Bicalho, B., Sinn, C., Shotyk, W., 2018. Selenium and sulphur in Athabasca bituminous sands mineral and bitumen fractions. Fuel 224: 718–725.

Givelet, N., Roos-Barraclough, F., Shotyk, W., 2003. Predominant anthropogenic sources and rates of atmospheric mercury accumulation in southern Ontario recorded by peat cores from three bogs: comparison with natural "background" values (past 8000 years). J. Environ. Monit. 5: 35–49.

Givelet, N., Roos-Barraclough, F., Goodsite, M.E., Cheburkin, A.K., Shotyk, W., 2004a. Atmospheric mercury accumulation rates between 5900 and 800 calibrated years BP in the High Arctic of Canada recorded by peat hummocks. Environ. Sci. Technol. 38: 4964–4972.

Givelet, N., Le Roux, G., Cheburkin, A., Chen, B., Frank, J., Goodsite, M.E., Kempter, H., Krachler, M., Noernberg, T., Rausch, N., Rheinberger, S., Roos-Barraclough, F., Sapkota, A., Scholz, C., Shotyk, W., 2004b. Suggested protocol for collecting, handling and preparing peat cores and peat samples for physical, chemical, mineralogical and isotopic analyses. J. Environ. Monit. 6: 481–492.

Glooschenko, W.A., Arafat, N., 1988. Atmospheric deposition of arsenic and selenium across Canada using *Sphagnum* moss as a biomonitor. Sci Tot. Environ. 73: 269–275.

Glooschenko, W.A., Holloway, L., Arafat, N., 1986. The use of mires in monitoring the atmospheric deposition of heavy metals. Aquat. Bot. 25: 179–190.

González, Z.I., Krachler, M., Cheburkin, A.K., Shotyk, W., 2006. Spatial distribution of natural enrichments of arsenic, selenium, and uranium in a minerotrophic peatland, Gola di Lago, Canton Ticino, Switzerland. Environ. Sci. Technol. 40: 6568–6574.

Harmens, H., Norris, D.A., Steinnes, E., Kubin, E., Piispanen, J., Alber, R., Aleksiayenak, Y., Blum, O., Coşkun, M., Dam, M., Temmerman, L.D., Fernández, J.A., Frolova, M., Frontasyeva, M., González-Miqueo, L., Grodzińska, K., Jeran, Z., Korzekwa, S., Krmar, M., Kvietkus, K., Leblond, S., Liiv, S., Magnússon, Maňkovská, B., Pesch, R., Rühling, Ǻ., Santamaria, J.M., Schröder, W., Spiric, Z., Suchara, I., Thöni, L., Urumov, V., Yurukova, L., Zechmeister, H.G., 2010. Mosses as biomonitors of atmospheric heavy metal deposition: Spatial patterns and temporal trends in Europe. Environ. Pollut. 158: 3144–3156.

Kelly, E.N., Schindler, D.W., Hodson, P.V., Short, J.W., Radmanovich, R., Nielsen, C. C., 2010. Oil sands development contributes elements toxic at low concentrations to the Athabasca River and its tributaries. Proc. Natl. Acad. Sci. USA, 107: 16178–16183.

Langner, P., Mikutta, C., Kretzschmar, R., 2011. Arsenic sequestration by organic sulphur in peat. Nature Geoscience 5: 66-73.

MacDonald, L.A., Wiklund, J.A., Elmes, M.C., Wolfe, B.B., Hall, R.I., 2016. Paleolimnological assessment of riverine and atmospheric pathways and sources of metal deposition at a floodplain lake (Salve River Delta, Northwest Territories, Canada). Sci Tot. Environ. 544: 811–823.

Magnan, G., van Bellen, S., Davies, L., Froese, D., Garneau, M., Mullan-Boudreau, G., Zaccone, C., Shotyk, W., 2018. Impact of the Little Ice Age cooling and 20th century climate change on peatland vegetation dynamics in central and northern Alberta using a multi-proxy approach and high-resolution peat chronologies. Quat. Sci. Rev. 185: 230–243.

McLinden, C.A., Fioletov, V., Boersma, K.F., Krotkov, N., Sioris, C.E., Veefkind, J.P., Yang, K., 2012. Air quality over the Canadian oil sands: A first assessment using satellite observations. Geophys. Res. Lett., 39: 1–8.

Mullan-Boudreau, G., Davies, L., Devito, K., Froese, D., Noernberg, T., Pelletier, R., Shotyk, W., 2017a. Reconstructing past rates of atmospheric dust deposition in the Athabasca bituminous sands region using peat cores from bogs. Land Degrad. Develop. 28: 2468–2481.

Mullan-Boudreau, G., Belland, R., Devito, K., Noernberg, T., Pelletier, R., Shotyk, W., 2017b. *Sphagnum* moss as an indicator of contemporary rates of atmospheric dust deposition in the Athabasca bituminous sands region. Environ. Sci. Technol. 51: 7422–7431.

Orbach, R.L., 2012 . Energy Production: A Global Perspective. In, Alberta Oil Sands: Energy, Industry and the Environment; Percy, K.E., Ed.; Elsevier Press, Oxford, UK, pp. 1–18.

Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmoshpere from anthropogenic sources worldwide. Environ. Rev. 9: 269–298.

Piper, L., Green, H., 2017. A province powered by coal: The renaissance of coal mining in the late Twentieth-Century Alberta. The Canadian Historical Review, University of Toronto Press 98: 532–567.

Riley, J.L., 1986. Laboratory methods for testing peat: Ontario peatland inventory project. Open File Report 5572. Ontario Geological Survey, Toronto. http://www.geologyontario.mndm.gov.on.ca/mndmfiles/pub/data/imaging/OFR5572/OFR5572.pdf.

Roos-Barraclough, F., Givelet, N., Cheburkin, A.K., Shotyk, W., Norton, S.A., 2006. Use of Br and Se in peat to reconstruct the natural and anthropogenic fluxes of atmospheric Hg: A 10000-year record from Caribou Bog, Maine. Environ. Sci. Technol. 40: 3188–3194.

Roos-Barraclough, F., Martinez-Cortizas, A., García-Rodeja, E., Shotyk, W., 2002. A 14 500 year record of the accumulation of atmospheric mercury in peat: volcanic signals, anthropogenic influences and a correlation to bromine accumulation. Earth Planet. Sci Lett. 202: 435–451.

Rudnick, R.L., Gao, S., 2003. The composition of the continental crust, in: Holland H, Turekian K, editors. Treatise on geochemistry, vol. 1, Oxford: Elsevier-Pergamon.

Shotyk, W., 1988. Review of the inorganic geochemistry of peats and peatland waters. Earth Sci. Rev. 25: 95–176.

Shotyk, W., 1994. Natural and anthropogenic enrichments of arsenic through three Canadian ombrtrophic *Sphagnum* bog profiles. In, Arsenic in the Environment Part I: Cycling and characterization; Nriagu, J.O., Ed.; John Wiley & Sons: New York, 1994; pp 381 – 401.

Shotyk, W., 1996a. Peat bog archives of atmospheric metal deposition: Geochemical evaluation of peat profiles, natural variations in metal concentrations, and metal enrichment factors. Environ. Rev. 4: 149–183.

Shotyk, W., Cheburkin, A.K., Appleby, P.G., Fankhauser, A., Kramers, J.D., 1996b. Two thousand years of atmospheric arsenic, antimony, and lead deposition recorded in an ombrotrophic peat bog profile, Jura Mountains, Switzerland. Earth Planet. Sci. Lett. 145: 1–7.

Shotyk, W., 1996c. Natural and anthropogenic enrichments of As, Cu, Pb, Sb, and Zn, in rainwater-dominated versus groundwater-dominated peat bogs profiles, Jura Mountains, Switzerland. Water Air Soil Pollut. 90: 375–405.

Shotyk, W., Weiss, D., Appleby, P.G., Cheburkin, A.K., Frei, R., Gloor, M., Kramers, J.D., Reese, S., Van Der Knaap, W.O., 1998. History of atmospheric lead deposition since 12,370 ^{14}C yr BP from a peat bog, Jura Mountains, Switzerland. Science, 281: 1635–1640.

Shotyk, W., Weiss, D., Kramers, J.D., Frei, R., Cheburkin, A.K., Gloor, M., Reese, S., 2001. Geochemistry of the peat bog at Etang de la Gruère, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace metals (Sc, Ti, Y, Zr, and REE) since 12,370 ^{14}C yr BP. Geochim. Cosmochim. Acta 65, 2337–2360.

Shotyk, W., Goodsite, M.E., Roos-Barraclough, F., Frei, R., Heinemeier, J., Asmund, G., Lohse, C., Hansen, T.S., 2003. Athropogenic contributions to atmospheric Hg, Pb and As accumulation recorded by peat cores from southern Greenland and Denmark dated using the 14C "bomb pulse curve". Geochim. Cosmochim. Acta 67: 3991–4011.

Shotyk, W., Belland, R., Duke, J., Kempter, H., Krachler, M., Noernberg, T., Pelletier, R., Vile, M.A., Wieder, K., Zaccone, C., Zhang, S., 2014. *Sphagnum* mosses from 21 ombrotrophic bogs in the Athabasca bituminous sands region show no significant atmospheric contamination of "heavy metals". Environ. Sci. Technol. 48: 12603–12611.

Shotyk, W., Bicalho, B., Cuss, C.W., Duke, M.J.M., Noernberg, T., Pelletier, R., Steinnes, E., Zaccone, C., 2016a. Dust is the dominant source of "heavy metals" to peat moss (*Sphagnum fuscum*) in the bogs of the Athabasca bituminous sands region of northern Alberta. Environ. Int. 92–93: 494–506.

Shotyk, W., Appleby, P.G., Bicalho, B., Davies, L., Froese, D., Grant-Weaver, I., Krachler, M., Magnan, G., Mullan-Boudreau, G., Noernberg, T., Pelletier, R., Shannon, B., van Bellen, S., Zaccone, C., 2016b. Peat bogs in northern Alberta, Canada reveal decades of declining atmospheric Pb contamination. Geophys. Res. Lett., 43: 1–11.

Shotyk, W., Appleby, P.G., Bicalho, B., Davies, L.J., Froese, D., Grant-Weaver, I., Magnan, G., Mullan-Boudreau, G., Noernberg, T., Pelletier, R., Shannon, B., van Bellen, S., Zaccone, C., 2017. Peat bogs document decades of declining atmospheric contamination by trace metals in the Athabasca bituminous sands region. Environ. Sci. Technol. 51: 6237–6249.

Shotyk, W., 2018a. A geochemical perspective on the natural abundance and predominant sources of trace elements in cranberries (Vaccinium oxycoccus) from remote bogs in the Boreal region of northern Alberta, Canada. Sci. Total Environ. 650: 1652–1663.

Shotyk, W., 2018b. Trace metals in soils of the bituminous sands mining region of Alberta: a critical, geochemical perspective on the study by Boutin and Carpenter (2017). Sci. Total. Environ. 618: 866–869.

Steinnes, E., Rambaek, J.P., Hanssen, J.E., 1992. Large scale multi-element survey of atmospheric deposition using naturally growing moss as biomonitor. Chemosphere 25: 735–752.

Steinnes, E., Rühling, Ǻ., Lippo, H., Mäkinen, A., 1997. Reference materials for large-scale metal deposition surveys. Accred. Qual. Assur. 2:243–249.

van Bellen, S., Magnan, G., Davies, L., Froese, D., Mullan-Boudreau, G., Zaccone, C. Garneau, G., Shotyk, W., 2018. Testate amoeba records indicate regional 20th-century lowering of water tables in ombrotrophic peatlands in central-northern Alberta, Canada. Global Change Biol. 24: 2758–2774.

Vejahati, F., Xu, Z., Gupta, R., 2010. Trace elements in coal: Associations with coal and minerals and their behavior during coal utilization – A review. Fuel 89: 904–911.

Wardenaar, E.C.P., 1987. A new hand tool for cutting peat profiles. Can. J. Bot. 65:1772–1773.

Wen, H., Carignan, J., 2007. Reviews on atmospheric selenium: Emissions, speciation and fate. Atmos. Environ. 41: 7151–7165.

Wiklund, J.A., Hall, R.I., Wolfe, B.B., Edwards, T.W.D., Farwell, A.J., Dixon, D.G., 2012. Has Alberta oil sands development increased far-field delivery of airborne contaminants to the Peace-Athabasca Delta? Sci Tot. Environ. 433: 379–382.

Zhang, Y., Shotyk, W., Zaccone, C., Noernberg, T., Pelletier, R., Bicalho, B., Froese, D.G., Davies, L., Martin, J.W., 2016. Airborne petcoke dust is a major source of polycyclic aromatic hydrocarbons in the Athabasca oil sands region. Environ. Sci Technol. 50: 1711–1720.

6.8 Figures

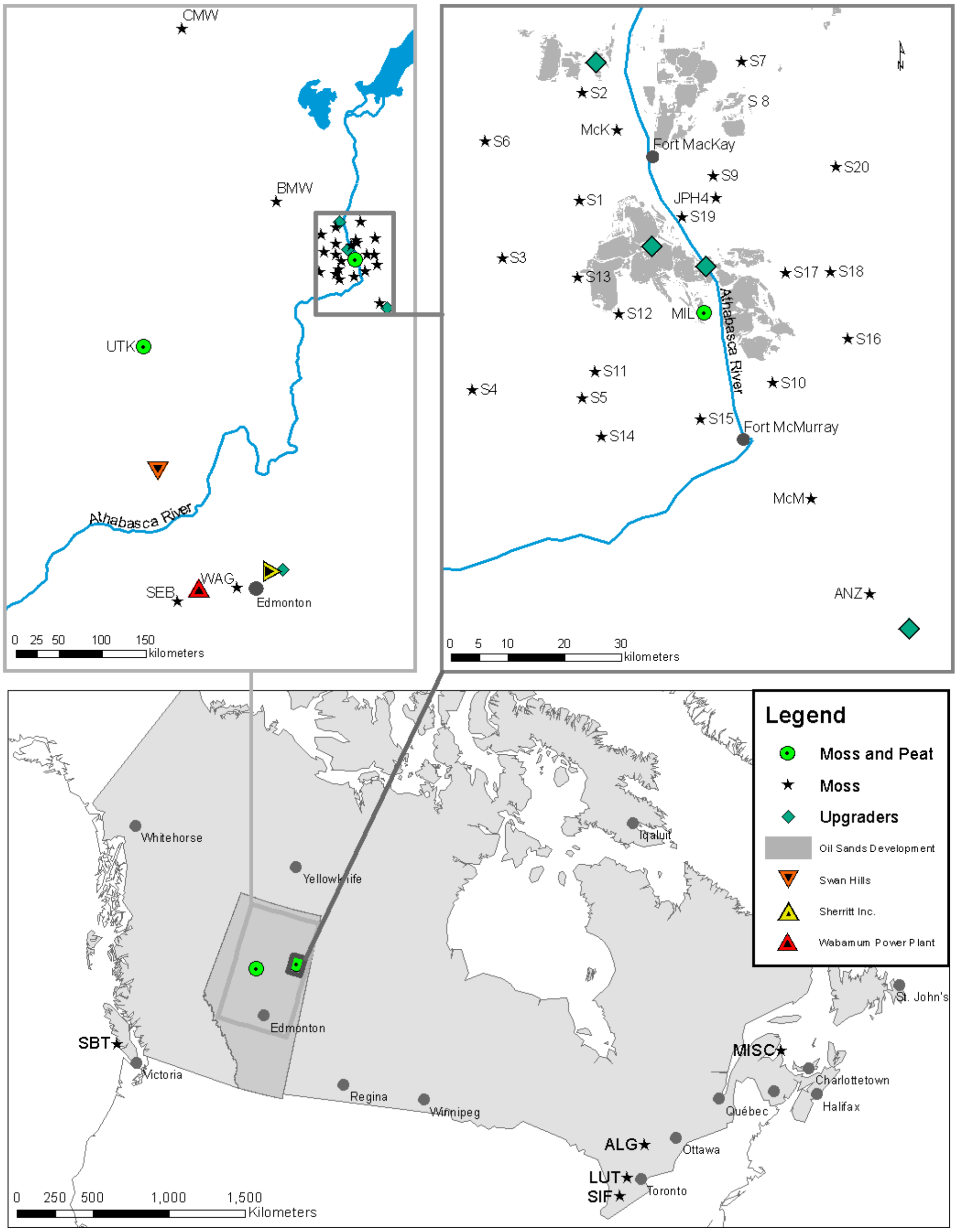

Figure 6.1 Map of study sampling sites for *Sphagnum sp*. moss and peat cores. Inset: location of sampling sites in the Athabasca Bituminous Sands Region and reference locations in northern Alberta.

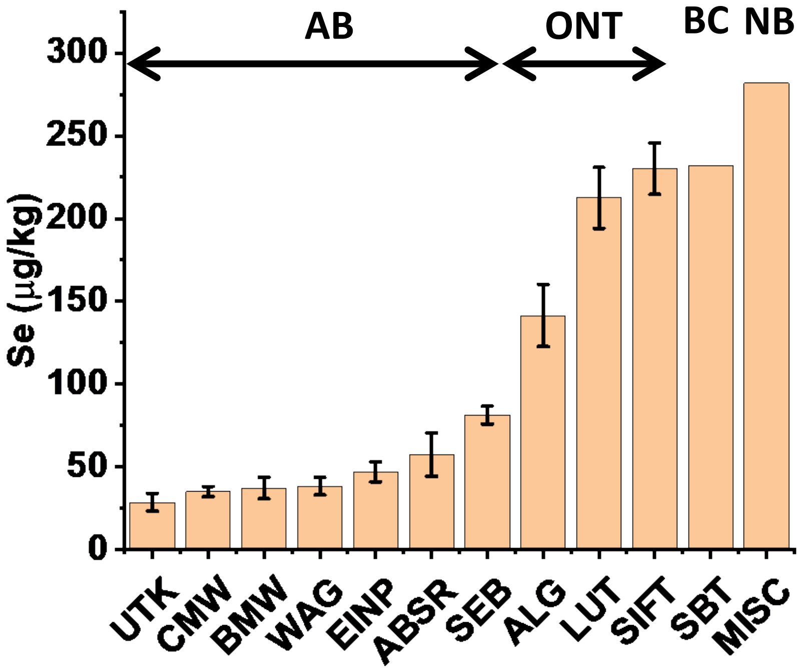

Figure 6.2 Average concentrations of Se determined in the living layer of moss from peat bogs in Canada using HG-AFS. The average concentration for the ABSR represents a total of 75 samples (25 bogs sampled in triplicate), while other locations (excluding SBT and MISC) are represented by the average concentration (± standard deviation) of samples from three different locations within a single bog. Sites are ordered from lowest to highest average concentration to emphasize the relative importance of different sources.

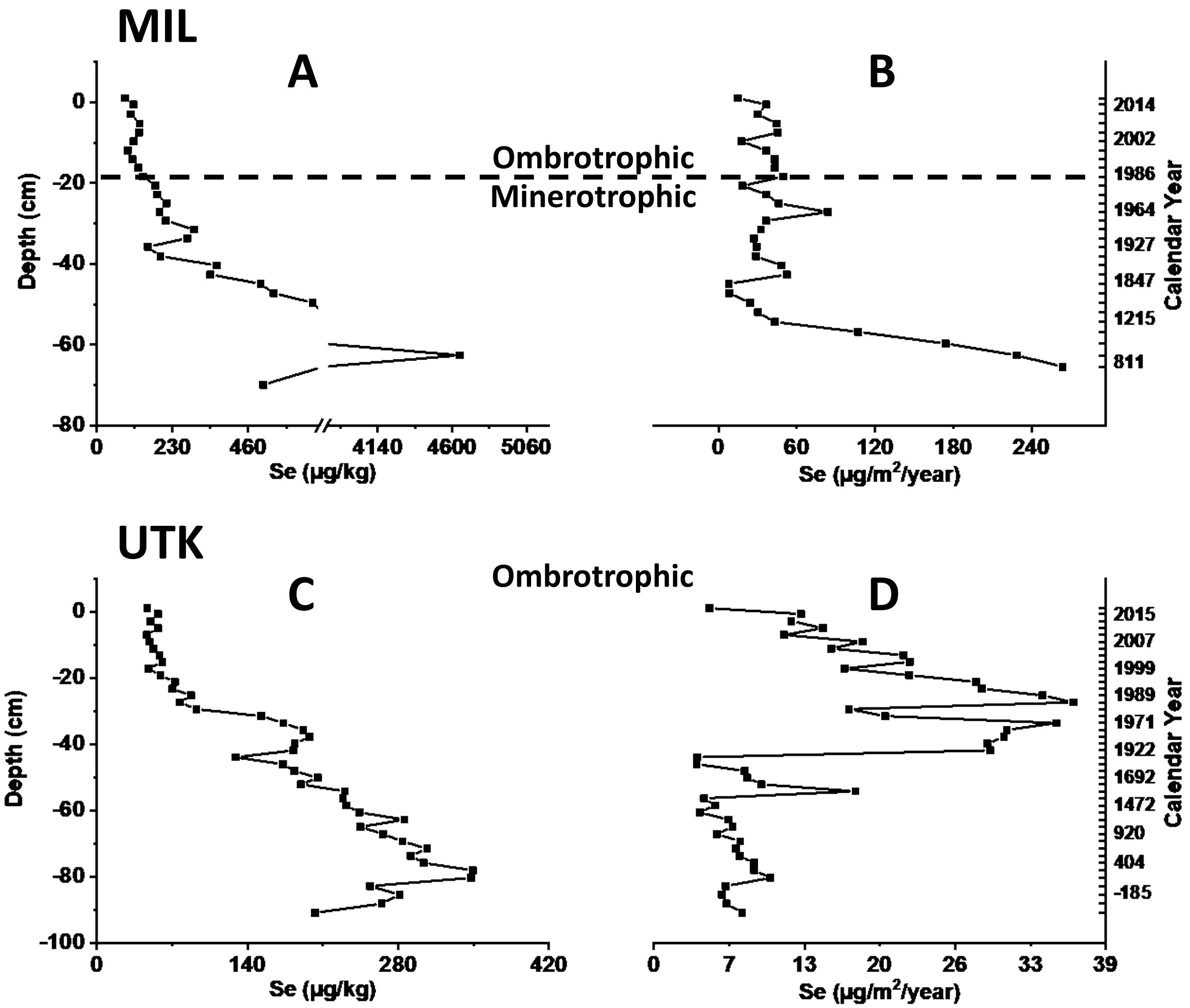

Figure 6.3 Selenium concentrations and accumulation rates determined in MIL (Panels A and B) and UTK (Panels C and D) peat cores. The peat age dates were taken from Davies et al., 2018. The transition between ombrotrophic (rain-fed) and minerotrophic (groundwater influenced) in MIL occurs at 17 cm and is indicated by a dashed line. The entire profile of UTK was determined to be ombrotrophic.

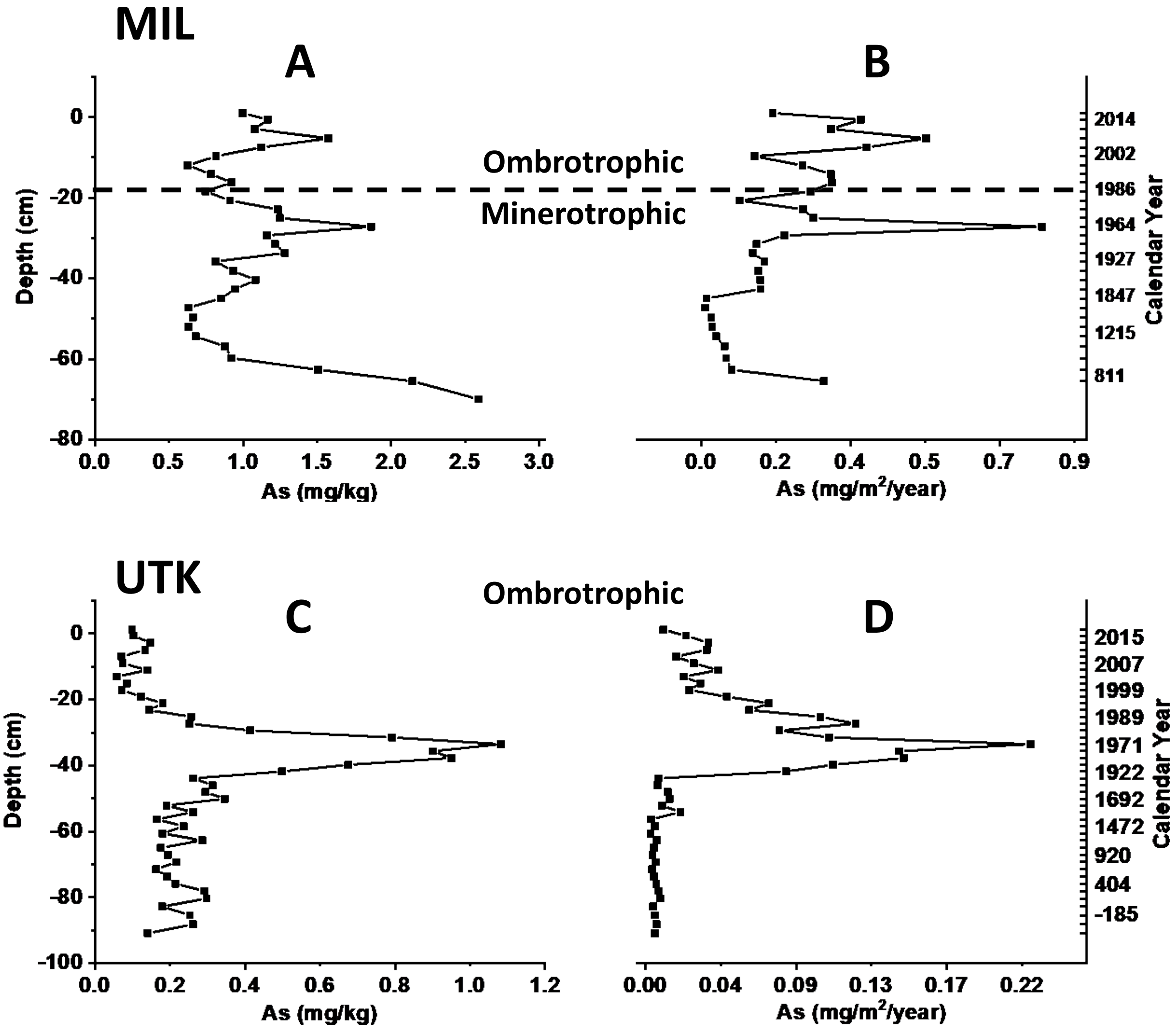

Figure 6.4 Arsenic concentrations and accumulation rates determined in MIL (Panels A and B) and UTK (Panels C and D) peat cores. The peat age dates were taken from Davies et al., 2018. The transition between ombrotrophic (rain-fed) and minerotrophic (groundwater influenced) in MIL occurs at 17 cm and is indicated by a dashed line. The entire profile of UTK was determined to be ombrotrophic.

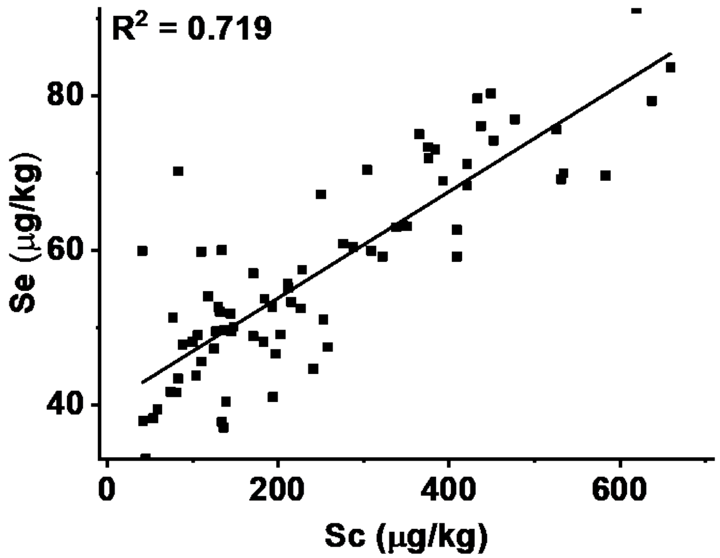

Figure 6.5 Linear regression of Se concentrations in moss (n=75) from the ABSR versus Sc. Selenium concentrations were determined by HG-AFS as part of this study, concentrations of Sc in the same moss samples were taken from Shotyk et al. (2016a).

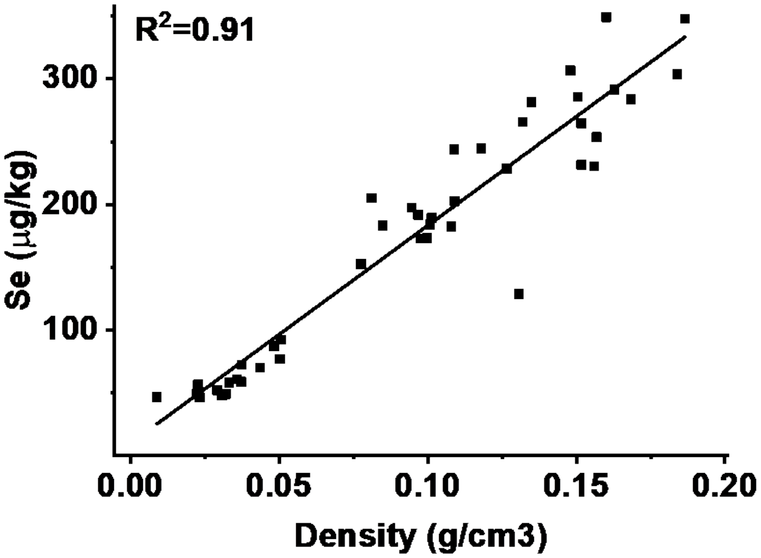

Figure 6.6 Linear regression of Se concentrations in peat from UTK versus compared to dry density of peat.

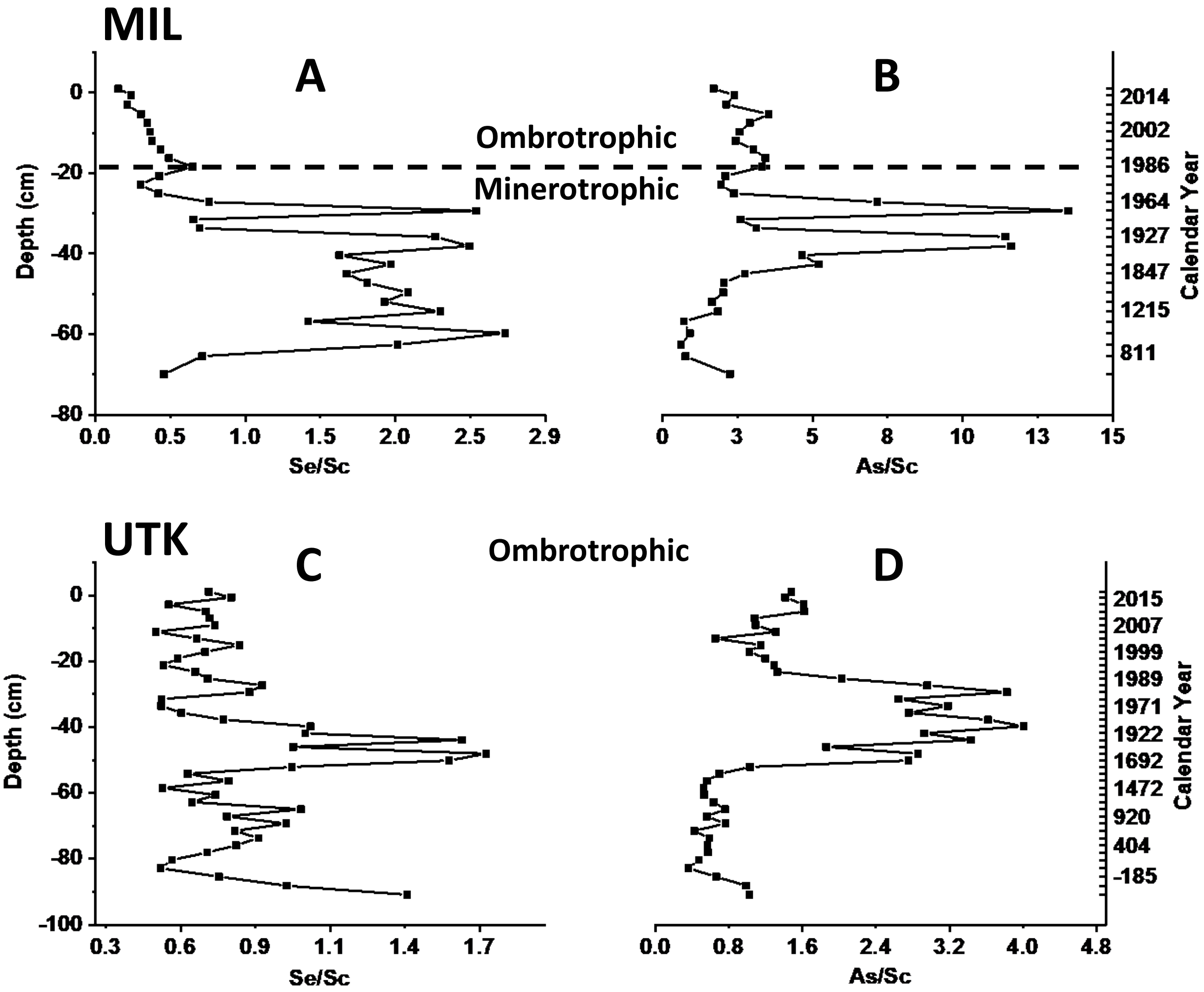

Figure 6.7 Ratios of As and Se with Sc determined in peat from MIL (Panels A and B) and UTK (Panels C and D). The peat age dates were taken from Davies et al., 2018. The transition between ombrotrophic (rain-fed) and minerotrophic (groundwater influenced) in MIL occurs at 17 cm and is indicated by a dashed line. The entire profile of UTK was determined to be ombrotrophic.

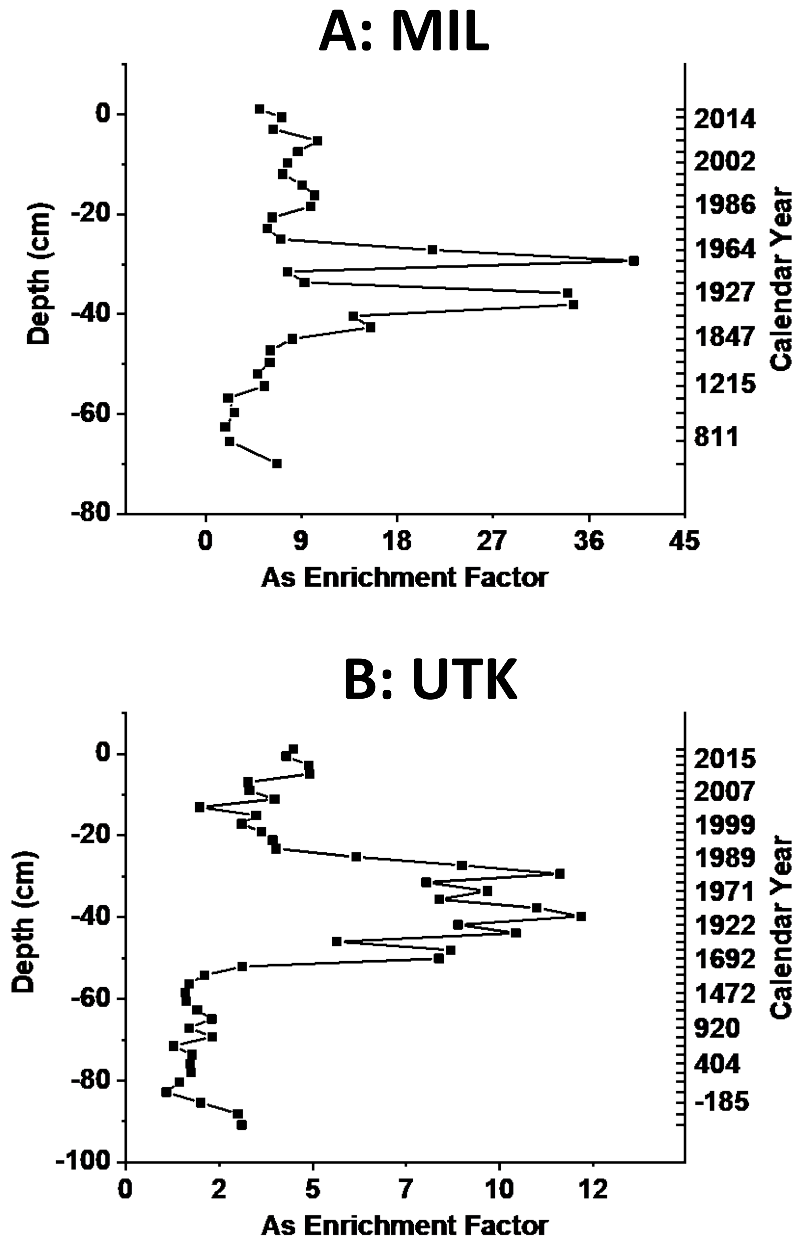

Figure 6.8 Crustal enrichment factors for As in peat from MIL (Panel A) and UTK (Panel B). Enrichment factors were determined by dividing the As/Sc ratio determined in peat by the ratio of As/Sc for the upper continental crust (Rudnick and Gao, 2003).

6.9 Tables

Table 6.1 Summary of moss sample collection locations and sources of detailed information.

Site name	Abbreviation	Location	Environmental significance	Date of collection	Detailed information
Caribou Mountain Wildlands	CMW	Northern Alberta	Remote	2015	Shotyk et al., 2018a; Mullan-Boudreau et al., 2017b
Birch Mountain Wildlands	BMW	Northern Alberta	Remote	2015	Shotyk et al., 2018a; Mullan-Boudreau et al., 2017b
Miscou Bog	MISC	New Brunswick	Coastal	2017	This study
Utikuma	UTK	Central Alberta	Remote	2014, 2015	Shotyk et al., 2014, 2016a; Mullan-Boudreau et al., 2017b
Shorepine Bog Trail	SBT	British Columbia	Coastal	2017	This study
Elk Island National Park	EINP	Central Alberta	National Park; downwind of industrial activity	2014, 2015	Shotyk et al., 2016a; Mullan-Boudreau et al., 2017b
Wagner Wetland	WAG	Central Alberta	Suburban	2014, 2015	Shotyk et al., 2016a; Mullan-Boudreau et al., 2017b
Seba Beach	SEB	Central Alberta	Suburban	2014	Shotyk et al., 2016a; Mullan-Boudreau et al., 2017b
Athabasca Bituminous Sands Region	ABSR	Northern Alberta	Bitumen mining and upgrading	2013, 2014	Shotyk et al., 2014, 2016a; Mullan-Boudreau et al., 2017b
Spruce Bog	ALG	Southern Ontario	Remote; National Park	2016	Givelet et al., 2003
Luther Bog	LUT	Southern Ontario	Rural area	2015	Givelet et al., 2003
Sifton Bog	SIFT	Southern Ontario	Urban area	2015	Givelet et al., 2003

Table 6.2 Selenium concentrations in various reference materials determined using HG-AFS.

Reference Material	**Se (µg/g)**
NIST 1575a (Pine Needles)[a]	
Average (n = 5)	0.107
SD	± 0.015
Reference value	0.099
Uncertainty	± 0.004
NIST 1547 (Peach Leaves)[a]	
Average (n = 17)	0.140
SD	± 0.009
Certified value	0.120
Uncertainty	± 0.009
NIST 1515 (Apple Leaves)[a]	
Average (n = 17)	0.057
SD	± 0.002
Certified value	0.050
Uncertainty	± 0.009
IAEA V-10 (Hay)[b]	
Average (n = 3)	0.023
SD	± 0.001
Informative value	0.022
95% CI	0.019 – 0.030
IAEA 336 (Lichen)[b]	
Average (n = 3)	0.249
SD	± 0.001
Recommended value	0.22
95% CI	0.18 – 0.26
M3 Moss (Norway Moss)[c]	
Average (n = 5)	0.127
SD	± 0.004
Recommended value	0.115
Uncertainty	± 0.016
OGS 1878P (peat)[d]	
Average (n = 6)	0.87
SD	± 0.06
Recommended value	0.6
Uncertainty	± 0.2

[a] National Institute of Standards and Technology

[b] International Atomic Energy Agency

[c] Steinnes et al., 1997

[d] Riley, J.L., 1986

Table 6.3 Arsenic concentrations in various reference materials determined using ICP-SMS.

Reference Material	**As (µg/g)**	**Sc (µg/g)**
NIST 1547 (Peach Leaves)[a]		
Average (n = 3)	0.064	0.037
SD	± 0.011	± 0.005
Certified value	0.060	na
Noncertified value	na	0.040
Uncertainty	± 0.018	na
OGS 1878P (peat)[b]		
Average (n = 6)	8.9	na
SD	± 0.8	na
Recommended value	9.2	na
Uncertainty	± 1.0	na

[a] National Institute of Standards and Technology

[d] Riley, J.L., 1986

na: not applicable

7.0 CONCLUSIONS

The goal of this study was to evaluate natural and anthropogenic inputs of As and Se to the environment from open-pit mining and upgrading of the Athabasca Bituminous Sands (ABS). The aquatic environment was assessed as part of a collaborative, multi-disciplinary study of groundwater-surface water interactions in the lower Athabasca River watershed. After two field seasons, no evidence of As or Se contamination was found in surface waters of the Athabasca River. Average concentrations of dissolved (i.e., < 0.45 µm) As were consistently low in 2014 (0.37 ± 0.01 µg/L) and 2015 (0.34 ± 0.01 µg/L), with As(V) as the predominant form. Dissolved As concentrations and chemical speciation in tributaries and groundwater were more variable (~ 0.5 – 50 µg/L), with As(III) dominating in waters with reducing conditions. The greatest concentration of As (50.4 µg/L) was observed in shallow groundwater near a large tailings pond. The source of As and its potential impact to the receiving environment remain unclear; however, given the close proximity of the tailings pond, further investigation is warranted. Concentrations of total (bulk, unfiltered) As determined in samples from 2014 (12.7 ± 2.8 µg/L) were greater than in samples collected in 2015 (3.3 ± 0.65 µg/L). However, a significant ($p < 0.05$) correlation was observed between As and Th in samples from 2014, but not 2015. This suggests that suspended mineral sediments were responsible for the change in total As concentrations. The considerable difference in concentration and variability of total As concentrations reflects physical inputs and erosional processes, which are driven by seasonal variation and other hydrologically processes.

Selenium concentrations in Athabasca River water were consistently low and comparable between 2014 (0.11 ± 0.02 µg/L) and 2015 (0.16 ± 0.02 µg/L). Similar to As, concentrations did not demonstrate an increasing trend with distance downstream. Due to the low concentrations of total dissolved Se, a novel analytical method (Chapter Four; Appendix IV) with enhanced sensitivity was developed to obtain suitable detection limits for chemical speciation. The predominant inorganic form determined in Athabasca River was Se(VI), however, it was apparent from sequential Se hydride generation analyses that a significant portion of the Se was present in a form that was not Se(IV) or Se(VI), and may have been as organic colloids < 0.45 µm in size. Determinations of Se in Trout-Perch muscle supported conclusions made regarding the absence of Se contamination in surface water, as concentrations were below relevant guideline values (e.g., BC MoE) and did not yield a significant increase ($p > 0.05$) for regions near or downstream of industry, compared to upstream.

The simplest explanation for the apparent lack of As contamination in the Athabasca River lies in the fact that it is contained predominantly in mineral fraction of bituminous sands, as the mineral fraction is expected to exhibit a high-degree of stability during the mining and upgrading process. This was also apparent in the assessment of atmospheric deposition to the landscape, as the contribution of As contained in mineral dust particles in the ABS region is represented by proportional increases in As and Sc concentrations in the MIL peat core over time. Although mineral dust exists as an environmental contaminant in the ABS region, the stability of As within the mineral complex, together with its concentration, must be considered before assigning As as an ecological threat.

The lack of Se contamination observed in this study is remarkable given that it is found predominantly in the bitumen fraction of ABS. Concentrations of Se (typically < 100 µg/kg) determined in *Sphagnum* moss from the ABS region were low relative to moss from other areas of Alberta and Canada, indicating that bitumen mining and upgrading is not likely an important source of atmospheric Se deposition to the region. Historical inputs of Se determined in the MIL core suggest that atmospheric Se deposition in the ABS region have not been on the rise, despite rapidly increasing oil production. The UTK peat core revealed an atmospheric record of As and Se deposition in central Alberta dating back more than 2700 years. Despite rapid industrial growth of bitumen mining and upgrading in the ABS region, the greatest industrial inputs of atmospheric As and Se to the province occurred in the past, prior to commercial development of the ABS in 1967.

Based on the determination of As and Se in a variety of environmental samples obtained from two multi-disciplinary studies (atmospheric deposition, Athabasca River groundwater-surface water interactions), the extent of As and Se contamination from open-pit mining and upgrading of ABS is difficult to distinguish from natural inputs. However, crude oil production from mining and upgrading of ABS continues to grow, along with rapidly evolving technologies and mining practices. Research and environmental monitoring will continue to be a critical component of assessing potential change in industrial emissions and their impact on the environment. Plans for future reclamation and potential discharge to the Athabasca River will require further study and monitoring of all constituents, including As and Se. The analytical techniques and methods of environmental assessment applied here should be viewed as a starting point for further investigation and continued monitoring.

BIBLIOGRAPHY

Addison, P.A., Puckett, K.J., 1980. Deposition of atmospheric pollutants as measured by lichen element content in the Athabasca oil sands area. Can. J. Bot. 58, 2323–2334.

Alberta Energy Regulator, 2017. ST98: 2017 Alberta's Energy Reserves & Supply/Demand Outlook. http://www1.aer.ca/st98/data/executive_summary/ST98-2017_Executive_Summary.pdf; 2017 [accessed 12.19.2017].

Alexander, D.A., Chambers, D.P., 2016. Assessment of seven Canadian Rivers in relation to stages in oil sands industrial development, 1972 to 2010. Environ. Rev. 24, 484–494.

Alexander, A.C., Chambers, P.A., Jeffries, D. S., 2017. Episodic acidification of 5 rivers in Canada's oil sands during snowmelt: A 25-year record. Sci. Total Environ. 599–600, 739–749.

Alfthan, G., Wang, D., Aro, A., Soveri, J., 1995. The geochemistry of selenium in groundwaters in Finland. Sci. Total Environ. 162, 93–103.

Andren, A.W., Klein, D.H., Talmi, Y., 1975. Selenium in coal-fired steam plant emissions. Environ. Sci. Technol. 9, 856–858.

Arafat, N.M., Glooschenko, W.A., 1982. The use of bog vegetation as an indicator of atmospheric deposition of arsenic in northern Ontario. Environ. Pollut. B. 4, 85–90.

Aren, C.J., Arens, J.C., Hogan, N.S., Kavanagh, R.J., Berrue, F., Van Der Kraak, G.J., van den Heuvel, M.R., 2017. Population impacts in white sucker (*Catostomus commersonii*) exposed to oil sands-derived contaminants in the Athabasca River. Environ. Toxicol. Chem. 36, 2058–2067.

Arndt, J., Calabrese, S., D'Alessandro, W., Planer-Friedrich, B., 2017. Using mosses as biomonitors to study trace element emissions and their distribution in six different volcanic areas. J. Volcanol. Geotherm. Res. 343, 220–232.

Azcue, J.M., Nriagu, J. O., 1994. Arsenic: historical perspectives, in: Nriagu, J.O. (Eds.), Arsenic in the Environment Part I: Cycling and Characterization. John Wiley and Sons, New York, NY, pp. 1–15.

BC MOE, 2014. British Columbia Ministry of the Environment. Water Quality Guidelines. Accssed at https://www2.gov.bc.ca/gov/content/environment/air-land-water/water/water-quality/water-quality-guidelines/approved-water-quality-guidelines

Beach, L.K., Shewmaker, J.E., 1957. The nature of vanadium in petroleum. Ind. Eng. Chem. 49, 1157–1164.

Berrow, M., Ure, A., 1989. Geological materials and soils, in: Inhat, M., (Eds.), Occurrence and distribution of selenium. CRC Press., Florida, pp. 213–242.

Berzelius, J.J., 1817. Lettre de M. Berzelius a M. Berthollet sur deux metaux nouveaux. Annales de Chimie et de Physique, 199–206.

Berzelius, J.J., 1818. Recherches sur un nouveau corps mineral trouve dans le souffre fabrique a Fahlun. Annales de Chimie et de Physique.

B'Hymer, C., Caruso, J.A., 2004. Arsenic and its speciation analysis using high-performance liquid chromatography and inductively coupled plasma mass spectrometry. J. Chromatogr. A. 1045, 1–13.

B'Hymer, C., Caruso, J.A., 2006. Selenium speciation analysis using inductively coupled plasma-mass spectrometry. J. Chromatogr. A. 1114, 1–20.

Bicalho, B., Grant-Weaver, I., Sinn, C., Donner, M.W., Woodland, S., Pearson, G., Larter, S., Duke, J.,Shotyk, W., 2017. Determination of ultratrace (<0.1 mg/kg) elements in Athabasca bituminous sands mineral and bitumen fractions using inductively coupled plasma sector field mass spectrometry (ICP-SFMS). Fuel. 206, 248–257.

Bird, S. M., Ge, H., Uden, P. C., Tyson, J. F., Block, E., Denoyer, E. J., 1997. High performance liquid chromatography of selenoamino acids and organo selenium compounds: speciation by inductively coupled plasma mass spectrometry. Chromatogr. A. 789, 349–359.

Blais, J. M. and Donahue, W.F., 2015. Comment on " sphagnum mosses from 21 ombrotrophic bogs in the Athabasca bituminous sands region show no significant atmospheric contamination of 'heavy metals'". Environ. Sci. Technol. 49, 6352–6353.

Borneuf, D., 1983. Springs of Alberta. Alberta Research Council; Earth Sciences Report 82–3, Edmonton, Alberta, Canada (280 pp). Accessed at http://ags.aer.ca/document/ESR/ESR_1982_03.PDF.

Boutin, C., Carpenter, D. J., 2017. Assessment of wetland/upland vegetation communities and evaluation of soil-plant contamination by polycyclic aromatic hydrocarbons and trace metals in regions near oil sands mining in Alberta. Sci. Total Environ. 576, 829–839.

Bowen, H.J.M., 1979. Environmental chemistry of the elements. London; New York: Academic Press.

Bruggeman, C., Maes, A., Vancluysen, J., 2007. The interaction of dissolved boom clay and gorleben humic substances with selenium oxyanions (selenite and selenate). Appl. Geochem. 22, 1371–1379.

Cannon, J. R., Edmonds, J.S., Francesconi, K.A., Raston, C.L., Saunders, J.B., Skelton, B.W., White, A.H., 1981. Isolation, crystal structure and synthesis of arsenobetaine, a constituent of the western rock lobster, the duskey shark, and some samples of human urine. Aust. J. Chem. 34, 787–798.

Cardoso, B.R., Ong, T.P., Jacob-Filho, W., Jaluul, O., Freitas, M.I., Cozzolino, S.M.F., 2010. Nutritional status of selenium in alzheimer's disease patients. Br. J. Nutr. 103, 803–806.

Cardoso, B.R., Hare, D.J., Lind, M., McLean, C.A., Volitakis, I., Laws, S.M., Masters, C.L., Bush, A.I., Roberts, B.R., 2017. The *APOE* ε4 allele is associated with lower selenium levels in the brain: implications for alzheimer's disease. ACS. Chem. Neurosci. 8, 1459–1464.

CCME, 1999. Canadian Environmental Quality Guidelines. Canadian Council of Ministers of the Environment. Environment Canada, Hull, Quebec 1999. Accessed at http://st-ts.ccme.ca/en/index.html?lang=en&factsheet=197#aql_fresh_date.

Challenger, F., 1945. Biological methylation. Chem. Rev. 36, 315–361.

Champlin, J.B.F., Dunning, H.N., 1960. A geochemical investigation of the Athabasca bituminous sands. Econ. Geol. 55, 797–804.

Chapman, A.C., 1926. On the presence of compounds of arsenic in marine crustaceans and shell fish. The Analyst. 51, 548–563.

Chapman, P.M., 2007. Selenium thresholds for fish from cold freshwaters. Hum. Ecol. Risk Assess. 13, 20–24.

Chen, Y-W., Belzile, N., Gunn, J.M., 2001. Antagonistic effect of selenium on mercury assimilation by fish populations near Sudbury metal smelters ? Limnol. Oceanogr. 46, 1814–

1818.

Chen, Y-W., Zhou, X-L., Tong, J., Truong, Y., Belzile, N., 2005. Photochemical behavior of inorganic and organic selenium compounds in various aqueous solutions. Anal. Chim. Acta, 545, 149–157.

Chilvers, D.C., Peterson, P.J., 1987. Global cycling of arsenic, in: Hutchinson, T.C., Memma, K.M. (Eds.), Lead, Mercury, Cadmium and Arsenic in the Environment. John Wiley & Sons., New York, pp. 279–301.

Conde, J. E., Sanz Alaejos, M., 1997. Selenium concentrations in natural and environmental water. Chem. Rev. 97, 1979–2004.

Cone, J.E., Del Río, R.M., Davis, J.N., Stadtman, T.C., 1976. Chemical characterization of the selenoprotein component of clostridial glycine reductase: identification of selenocysteine as the organoselenium moiety. Proc. Natl. Acad. Sci. USA. 73, 2659–2663.

Conly, F.M., Crosley, R.W., Headley, J.V.; Quagraine, E.K., 2007. Assessment of metals in bed and suspended sediments in tributaries of the lower Athabasca River. J. Environ. Sci. Health, 42:8, 1021–1028.

Cooke, C.A., Kirk, J.L., Muir, D.C.G., Wiklund, J.A., Wang, X., Gleason, A., Evans, M.S., 2017. Spatial and temporal patterns in trace element deposition to lakes in the Athabasca oil sands region (Alberta, Canada). Environ. Res. Lett. 12: 124001–124011.

Cullen, W. R., Reimer, K. J., 1989. Arsenic speciation in the environment. Chem. Rev. 89, 713–764.

Cullen, W.R., Reimer, K.J., 2016. Arsenic is everywhere: cause for concern? Royal Society of

Chemistry, Cambridge, United Kingdom, pp. 257.

Cuss, C. W., Grant-Weaver, I., Shotyk, W., 2017. AF4-ICPMS with the 300 Da Membrane To Resolve Metal-Bearing “Colloids” < 1 kDa: Optimization, Fractogram Deconvolution, and Advanced Quality Control. Anal. Chem. 89, 8027-8035.

Cuss, C.W., Donner, M.W., Grant-Weaver, I., Noernberg, T., Pelletier, R., Sinnatamby, R.N., Shotyk, W., 2018. Fingerprinting sources of trace elements in aquatic systems by measuring their distribution amongst colloidal species. Sci. Total Environ., 642, 1242–1251.

Cuss, C.W., Donner, M.W., Noernberg, T., Pellletier, R., Shotyk, W. Disentangling the seasonal and source-based variation of dissolved organic matter quality in a large river and its source waters using EEM-PARAFAC-SOM. J. Geophys. Res. Biogeosci. (In review).

Cutter, G. A., 1978. Species determination of selenium in natural waters. Anal. Chim. Acta. 98, 59–66.

Cutter, G. A., 1982. Selenium in reducing waters. Science. 217, 829–831.

Cutter, G. A., 1985. Determination of selenium speciation in biogenic particles and sediments. Anal. Chem. 57, 2951-2955.

Cutter, G. A. 1989. Fresh water systems, in: Ihnat. M, (Eds.), Occurrence and Distribution of Selenium. CRC Press., Boca Raton, Fla, pp. 243–262.

Cutter, G.A., San Diego-McGlone, M. L. C., 1990. Temporal variability of selenium fluxes in San Francisco Bay. Sci. Total. Environ. 97, 235–50.

D’albe, Fournier, E. E., 1924. Data and data concerning selenium and selenium cells, in: The

Moon-Element: An Introduction to the Wonders of Selenium. T. Fisher Unwin Ltd. London: Adelphi Terrace, pp. 33–45.

Davies, L.J., Appleby, P., Jensen, B.J.L., Magnan, G., Mullan-Boudreau, G., Noernberg, T., Shannon, B., Shotyk, W., van Bellen, S., Zaccone, C., Froese, D.G., 2018. High-resolution age modelling of peat bogs from northern Alberta, Canada, using pre- and post-bomb ^{14}C, ^{210}Pb and historical cryptotephra. Quat. Geochronol. 47, 138–162.

Deforest, D.K., Brix, K.V, Adams, W.J., 1999. Critical review of proposed residue-based selenium toxicity thresholds for freshwater. Hum. Ecol. Risk Assess, 5, 1187–1228.

Devito, K.J., Mendoza, C., Petrone, R.M., Kettridge, N., Waddington, J.M., 2016. Utikuma Region Study Area (URSA) – Part 1 : Hydrogeological and ecohydrological studies (HEAD). For. Chron. 92, 57–61.

Donner, M.W., Javed, M.B., Shotyk, W., Francesconi, K.A., Siddique, T., 2017. Arsenic speciation in the lower Athabasca River watershed: A geochemical investigation of the dissolved and particulate phases. Environ. Pollut. 224, 265–274

Donner, M.W., Bicalho, B., Sinn, C., Shotyk, W., 2018. Selenium and sulphur in Athabasca bituminous sands mineral and bitumen fractions. Fuel. 224, 718–725.

Donner, M.W., Siddique, T., 2018. A rapid and sensitive IC-ICP-MS method for determining selenium speciation in natural waters. Can. J. Chem. 96, 795–802.

Dopp, E., Hartmann, L.M., Florea, A.M., Von Recklinghausen, U., Pieper, R., Shokouhi, B., Rettenmeier, A.W., Hirner, A.V., Obe, G., 2004. Uptake of inorganic and organic derivatives of arsenic associated with induced cytotoxic and genotoxic effects in Chinese hamster ovary (CHO) cells. Toxicol. Appl. Pharmacol. 201, 156–165.

Dufresne, M.B., Eccles, D.R., Leckie, D.A., 2001. The geological and geochemical setting of the mid-cretaceous shaftesbury formation and other Colorado group sedimentary units in northern Alberta. Alberta Energy and Utilities Board and Alberta Geological Survey. Special Report 09 (654 pp). Accessed at http://ags.aer.ca/document/SPE/SPE_009.PDF.

Durkee, J., Bartrem, C., Möller, G., 2017. Legacy lead arsenate soil contamination at childcare centers in the Yakima valley, central Washington, USA. Chemosphere 168, 1126–1135.

Edmonds, J. S., Francesconi, K. A., Cannon, J. R., Raston, C. L., Skelton, B. W., White, A. H., 1977. Isolation, crystal structure and synthesis of arsenobetaine, the arsenical constituent of the western rock lobster *panulirus longipes cygnus* George. Tetrahedron Lett. 18, 1543–1546.

Ellis, J., Jasechko, S., 2018. Formation waters discharge to rivers near oil sands projects. Hydrol. Processes 32, 533–549.

Essington, M., 2015. Oxidation-reduction reactions in soils, in: Soil and Water Chemistry An Integrative Approach. CRC Press., Boca Raton, Florida, pp. 349–381.

Ferguson, J. F., Gavis, J., 1972. A review of the arsenic cycle in natural waters. Water Res. 6, 1259–1274.

Fernández-Martínez, A., Charlet, L., 2009. Selenium environmental cycling and bioavailability: a structural chemist point of view. Rev. Environ. Sci. Biotechnol. 8, 81–110.

Fiera (Fiera Biological Consulting Ltd), 2013. State of the watershed report e phase 3: water quantity and basic water quality in the Athabasca watershed. Report prepared for the Athabasca Watershed Council, Fiera Biological Consulting report #1234. Accessed at. http://www.awc-wpac.ca/sites/default/files/SOW3complete.pdf.

Filella, M., 2007. Colloidal properties of submicron particles in natural waters, in Wilkinson, K.J., Lead, J.R. (Eds.) Environmental colloids and particles behaviour, separation and characterisation. John Wiley & Sons, Ltd, England, pp. 17–93.

Floor, G. H.;, Iglesías, M., Román-Ross, G., Corvini, P. F., Lenz, M., 2011. Selenium speciation in acidic environmental samples: application to acid rain-soil interaction at Mount Etna volcano. Chemosphere. 84, 1664–1670.

Francesconi, K.A., Kuehnelt, D., 2004. Determination of arsenic species: a critical review of methods and applications, 2000-2003. Analyst. 129, 373–395.

Francesconi, K.A., 2010. Arsenic species in seafood: origin and human health implications. Pure Appl. Chem. 82, 373–381.

Frank, R.A., Roy, J.W., Bickerton, G., Rowland, S.J., Headley, J.V., Scarlett, A.G., West, C.E., Peru, K.M., Parrott, J.L., Conly, F.M., Hewitt, L.M., 2014. Profiling oil sands mixtures from industrial developments and natural groundwaters for source identification. Environ. Sci. Technol. 48, 2660–2670.

Frost, D.V, Olson, O.E., 1972. The two faces of selenium – can selenophobia be cured? CRC Critical Reviews in Toxicology, 1:4, 467–514.

Gailer, J., George, G.N., Pickering, I.J., Prince, R.C., Ringwald, S.C., Pemberton, J.E., Glass, R.S., Younis, H.S., DeYoung, D.W., Aposhian, H.V., 2000. A metabolic link between arsenite and selenite: the seleno-bis(*S*-glutathionyl) arsinium ion. J. Am. Chem. Soc. 122, 4637–4639.

Gantner, N., Power, M., Babaluk, J.A., Reist, J.D., Köck, G., Lockhart, L.W., Solomon, K.R., Muir, D.C.G., 2009. Temporal trends of mercury, cesium, potassium, selenium, and thallium in Arctic Char (*Salvelinus alpinus*) from Lake Hazen, Nunavut, Canada: Effects of trophic position, size, and age. Environ. Toxicol. Chem. 28, 254–263.

Garven, G.,1989. A hydrogeologic model for the formation of the giant oil sands deposits of the Western Canada sedimentary basin. Am. J. Sci. 289, 105–166.

Gibbons, W.N., Munkittrick, K.R., McMaster, M.E., Taylor, W.D., 1998. Monitoring aquatic environments receiving industrial effluents using small fish species 2: comparison between responses of trout-perch (*percopsis omiscomaycus*) and white sucker (*catostomus commersoni*) downstream of a pulp mill. Environ. Toxicol. Chem. 17, 2238–2245.

Gibson, J.J., Fennell, J., Birks, S.J., Yi, Y., Moncur, M.C., Hansen, B., Jasechko, S., 2013. Evidence of discharging saline formation water to the Athabasca river in the oil sands mining region, northern Alberta, Can. J. Earth Sci. 50, 1244–1257.

Givelet, N., Roos-Barraclough, F., Shotyk, W., 2003. Predominant anthropogenic sources and rates of atmospheric mercury accumulation in southern Ontario recorded by peat cores from three bogs: comparison with natural “background” values (past 8000 years). J. Environ. Monit. 5, 35–49.

Givelet, N., Le Roux, G., Cheburkin, A., Chen, B., Frank, J., Goodsite, M.E., Kempter, H., Krachler, M., Noernberg, T., Rausch, N., Rheinberger, S., Roos-Barraclough, F., Sapkota, A., Scholz, C., Shotyk, W., 2004. Suggested protocol for collecting, handling and preparing peat cores and peat samples for physical, chemical, mineralogical and isotopic analyses. J. Environ. Monit. 6, 481–492.

Givelet, N., Roos-Barraclough, F., Goodsite, M.E., Cheburkin, A.K., Shotyk, W., 2004. Atmospheric mercury accumulation rates between 5900 and 800 calibrated years BP in the High Arctic of Canada recorded by peat hummocks. Environ. Sci. Technol. 38, 4964–4972.

Glabonjat, R.A., Raber, G., Van Mooy, B.A.S., Francesconi, K.A., 2017. Arsenobetaine in seawater: depth profiles from selected sites in the north Atlantic. Env. Sci. Technol. 52, 522–530.

Glooschenko, W.A., Holloway, L., Arafat, N., 1986. The use of mires in monitoring the atmospheric deposition of heavy metals. Aquat. Bot. 25, 179–190.

Glooschenko, W.A., Arafat, N., 1988. Atmospheric deposition of arsenic and selenium across Canada using *Sphagnum* moss as a biomonitor. Sci Tot. Environ. 73, 269–275.

Goldschmidt, V.M., 1937. The principles of distribution of chemical elements in minerals and rocks. J. Chem. Soc. 655–673.

Gong, Z., Lu, X., Ma, M., Watt, C., Le, X.C., 2002. Arsenic speciation analysis. Talanta. 58, 77–96.

González, Z.I., Krachler, M., Cheburkin, A.K., Shotyk, W., 2006. Spatial distribution of natural enrichments of arsenic, selenium, and uranium in a minerotrophic peatland, Gola di Lago, Canton Ticino, Switzerland. Environ. Sci. Technol. 40, 6568–6574.

Gorny, J., Billon, G., Lesven, L., Dumoulin, D., Mad_e, B., Noiriel, C., 2015. Arsenic behavior in river sediments under redox gradient: a review. Sci. Total Environ. 505, 423–434.

Gorny, J., Dumoulin, D., Lesven, L., Noiriel, C., Madé, B., Billon. G., 2015. Development and application of HPIC-ICP-MS method for the redox arsenic speciation in river sediment pore waters. J. Anal. At. Spectrom. 30, 1562–1570.

Gosselin, P., Hrudey, S.E., Naeth, M.A. Plourde, A., Therrien, R., Van Der Kraak, G., Xu, Z., 2010. Environmental and health impacts of Canada's oil sands industry. The Royal Sciety of Canada (RSC), Ottawa, Ontario, Canada (414 pp). https://rsc-src.ca/sites/default/files/pdf/RSCreportcompletesecured9Mb_Mar28_11.pdf

Government of Alberta, 2004. The micronutrient and trace element status of forty-three soil quality benchmark sites in Alberta: results and summary. http://www1.agric.gov.ab.ca/$department/deptdocs.nsf/all/aesa8885

Government of Canada, 2008. Environmental Petition: No. 238. Water and sediment contamination of the Athabasca river due to oilsands production. Office of the Auditor General of Canada. Commissioner of the Environment and Sustainable Development, Ottawa, Canada.

Gue, A.E., Mayer, B., Grasby, S.E., 2015. Origin and geochemistry of saline spring waters in the Athabasca oil sands region, Alberta, Canada. Appl. Geochem. 61, 132–145.

Guéguen, C., Clarisse, O., Perroud, A., McDonald, A., 2011. Chemical speciation and partitioning of trace metals (Cd, Co, Cu, Ni, Pb) in the lower Athabasca river and its tributaries (Alberta, Canada). J. Environ. Monit. 13, 2865–2872.

Gustafsson, J.P., Johnsson, L., 1994. The association between selenium and humic substances in forested ecosystems–laboratory evidence. Appl. Organomet. Chem. 8, 141–147.

Hamilton, S.J., 2002. Rationale for a tissue-based selenium criterion for aquatic life. Aquat. Toxicol. 57, 85–100.

Hamilton, S.J., 2003. Review of residue-based selenium toxicity thresholds for freshwater fish. Ecotoxicol. Environ. Saf. 56, 201–210.

Hamilton ,S.J., 2004. Review of selenium toxicity in the aquatic food chain. Sci. Total. Environ. 326, 1–31.

Hargesheimer, E.E., Apps, M.J., Malhotra, S.S., 1980. Determination of vanadium in jack pine needles using neutron activation analysis. Environ. Technol. Lett. 1, 273–282.

Harmens, H., Norris, D.A., Steinnes, E., Kubin, E., Piispanen, J., Alber, R., Aleksiayenak, Y., Blum, O., Coşkun, M., Dam, M., Temmerman, L.D., Fernández, J.A., Frolova, M., Frontasyeva, M., González-Miqueo, L., Grodzińska, K., Jeran, Z., Korzekwa, S., Krmar, M., Kvietkus, K., Leblond, S., Liiv, S., Magnússon, Maňkovská, B., Pesch, R., Rühling, Ǻ., Santamaria, J.M., Schröder, W., Spiric, Z., Suchara, I., Thöni, L., Urumov, V., Yurukova, L., Zechmeister, H.G., 2010. Mosses as biomonitors of atmospheric heavy metal deposition: Spatial patterns and temporal trends in Europe. Environ. Pollut. 158, 3144–3156.

Hasegawa, H., 1997. The behavior of trivalent and pentavalent methylarsenicals in Lake Biwa. Appl. Organometal. Chem. 11, 305–311.

Hasegawa, H., Rahman, M.A., Kitahara, K., Itaya, Y., Maki, T., Ueda, K., 2010. Seasonal changes of arsenic speciation in lake waters in relation to eutrophication. Sci. Total. Environ. 408, 1684–1690.

Hayes, K.F., Roe, A.L., Brown, G. E. Jr., Hodgson, K.O., Leckie, J.O., Parks, G.A., 1987. In situ x-ray absorption study of surface complexes: selenium oxyanions on α-FeOOH. Science. 238, 783–786.

Haygarth, P. M., 1994. Global importance and global cycling of selenium, in: Frankenberger, W. T., Jr., Benson, S, (Eds.), Selenium in the Environment. Marcel Dekker., New York, pp. 1–27.

Headley, J. V., Barrow, M. P., Peru, K. M., Fahlman, B., Frank, R. A., Bickerton, G., McMaster, M. E., Parrott, J., Hewitt, L. M., 2011. Preliminary fingerprinting of Athabasca oil sands polar organics in environmental samples using electrospray ionization fourier transform ion cyclotron resonance mass spectrometry. Rapid Commun. Mass. Spectrom. 25, 1899–1909.

Hillwalker, W.E., Jepson, P.C., Anderson, K.A., 2006. Selenium accumulation patterns in lotic and lentic aquatic systems. Sci. Total Environ. 366, 367–379.

Hinrichsen, S., Geist, F., Planer-Friedrich, B., 2015. Inorganic and methylated thioarsenates pass the gastrointestinal barrier. Chem. Res. Toxicol. 28, 1678–1680.

Hitchon, B., Filby, R., Shah, K., 1975. Geochemistry of trace elements in crude oils, Alberta, Canada, in: Yen, T., (Eds.), The role of trace metals in petroleum. Ann Arbor Science., MI, pp. 111–121.

Hitchon, B., Filby, R.H., 1983. Geochemical studies – 1: trace elements in Alberta crude oils. Alberta. Research. Council. Open. File. Report. 1983-02. p. 38.

Hitchon, B., Filby, R.H., 1984. Use of trace elements for classification of crude oils into families– example from Alberta, Canada. Am. Assoc. Pet. Geologists. Bull. 68, 838–849.

Hodson, P.V., Reash, R.J., Canton, S.P., Campbell, P.V., Delos, C.G., Faribrother, A., Hitt, N.P., Miller, L.L., Ohlendorf, H.M. Selenium risk characterization, in: Chapman, P.M., Adam s, W.J., Brooks, M.L., Delos, C.G., Luoma, S.N., Maher, W.A., Ohlendorf, H.M., Presser, T.S., Shaw, D.P. (Eds.), Ecological assessment of selenium in the aquatic environment, 2010, CRC Press, Taylor & Francis Group, Boca Raton, pp. 233–256.

Hosterman, J.W., Meyer, R.F., Palmer, C.A., Doughten, M.W., Anders, D.E., 1990. Chemistry and mineralogy of natural bitumens and heavy oils and their reservoir rocks from the United States, Canada, Trinidad and Tobago, and Venezuela. U.S. Geological. Survey. Circular. 1047. p. 28.

Ikemoto, T., Kunito, T., Tanaka, H., Baba, N., Miyazaki, N., Tanabe, S., 2004. Detoxification mechanism of heavy metals in marine mammals and seabirds: Interaction of selenium with mercury, silver, copper, zinc, and cadmium in liver. Arch. Environ. Contam. Toxicol. 47, 402–413.

Innes, E.D., Fear, J.V.D., 1967. Canada's first commercial tar sands development. 7th. World. Petrol. Congr. Proc. 3, 633–643.

Jackson, B.P., Liba, A., Nelson, J., 2015. Advantages of reaction cell ICP-MS on doubly charged interferences for arsenic and selenium analysis in foods. J. Anal. At. Spectrom. 30, 1179–1183.

Jacobs, F.S., Filby, R.H., 1983. Solvent extraction of oil-sand components for determination of trace elements by neutron activation analysis. Anal. Chem. 55, 74–77.

Javed, M. B., 2015. Distribution of arsenic in surficial deposits in the Cold Lake area of Alberta, Canda. Ph.D Thesis, University of Alberta, Edmonton, Alberta.

Javed, M.B., Siddique, T., 2016. Thermally released arsenic in porewater from sediments in the Cold Lake area of Alberta, Canada. Environ. Sci. Technol. 50, 2191–2199.

Javed, M.B., Cuss, C.W., Grant-Weaver, I., Shotyk, W., 2017. Size-resolved Pb distribution in the Athabasca river shows snowmelt in the bituminous sands region an insignificant source of dissolved Pb. Sci. Rep. 7, 43622–43633

Jervis, R.E., Richard Ho, K.L,, Tiefenbach, B., 1982. Trace impurities in Canadian oil-sands, coals and petroleum products and their fate during extraction, up-grading and combustion. J. Radioanal. Chem. 71, 225–241.

Jia, B., 2010. Distribution of oil sands formation water in bitumen froth. Thesis Edmonton: University of Alberta; 2010.

Jones, G.D., Droz, B., Greve, P., Gottschalk, P., Poffet, D., McGrath, S.P., Seneviratne, S.I., Smith, P., Winkel, L.H.E., 2017. Selenium deficiency risk predicted to increase under future climate change. Proc. Natl. Acad. Sci. USA. 114, 2848–2853.

Kelly, E.N., Schindler, D.W., Hodson, P.V., Short, J.W., Radmanovich, R., Nielsen, C. C., 2010. Oil sands development contributes elements toxic at low concentrations to the Athabasca river and its tributaries. Proc. Natl. Acad. Sci. USA. 107, 16178–16183.

Khan, M.A.K., Wang F., 2009. Mercury–selenium compounds and their toxicological significance: toward a molecular understanding of the mercury–selenium antagonism. Environ. Toxicol. Chem., 28, 1567–1577.

Kirk, J.L., Muir, D.C.G., Gleason, A., Wang, X., Lawson, G., Frank, R.A., Lehnherr, I., Wrona, F., 2014. Atmospheric deposition of mercury and methylmercury to landscapes and waterbodies of the Athabasca Oil Sands Region. Environ. Sci. Technol. 48, 7374–7383.

Kölbl, G., Kalcher, K., Irgolic, K. J., Magee, R. J., 1993. Identification and quantification of inorganic and organic selenium compounds with high performance liquid chromatography. Appl. Organomet. Chem. 7, 443–466.

Kumar, A.R., Riyazuddin, P., 2010. Preservation of inorganic arsenic species in environmental water samples for reliable speciation analysis. Trends Anal. Chem. 29, 1212–1223.

Langner, P., Mikutta, C., Kretzschmar, R., 2011. Arsenic sequestration by organic sulphur in peat. Nature Geoscience 5, 66–73.

Larter, S.R., Head, I.M., 2014. Oil sands and heavy oil: origin and exploitation. Elements. 10, 277–283.

Lead, J.R., Wilkinson, K.J., 2007. Environmental colloids and particles: Current knowledge and future developments, in Wilkinson, K.J., Lead, J.R. (Eds.) Environmental colloids and particles behaviour, separation and characterisation. John Wiley & Sons, Ltd, England, pp. 1–15.

Leblanc, K.L., Ruzicka, J., Wallschläger, D., 2016. Identification of trace levels of selenomethionine and related organic selenium species in high-ionic-strength waters. Anal. Bioanal. Chem. 408, 1033–1042.

Leblanc, K.L., Wallschläger, D., 2016. Production and release of selenomethionine and Rrlated organic selenium species by microorganisms in natural and industrial waters. Environ. Sci. Technol. 50, 6164–6171.

Lemly, D.A., 1998. Pathology of selenium poisoning in fish, in Frankenberger, W.T. Jr., Engberg, R.A. (Eds.) Environmental chemistry of selenium. Marcel Dekker, Inc. New York, NY, pp. 281–296.

Lenz, M., Lens, P.N.L., 2009. The essential toxin: The changing perception of selenium in environmental sciences. Sci. Total Environ. 407, 3620–3633.

Levander, O.A., Argrett, L.C., 1969. Effects of arsenic, mercury, thallium, and lead on selenium metabolism in rats. Toxicol. Appl. Pharmacol. 14, 308–314.

Li, H.-F., McGrath, S. P., Zhao, F.-J., 2008. Selenium uptake, translocation and speciation in wheat supplied with selenate or selenite. New. Phytol. 178, 92–102.

Liu, P., Shi, Q., Chung, K.H., Zhang, Y., Pan, N., Zhao, S., Xu, C., 2010. Molecular characterization of sulfur compounds in Venezuela crude oil and its SARA fractions by electrospray ionization fourier transform ion cyclotron resonance mass spectrometry. Energy. Fuels. 24, 5089–5096.

Lum, T., Leung, K.S., 2016. Strategies to overcome spectral interference in ICP-MS detection. J. Anal. At. Spectrom. 3, 1078–1088.

Luoma, S.N., Rainbow, P.S., 2008. Selenium: Dietary exposure, trophic transfer and food web effects, in: Metal contamination in aquatic environments: Science and lateral management. Cambridge University Press, New York, NY, 573p.

Luoma, S.N., 2009. Emerging opportunities in management of selenium contamination. Environ. Sci. Technol. 43, 8483–8487.

MacDonald, L.A., Wiklund, J.A., Elmes, M.C., Wolfe, B.B., Hall, R.I., 2016. Paleolimnological assessment of riverine and atmospheric pathways and sources of metal deposition at a floodplain lake (Salve River Delta, Northwest Territories, Canada). Sci Tot. Environ. 544, 811–823.

Magnan, G., van Bellen, S., Davies, L., Froese, D., Garneau, M., Mullan-Boudreau, G., Zaccone, C., Shotyk, W., 2018. Impact of the Little Ice Age cooling and 20th century climate change on peatland vegetation dynamics in central and northern Alberta using a multi-proxy approach and high-resolution peat chronologies. Quat. Sci. Rev. 185, 230–243.

Magos, L., Webb, M., Clarkson, T.W., 2008. The interactions of selenium with cadmium and mercury. Crit. Rev. Toxicol. 8, 1–42.

Maher, W., Roach, A., Doblin, M., Fan, T., Foster, S., Garrett, R., Möller, G., Oram, L., Wallschläger, D., 2009. Environmental sources, speciation, and partitioning of selenium, in: Ecological assessment of selenium in the aquatic environment, in: Ecological assessment of selenium in the aquatic environment; in: Chapman, P. M., Adams, W. J., Brooks, M. L., Delos, C. G., Luoma, S. N., Maher, W. A., Ohlendorf, H. M., Presser, T. S., Shaw, D. P, (Eds.), CRC Press., Boca Raton, Fla, pp. 47–91.

Martin, D.P., Seiter, J.M., Lafferty, B.J., Bednar, A.J., 2017. Exploring the ability of cations to facilitate binding between inorganic oxyanions and humic acid. Chemosphere 166, 192–196.

McCleskey, R.B., Nordstrom, D.K., Maest, A.S., 2004. Preservation of water samples for arsenic(III/V) determinations: an evaluation of the literature and new analytical results. Appl. Geochem 19, 995–1009.

McLinden, C.A., Fioletov, V., Boersma, K.F., Krotkov, N., Sioris, C.E., Veefkind, J.P., Yang, K., 2012. Air quality over the Canadian oil sands: A first assessment using satellite observations. Geophys. Res. Lett. 39, 1–8.

Mikutta, C., Rothwell, J. J., 2016. Peat bogs as hotspots for organoarsenical formation and persistence. Environ. Sci. Technol. 50, 4314–4323.

Milne, J.B., 1998. The uptake and metabolism of inorganic selenium species, in: Frankenberger, Jr.W.T. (Eds.), Environmental Chemistry of Selenium. Marcel Dekker Inc., New York, pp. 459–477.

Mok, W.M., Wai, C.M., 1994. Mobilization of arsenic in contaminated river waters, in: Nriagu, J.O. (Ed.), Arsenic in the Environment Part I: Cycling and Characterization. John Wiley and

Sons, New York, NY, pp. 99–114.

Moncur, M.C., Paktunc, D., Jean Birks, S., Ptacek, C.J., Welsh, B., Thibault, Y., 2015. Source and distribution of naturally occurring arsenic in groundwater from Alberta's Southern Oil Sands Regions. Appl. Geochem. 62, 171–185.

Morris, D.L., 2015. Chemistry and activity of selenium dioxide and selenite ions, in: Preedy, V.R. (Eds.), Selenium: chemistry, analysis, function and effects. The Royal Society of Chemistry., Cambridge, UK, pp. 65–80.

Mosher, B.W., Duce, R.A., 1987. A global atmospheric selenium budget. J. Geophys. Res. Atmos. 92, 289–13298.

Mossop, G.D., 1980. Geology of the Athabasca oil sands. Science. 207, 145–152.

Mullan-Boudreau, G., Belland, R., Devito, K., Noernberg, T., Pelletier, R., Shotyk, W., 2017. *Sphagnum* moss as an indicator of contemporary rates of atmospheric dust deposition in the Athabasca bituminous sands region. Environ. Sci. Technol. 51, 7422–7431.

Mullan-Boudreau, G., Davies, L., Devito, K., Froese, D., Noernberg, T., Pelletier, R., Shotyk, W., 2017. Reconstructing past rates of atmospheric dust deposition in the Athabasca bituminous sands region using peat cores from bogs. Land Degrad. Dev. 28, 2468–2481.

Nasrabadi, T., Ruegner, H., Sirdari, Z.Z., Schwientek, M., Grathwohl, P., 2016. Using total suspended solids (TSS) and turbidity as proxies for evaluation of metal transport in river water. Appl. Geochem. 68, 1–9.

Navarro-Alarcon, M., Cabrera-Vique, C., 2008. Selenium in food and the human body: a review. Sci. Total. Environ. 400, 115–141.

Nriagu, J.O., Wong, H.K., 1983. Selenium pollution of lakes near the smelters at Sudbury, Ontario. Nature. 301, 55–57.

Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature. 333, 134–139.

Nriagu, J.O., 1989. Global cycling of selenium, in: Inhat, M., (Eds.), Occurrence and distribution of selenium. Boca Raton. CRC Press., Florida, pp. 327–340.

Nriagu, J. O., 2002. Arsenic poisoning through the ages, in: Frankenberger, Jr. W.T. (Eds.), Environmental Chemistry of Arsenic. Marcel Dekker Inc., New York, pp. 1–26.

Ogra, Y., Ishiwata, K., Suzuki, K. T., 2005. Effects of deuterium in octopole reaction and collision cell ICP-MS on detection of selenium in extracellular fluids. Anal. Chim. Acta. 554, 123–129.

Ohlendorf, H.M., Hoffman, D.J., Saiki, M.K., Aldrich, T.W., 1986. Embryonic mortality and abnormalities of aquatic birds: apparent impacts of selenium from irrigation drainwater. Sci. Total Environ. 52, 49–63.

Ohlendorf , H.M., Hothem, R.L., Bunck, C.M., Marois, K.C., 1990. Bioaccumulation of selenium in birds at Kesterson Reservoir, California. Arch. Environ. Contam. Toxicol. 19, 495–507.

Orbach, R.L., 2012 . Energy Production: A Global Perspective. In, Alberta Oil Sands: Energy, Industry and the Environment; Percy, K.E., Ed.; Elsevier Press, Oxford, UK, pp. 1–18.

Orr, W.L., 1978. Sulfur in heavy oils, oil sands and oil shales. Oil Sand Oil Shale Chem New York, Verlag Chemie 223–243.

Outridge, P.M., Scheuhammer, A.M., Fox, G.A., Braune, B.M., White, L.M., Gregorich, L.J., Keddy, C., 1999. An assessment of the potential hazards of environmental selenium for Canadian water birds. Environ. Rev. 7, 81–96.

Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environ. Rev. 9, 269–298.

Papoff, P., Bocci, F., Lanza, F., 1998. Speciation in natural waters and snow by DPCSV at the hanging mercury drop electrode. Microchem. J. 59, 50–76.

Pedersen, G. A., Larsen, E. H., 1997. Speciation of four selenium compounds using high performance liquid chromatography with on-line detection by inductively coupled plasma mass spectrometry or flame atomic absorption spectometry. Fresenius' J. Anal. Chem. 358, 591–598.

Peel, H.R., Martin, D.P., Bednar, A.J., 2017. Extraction and characterization of ternary complexes between natural organic matter, cations, and oxyanions from a natural soil. Chemosphere 176, 125–130.

Petrov, P.K., Charters, J.W., Wallschläger, D., 2012. Identification and determination of selenosulfate and selenocyanate in flue gas desulfurization waters. Environ. Sci. Technol. 46, 1716–1723.

Pettine, M., McDonald, T.J., Sohn, M., Anquandah, G.A.K., Zboril, R., Sharma, V.K., 2015. A critical review of selenium analysis in natural water samples. Trends. Environ. Anal. Chem. 5, 1–7.

Pilote, M., Turcotte, A.C., Gagné, F., Gagnon, C., 2018. Metal bioaccumulation and biomarkers of effects in caged mussels exposed in the Athabasca oil sands area. Sci. Total Environ. 610–

611, 377–390.

Piper, L., Green, H., 2017. A province powered by coal: The renaissance of coal mining in the late Twentieth-Century Alberta. The Canadian Historical Review, University of Toronto Press 98, 532–567.

Planer-Friedrich, B., London, J., Mccleskey, R.B., Nordstrom, D.K., Wallschl€ager, D., 2007. Thioarsenates in geothermal waters of yellowstone national park: determination, preservation, and geochemical importance. Environ. Sci. Technol. 41, 5245–5251.

Pollock, S.M., Goodarzi, F., Riediger, C.L., 2000. Mineralogical and elemental variation of coal from Alberta, Canada: an example from the no. 2 seam, Genesee Mine. Int. J. Coal. Geol. 43, 259–286.

Polya, D.A., Lythgoe, P.R., Abou-Shakra, F., Gault, A.G., Brydie, J.R., Webster, J.G., Brown, K.L., Nimfopoulos, M.K., Michailidis, K.M., 2003. IC-ICP-MS and IC-ICPHEX-MS determination of arsenic speciation in surface and groundwaters: preservation and analytical issues. Mineral. Mag. 67, 247–261.

Potin-Gautier, M., Boucharat, C., Astruc, A., Astruc, M., 1993. Speciation of selenoamino acids by on-line HPLC ETAA. Appl. Organomet. Chem. 7, 593–598.

Rahman, M.A, Hasegawa, H., 2012. Arsenic in freshwater systems: influence of eutrophication on occurrence, distribution, speciation, and bioaccumulation. Appl. Geochem. 27, 304–314.

Rahn, K.A., 1976. The chemical composition of the atmospheric aerosol: technical report. Graduate School of Oceanography, University of Rhode Island, Kinston, R.I., USA.

Rayman, M.P., 2000. The importance of selenium to human health. Lancet. 356, 233–241.

Reilly, C., 2006. Selenium in diets, in: Selenium in Food and Health, second ed. Springer, New York, New York, pp. 173–199.

Reilly, C., 2006. Selenium in food and health, second ed. Springer, New York, New York.

Riedel, G. F., Ferrier, D. P., Sanders, J. G., 1991. Uptake of selenium by freshwater phtoplankton. Water, Air, and Soil Pollut. 57–58, 23–30.

[48] Riley, J.L., 1986. Laboratory methods for testing peat: Ontario peatland inventory project. Open File Report 5572. Ontario Geological Survey, Toronto. http://www.geologyontario.mndm.gov.on.ca/mndmfiles/pub/data/imaging/OFR5572/OFR5572.pdf.

Roos-Barraclough, F., Martinez-Cortizas, A., García-Rodeja, E., Shotyk, W., 2002. A 14 500 year record of the accumulation of atmospheric mercury in peat: volcanic signals, anthropogenic influences and a correlation to bromine accumulation. Earth Planet. Sci Lett. 202, 435–451.

Roos-Barraclough, F., Givelet, N., Cheburkin, A.K., Shotyk, W., Norton, S.A., 2006. Use of Br and Se in peat to reconstruct the natural and anthropogenic fluxes of atmospheric Hg: A 10000-year record from Caribou Bog, Maine. Environ. Sci. Technol. 40, 3188–3194.

Ross, M.S., Pereira, A.D.S., Fennell, J., Davies, M., Johnson, J., Sliva, L., Martin, J.W., 2012. Quantitative and qualitative analysis of naphthenic acids in natural waters surrounding the canadian oil sands industry. Environ. Sci. Technol. 46, 12796–12805.

Rotruck, J.T., Pope, A.L., Ganther, H.E., Swanson, A.B. Hafeman, D.G., Hoekstra, W.G., 1972. Selenium: biochemical role as a component of glutathione peroxidase. Science. 179, 588–590.

Roy, J.W., Bickerton, G., Frank, R.A., Grapentine, L., Hewitt, L.M., 2016. Assessing risks of shallow riparian groundwater quality near an oil sands tailings pond. Groundwater 54, 545–558.

Rudnick, R.L., Gao, S., 2003. The composition of the continental crust, in: Holland H, Turekian K, editors. Treatise on geochemistry, vol. 1, Oxford: Elsevier-Pergamon.

Saiki, M.K., Lowe, P.T., 1987. Selenium in aquatic organisms from subsurfaec agricultural drainage water, San Joaquin Valley, California. Arch. Environ. Contam. Toxicol. 16, 657–670.

Sánchez-Rodas, D., Corns, W.T., Chen, B., Stockwell, P.B., 2010. Atomic fluorescence spectrometry: a suitable detection technique in speciation studies for arsenic, selenium, antimony and mercury. J. Anal. At. Spectrom. 25, 933–946.

Schindler, D.W, 2010. Tar sands need solid science. Nature. 468, 499–501.

Schindler, D.W., 2013. Geoscience of climate and energy 12. Water quality issues in the oil sands region of the lower Athabasca river, Alberta. Geosci. Can. 40, 202–214.

Schindler, D.W., 2013. Water quality issues in the oil sands region of the lower Athabasca river, Alberta. Geosci. Canada. 40, 202–14.

Schwarz, K., Foltz, C.M., 1957. Selenium as an integral part of factor 3 against dietary necrotic liver degeneration. J. Am. Chem. Soc. 79, 3292–3293.

Scott, J., Collins, G.A., Hodgson, G., 1954. Trace metals in the McMurray oil sands and other cretaceous reservoirs of Alberta. Can. Min. Metall. 57, 34–40.

Selby, D., 2005. Direct radiometric dating of hydrocarbon deposits using rhenium-osmium isotopes. Science. 308, 1293–1295.

Senior, C.L., Tyree, C.A., Meeks, N.D., Acharya, C., McCain, J.D., Cushing, K.M., 2015.

Selenium partitioning and removal across a wet FGD scrubber at a coal-fired power plant. Envrion. Sci. Technol. 49, 14376–14382.

Shendrikar, A.D., Ensor, D.S., Cowent, S.J., Woffindei, G.J., 1983. Size-dependent penetration through a utility of trace elements baghouse. Atmos. Environ. 17, 1411–1421.

Shotyk, W., 1988. Review of the inorganic geochemistry of peats and peatland waters. Earth Sci. Rev. 25, 95–176.

Shotyk, W., 1994. Natural and anthropogenic enrichments of arsenic through three Canadian ombrtrophic *Sphagnum* bog profiles. In, Arsenic in the Environment Part I: Cycling and characterization; Nriagu, J.O., Ed.; John Wiley & Sons: New York, 1994; pp 381 – 401.

Shotyk, W., 1996. Natural and anthropogenic enrichments of As, Cu, Pb, Sb, and Zn, in rainwater-dominated versus groundwater-dominated peat bogs profiles, Jura Mountains, Switzerland. Water Air Soil Pollut. 90, 375–405.

Shotyk, W., 1996. Peat bog archives of atmospheric metal deposition: Geochemical evaluation of peat profiles, natural variations in metal concentrations, and metal enrichment factors. Environ. Rev. 4, 149–183.

Shotyk, W., Cheburkin, A.K., Appleby, P.G., Fankhauser, A., Kramers, J.D., 1996. Two thousand years of atmospheric arsenic, antimony, and lead deposition recorded in an ombrotrophic peat bog profile, Jura Mountains, Switzerland. Earth Planet. Sci. Lett. 145, 1–7.

Shotyk, W., Weiss, D., Appleby, P.G., Cheburkin, A.K., Frei, R., Gloor, M., Kramers, J.D., Reese, S., Van Der Knaap, W.O., 1998. History of atmospheric lead deposition since 12,370 ^{14}C yr BP from a peat bog, Jura Mountains, Switzerland. Science 281, 1635–1640.

Shotyk, W., Weiss, D., Kramers, J.D., Frei, R., Cheburkin, A.K., Gloor, M., Reese, S., 2001. Geochemistry of the peat bog at Etang de la Gruère, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace metals (Sc, Ti, Y, Zr, and REE) since 12,370 ^{14}C yr BP. Geochim. Cosmochim. Acta 65, 2337–2360.

Shotyk, W., Goodsite, M.E., Roos-Barraclough, F., Frei, R., Heinemeier, J., Asmund, G., Lohse, C., Hansen, T.S., 2003. Athropogenic contributions to atmospheric Hg, Pb and As accumulation recorded by peat cores from southern Greenland and Denmark dated using the 14C "bomb pulse curve". Geochim. Cosmochim. Acta 67, 3991–4011.

Shotyk, W., Krachler, M., 2009. Determination of trace element concentrations in natural freshwaters: how low is "low", and how low do we need to go? J. Environ. Monit. 11, 1747–1753.

Shotyk, W., Krachler, M., Aeschbach-Hertig, W., Hillier, S., Zheng, J., 2010. Trace elements in recent groundwater of an artesian flow system and comparison with snow: enrichments, depletions, and chemical evolution of the water. J. Environ. Monit. 12, 208–217.

Shotyk, W., Belland, R., Duke, J., Kempter, H., Krachler, M., Noernberg, T., Pelletier, R., Vile, M.A., Wieder, K., Zaccone, C., Zhang, S., 2014. *Sphagnum* mosses from 21 ombrotrophic bogs in the Athabasca bituminous sands region show no significant atmospheric contamination of "heavy metals". Environ. Sci. Technol. 48, 12603–12611.

Shotyk, W., Appleby, P.G., Bicalho, B., Davies, L., Froese, D., Grant-Weaver, I., Krachler, M., Magnan, G., Mullan-Boudreau, G., Noernberg, T., Pelletier, R., Shannon, B., van Bellen, S., Zaccone, C., 2016. Peat bogs in northern Alberta, Canada reveal decades of declining atmospheric Pb contamination. Geophys. Res. Lett. 43, 1–11.

Shotyk, W., Bicalho, B., Cuss, C.W., Duke, M.J.M., Noernberg, T., Pelletier, R., Steinnes, E., Zaccone, C., 2016. Dust is the dominant source of “heavy metals” to peat moss (*Sphagnum fuscum*) in the bogs of the Athabasca bituminous sands region of northern Alberta. Environ. Int. 92–93, 494–506.

Shotyk, W., Appleby, P.G., Bicalho, B., Davies, L., Froese, D., Grant-Weaver, I., Magnan, G., Mullan-Boudreau, G., Noernberg, T., Pelletier, R., Shannon, B., van Bellen, S., Zaccone, C., 2017. Peat bogs document decades of declining atmospheric contamination by trace metals in the Athabasca bituminous sands region. Environ. Sci. Technol. 51, 6237–6249.

Shotyk, W., Bicalho, B., Cuss, C.W., Donner, M.W., Grant-Weaver, I., Haas-Neill, S., Javed, M.B., Krachler, M., Noernberg, T., Pelletier, R. Zaccone, C., 2017. Trace metals in the dissolved fraction (< 0.45 μm) of the lower Athabasca River: Analytical challenges and environmental implications. Sci. Total Environ. 580, 660–669.

Shotyk, W., 2018. A geochemical perspective on the natural abundance and predominant sources of trace elements in cranberries (Vaccinium oxycoccus) from remote bogs in the Boreal region of northern Alberta, Canada. Sci. Total Environ. 650, 1652–1663.

Shotyk, W., 2018. Trace metals in soils of the bituminous sands mining region of Alberta: a critical, geochemical perspective on the study by Boutin and Carpenter (2017). Sci. Total. Environ. 618, 866–869.

Simmons, D.B.D., Wallschläger, D., 2005. A critical review of the biogeochemistry and ecotoxicology in lotic and lentic environments. Environ. Toxicol. Chem. 24, 1331–1343.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517–568.

Smith, W., 1873. Effect of light on selenium during the passage of an electric current. Nature. 303.

Soignet, S.L., Maslak, P., Wang, Z., Jhanwar, S., Calleja, E., Dardashti, L.J., Corso, D., DeBlasio, A., Gabrilove, J., Scheinberg, D.A., Pandolfi, P.P., Warrell, R.P. Jr., 1998. Complete remission after treatment of acute promyelocytic leukemia with arsenic trioxide. N. Engl. J. Med. 339, 1341–1348.

Sørmo, E.G., Ciesielski, T.M., Øverjordet, I.B., Lierhagen, S., Eggen, G.S., Berg, T., Jenssen, B. M., 2011. Selenium moderates mercury toxicity in free-ranging freshwater fish. Environ. Sci. Technol. 45, 6561–6566.

Spafford, M.D., 1999. Trout-perch *Percopsis omiscomaycus* (Walbaum) and lake chub Couesius plumbeus (Agassiz), as sentinel monitoring species in the Athabasca River, Alberta. Thesis. University of Alberta. Edmonton, Alberta.

Sposito, G., 1995. Adsorption as a problem in coordination chemistry: the concept of the surface complex, in: Huang, C.P., O'Melia, C.R., Morgan, J.J. (Eds.), Aquatic Chemistry Interfacial and Interspecies Processes. American Chemical Society., Washington, DC, pp. 33–57.

Steinnes, E., Rambaek, J.P., Hanssen, J.E., 1992. Large scale multi-element survey of atmospheric deposition using naturally growing moss as biomonitor. Chemosphere 25, 735–752.

Steinnes, E., Rühling, Ǻ., Lippo, H., Mäkinen, A., 1997. Reference materials for large-scale metal deposition surveys. Accred. Qual. Assur. 2, 243–249.

Steudel, R., Strauss, E.M., Papavassiliou, M., Brätter, P., Gatschke, W., 1986. Selenium content of naturally occurring elemental sulfur, of industrially produced sulfur and of the mineral selensulfur. Phosphorus. Sulfur. 29, 17–21.

Stewart, R., Grosell, M., Buchwalter, D., Fisher, N., Luoma, S., Mathews, T., Orr, P., Wang, W-X., 2010. Bioaccumulation and trophic transfer of selenium, in: Chapman, P.M., Adam s, W.J., Brooks, M.L., Delos, C.G., Luoma, S.N., Maher, W.A., Ohlendorf, H.M., Presser, T.S., Shaw, D.P. (Eds.), Ecological assessment of selenium in the aquatic environment. CRC Press, Taylor & Francis Group, Boca Raton, pp. 93–139.

Stiboller, M., Raber, G., Lenters, V., Gjengedal, E.L.F., Eggesbø, M., Francesconi, K.A., 2017. Arsenolipids detected in the milk of nursing mothers. Environ. Sci. Technol. Lett. 4, 273–279.

Stoeppler, M., Vahter, M., 1994. Arsenic, in: Herber, R.F.M., Stoeppler, M. (Eds.), Trace element analysis in biological specimens. Elsevier., Amsterdam, pp. 291–320.

Stoeppler, M., 2004. Arsenic, in: Merian, E., Anke, M., Ihnat, M., Stoeppler, M. (Eds.), Elements and their compounds in the environent occurrence, analysis and biological relevance, second edition. Wiley-VCH Verlag, GmbH & Co. KGaA, pp. 1321–1364.

Suess, E., Mehlhorn, J., Planer-Friedrich, B., 2015. Anoxic, ethanolic, and cool – an improved method for thioarsenate preservation in iron-rich waters. Appl. Geochem 62, 224–233.

Sun, C., Shotyk, W., Cuss, C.W., Donner, M.W., Fennell, J., Javed, M., Noernberg, T., Poesch, M., Pelletier, R., Sinnatamby, N., Siddique, T., Martin, J.W, 2017. Characterization of naphthenic acids and other dissolved organics in natural water from the Athabasca Oil Sands Region, Canada. Environ. Sci. Technol. 51, 9524–9532.

Takamura, K., 1982. Microscopic structure of Athabasca oil sand. Can. J. Chem. Eng. 60, 538–

545.

Terlecka, E., 2005. Arsenic speciation analysis in water samples: a review of the hyphenated techniques. Environ. Monit. Assess. 107, 259–284.

Timoney, K., Lee, P., 2009. Does the Alberta tar sands industry pollute? The scientific evidence. The Open Conservation Biology Journal. 3, 65–81.

Timoney, K., 2012. Environmental and health impacts of Canada's bitumen industry: in search of answers. Environ. Sci. Technol. 46, 2496–2497.

Trelease, S.F., Beath, O.A., 1949. History, in: Selenium: Its Geological Occurrence and its Biological Effects in Relation to Botany, Chemistry, Agriculture, Nutrition, and Medicine. New York, pp. 1–12.

USEPA, 1995. National recommended water quality criteria aquatic life criteria table. Accessed at. https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table.

USEPA, 2016. Aquatic Life Ambient Water Quality Criterion for Selenium – Freshwater, 2016, United States Environmental Protection Agency. https://www.epa.gov/sites/production/files/2016-07/documents/aquatic_life_awqc_for_selenium_-_freshwater_2016.pdf

Vahter, M., 2002. Mechanisms of arsenic biotransformation. Toxicology 181–182, 211–217.

van Bellen, S., Magnan, G., Davies, L., Froese, D., Mullan-Boudreau, G., Zaccone, C. Garneau, G., Shotyk, W., 2018. Testate amoeba records indicate regional 20th-century lowering of water tables in ombrotrophic peatlands in central-northern Alberta, Canada. Global Change Biol. 24, 2758–2774.

Vejahati, F., Xu, Z., Gupta, R., 2010. Trace elements in coal: Associations with coal and minerals and their behavior during coal utilization – A review. Fuel 89: 904–911.

Wallschläger, D., London, J., 2004. Determination of inorganic selenium species in rain and sea waters by anion exchange chromatography-hydride generation-inductively-coupled plasma-dynamic reaction cell-mass spectrometry (AEC-HG-ICP-DRC-MS). J. Anal. At. Spectrom. 19, 1119–1127.

Wallschläger, D., Feldmann, J., 2010. Formation, occurrence, significance, and analysis of organoselenium and organotellurium compounds in the environment, in: Sigel, A., Sigel, H., Sigel, R.K.O (Eds.), Organometallics in Environment and Toxicology: Metal Ions in Life Sciences. Royal Society of Chemistry., Cambridge, UK, pp. 319–364.

Wang, D., Alfthan, G., Aro, A., 1994. Determination of total selenium and dissolved selenium species in natural waters by fluorometry. Environ. Sci. Technol. 28, 383–387.

Wang, S., Mulligan, C.N., 2006. Occurrence of arsenic contamination in Canada: sources, behavior and distribution. Sci. Total. Environ. 366, 701–721.

Wang, W., Chen, Z., Davey, D. E., Naidu, R., 2010. Speciation of selenium in biological samples by ion chromatography with inductively coupled plasma mass spectrometry. J. Liq. Chromatogr. Relat. Technol. 33, 1151–1173.

Wardenaar, E.C.P., 1987. A new hand tool for cutting peat profiles. Can. J. Bot. 65, 1772–1773.

Wedepohl, K.H., 1995. The composition of the continental crust. Geochim. Cosmochim. Acta. 59, 1217–1232.

Weiss, J., 2004. Handbook of Ion Chromatography. Wiley-VCH: Weinheim, Germany, Vol. 1, pp. 63, 182, and 528.

Wen, H., Carignan, J., 2007. Reviews on atmospheric selenium: Emissions, speciation and fate. Atmos. Environ. 41, 7151–7165.

White, A.F., Dubrovsky, N.M., 1994. Chemical oxidation–reduction controls on selenium mobility in groundwater systems, in: Frankenberger, W.T., Benson, S., (Eds.), Selenium in the environment. Marcel Dekker Inc., New York, pp. 185–221.

Wieder, R.K., Vile, M.A., Scott, K.D., Albright, C.M., McMillen, K.J., Vitt, D.H., Fenn, M. E., 2016. Differential effects of high atmospheric N and S deposition on bog plant/lichen tissue and porewater chemistry across the Athabasca oil sands region. Environ. Sci. Technol. 50, 12630–12640.

Wiklund, J.A., Hall, R.I., Wolfe, B.B., Edwards, T.W.D., Farwell, A.J., Dixon, D.G., 2012. Has Alberta oil sands development increased far-field delivery of airborne contaminants to the Peace-Athabasca Delta? Sci Tot. Environ. 433, 379–382.

Wiklund, J.A., Hall, R.I., Wolfe, B.B., Edwards, T.W.D., Farwell, A.J., Dixon, D.G., 2014. Use of pre-industrial floodplain lake sediments to establish baseline river metal concentrations downstream of Alberta oil sands: A new approach for detecting pollution of rivers. Environ. Res. Lett. 9, 124019–124028.

Willis, C.E., Kirk, J.L., Louis, V.L.S., Lehnherr, I., Ariya, P.A., Rangel-Alvarado, R.B., 2018. Sources of methylmercury to snowpacks of the Alberta Oil Sands Region: A study of in situ methylation and particulates. Environ. Sci. Technol. 52, 531–540.

Winkel, L.H.E., Vriens, B., Jones, G.D., Schneider, L.S., Pilon-Smits, E., Bañuelos, G.S., 2015. Selenium cycling across soil-plant-atmosphere interfaces: a critical review. Nutrients. 7, 4199–4239.

Wolfe, B.B., Karst-Riddoch, T.L., Hall, R.I., Edwards, T.W.D., English, M.C., Palmini, R., McGowan, S., Leavitt, P.R., Vardy, Sheila, R., 2007. Classification of hydrological regimes of northern floodplain basins (Peace-Athabasca Delta, Canada) from analysis of stable isotopes ($\delta^{18}O$, $\delta^{2}H$) and water chemistry. Hydrol. Process 21, 151–168.

Wu, D., Sun, S., 2016. Speciation analysis of As, Sb and Se. Trends Environ. Anal. Chem. 11, 9–22.

Xing, L., Beauchemin, D. J., 2010. Chromium speciation at trace level in potable water using hyphenated ion exchange chromatography and inductively coupled plasma mass spectrometry with collision/reaction interface. J. Anal. At. Spectrom. 25, 1046–1055.

Young, T.G., Finley, K., Adams, W.J., Besser, J., Hopkins, W.D., Jolley, D.F, McNaughton, E., Presser, T.S., Shaw, P., Unrine, J., 2010. What you need to know about selenium, in: Chapman, P.M., Adams, W.J., Brooks, M.L., Delos, C.G., Luoma, S.N., Maher, W.A., Ohlendorf, H.M., Presser, T.S., Shaw, D.P. (Eds.), Ecological assessment of selenium in the aquatic environment. CRC Press, Taylor & Francis Group., Boca Raton, pp. 7–46.

Zhang, P., Sparks, D.L., 1990. Kinetics of selenate and selenite adsorption/desorption at the goethite/water Interface. Environ. Sci. Technol. 24, 1848–1856.

Zhang, Y. and Moore, J.N., 1996. Selenium fractionation and speciation in a wetland system. Environ. Sci. Technol. 30, 2613–2619.

Zhang, Y., Shotyk, W., Zaccone, C., Noernberg, T., Pelletier, R., Bicalho, B., Froese, D.G., Davies, L., Martin, J.W. 2016. Airborne petcoke dust is a major source of polycyclic aromatic hydrocarbons in the Athabasca oil sands region. Environ. Sci. Technol. 50, 1711–1720.

Zhu, Y. and Guéguen, C., 2016. Evaluation of free/labile concentrations of trace metals in Athabasca oil sands region streams (Alberta, Canada) using diffusive gradient in thin films and a thermodynamic equilibrium model. Environ. Pollut. 219, 1140–1147.

Ziegler, B.A., McGuire, J.T., Cozzarelli, I.M., 2015. Rates of as and trace-element mobilization caused by Fe reduction in mixed BTEX-ethanol experimental plumes. Environ. Sci. Technol. 49, 13179–13189.

APPENDICES

Appendix I: Journal article-formatted version of Chapter Two

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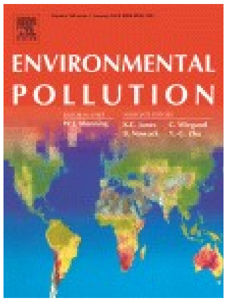

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Arsenic speciation in the lower Athabasca River watershed: A geochemical investigation of the dissolved and particulate phases☆

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ABSTRACT

Human and ecosystem health concerns for arsenic (As) in the lower Athabasca River downstream of Athabasca Bituminous Sands (ABS) mining (Alberta, Canada) prompted an investigation to determine its forms in surface and groundwater upstream and downstream of industry. Dissolved As species, together with total and particulate As, were used to evaluate the potential bioavailability of As in water as well as to decipher inputs from natural geological processes and ABS mining and upgrading activities. Water samples were collected from the river in October at 13 locations in 2014 and 19 locations in 2015, spanning up to 125 km. Additional samples were collected from groundwater, tributaries and springs. "Dissolved" (<0.45 μm) As was consistently low in the Athabasca River (average 0.37 ± 0.01 and 0.34 ± 0.01 μg L^{-1} in 2014 and 2015, respectively) as well as tributaries and springs (<1 μg L^{-1}), with As(V) as the predominant form. The average total As concentration was higher in 2014 (12.7 ± 2.8 μg L^{-1}) than 2015 (3.3 ± 0.65 μg L^{-1}) with nearly all As associated with suspended solids (>0.45 μm). In 2014, when total As concentrations were greater, a significant correlation ($p < 0.05$) was observed with thorium in particles > 0.45 μm, suggesting that mineral material is an important source of As. Naturally saline groundwater contained low dissolved As (<2 μg L^{-1}) and did not appear to be a significant source to the river. Arsenic in shallow groundwater near a tailings pond exceeded 50 μg L^{-1} predominantly as As(III) warranting further investigation.

1. Introduction

Extending over 1300 km across the province of Alberta, Canada, the Athabasca River (AR) and its watershed is an ecologically rich and diverse aquatic system that forms part of the Peace-Athabasca Delta, the largest freshwater boreal delta in the world (Wolfe et al., 2007). While the Athabasca River as a whole faces numerous environmental stresses, the area of the river under the most intense scrutiny is the lower reach where surface mining of the Athabasca Bituminous Sands (ABS) is located. Development of the ABS deposit is one of the largest surface mining operations in the world, generating enormous volumes of waste as fluid fine tailings that now have a total storage volume approaching 1 billion m^3 (http://osip.alberta.ca/map/). Due to the continual growth and development of ABS mining, the current and future status of water quality in the lower Athabasca River and watershed has received significant national and international attention (Gosselin et al., 2010; Schindler, 2010, 2013).

Arsenic (As) has been described as a contaminant from ABS industrial operations in reports, peer-reviewed publications (Timoney and Lee, 2009; Kelly et al., 2010) and even an environmental petition to the government of Canada (Government of Canada, 2008). The negative health effects of long-term exposure to elevated concentrations of As are well known, with specific As compounds classified as carcinogens, teratogens, and mutagens (Stoeppler, 2004). Despite these concerns, no study has examined As in-depth and there have been no source assessments or studies of its chemical speciation, in this region. Health concerns for residents and aquatic life downstream of mining operations is a priority, as previous reports have suggested that As concentrations in water and sediments may have increased over time (Timoney and

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☆ This paper has been recommended for acceptance by Prof. W. Wen-Xiong.

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Lee, 2009). In addition, an evaluation of metals in snow around the region of the ABS described As concentrations (along with other potentially toxic elements) as being greater near ABS industrial development (Kelly et al., 2010). The same study also concluded that As concentrations were greater in the Athabasca River downstream of mining suggesting ABS development as the potential source of As (Kelly et al., 2010). That information generated considerable attention and has recently been disputed by studies that suggest a lack of metal pollution around the region of the ABS (Shotyk et al., 2014; Wiklund et al., 2014). To further examine atmospheric deposition of heavy metals, *Sphagnum* moss was collected around the region of the ABS and analyzed for a variety of potentially toxic metals (Ag, Cd, Ni, Pb, Sb and Tl); but no evidence of atmospheric contamination of heavy metals was found (Shotyk et al., 2014). Similarly, a study of sediment cores from the Peace-Athabasca Delta provided evidence that the Athabasca River had been depositing metals (Be, Cd, Cr, Cu, Pb, Ni, Zn, V) for many years prior to industrial development of the ABS (Wiklund et al., 2014). However, neither of these two preceding studies addressed the potential contribution of As, an element of concern for people living downstream in the First Nations communities of Fort McKay and Fort Chipewyan.

To address this information gap, water samples were collected in October 2014 and 2015 from the lower Athabasca River as well as surrounding tributaries and groundwater as part of a multidisciplinary study to investigate natural and anthropogenic inputs to the river. Because the river is known for its unique natural chemical inputs, primarily as high salinity groundwater intrusions and hydrocarbons from the erosion of bitumen-laden banks, sampling was focused on studying As from areas with suspected influence from these potential sources. While measurements of total As provide important preliminary information, chemical speciation is a crucial component of any study assessing the fate and behavior of As in aquatic systems (Gong et al., 2002). Arsenite [As(III)] and arsenate [As(V)] are known to be carcinogenic to humans (Vahter, 2002) and tend to be the predominant forms in natural waters (Smedley and Kinniburgh, 2002). In surface waters with circumneutral pH, As is thermodynamically stable as As(V) whereas anoxic waters such as groundwaters yield As(III) as the stable and more abundant form (Cullen and Reimer, 1989). Methylated As(V) species (monomethylarsonic acid, MMA and dimethylarsinic acid, DMA) are less toxic than the inorganic forms (Dopp et al., 2004) and may also occur in natural waters in significant concentrations as a result of biological activity (Hasegawa, 1997; Hasegawa et al., 2010). Here, we present data for As in the dissolved (<0.45 μm) and suspended particulate phases (>0.45 μm) in the Athabasca River, tributaries and groundwater, as well as common chemical species [As(V), As(III) and DMA] of As.

2. Materials and methods

2.1. Study area

Water samples were collected from the Athabasca River at 13 locations in October 2014 (Fig. S1) and 19 locations in October 2015 (Fig. 1). Sampling took place during the autumn when water levels are typically at their lowest and under the greatest influence of groundwater inputs. Sampling sites began upstream of the town of Fort McMurray and extended over 125 km downstream to the confluence of the Firebag River. Additional water samples were collected from a total of 11 tributaries, 5 shallow (0.7–3.0 m) groundwater aquifers, 3 saline springs and a saline lake during 2014–2015. Many of the tributaries selected (Steepbank River, Beaver Creek, McLean Creek, Ells River, Tar River) drain areas heavily disturbed by mining operations. The Firebag River, which is relatively far downstream of industrial areas, was sampled for comparison. Water samples were also collected from streams flowing through banks containing large bitumen outcrops (A20e Spring, A9w Creek) and from Pierre River which is known for naturally elevated concentrations of heavy metals due to the occurrence of metalliferous black shales in the Birch Mountains, the source water for the river (Dufresne et al., 2001). Input of saline waters in the Athabasca River has been shown to be extensive in the study area (Gibson et al., 2013), raising questions about the contribution of trace elements such as As from naturally saline groundwater. The area of the Athabasca River under the greatest influence of saline water was identified in a previous study using terrain conductivity mapping (Gibson et al., 2013) which provided insight into potential sampling locations for high salinity ($>20\,000$ μS cm^{-1}) shallow groundwater. Site A5w is located in an area well removed from industrial activity but with a significant amount of saline groundwater seepage (Fig. 1). Samples were also collected from artesian saline springs (FMSS, NSS, SLSP) at various locations on the river as well as at Saline Lake, a naturally saline body of water on the shore of the Athabasca River.

From each location, samples were collected and analyzed for a variety of chemical and physical parameters (e.g. organic pollutants, trace metals, stable and radiogenic isotopes) to expand on existing water quality knowledge in the region. Here, the focus is exclusively As with select physicochemical properties as complementary information.

2.2. Sample collection and handling

Surface water samples from the Athabasca River were collected beneath the surface (~30 cm) from the bow of a small boat anchored approximately 80 m from shore. Water was collected from the mouth of tributaries upstream of the Athabasca River. Samples were collected from the central portion of the stream, upstream from where the person sampling was positioned. For logistical reasons, and in anticipation of a wide variety of water sample compositions, a broad and practical approach comprising field filtration (0.45 μm), acidification using hydrochloric acid (HCl) and dark refrigeration was used to preserve As(III) and As(V) (Kumar and Riyazuddin, 2010; McCleskey et al., 2004; Polya et al., 2003). Hydrochloric acid is the preferred acid for hydride generation atomic fluorescence spectrometry (HG-AFS), the instrument used for analyzing high salinity samples for As. Samples for dissolved As and chemical speciation were filtered in the field using 30 mL plastic syringes (Thermo Scientific™; Cat. #S7510-30) through 0.45 μm polytetrafluoroethylene (PTFE) disk filters (Thermo Scientific™; 30 mm; Cat. # 03-391-1C) into 125 mL low density polyethylene (Thermo Scientific™; Cat. #02-893-4B) or fluorinated high density polyethylene Nalgene™ bottles (Thermo Scientific™; Cat. #0331220); higher volume samples were also collected in 250 mL fluorinated high density polyethylene Nalgene™ bottles (Thermo Scientific™; Cat. # 0331 213). Syringes and filters were pre-cleaned as described in detail elsewhere (Shotyk et al., 2016). Samples were acidified ($pH < 2$) in the field using Optima™ HCl (Fisher Scientific; Cat. # A466-500; certified test value < 1 ng L^{-1} As) and kept in a cool box until being refrigerated (4 °C) at the end of the day. Samples for As speciation were kept in the dark and analyzed immediately upon arrival at the laboratory. To determine As associated with suspended particulate matter in river water, filters containing the particles >0.45 μm were retained after filtration. Unfiltered and unacidified water samples were also collected in 125 mL polypropylene (PP) bottles to determine the total As (dissolved + particulate As) and major anions. Particulate As was estimated by subtracting the dissolved As (<0.45 μm) from total As. Samples for major cation analysis were filtered in the field

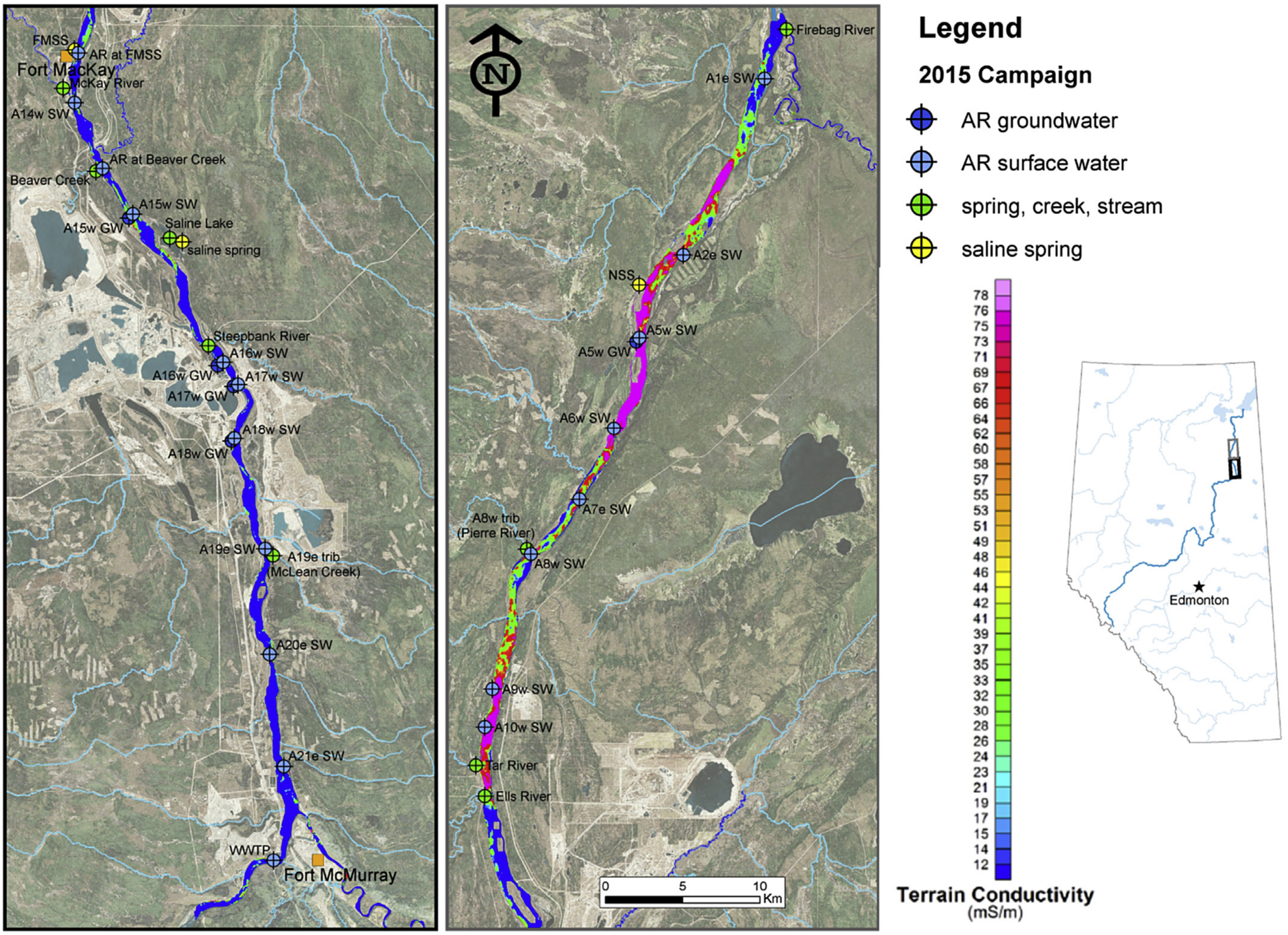

Fig. 1. Map of study area and sampling locations during the 2015 sampling campaign. Map begins at Fort McMurray (bottom of left panel), moving downstream to Fort MacKay, then from Ells River (bottom of right panel) downstream to the Firebag River. Sampling locations were selected for their proximity to ABS industrial development or to assess areas of known saline groundwater influence. Lower terrain conductivity data were provided by Gibson et al., (2013). Letters "e" or "w" indicate whether sampling took place on the East or West portion of the Athabasca River (AR).

into 125 mL PP bottles containing 100 μL of double-distilled nitric acid (HNO_3).

Groundwater samples were obtained using a peristaltic pump by inserting a stainless steel drive point well casing into the sediment and pumping water to the surface through acid cleaned PP tubing. A custom PP cap fitting was constructed so that sample bottles could be attached directly to the line minimizing exposure to the atmosphere. Prior to any sampling, the wells were purged and monitored for basic water quality parameters using a portable multimeter (YSI Pro Plus, Yellow Springs, OH, USA). Samples were collected after stable readings were obtained. For the 2015 sampling campaign, custom PP wells were constructed in advance and installed at sites A18, A15 and A5 approximately 6 weeks prior to water sampling. All samples were filtered and acidified immediately after collection, well within a suggested 10 min time frame for inorganic As speciation in Fe-rich waters (Kumar and Riyazuddin, 2010). Due to the disturbance of the aquifer during drive-point well installation, total As concentrations are not representative. Furthermore, the oxidation of dissolved Fe(II) to Fe(III) was manifested as precipitates on the container wall and these may have scavenged As; therefore, total As in groundwater and saline springs will not be presented.

2.3. *Arsenic quantification*

Inorganic As(III) and As(V) were separated using a high performance ion chromatograph (HPIC; Thermo Scientific Dionex ICS-5000^{+}) equipped with a Dionex Ion Pac™ AS7 anion exchange column (4 mm ID x 250 mm length) and a 25 μL sample loop. The method also included use of a Dionex IonPac™ AG7 guard column (4 mm ID x 50 mm length) for greater separation of DMA from As(V). The system mobile phase consisted of dilute HNO_3 operated using a step-wise program with concentrations from 2.5 mM to 50 mM HNO_3 and a constant flow rate of 1 mL min^{-1}. After chromatographic separation, column effluent was pumped to the inductively coupled plasma mass spectrometer (ICP-MS; iCap Q, Thermo Scientific) for As determination and quantification. Owing to the extremely low concentrations of As, sample groups were analyzed in triplicate to evaluate repeatability. Calculated limits of detection (LOD) for As(III), As(V) and DMA were 6.3 ng L^{-1}, 8.9 ng L^{-1} and 5.4 ng L^{-1}, respectively. Limits of quantification (LOQ) for As species were also calculated and assessed experimentally, with the greatest accuracy and precision at concentrations ~ 20 ng L^{-1}. The LODs for dissolved As using ICP-MS and HG-AFS were 10 ng L^{-1} and 55 ng L^{-1}, respectfully.

All surface water samples were analyzed undiluted whereas groundwater and highly saline surface water samples were diluted up to ten-fold (1 mL + 9 mL) to reduce potential chromatographic or spectral interferences. Dissolved As was measured using ICP-MS under kinetic energy discrimination mode, with 0.05 s dwell time and 120 sweeps. A multi-element internal standard solution (SPEX CertiPrep) was added at a concentration of 1 μg L^{-1} during analysis using a continuous on-line approach. For an independent confirmation of dissolved As in high salinity water, numerous samples were also measured using HG-AFS (Millennium Excalibur, P S Analytical). This procedure converts As species [As(III), As(V), MMA, DMA] into a gaseous hydride when reduced with $NaBH_4$ under acidic conditions; since other organic forms of As (which do not readily form a hydride) were not of interest, no additional oxidation pre-treatments were performed (Sánchez-Rodas et al., 2010). For HG-AFS analysis, 10 mL of sample was combined with 15 mL HCl (12 M), reduced with 1 mL of a potassium iodide and L-ascorbic acid solution (30 min hold time) then diluted and analyzed. The lengthy storage time of saline samples in 2014 precluded reliable chemical speciation data for saline samples and therefore only dissolved As was measured.

To determine total As concentration in untreated water samples, 2 mL of sample was digested with 3 mL double-distilled HNO_3 and 0.1 mL tetrafluoroboric (HBF_4) in PTFE digestion vessels inside a high pressure UltraClave (Milestone, Germany). Optimized parameters and full methodology for digestion of samples is described elsewhere (Shotyk et al., 2014). Diluted samples after digestion were analyzed for As and thorium (Th) using quadrupole ICP-MS housed in the metal-free ultraclean SWAMP laboratory at the University of Alberta. Arsenic and Th concentrations were calculated by averaging three main runs (0.03 s dwell time, 30 sweeps) after adjusting instrumental drift using indium (In) as an internal standard. To determine As and Th in the suspended (>0.45 μm) particulate fraction, filter discs used for filtration in the field were vacuum dried to remove excess water and increase adherence of particles to the membrane. A mechanical lathe was used to remove the filter membrane without any loss of particulate matter. Membranes laden with particulate matter were then digested in double-distilled HNO_3 (6 mL) and HBF_4 (0.2 mL) following the same analytical protocol used for untreated water digestion.

Description of water analyses conducted on samples collected in 2014 for basic measurements (pH, electrical conductivity, temperature, redox potential, etc.) and other complementary chemical data such as dissolved organic carbon (DOC), major cations (Na, Ca, Mg, K, Fe, and Mn) and anions (Cl^-, SO_4^{2-}, NO_3^-) in AR water and tributaries is published separately (Shotyk et al., 2016); however, groundwater data for 2014 and 2015 is presented here (Tables S1 and S2). Site coordinates and their distance relative to the city of Fort McMurray are provided in Table S5.

2.4. Quality control

All analyses followed a strict and detailed quality control protocol that included experimental blanks, certified standard reference materials (SRM; SLRS-5 and NIST 1640a), continuous calibration verification, and matrix spikes to assess the accuracy and precision of measurements. The average value obtained for each SRM was within 5% of the certified value (see full details in Table S3). Experimental blanks and triplicate laboratory and field blanks (ultrapure water plus preservative i.e., HNO_3 or HCl) were included to indicate any sources of contamination. Field duplicates were collected at 7 sites to provide insight on sampling reproducibility. Dissolved As was also analyzed in 2 different sample bottles collected from each site at the same time, but for a collaborative study examining trace metals (Shotyk et al., 2016). Aliquots from samples were also sent to an independent lab (University of Graz, Austria) and analyzed blind. Results of independent laboratory measurements confirm the reproducibility of both sampling and analytical measurements (detailed results for analyses of QC solutions and independent laboratory analyses are provided in Table S3 and Figs. S2, S3, S4). Written details regarding the acid cleaning procedure (Text S1), laboratory reagents (Text S2), calculation of LOD/LOQ (Text S3), independent laboratory methodology (Text S4) and upstream water samples (Text S5) are also provided in the Supplementary Data.

3. Results and discussion

3.1. Athabasca River water

Arsenic in the dissolved fraction of Athabasca River water averaged 0.37 ± 0.01 μg L^{-1} in 2014 (n = 14, Fig. 2A) and 0.34 ± 0.01 μg L^{-1} in 2015 (n = 21, Fig. 2B). These concentrations fluctuated very little both spatially and temporally (2014–2015) showing no discernable increase in As downstream of ABS mines

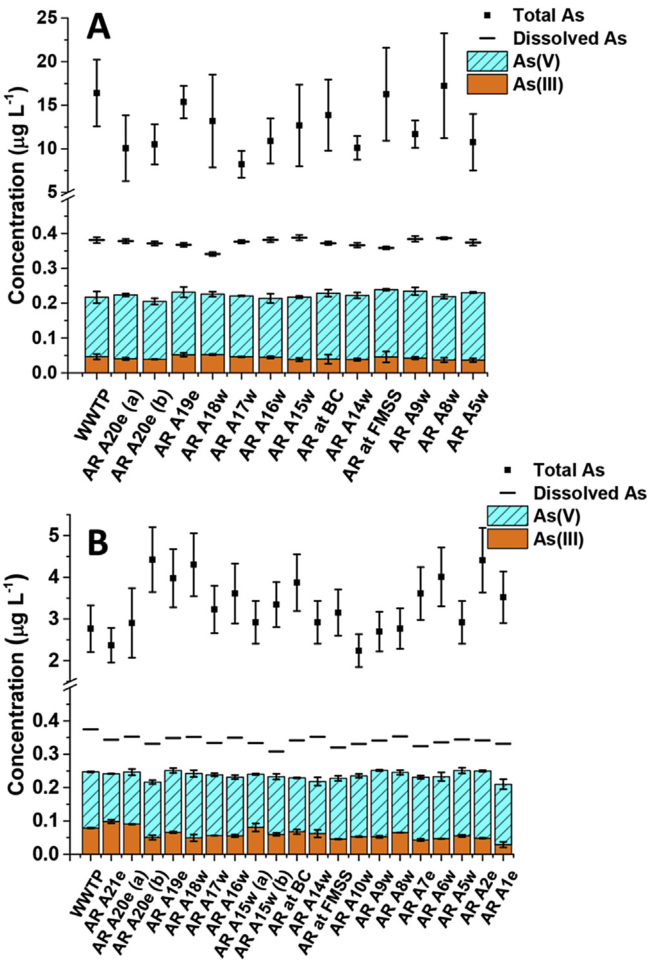

Fig. 2. Total (particulate plus dissolved), dissolved and chemical speciation of As (III, V) in surface water of the Athabasca River (AR) during autumn 2014 (A) and 2015 (B). Site WWTP is located upstream of the town of Fort McMurray and far upstream of ABS industrial activities. The area of greatest industrial activity is located between sites A18w and A9w. Error bars represent the standard deviation of triplicate measurements of an individual sample. Site duplicates are denoted with (a) or (b). Duplicates in 2014 (panel A) were collected 3 days apart; duplicates in 2015 (panel B) were collected 8 and 3 days apart for sites A20e and A15, respectively.

and upgraders in either year. As an additional control to this study, triplicate water samples were provided by Alberta Environment from 3 locations (Fig. S1) upstream of Fort McMurray and were analyzed at the SWAMP laboratory, University of Alberta. Concentrations of dissolved As in water collected near mountain headwaters were extremely low (0.08 μg L^{-1} ± 0.005) whereas the other 2 upstream sites were very similar (0.39 ± 0.01 μg L^{-1} and 0.33 ± 0.01 μg L^{-1}) to water collected in the lower Athabasca River in our study. Dissolved As concentrations in the main stem of the Athabasca River are consistent with the data presented in the Athabasca State of the Watershed Phase III Report from the years 2007–2012, for both Fall/Winter and Spring/Summer periods (Fiera Biological Consulting Ltd, 2013). Until now, the chemical speciation of As has not yet been investigated in the Athabasca River but a number of (non-peer reviewed) reports produced by government and environmental consulting groups exist that contain information about total and dissolved As. A complete review and comparison between these data sets and ours is difficult due to differences in the analytical capabilities of the various laboratories, with concomitant variations in the accuracy and precision of previous work: this is a fundamental issue when comparing data with historical measurements of trace elements in water. For accurate and precise measurements of elements in trace concentrations, strict QA/QC is needed and can only be obtained using suitable instruments capable of detecting analytes in very low concentrations (parts per trillion or lower); this is especially important in determining concentrations of individual species.

Regarding redox state speciation, concentrations of As(V) and As(III) and their ratio remained consistent in Athabasca River water (Fig. 2) with no noticeable change in values downstream of ABS development. The predominant form in Athabasca River surface water was As(V), with an average concentration of 0.18 μg L^{-1} ± 0.09 in 2014 and 0.18 μg L^{-1} ± 0.02 in 2015. Arsenite was present in trace amounts, averaging 43 ng L^{-1} ± 5 ng L^{-1} in 2014 and 60 ng L^{-1} ± 17 in 2015. Samples from 2014 were later screened for MMA and DMA by an independent laboratory, but all Athabasca River samples had concentrations below the LOD (50 ng L^{-1}). River water samples collected in 2015 were analyzed for DMA only, with a slightly lower limit of detection, however no trends or anomalous values were observed and all samples contained < 20 ng L^{-1} (data not shown). Seasonal variation might affect As speciation because changes in methylated As has been shown to correspond with water temperature, with greater concentrations of methylated As compounds occurring in biologically productive warm summer months (Azizur Rahman and Hasegawa, 2012). In our study, cooler water temperature in the Athabasca River (7–8 °C) at the time of sample collection might have caused low yield of methylated As. The effect of seasonal variation on As speciation was not investigated because the primary focus of our study was to determine As inputs from water sources such as natural seepages and shallow groundwater to Athabasca River surface water; groundwater-surface water interactions are more pronounced during fall season when sampling was performed because groundwater inputs become relatively more important. Quantitative data for methylated As species (e.g., MMA, DMA) would be an asset in any study determining seasonal changes in As speciation in the lower Athabasca River Watershed; the extremely low As concentrations, however, present a considerable analytical challenge.

Total As concentrations averaged 12.7 ± 2.8 μg L^{-1} ($n = 14$; Fig. 2A) in 2014 and 3.3 ± 0.65 μg L^{-1} in 2015 ($n = 21$; Fig. 2B). Similar to the dissolved phase, no increasing trend was observed from upstream to downstream in AR water and concentrations were considerably lower in 2015 than 2014. Comparing with dissolved As (0.34–0.37 μg L^{-1}), total As reflects the abundance of suspended particulates in water (Fig. 3). To further investigate As association with mineral or organic constituents of the particulate fraction, particles on the 0.45 μm filters were digested and measured for both As and Th. Concentrations of As were variable, with an average of 24.8 ± 14 μg g^{-1} ($n = 13$) in 2014 and 13.2 ± 9.3 μg g^{-1} ($n = 20$) in 2015 (Table S4). Thorium, a conservative lithophile element, was used as an indicator of mineral abundance. In 2014, when greater total (i.e. particulate) As concentrations were observed, there was a significant correlation ($p < 0.05$) between Th and As in particles retained on the filter (Fig. 3). This is in contrast to 2015, when As concentrations were lower and the correlation with Th was not significant ($p > 0.05$; Fig. 3). Therefore, it would seem that mineral material (i.e. > 0.45 μm fraction) was the dominant source of As in 2014, but not 2015. The use of Th offers some preliminary information but additional study is required to examine the exact composition of particulate matter, including the role of organic matter in As cycling. However, the consistent concentrations upstream to downstream within a given year suggests that the considerable difference in total As concentrations between 2014 and 2015 is likely driven by natural processes, and the concentrations fluctuate independently of industrial activities (Fig. 3). During springmelt when erosion is greatest, river water contains more particles carrying As and other trace elements (Fiera Biological Consulting Ltd, 2013). On this basis, measuring total suspended solids (TSS) or turbidity can be used to estimate metal loading in river water (Nasrabadi et al., 2016).

Permissible levels of As set by the United States Environmental Protection Agency (US EPA) for the protection of aquatic life is 150 μg L^{-1} of dissolved As (U.S EPA, 1995). In contrast, the critical value set by the Canadian Council of Ministers for the Environment (CCME) is much lower, at 5 μg L^{-1} total As (CCME, 1999). Given the discrepancy between two bordering nations with some of the world's largest watersheds in common, the concentrations of As acceptable for aquatic life should perhaps be re-examined. In the case of the Athabasca River, dissolved As concentrations (<0.4 μg L^{-1}) are on the order of 375× below the US EPA guideline value, but during 2014, exceeded the CCME recommended value for total As by a factor of 2× at most locations.

3.2. Tributary water

Tributary waters were highly variable in both concentration and ratio of As(III)/As(V) with all waters containing < 1 μg L^{-1} dissolved As (Fig. 4). In both 2014 and 2015, Pierre River contained the highest concentration of dissolved As compared to tributaries draining heavily mined areas such as Beaver Creek, Steepbank River, Ells River, Muskeg River and McLean Creek. Arsenic concentrations are considerably higher in Pierre River most likely due to inputs of As and many trace metals from metalliferous black shale (Dufresne et al., 2001). Similar to Athabasca River water, the total As in tributary water was much greater than the dissolved phase and noticeably lower in 2015 (Fig. 4). This discrepancy is again an indication that the difference in total As values observed between years is likely due to natural variations, probably related to water flow rates and erosion in each year. It was observed by the field team that water levels in the Athabasca River and tributaries were noticeably higher in 2015 compared to 2014, and this may be the simplest explanation for the much lower concentrations of total As during 2015.

Significant variation in the distribution of As species in tributaries is expected due to the different physical and chemical characteristics of each waterbody. However in general, the chemical speciation is consistent with measured redox conditions (Tables S2 and S3) with As(V) relatively more important in streams with

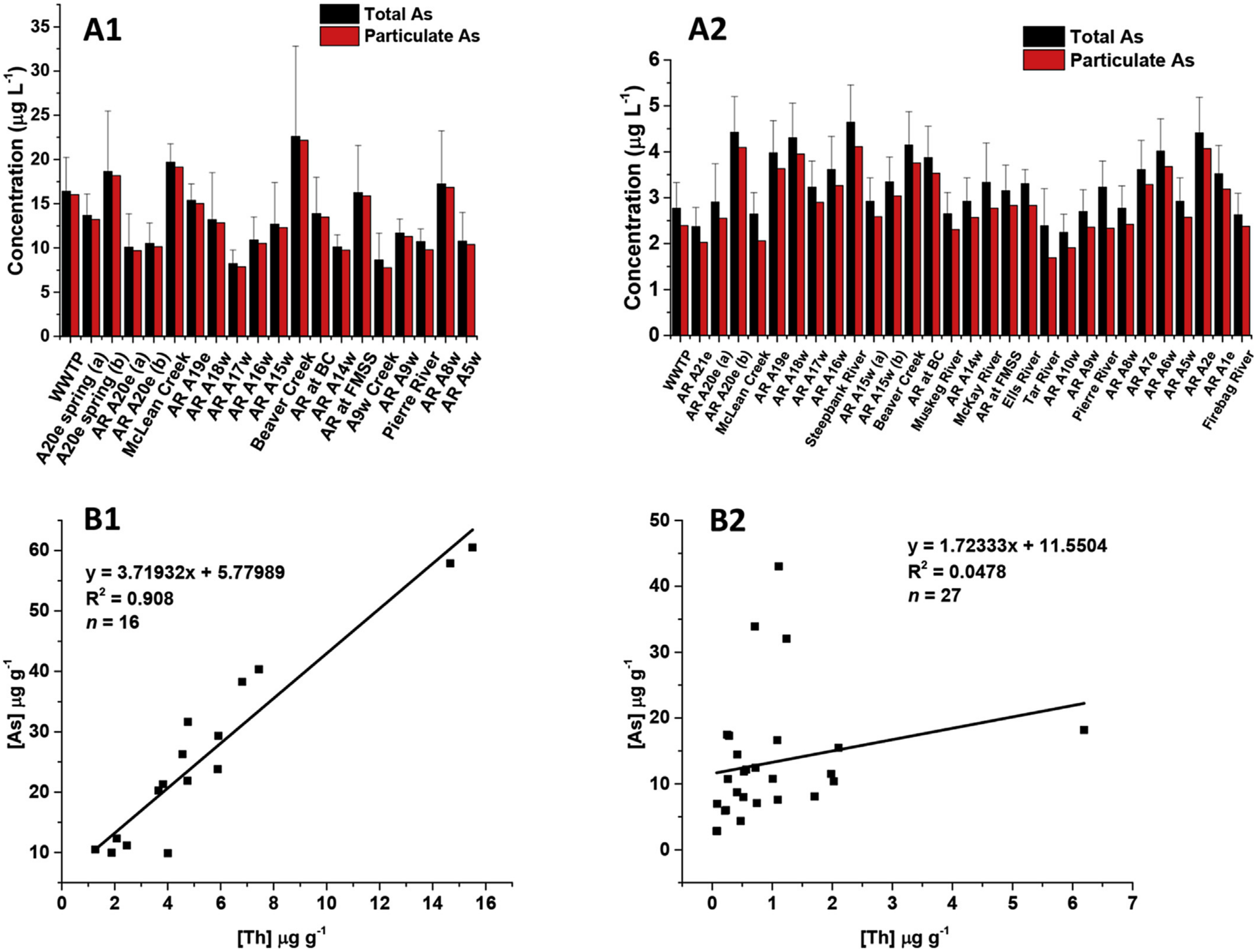

Fig. 3. Total and particulate As in surface water of the Athabasca River (AR) and tributaries during autumn 2014 (A1) and 2015 (A2). A significant ($p < 0.05$) correlation between As and Th was observed for the particulate phase (>0.45 µm) in 2014 (B1), but no significant ($p > 0.05$) correlation was observed for 2015.

higher redox potentials, and As(III) relatively more abundant at lower redox values. For example, a small turbulent creek (A20e) with elevated dissolved oxygen (DO, 13 mg L^{-1}) and redox potential (Eh, 232 mV) contained almost all As in As(V) form. The notable exception to the tributaries was Beaver Creek which contained mostly As(III). This anomaly may indicate a greater influence of groundwater seepage in the area as the redox potential measurements in 2014 in Beaver Creek were quite low (~29 mV). Based on the incomplete sum of inorganic As species relative to (total) dissolved As in Athabasca River water (Fig. 2; 55–70% in 2014 and 63–73% in 2015) and tributaries (Fig. 4; 53–76% in 2014 and 28–75% in 2015), there also appears to be a variable portion of unidentified As species present in surface water. However, because the tributaries drain water from the extensive boreal forest with its numerous, vast peatlands, there is also considerable input of DOC (Shotyk et al., 2016). It seems likely, therefore, that there may be important contributions of organo-As species from peatlands surrounding the Athabasca River. Support for this hypothesis comes from the recent report of an abundance of organic (arsenobetaine) and unidentified As species in peatland surface waters, with low proportions of inorganic As species relative to total dissolved As (Mikutta and Rothwell, 2016).

3.3. *Naturally saline waters*

A confounding factor for assessing water quality in the lower Athabasca River has been the input of naturally saline groundwater from Devonian and other geological formations of marine origin. Overall, there is only limited information on As in these types of saline groundwaters. A recent study of saline springs along the Athabasca River and Clearwater River, a major tributary of the Athabasca River, indicated that only 1 spring on the Clearwater River contained a relatively high concentration of total As (9.63 µg L^{-1}) and neither of the saline springs sampled along the Athabasca River was an important source of As (Gue et al., 2015).

As a part of this study, 3 saline springs (SLSP, NSS, and FMSS) and 1 saline groundwater aquifer (site A5w) on the Athabasca River were sampled to further investigate the potential contribution of As by saline waters. SLSP is an artesian spring located in La Saline Natural Area approximately 15 m above Saline Lake (Borneuf, 1983); NSS also comes to surface naturally. Site FMSS, near Fort McKay (Fig. 1) is unique as it flows up directly from the saline aquifer through an abandoned well casing suspected to have been drilled decades earlier. As a result, FMSS water is undiluted and extremely saline (see Table S1). Groundwater sampled at site A5w was collected with drive point wells at a depth of ~3 m below the

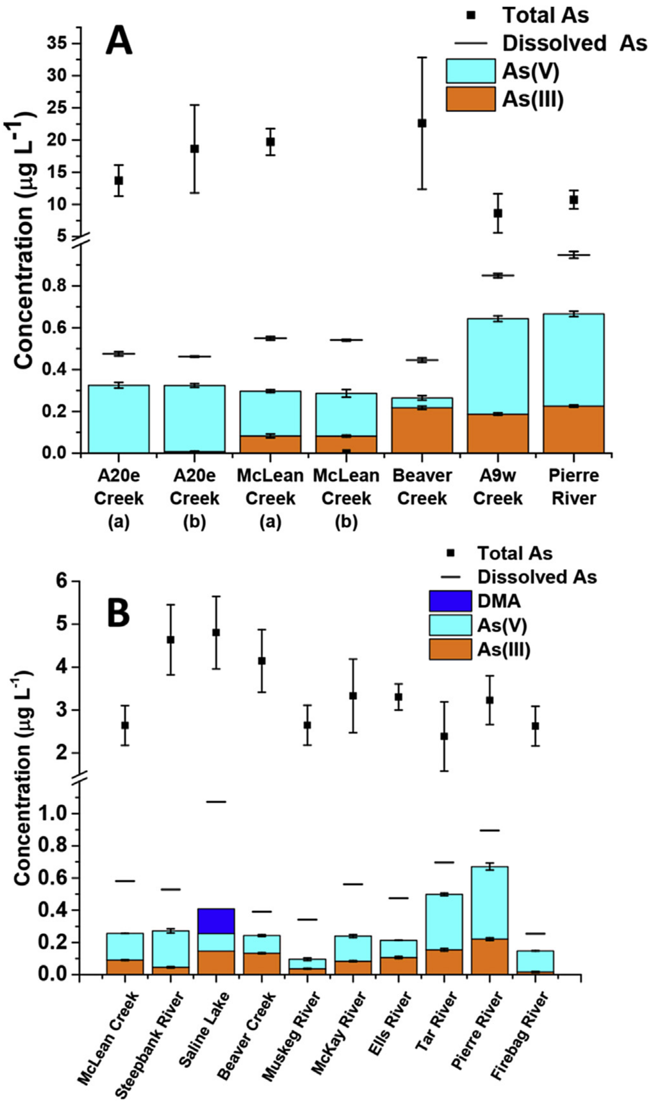

Fig. 4. Total (particulate + dissolved), dissolved and chemical speciation of As [As(III), As(V) and DMA] in Saline Lake and selected tributaries along the Athabasca River during autumn 2014 (A) and 2015 (B). Tributaries were selected based on their proximity to ABS industrial development (Beaver Creek, McLean Creek, Steepbank River, Tar River, Muskeg River, McKay River), drainage of an area with little to no ABS industrial disturbance (Firebag River) or to assess low volume, high flow rate creeks (A20e and A9w) in areas of natural bitumen outcrops. Error bars represent the standard deviation of triplicate measurements of an individual sample. Site duplicate bottles are denoted with (a) and (b) and were collected approximately 1 h apart. Sample McLean Creek (b) was not analyzed for total As.

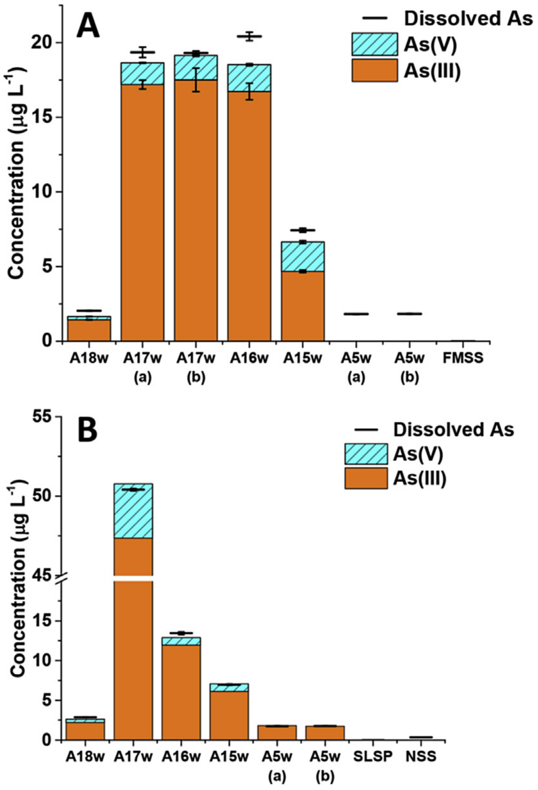

Fig. 5. Dissolved As and inorganic As(III) and As(V) in shallow groundwater and saline springs (FMSS, NSS, SLSP) of the Athabasca River during autumn 2014 (A) and 2015 (B). Sites A18w, A17w, A16w and A15w are located in areas of industrial activity, whereas A5w is well removed from industry but naturally high in salinity. Samples from saline springs were analyzed for total As using HG-AFS, while groundwater samples were measured with ICP-MS and IC-ICP-MS for speciation. Samples A5w (a) and A5w (b) in 2014 were not analyzed for speciation. Error bars represent the standard deviation of triplicate measurements of an individual sample. Site duplicate bottles are denoted with (a) and (b) and were collected approximately 1 h apart.

sediment on a seasonally dry section of the Athabasca River. Concentrations of dissolved As in A5w groundwater were consistent in both years with an average concentration of ~1.8 μg L^{-1} in both 2014 and 2015 (Fig. 5A and B). Chemical speciation by IC-ICP-MS revealed that As is almost entirely As(III) (Fig. 5B). Samples collected from NSS, SLSP and FMSS were taken at the surface before these naturally flowing artesian springs reached the Athabasca River. The concentration of dissolved As (measured by HG-AFS) in NSS was 0.37 μg L^{-1}, while values were < LOD (0.05 μg L^{-1}) in FMSS and SLSP spring water (Fig. 5).

Saline Lake, located in the La Saline Natural Area, is a highly productive, shallow oxbow lake on the shore of the Athabasca River that is naturally saline due to input from underground springs (Borneuf, 1983). In terms of As speciation, this area is anomalous compared to samples from Athabasca River water, tributaries, saline springs and groundwater. Chemical speciation (Fig. 4) of surface water from the lake showed that DMA was actually a significant component of dissolved As (1.07 μg L^{-1}). The breakdown of the three species was as follows: 0.18 μg L^{-1} As(III), 0.12 μg L^{-1} As(V) and 0.15 μg L^{-1} DMA. It is likely that many biological processes are responsible for cycling As within this unique ecosystem. Saline Lake was the only site where reliable concentrations of DMA were found, but a more detailed study of the As speciation at this site is beyond the project scope.

3.4. *The analytical challenges posed by saline waters*

The measurement of trace elements such as As in highly saline water poses a significant analytical challenge. Even with dilution, water collected from saline springs clearly strained the operational capabilities of ICP-MS showing severe changes in the peak intensity of internal standard and yielded a positive bias. For an independent method check of As in saline waters, HG-AFS and ICP-QQQ-MS (triple quadrupole) were employed. Measurements of As by HG-AFS and ICP-MS (single quadrupole) yielded similar results (<10% difference) for groundwater at site A5w (Table S3). However, for FMSS, NSS and SLSP, HG-AFS yielded lower results suggesting a potential positive bias for measurements made using ICP-MS. Also, values for As from FMSS with (single quadrupole) ICP-MS were >17× higher than measurements by ICP-QQQ-MS (data not shown). This discrepancy in As values is due to the well-documented interference on As ($m/z = 75$) by $^{40}Ar^{35}Cl^{+}$ ($m/z = 75$) polyatomic ions formed in the Ar plasma gas and in samples containing elevated chloride (B'Hymer and Caruso, 2004). Collision cell technology can reduce this positive bias but it may not completely eliminate this effect in high salinity samples. It is recommended that these types of waters be analyzed with caution when using conventional single quadrupole ICP-MS; spectral interference can be overcome by using HG-AFS (Terlecka, 2005; Wu and Sun, 2016), high resolution sector field ICP-MS (Jackson et al., 2015), or ICP-QQQ-MS (Jackson et al., 2015). Due to the extremely high salinity in comparison with low As concentrations in the saline springs, these samples could not be reliably analyzed for As species. Furthermore because of the high sulfur content and unique chemistry of these springs, comprehensive As speciation analysis should include thio-based As species, which have been shown to be abundant in sulfidic waters (Planer-Friedrich et al., 2007); these As forms also require specialized collection and preservation techniques for representative measurements (Suess et al., 2015).

Although chloride concentrations increase with distance downstream of Fort McMurray due to saline groundwater inputs (Gibson et al., 2013; Shotyk et al., 2016) the low, uniform As concentrations in the main stem Athabasca River combined with the low concentrations of As in the saline groundwater suggest that naturally saline groundwater is not a significant source of As to the river.

3.5. *Groundwater*

In contrast to many other potentially toxic trace elements which may be present at ultra-low concentrations in groundwater (Shotyk et al., 2010), As is often found to be naturally enriched relative to meteoric water due to mineral dissolution combined with anoxia, particularly when organic matter is present (Ziegler et al., 2015). More importantly, because it forms anionic species, removal processes in soils and sediments which are so effective for cationic species such as Pb^{2+}, are ineffective for adsorbing $H_3As^{III}O_3^0$ (Shotyk and Krachler, 2009; Shotyk et al., 2010). In shallow groundwater wells sampled on the Athabasca River near the banks (Fig. 5), dissolved As concentrations varied substantially (1.8–50.4 $\mu g\ L^{-1}$) between the five locations. The predominant form in all groundwater samples was As(III), constituting 63–103% of the dissolved As. Given the abundance of DOC (8–61 $mg\ L^{-1}$) and low redox potentials (Tables S1 and S2), As(III) was expected to predominate due to biotic/abiotic reduction of As(V) (Cullen and Reimer, 1989). Although a small portion of As(V) was found, this may be attributed to changes which occurred during field sampling or storage. Only by comparing multiple preservation techniques with immediate analysis could the appearance of As(V) in the groundwater thoroughly be assessed.

Concentrations of dissolved As in groundwater situated near a bitumen upgrader (A16w) and a tailings pond (A17w) were anomalous. This finding contrasts with a recent survey of shallow riparian groundwater near a tailings pond (site A17w in this study) which found no significant difference between As concentrations in "Pond Site" groundwater versus nearby control sites (Roy et al., 2016); it appears that the groundwater in this area contains variable concentrations of As. While As concentrations at site A16w remained similar in both years, concentrations at A17w were greater in 2015 than 2014 (50 $\mu g\ L^{-1}$ versus 20 $\mu g\ L^{-1}$, respectively; Fig. 5A and B). In comparison to other groundwater sites (A5w, A15w, and A18w), which showed almost no change in As concentration between 2014 and 2015, a 30 $\mu g\ L^{-1}$ difference at site A17w is substantial. Given the close proximity of this sampling location to industrial activity, a more detailed investigation of As in groundwater at this site is warranted. This could be accomplished by focusing on i) long term monitoring ii) biogeochemical processes taking place at the groundwater – surface water interface iii) quantifying the fluxes of groundwater entering the river during different water level (or seasonal) conditions and iv) comparing data with isotopic tracers and other sourcing techniques to determine the source of water.

Long term monitoring would be complemented by understanding the precipitation and complexation reactions occurring at the groundwater – surface water interface. These processes are driven by many chemical and physical factors (pH, sediment texture and mineralogy, speciation, redox potential, etc.) and may contribute to natural As removal processes (Mok and Wai, 1994). For example, scavenging of As(V) by Fe and Mn (hydr)oxides formed during the transition of groundwater from anoxic to oxic (groundwater – surface water interface) is a natural removal processes which is known to be a major controlling factor for As in river sediment (Gorny et al., 2015). Elucidating which biogeochemical processes are at work in sediments of the Athabasca River would aid in further understanding the source(s) of As and may help explain the observed variability in concentrations between years; laboratory experiments focused on the host phases of As in sediments and the microorganisms present are underway to determine the source and fate of As in shallow groundwater.

It is important to note that when discussing As contamination in relation to bituminous sands in Alberta, the distinction must be made between surface mining (*ex-situ*) in the Athabasca formation and *in-situ* extraction in the Cold Lake Region of Alberta (CLRA) as the CLRA is known for naturally high concentrations of As (up to 179 $\mu g\ L^{-1}$) in shallow groundwater (Moncur et al., 2015). Laboratory trials of simulated *in-situ* bituminous sand mining processes (underground heating via steam injection) has demonstrated the potential for substantial release of As from sediments and its mobilization in groundwater aquifers (Javed and Siddique, 2016).

4. Conclusion

The purpose of this study was to determine the form of As in the lower Athabasca River and distinguish between natural and anthropogenic inputs. The lack of change in As concentrations in surface water upstream versus downstream of industry during two intensive water sampling campaigns suggests that natural inputs dominate the As inventory of the river. Total concentrations of As show considerable spatial and temporal variation, but there was no observed increase in concentration downstream of industry. In contrast, "dissolved" As concentrations (ie < 0.45 μm) are remarkably consistent in space and time and again, show no increasing trend downstream of industry. Total concentrations of As reflect physical inputs to the river from erosion within the watershed, and these vary seasonally. Dissolved As, on the other hand, is supplied by chemical processes such as mineral weathering and these inputs are expected to be rather uniform and constant, given the pH buffering of surface and groundwaters in this basin by abundant carbonate alkalinity. High and variable As concentrations in groundwater near an industrial site warrants additional study to determine the source and biogeochemical cycling at the sediment-water interface. These findings are important not only for communities living downstream of ABS industrial activity concerned about As contamination, but also for water monitoring agencies tasked with understanding the partitioning of As in the dissolved or particulate phase of water. While the primary focus of this study was groundwater – surface water interactions, additional work is ongoing to evaluate atmospheric inputs to the snowpack and release during spring melt.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2017.02.004.

References

Azizur Rahman, M., Hasegawa, H., 2012. Arsenic in freshwater systems: influence of eutrophication on occurrence, distribution, speciation, and bioaccumulation. Appl. Geochem 27, 304–314. http://dx.doi.org/10.1016/j.apgeochem.2011.09.020.

B'Hymer, C., Caruso, J.A., 2004. Arsenic and its speciation analysis using high-performance liquid chromatography and inductively coupled plasma mass spectrometry. J. Chromatogr. A 1045, 1–13. http://dx.doi.org/10.1016/j.chroma.2004.06.016.

Borneuf, D., 1983. Springs of Alberta. Alberta Research Council; Earth Sciences Report 82–3, Edmonton, Alberta, Canada (280 pp). Accessed at http://ags.aer.ca/document/ESR/ESR_1982_03.PDF.

CCME, 1999. Canadian Environmental Quality Guidelines. Canadian Council of Ministers of the Environment. Environment Canada, Hull, Quebec, 8 Chapters. Accessed at. http://st-ts.ccme.ca/en/index.html?chems=9&chapters=1,2.

Cullen, W.R., Reimer, K.J., 1989. Arsenic speciation in the environment. Chem. Rev. 89, 713–764.

Dopp, E., Hartmann, L.M., Florea, A.-M., von Recklinghausen, U., Pieper, R., Shokouhi, B., Rettenmeier, A.W., Hirner, A.V., Obe, G., 2004. Uptake of inorganic and organic derivatives of arsenic associated with induced cytotoxic and genotoxic effects in Chinese hamster ovary (CHO) cells. Toxicol. Appl. Pharmacol. 201, 156–165. http://dx.doi.org/10.1016/j.taap.2004.05.017.

Dufresne, M.B., Eccles, D.R., Leckie, D.A., 2001. The Geological and Geochemical Setting of the Mid-cretaceous Shaftesbury Formation and Other Colorado Group Sedimentary Units in Northern Alberta. Alberta Energy and Utilities Board and Alberta Geological Survey. Special Report 09 (654 pp). Accessed at http://ags.aer.ca/document/SPE/SPE_009.PDF.

Fiera (Fiera Biological Consulting Ltd), 2013. State of the Watershed Report – Phase 3: Water Quantity and Basic Water Quality in the Athabasca Watershed. Report prepared for the Athabasca Watershed Council, Fiera Biological Consulting report #1234. Accessed at. http://www.awc-wpac.ca/sites/default/files/SOW3complete.pdf.

Gibson, J.J., Fennell, J., Birks, S.J., Yi, Y., Moncur, M.C., Hansen, B., Jasechko, S., 2013. Evidence of discharging saline formation water to the Athabasca River in the oil sands mining region. North. Alta. Can. J. Earth Sci. 50, 1244–1257. http://dx.doi.org/10.1139/cjes-2013-0027.

Gong, Z., Lu, X., Ma, M., Watt, C., Le, X.C., 2002. Arsenic speciation analysis. Talanta 58, 77–96. http://dx.doi.org/10.1016/S0039-9140(02)00258-8.

Gorny, J., Billon, G., Lesven, L., Dumoulin, D., Madé, B., Noiriel, C., 2015. Arsenic behavior in river sediments under redox gradient: a review. Sci. Total Environ. 505, 423–434. http://dx.doi.org/10.1016/j.scitotenv.2014.10.011.

Gosselin, P., Hrudey, S.E., Naeth, M.A., Plourde, A., Therrien, R., Van Der Kraak, G., Xu, Z., 2010. Environmental and Health Impacts of Canada's Oil Sands Industry. Royal Society of Canada (RSC), Ottawa, Ontario, Canada (414 pp). Accessed at. https://rsc-src.ca/sites/default/files/pdf/RSC%20Oil%20Sands%20Panel%20Main%20Report%20Oct%202012.pdf.

Government of Canada, 2008. Environmental Petition: No. 238. Water and Sediment Contamination of the Athabasca River Due to Oilsands Production. Office of the Auditor General of Canada. Commissioner of the Environment and Sustainable Development, Ottawa, Canada.

Gue, A.E., Mayer, B., Grasby, S.E., 2015. Origin and geochemistry of saline spring waters in the Athabasca oil sands region, Alberta, Canada. Appl. Geochem 61, 132–145. http://dx.doi.org/10.1016/j.apgeochem.2015.05.015.

Hasegawa, H., 1997. The behavior of trivalent and pentavalent methylarsenicals in Lake Biwa. Appl. Organometal. Chem. 11, 305–311.

Hasegawa, H., Rahman, M.A., Kitahara, K., Itaya, Y., Maki, T., Ueda, K., 2010. Seasonal changes of arsenic speciation in lake waters in relation to eutrophication. Sci. Total Environ. 408, 1684–1690. http://dx.doi.org/10.1016/j.scitotenv.2009.11.062.

Jackson, B.P., Liba, A., Nelson, J., 2015. Advantages of reaction cell ICP-MS on doubly charged interferences for arsenic and selenium analysis in foods. J. Anal. At. Spectrom. 30, 1179–1183. http://dx.doi.org/10.1039/c4ja00310a.

Javed, M.B., Siddique, T., 2016. Thermally released arsenic in porewater from sediments in the Cold Lake area of alberta, Canada. Environ. Sci. Technol. 50, 2191–2199. http://dx.doi.org/10.1021/acs.est.5b04555.

Kelly, E.N., Schindler, D.W., Hodson, P.V., Short, J.W., Radmanovich, R., Nielsen, C.C., 2010. Oil sands development contributes elements toxic at low concentrations to the Athabasca River and its tributaries. Proc. Natl. Acad. Sci. U. S. A. 107, 16178–16183. http://dx.doi.org/10.1073/pnas.1008754107.

Kumar, A.R., Riyazuddin, P., 2010. Preservation of inorganic arsenic species in environmental water samples for reliable speciation analysis. Trends Anal. Chem. 29, 1212–1223. http://dx.doi.org/10.1016/j.trac.2010.07.009.

McCleskey, R.B., Nordstrom, D.K., Maest, A.S., 2004. Preservation of water samples for arsenic(III/V) determinations: an evaluation of the literature and new analytical results. Appl. Geochem 19, 995–1009. http://dx.doi.org/10.1016/j.apgeochem.2004.01.003.

Mikutta, C., Rothwell, J.J., 2016. Peat bogs as hotspots for organoarsenical formation and persistence. Environ. Sci. Technol. 50, 4314–4323. http://dx.doi.org/10.1021/acs.est.5b06182.

Mok, W.M., Wai, C.M., 1994. Mobilization of arsenic in contaminated River Waters. In: Nriagu, J.O. (Ed.), Arsenic in the Environment Part I: Cycling and Characterization. John Wiley and Sons, New York, NY, pp. 99–114.

Moncur, M.C., Paktunc, D., Jean Birks, S., Ptacek, C.J., Welsh, B., Thibault, Y., 2015. Source and distribution of naturally occurring arsenic in groundwater from Alberta's Southern Oil Sands Regions. Appl. Geochem 62, 171–185. http://dx.doi.org/10.1016/j.apgeochem.2015.02.015.

Nasrabadi, T., Ruegner, H., Sirdari, Z.Z., Schwientek, M., Grathwohl, P., 2016. Using total suspended solids (TSS) and turbidity as proxies for evaluation of metal transport in river water. Appl. Geochem 68, 1–9. http://dx.doi.org/10.1016/j.apgeochem.2016.03.003.

Planer-Friedrich, B., London, J., Mccleskey, R.B., Nordstrom, D.K., Wallschläger, D., 2007. Thioarsenates in geothermal waters of yellowstone National Park: determination, preservation, and geochemical importance. Environ. Sci. Technol. 41, 5245–5251. http://dx.doi.org/10.1021/es070273v.

Polya, D.A., Lythgoe, P.R., Abou-Shakra, F., Gault, A.G., Brydie, J.R., Webster, J.G., Brown, K.L., Nimfopoulos, M.K., Michailidis, K.M., 2003. IC-ICP-MS and IC-ICP-HEX-MS determination of arsenic speciation in surface and groundwaters: preservation and analytical issues. Mineral. Mag. 67, 247–261. http://dx.doi.org/10.1180/0026461036720098.

Roy, J.W., Bickerton, G., Frank, R.A., Grapentine, L., Hewitt, L.M., 2016. Assessing risks of shallow riparian groundwater quality near an oil sands tailings pond. Groundwater 54, 545–558. http://dx.doi.org/10.1111/gwat.12392.

Schindler, D., 2010. Tar sands need solid science. Nature 468, 499–501. http://dx.doi.org/10.1038/468499a.

Schindler, D.W., 2013. Geoscience of climate and energy 12. Water quality issues in the oil sands region of the lower Athabasca River, Alberta. Geosci. Can. 40, 202–214. http://dx.doi.org/10.12789/geocanj.2013.40.012.

Sánchez-Rodas, D., Corns, W.T., Chen, B., Stockwell, P.B., 2010. Atomic Fluorescence Spectrometry: a suitable detection technique in speciation studies for arsenic, selenium, antimony and mercury. J. Anal. At. Spectrom. 25, 933–946. http://dx.doi.org/10.1039/b917755h.

Shotyk, W., Krachler, M., 2009. Determination of trace element concetrations in natural freshwaters: how low is “low”, and how low do we need to go? J. Environ. Monit. 11, 1747–1753. http://dx.doi.org/10.1039/B917090C.

Shotyk, W., Belland, R., Duke, J., Kempter, H., Krachler, M., Noernberg, T., Pelletier, R., Vile, M.A., Wieder, K., Zaccone, C., Zhang, S., 2014. Sphagnum mosses from 21 ombrotrophic bogs in the athabasca bituminous sands region show no significant atmospheric contamination of “Heavy Metals”. Environ. Sci. Technol. 48, 12603–12611. http://dx.doi.org/10.1021/es503751v.

Shotyk, W., Krachler, M., Aeschbach-Hertig, W., Hillier, S., Zheng, J., 2010. Trace elements in recent groundwater of an artesian flow system and comparison with snow: enrichments, depletions, and chemical evolution of the water. J. Environ. Monit. 12, 208–217. http://dx.doi.org/10.1039/b909723f.

Shotyk, W., Bicalho, B., Cuss, C.W., Donner, M.W., Grant-Weaver, I., Haas-Neill, S., Javed, M.B., Krachler, M., Noernberg, T., Pelletier, R., Zaccone, C., 2016. Trace metals in the dissolved fraction (<0.45μm) of the lower Athabasca River: analytical challenges and environmental implications. Sci. Total Environ. (in press) http://dx.doi.org/10.1016/j.scitotenv.2016.12.012.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem 17, 517–568. http://dx.doi.org/10.1016/S0883-2927(02)00018-5.

Stoeppler, M., 2004. Arsenic. In: Merian, E., Anke, M., Ihnat, M., Stoeppler, M. (Eds.), Elements and Their Compounds in the Environment. Volume 3: Nonmetals, Particular Aspects. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, pp. 1321–1364.

Suess, E., Mehlhorn, J., Planer-Friedrich, B., 2015. Anoxic, ethanolic, and cool - an improved method for thioarsenate preservation in iron-rich waters. Appl. Geochem 62, 224–233. http://dx.doi.org/10.1016/j.apgeochem.2014.11.017.

Terlecka, E., 2005. Arsenic speciation analysis in water samples: a review of the hyphenated techniques. Environ. Monit. Assess. 107, 259–284. http://dx.doi.org/10.1007/s10661-005-3109-z.

Timoney, K.P., Lee, P., 2009. Does the Alberta tar sands industry pollute? The scientific evidence. Open Conserv. Biol. J. 3, 65–81. http://dx.doi.org/10.2174/1874839200903010065.

U.S. Environmental Protection Agency, 1995. National Recommended Water Quality Criteria – Aquatic Life Criteria Table. Accessed at. https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table.

Vahter, M., 2002. Mechanisms of arsenic biotransformation. Toxicology 181–182, 211–217. http://dx.doi.org/10.1016/S0300-483X(02)00285-8.

Wiklund, J.A., Hall, R.I., Wolfe, B.B., Edwards, T.W.D., Farwell, A.J., Dixon, D.G., 2014. Use of pre-industrial floodplain lake sediments to establish baseline river metal concentrations downstream of Alberta oil sands: a new approach for detecting pollution of rivers. Environ. Res. Lett. 9, 124019. http://dx.doi.org/10.1088/1748-9326/9/12/124019.

Wolfe, B.B., Karst-Riddoch, T.L., Hall, R.I., Edwards, T.W.D., English, M.C., Palmini, R., McGowan, S., Leavitt, P.R., Vardy, Sheila, R., 2007. Classification of hydrological regimes of northern floodplain basins (Peace-Athabasca Delta, Canada) from analysis of stable isotopes ($\delta^{18}O$, $\delta^{2}H$) and water chemistry. Hydrol. Process 21, 151–168. http://dx.doi.org/10.1002/hyp.6229.

Wu, D., Sun, S., 2016. Speciation analysis of As, Sb and Se. Trends Environ. Anal. Chem. 11, 9–22. http://dx.doi.org/10.1016/j.teac.2016.05.001.

Ziegler, B.A., McGuire, J.T., Cozzarelli, I.M., 2015. Rates of as and trace-element mobilization caused by Fe reduction in mixed BTEX-ethanol experimental plumes. Environ. Sci. Technol. 49, 13179–13189. http://dx.doi.org/10.1021/acs.est.5b02341.

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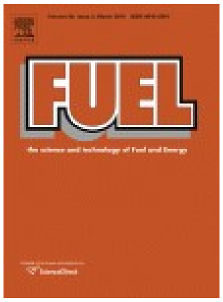

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Selenium and sulphur in Athabasca bituminous sands mineral and bitumen fractions

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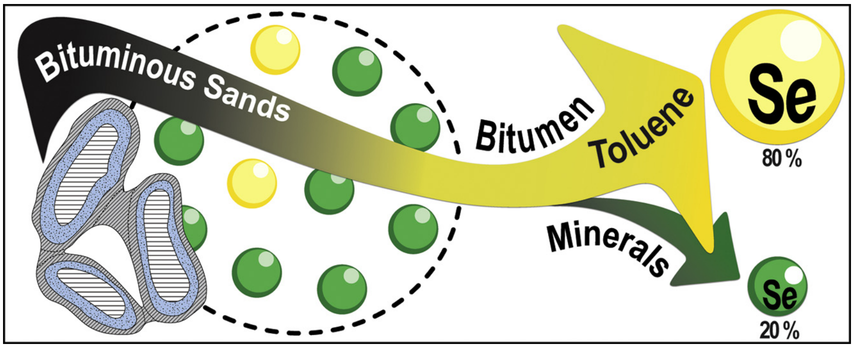
GRAPHICAL ABSTRACT



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ABSTRACT

There is increasing environmental concern regarding the emission of selenium (Se) from mining and upgrading of bitumen extracted from the Athabasca bituminous sands (ABS) in northern Alberta, Canada. However, there remains a lack of high quality analytical data for Se in this massive hydrocarbon reserve. Accurate analytical determinations of Se in bitumen from ABS are an important first step toward understanding its potential to be emitted to the environment. This has been a challenge due to the low abundance of Se combined with the preponderance of entrained mineral material (sand, clay) and the generally inadequate sensitivity of analytical methods used in the past. To overcome these issues, samples of ABS ores (McMurray Formation) underwent a toluene extraction procedure under ultra-clean lab conditions to separate bitumen from mineral particles. Separated bitumen, residual mineral material, and bulk ores were then subjected to acid-digestion and analysis using inductively coupled plasma sector-field mass spectrometry (ICP-SFMS) as well as hydride generation atomic fluorescence spectroscopy (HG-AFS). Unlike many other potentially toxic trace elements (Ag, As, Be, Cd, Cu, Pb, Sb, Tl and Zn) which exist almost exclusively in the mineral fraction, Se was found primarily (ca. 80%) in the organic (bitumen) fraction. Sulphur was determined in the same acid digests using both ICP-SFMS and inductively coupled plasma-optical emission spectroscopy (ICP-OES) and it too, was found almost exclusively in the bitumen fraction. Despite the limited number of samples available to our study, the positive, linear correlation between Se and S concentrations in bitumen suggests that S concentrations can be used as a guide to estimate their Se content. Given that Se is found mainly in the organic fraction of the ABS, there is considerable potential for mobilization of this element during upgrading and refining. The analytical methods successfully employed here have sufficient sensitivity to support studies of Se contamination of environmental media in the ABS region.

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1. Introduction

Bituminous sands are hydrocarbon reserves consisting of mixtures of sand, clay, water and bitumen – a heavily biodegraded crude oil [1]. The largest known group of bitumen deposits is the Lower Cretaceous Mannville group (Athabasca-Wabasca, Peace River, Cold Lake) in Alberta, Canada [2], which together contains an estimated 165.4×10^9 barrels of (remaining) established reserves [3]. Of this group, the Athabasca bituminous sands (ABS) region is the largest deposit [2] (initial established reserve = $6.16 \times 10^9\ m^3$) and contains an estimated 32.09×10^9 barrels remaining established reserves [3]. The Athabasca deposit is also well known for its shallow (average) pay-zone (~30 m deep) accessible by surface mining [4]. Geochemical characterization of bitumen from the ABS region was a priority during the early stages of development (ca. 1950–1985). This included determining the trace element content to provide information on the type of petroleum (i.e., origin, geological formation, maturation, etc.) as well as the abundance of elements known to be problematic during the bitumen upgrading processes [5]. Much of the trace element research at that time was focused on vanadium (V) and nickel (Ni) due to their enrichment in bitumen as metal-porphyrin complexes and ability to cause significant corrosion of equipment and impair the catalytic cracking process [6,7]. Atmospheric emissions of trace elements to the environment were also of interest, with monitoring efforts concentrated on V as an indicator of ABS mining and upgrading emissions [8,9].

Aside from V and Ni, there have been very few published studies examining the trace element content of bitumen in the ABS region since the pioneering work over 30 years ago [5,10–13]. This is despite: i) considerable improvements in relevant analytical techniques ii) extremely rapid industrial growth and iii) growing concerns in regard to contamination of potentially toxic trace elements such as Ag, As, Be, Cd, Cr, Cu, Ni, Hg, Pb, Sb, Se, Tl and Zn [14–16]; for these reasons, a contemporary investigation of the trace element content in bitumen from the ABS was undertaken [17]. In that study [17], bitumen and mineral phases were separated under ultra-clean lab conditions using toluene, then digested and analyzed using inductively coupled plasma sector-field mass spectrometry (ICP-SFMS). The results confirmed the enrichment of V, Ni and Mo in bitumen, which is consistent with the historical work by Goldschmidt [18]. Rhenium (Re) was also found to be hosted predominantly in the bitumen fraction, in agreement with the more recent work on Re-Os dating by Creaser and Selby [19]. In contrast to V, Ni, Mo and Re, potentially toxic trace elements such as Ag, As, Be, Bi, Cd, Cu, Pb, Sb, Tl and Zn were found almost exclusively in the mineral fraction [17]. Unfortunately, the work by Bicalho et al. [17] provided no information about selenium (Se), a non-metallic trace element with properties chemically analogous to sulphur (S) [20].

Depending on its concentration and chemical form, Se may act either as an essential micro-nutrient [21,22] or environmental toxin [23]. The concentration range between toxic and beneficial can be relatively narrow, particularly for aquatic organisms such as fish [24–26] and waterfowl [27]. This highlights the importance of understanding human activities that could mobilize Se or change its speciation, thereby increasing the potential for bioaccumulation within the food chain [28]. Industrial combustion and roasting processes involving crude oil, coal and metal sulphide ores dominate anthropogenic Se emissions to the atmosphere [29–33]. Selenium emissions can be especially problematic during industrial processing of fossil fuels (particularly coal) due to its ability to form sub-micron or gaseous species which by-pass many engineered air pollution controls such as electrostatic precipitators and baghouse filters [34–36]. However, due to its chemical similarity to S, the use of modern wet-scrubber technologies (e.g., flue gas desulphurization; FGD) can be effective in reducing atmospheric Se emissions [37,38]. The impacts of atmospheric emissions can be assessed by determining Se concentrations in various environmental compartments (soil, water, plants, etc.), but even in polluted areas this can still be a challenge due to its low abundance and complexity of chemical transformations. The most common method of analysis currently used for Se determination is ICP-MS, however, accurate and precise measurements of Se are often hindered by its high ionization potential and a large number of molecular interferences for an array of stable isotopes (^{74}Se, ^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se) [39–42].

Early work on bitumen from the ABS region that examined a wide spectrum of trace elements either did not include Se in the list of elements studied [43], or reported inadequate limits of detection [44]. Previous studies were also limited to only one or two samples and therefore provided no information about possible relations between Se concentrations and ore quality. The analytical challenges and paucity of information on the abundance and forms of Se in ABS makes it difficult to fully evaluate the potential environmental impacts of resource development, from open pit mining to upgrading and eventually refining. Here we provide an accurate assessment of the distribution of Se between the mineral and bitumen fractions of the ABS. Due to the chemical similarities between Se and S, we also examined the abundance of S in the two fractions, with a view toward using it as a proxy for estimating the abundance of Se in bitumen.

2. Materials and methods

2.1. General

All experimental procedures were carried out within class 100, metal-free clean air cabinets. High-purity water (18 MΩ·cm, Q-Pod Element, Millipore) was used throughout the study. Laboratory soap (Versa-Clean, Fisherbrand) and trace grade acids (Fisherbrand HNO_3 and HCl) were used in material cleaning routines. Trace metal grade HNO_3 used for sample digestion and preparation of working solutions was purified twice by sub-boiling distillation and stored in cleaned polytetrafluoroethylene (PTFE) bottles. ACS certified toluene (> 99.5%, Fisher Scientific) was used for the bitumen extractions. Polypropylene (PP) syringes and filters (30 mm PTFE membrane, 0.45 μm, PP housing, Target-2, ThermoFisher) were cleaned by filtering 20 mL of 2% double-distilled HNO_3, water, toluene and methanol (LC-MS grade, Fisher Scientific). Chemical reductant solution for HG-AFS analysis consisted of NaOH (BioXtra, ≥98%) and $NaBH_4$ (98%) purchased from Sigma Aldrich; HCl used for sample acidification and preparing the reagent blank was trace metal grade (Fisherbrand).

2.2. Athabasca bituminous sands

Seven samples from the McMurray Formation of the ABS region were obtained for analysis. The bitumen content of the samples ranged from 8.0 to 15.6 wt%. This range is ideal for study, as ores are typically graded into three categories based on their bitumen content: rich (> 10 wt% bitumen), moderate (6–10 wt% bitumen), and lean (< 6 wt%) [45]; an ore containing less than 8 wt% bitumen is generally considered uneconomical and is not desirable for mining [46]. Depending on the amount of mineral material, a typical ore also contains ~3–5 wt% connate water present as an ultra-thin film (estimated ~10 nm) between mineral particles and the bitumen [45,47].

Each ore sample was separated into its bitumen and mineral fractions by extraction with toluene three times then twice using methanol [17]. Bulk ore samples and the extracted bitumen and minerals were digested in a mixture of HNO_3 and HBF_4 using a high pressure microwave (ULTRAclave, MLS, Leutkirch, Germany). The mineral phases were also digested using an HF-HNO_3 procedure. The extraction and digestion procedures are described in detail elsewhere [17]. We assume that any connate water present would end up in the organic fraction (bitumen) following the methanol wash. The potential significance of connate water is discussed in greater detail in the Results and Discussion. To calculate the mass balance for Se and S, the concentrations determined using ICP-SFMS and hydride generation atomic fluorescence spectroscopy (HG-AFS), for Se, and ICP-SFMS and inductively coupled plasma optical emission spectroscopy (ICP-OES), for S, were combined to produce an average value for each of the following samples: 1) bulk ABS, 2) extracted bitumen and 3) remaining mineral fraction. Then, by assuming that the bulk sample represents the total (100%), the mass fractions of an element associated to the organic and mineral matters were calculated using Eqs. (1) and (2):

$$[E]_{ABS(b)} = [E]_{of}.(M_{of}/\ M_{ABS}) \tag{1}$$

$$[E]_{ABS(m)} = [E]_{mf}.(M_{mf}/\ M_{ABS}) \tag{2}$$

where

$[E]_{ABS(b)}$ = concentration of element associated with bitumen in bulk ABS.
$[E]_{ABS(m)}$ = concentration of element associated with minerals in bulk ABS.
$[E]_{of}$ = concentration of element in the organic fraction separated from bulk ABS.
$[E]_{mf}$ = concentration of element in the mineral fraction separated from bulk ABS.
M_{of} = mass of organic fraction separated from bulk ABS.
M_{mf} = mass of mineral fraction separated from bulk ABS.
M_{ABS} = mass of bulk ABS.

2.3. Selenium and S determination using ICP-SFMS

An ICP-SFMS (Element XR, Thermo-Finnigan, Bremen, Germany) was used to determine the concentrations of Se and S in the acid digests of bulk ABS and its mineral and bitumen fractions. Relevant data acquisition parameters specific to Se and S are provided in Table 1, and all other general instrument features and operating parameters related to ICP-SFMS are provided elsewhere [17]. For calibration, the external standards were diluted from a 10 mg/L stock solution (Spex CertiPrep; Metuchen, NJ) with 2% HNO_3 to make solutions ranging in concentration from 0.01 to 10 µg/L. To correct for any minor instrument drift over time, indium (In) was spiked into each sample as an internal standard (IS) for a final concentration of 0.5 µg/L. Due to the substantial difference between Se and S concentrations, digestate stocks were diluted 10x and 1000x for Se and S analysis, respectively. Samples were analyzed following the measurement of 5 method blank solutions (2% HNO_3 + IS) and instrument calibration; a trio of additional quality control solutions (0.1, 1, and 10 µg/L) was analyzed periodically throughout the analysis.

2.4. Selenium determination using HG-AFS

For pre-reduction of Se in the digestates from Se(VI) to Se(IV), aliquots of digestate (1–3 mL) were combined with Milli-Q water and HCl in PTFE digestion vessels to obtain a final acid concentration of 60% (v/v). Solutions were heated to 90 °C using a microwave digestion unit (MARS, CEM Corporation, USA) and held for 60 min. After cooling, the full volume of solution was transferred to graduated 50 mL polypropylene vessels (certified for low background metal analysis). The digestion vessels were rinsed a minimum of 3 times with Milli-Q water, which was added to the beaker until a final volume of 25 mL was achieved. Diluted, pre-reduced, samples were analyzed using a Millennium Excalibur 10.055 HG-AFS system (PS Analytical, Orpington, UK) operated with a continuous flow of sample/reagent (30% HCl v/v) and chemical reductant (7 g/L $NaBH_4$ stabilized in 4 g/L NaOH; prepared fresh daily). Gaseous Se produced in the reaction with $NaBH_4$ was swept from the gas-liquid separator by argon (Ar) gas and passed through a hygroscopic membrane to remove moisture. The gas stream was then atomized by a hydrogen diffusion flame, fueled by the production of excess hydrogen during hydride generation. Selenium atoms were radiated by a boosted discharge hollow cathode lamp with primary and boost settings of 20 mA and 25 mA, respectively. A photomultiplier tube served to detect atomic fluorescence and the electronic signals were recorded as peak areas. Signals were quantified by a 6-point calibration curve (0.05, 0.1, 0.2, 0.4, 0.8, 2 µg/L) with R^2 values always > 0.999. Instrument calibration solutions were prepared fresh daily by serially diluting a 1000 mg/L stock solution of Se (Fluka Analytical; TraceCERT®). The reagent blank, samples, and calibration standards were prepared using the same source of HCl to ensure consistency.

2.5. Quality control

Procedural blanks for the toluene extraction and digestion blanks for non-extract samples were prepared in triplicate and included in the analysis. Certified Standard Reference Materials (SRMs) were analyzed to assess the performance of the analytical procedure. These included two materials developed by the National Institute of Standards and Technology: NIST 1635 (sub-bituminous coal) and NIST 2711 (Montana soil). Both materials are certified for Se and S, but differ in respect to their mineral matter contents. For additional quality control, an in-house peat reference material (OGS-1878P) was also analyzed. Reference values for Se in OGS-1878P are based on past measurements performed using hydride generation atomic absorption spectroscopy (HG-AAS) at the Environmental Specimen Bank (Jülich, Germany). Details on the development and analysis of OGS-1878 can be found elsewhere [48]. For an independent verification of S concentrations, aliquots of the HNO_3-HBF_4 digests (bulk ore, bitumen, minerals) were diluted 10x with 2% HNO_3 and submitted to the Natural Resources Analytical Laboratory, University of Alberta, for ICP-OES analysis (Thermo iCAP 6300Duo, Cambridge, UK). To confirm the pre-reduction of Se(VI) required for HG-AFS analysis, selected samples were spiked with a representative concentration of Se(VI) prepared from a sodium selenate salt (Sigma Aldrich; 99.999%) and diluted appropriately (final concentration of 0.8 µg/L in the sample).

3. Results

3.1. Method performance

The use of certified SRMs (NIST 2711, NIST 1635) in this study served two purposes: i) to evaluate the performance of each analytical method based on the element recoveries and ii) to determine the suitability of the digestion techniques (HF-HNO_3 and HBF_4-HNO_3). Both instruments yielded good recoveries (100 ± 10%) for Se in NIST 1635 (subbituminous coal), regardless of which acid digestion procedure was applied (Table 2). However, similar to the findings of Bicalho et al. [17], the application of HNO_3-HBF_4 for digesting NIST 2711 (Montana Soil) resulted in a slightly lower recovery (70 ± 10%) than HF-HNO_3 (80 ± 10%; Table 2). This is due to the abundance of mineral material in NIST 2711 (presumably > 95 wt% mineral matter) compared to

Table 1
ICP-SFMS data acquisition parameters.

Parameter	Settings	
Forward power	1100 W	
Argon flow rates	Coolant gas: 16.0 L/min; Auxiliary gas: 1.0 L/min; Sample gas: 1.1 L/min	
Sample uptake rate	30 µL/min	
Take up time	120 s	
Wash time	120 s	
Acquisition mode	High resolution (10,000)	
Isotope (samples)	^{32}S (100)	^{77}Se (200)
Sample time (ms)	5	5
Mass window (%)	200	125
Integration window (%)	70	50
Run × Passes	3 × 10	3 × 10

NIST 1635 (ash content = 4.6%): the mineral soil requires more HF than that generated by HBF_4 in the HNO_3-HBF_4 digestion procedure. For S determination by ICP-SFMS, SRM recoveries were in excellent agreement with the certified values and showed no indication of being influenced by the acid digestion procedure. Sulphur concentrations obtained using ICP-OES were in good agreement with ICP-SFMS (Table 3).

As mentioned in the Introduction, the use of ICP-MS for determining Se concentrations can be challenging due to a plethora of polyatomic interferences. Evidence of a common interference is depicted in Fig. 1, where the resolving power of sector-field mass spectrometry is required to distinguish ^{77}Se from ^{37}Cl^{40}Ar. Despite its abundance, S also requires the high mass resolution offered by ICP-SFMS due to the ^{16}O^{16}O interference on ^{32}S (Fig. 1). Clearly, both Se and S require high mass resolution to eliminate interferences. Moreover, the data in Fig. 1 suggest that determination of Se and S using ICP-MS with a single quadrupole mass analyzer is potentially problematic. In the case of HG-AFS for Se measurements, polyatomic interferences are mostly eliminated by the hydride generation step – as only the hydride forming elements are reduced to a gaseous state for measurement by atomic fluorescence. Analysis by HG-AFS is an ideal way to complement the data produced by ICP-SFMS because it operates on completely different physical principles. Both instruments yielded sufficiently low limits of detection for the reliable determination of Se in bitumen. However, because ion transmission is reduced at the high mass resolution required for baseline separation of Se, the ICP-SFMS was less sensitive (0.04 ng/ml) than HG-AFS (0.003 ng/ml). On the other hand, the pre-reduction step required by HG-AFS introduces an additional dilution of the sample by up to 25 times. Thus, when the method detection limit is expressed on a dry weight basis (Table 2), the two techniques provide comparable MDLs, namely 0.02 mg/kg (ICP-SFMS) and 0.04 mg/kg (HG-AFS).

3.2. Concentration and distribution of S and Se

The concentrations of Se and S in the studied samples for each analytical technique are presented in Table 3. Overall, there was good agreement for all the sample types (bulk ore, minerals, bitumen), with the differences in the data between the methods for determining Se concentrations being in the range of 30 ± 15% and the differences in the methods for determining S in the range of 20 ± 15% (Table 3). Not surprisingly, sample type influenced analytical performance, with the bitumen samples resulting in the greatest differences in Se and S between instruments; for bitumen samples alone, the average differences for Se and S were 42 ± 13% and 36 ± 16%, respectively. With these differences assessed, the two sets of results for each element were combined to give an average concentration per sample, to better represent the concentration values obtained (Fig. 2). Determination of Se in extracted bitumen and mineral fractions revealed elevated concentrations in the bitumen fraction (390 ± 45 µg/kg) relative to the mineral fraction (15 ± 7 µg/kg), with an average Se concentration in the native ore of 75 ± 15 µg/kg (Fig. 2). Sulphur concentrations in bitumen averaged 6 ± 1 wt% versus 0.1 ± 0.04 wt% in the extracted minerals; the average concentration in the ore was 0.9 ± 0.3 wt% (Fig. 2). Not only are Se and S both enriched in bitumen, relative to the ore, but there is a positive correlation between the two elements (Fig. 3). In contrast, there is a negative correlation between the two elements in the mineral fraction (Fig. 3). Using the mass balance equations previously described [17], the relative abundances of Se and S in the ore compartments are illustrated in Fig. 4. There is a positive correlation between the concentrations of Se and S, and the bitumen content (i.e. grade) of the ores (Fig. 5). Similar trends were reported earlier [17] for four other elements (V, Ni, Mo, Re) which are found primarily in the bitumen fraction of ABS. Despite the limited number of samples available for this study, the data obtained thus far certainly suggests that the abundances of Se and S increase with ore grade.

Table 3
Concentrations of Se and S in ABS ore samples[a] and subsamples[b] (separated bitumen and minerals), as determined using HG-AFS, ICP-OES and ICP-SFMS.

Se	Min	Med	Max	Min	Med	Max
		HG-AFS			ICP-SFMS	
	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
Bulk	48.9	83.4	108.5	47.5	66.7	82.6
Bitumen	345.9	463.2	504.7	257.4	326.6	425.2
Mineral	4.4	13.4	26.8	5.6	15.0	24.1
Mineral-HF	na	na	na	9.8	22.1	41.9
S		ICP-OES			ICP-SFMS	
	%	%	%	%	%	%
Bulk	0.3	0.7	1.4	0.3	0.8	1.3
Bitumen	3.4	4.9	5.3	4.0	8.2	10.4
Mineral	0.04	0.08	0.15	0.05	0.09	0.18
Mineral-HF	0.02	0.06	0.31	na	na	na

[a] Experimental set = 7 sample units representing different ore locations. [b] Each n = 7. Mineral-HF refers to the digestion method using HF and HNO_3 instead of HBF_4 and HNO_3 (Minerals). “na” denotes samples with concentrations below the MDL.

Two potentially relevant artefacts of the extraction are worth noting: i) the presence of Se and S in connate water and ii) the retention of ultra-fine mineral particles < 0.45 µm in the bitumen extract. While

Table 2
Determination of Se and S in Standard Reference Materials (SRM) using ICP-SFMS and HG-AFS.

Element	Analytical Technique	IDL[a] (ng/ml)	MDL[b] (mg/kg)	SRM[c]	Nominal value	Digestion method	Recovery (%)	(n)[d]
Se	ICP-SFMS	0.04	0.02	OGS 1878P	0.6 ± 0.2 mg/kg	HNO_3-HBF_4	106 ± 2	2
				NIST 1635	0.9 ± 0.3 mg/kg	“	107 ± 13	4
				NIST 2711	1.5 ± 0.1 mg/kg	“	62 ± 4	3
				“	“	HF-HNO_3	71	1
Se	HG-AFS	0.003	0.04	OGS 1878P	0.6 ± 0.2 mg/kg	HNO_3-HBF_4	117	1
				NIST 1635	0.9 ± 0.3 mg/kg	“	95	1
				NIST 2711	1.5 ± 0.1 mg/kg	“	78	1
				“	“	HF-HNO_3	90 ± 3	2
S	ICP-SFMS	5.8	58	NIST 1635	0.4 ± 0.002%	HNO_3-HBF_4	107 ± 13	4
				NIST 2711	0.04 ± 0.01%	“	111 ± 10	4
				“	“	HF-HNO_3	91 ± 5	3

[a] Instrument detection limit calculated as follows: (BLK cps AVG + 3*BLK cps SD)*[STD]/(STD cps – BLK cps AVG), where BLK = blank (2% HNO_3); cps = counts per second; AVG = average; SD = standard deviation; [STD] = nominal concentration of the element in a primary standard; (STD cps – BLK cps AVG) = intensity difference between STD and BLK. Method detection limit calculated as follows: IDL (m/v)*sample dilution factor, as per method. [c] Ontario Geological Survey Peat (1878); NIST 1635 Coal Subbituminous; NIST 2711 Montana Soil. [d] n = number of replicates analyzed along current ABS samples and subsamples.

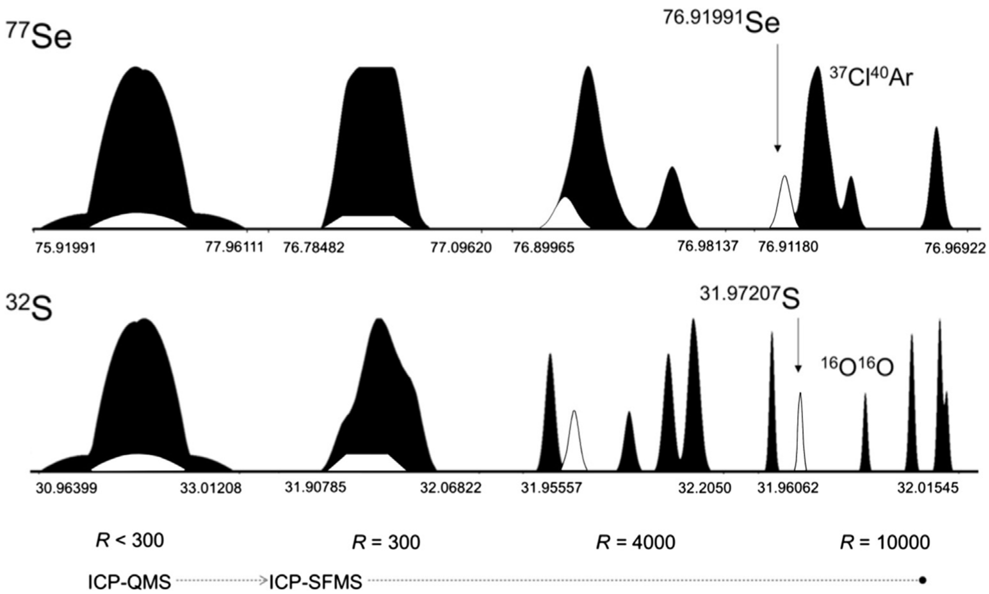

Fig. 1. Mass spectrometric determination of Se and S (white peaks) as a function of the mass analyzer resolution ($R = m/\Delta m$) power. Multiple near isobaric interferences (black peaks) need to be investigated and resolved before Se and S can be determined accurately using ICP-MS. From left to right: the detection of Se and S enabled by a single quadrupole mass spectrometer (QMS) next to the detection of Se and S enabled by a sector field mass spectrometer (SFMS) in low (R = 300), medium (R = 4000) and high (R = 10000) mass resolution modes. Adapted from Element2 Tour and Interferences (Demo Version 3.2), Thermo Electron, Bremen, Germany.

it was not evaluated experimentally, the presence of Se or S in connate water did not appear to influence the results. This is suggested from the fact that the proportion of connate water content in ABS is known to increase with greater mineral (fines) content [46,49]. Therefore, assuming that a greater proportion of connate water was present in ores with a greater mineral content, we would have expected to see greater concentrations of Se in the analysis of low quality (high mineral) ores than high quality (low mineral); this however is contrary to our results, further indicating that Se is predominantly in the bitumen. Lastly, a very small amount of ultra-fine mineral material is predicted to have been present in the bitumen extract, even after additional syringe filtration (0.45 μm). Evidence of this comes from the analysis of ultra-trace concentrations of lithophile elements (Sc, Y, Dy, Sm, Th), which behave conservatively during chemical weathering and serve as indicators of the presence of mineral material [18]; this analysis was performed on the same digests, with details presented in Bicalho et al. [17]. The low concentrations of lithophile elements (Sc, Y, Dy, Sm, Th) suggest that the contribution of Se and S from any such mineral material remaining in the bitumen extract is negligible. Further study of trace elements in both connate water and ultra-fine clays would be of value but would require lab techniques and methods beyond the scope of this study.

4. Discussion

4.1. Selenium in bitumen from the ABS region compared to other geological materials

The abundance of Se in soils, rocks, sediments, and other materials can vary considerably. For perspective, a brief compilation of Se concentrations in some relevant geological materials is provided in Table 4. The average Se concentration in bulk ABS ore (75 ± 15 μg/kg) is comparable to its abundance provided by Rudnick and Gao [50] for the Upper Continental Crust (UCC; 90 μg/kg). However, Se in bitumen from oil sands is enriched relative to the UCC, with concentrations comparable to the global average for crude oil, but lower than averages for coal and oil shale (Table 4). For a more local perspective on Se abundance, the average concentration of Se in soils from across Alberta (129 sites) and coal from the Genesee coal mine (~70 km from Edmonton, Alberta) are also presented in Table 4. The concentrations of Se in coal, soil, and other geological materials vary considerably depending on the environment of formation, accumulation, or deposition. For example, in the case of coal from the Genesee mine, the average Se content for coal samples (No. 2 seam) is relatively consistent; however, higher concentrations are observed for samples collected from rheotrophic (groundwater influenced) zones, while lower concentrations were found in coal formed under ombrotrophic (rain-fed) conditions [51].

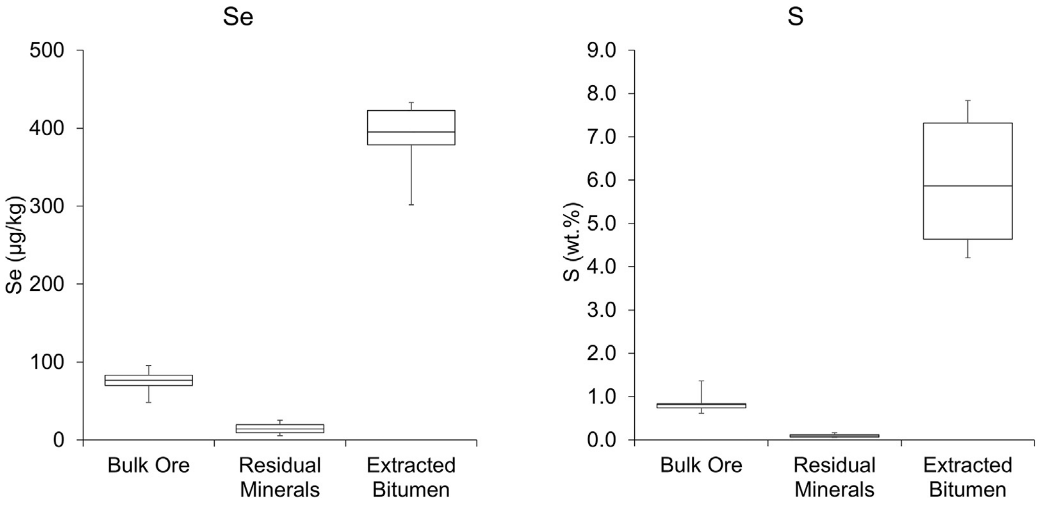

Fig. 2. Box-and-whisker plots of absolute concentrations of Se and S in the studied ABS samples and subsamples (each n = 7). Plot whiskers denote concentration range, box length represents the upper and lower quartiles, and the horizontal line within the box represents the median. From left to right: native samples (bulk ore), the mineral fraction left over after bitumen removal using toluene (residual minerals) and the separated bitumen (extracted bitumen). Bulk ores consisted of 86 ± 4 wt% mineral matter and 12 ± 3 wt% bitumen.

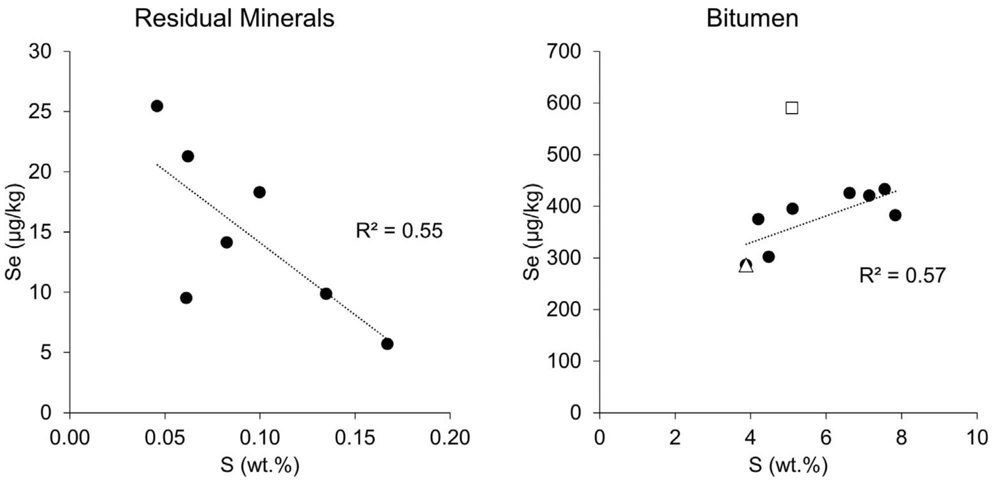

Fig. 3. Correlations of Se and S concentrations in ABS ore mineral and bitumen subsamples. Apparent trends illustrate a negative correlation for Se and S in the mineral matter and a positive correlation for these elements in the bitumen. In addition to current results (●), previous results by Hitchon and Filby [12] (Δ) and by Hosterman et al. [44] (□) for Se and S in the ABS bitumen are shown for comparison.

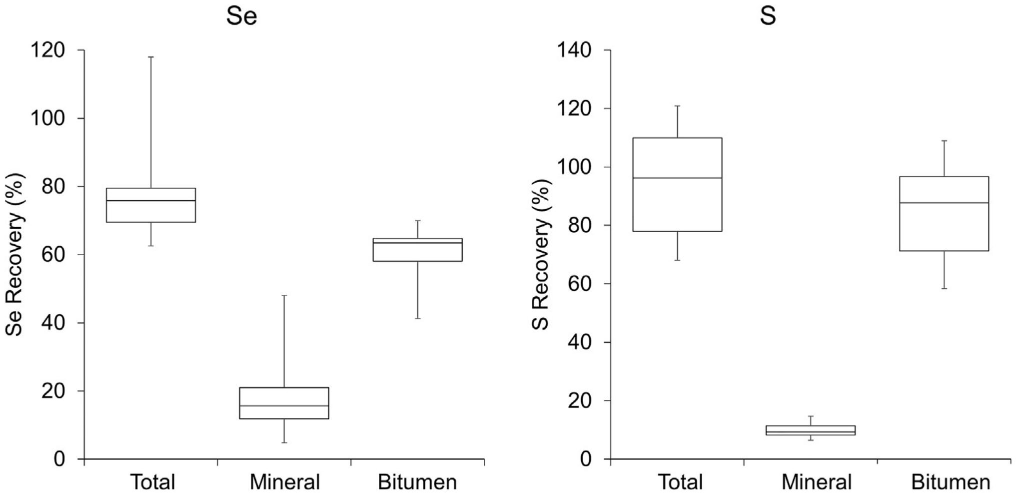

Fig. 4. Box-and-whisker plots showing relative abundance of Se and S in the studied ABS samples (n = 7). Plot whiskers denote concentration range, box length represents the upper and lower quartiles, and the horizontal line within the box represents the median. From left to right: relative abundance of the element content recovered from bulk ore, mineral fraction, and bitumen fraction.

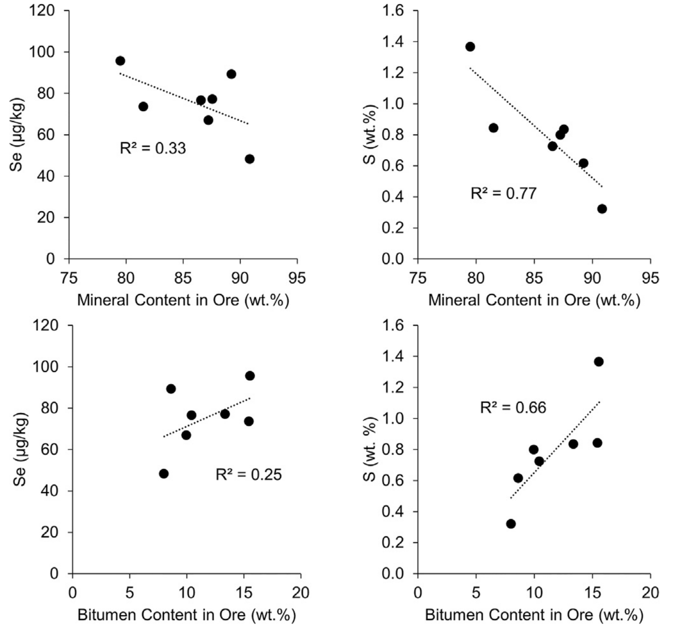

Fig. 5. Variation in Se and S concentrations versus ore grade (expressed both in terms of bitumen and mineral matter abundance). Although the number of samples is small (n = 7), the concentrations of Se and S tend to increase with the ore grade.

Table 4
Average Se concentrations in some relevant geological materials. Where necessary and available, the range is provided in parenthesis next to the average concentration.

Material type	Concentration (mg/kg)	Source
Upper Continental Crust	0.09	[50]
Soil	0.4	[60]
Soil organic matter	0.2	[61]
Coal	3.4	[61]
Oil shale	2.3	[61]
Crude oil	0.2	[61]
Alberta soil (0–15 cm)	0.48 (0.1–1.6)	[62]
Alberta soil (15–30 cm)	0.47 (0.001–2.3	[62]
[a]Genesee Coal	0.77 (0.64–1.24)	[51]
[b]Bitumen (ABS) #43	0.29	[12]
[b]Bitumen (ABS) #94	0.52	[12]
[b]Bitumen (ABS)	0.59	[44]
[b]Bitumen (ABS)	0.4	This study

[a] Se value refers to an average of blends (1–5) for the No. 2 seam. [b] Bitumen refers to samples where mineral particles have been extracted.

For one sample, there was also evidence of a volcanic event which in turn greatly increased the concentration of Se in the coal (13 mg/kg) [51]. Although consistent Se concentrations were found in the limited number of ABS samples measured in this study, it would be beneficial to conduct a survey of bitumen from the ABS region using a suitable number of samples to evaluate the geochemical heterogeneity of the deposits.

4.2. Comparing Se abundance with S

The behavior and fate of Se and S during endogenic (bio) geochemical processes are extremely similar and often leads to the concomitant occurrence of these elements in both minerals and organic materials [52]. The similar ionic radii of Se(-II) (1.91 Å) and S(-II) (1.84 Å) allows Se to readily substitute for S in sulfide minerals under reducing conditions [52]. The uptake and transformation of Se and S by organisms is also extremely similar, leading to analogous biomolecules such as amino acids [53]. Owing to the fact that S is found primarily in the form of organic compounds in crude oil [54] as well as ABS [55], it is reasonable to assume, given the positive correlation reported here between concentrations of Se and S in bitumen (Fig. 3), that most of the Se in the ABS is also in the form of organic compounds.

In a previous survey of Alberta crude oils, 86 conventional and two unconventional (ABS region) crude oil samples were analyzed for 22 trace elements, including S and Se [12]. Using factor analysis, their results indicated that more than 25% of the cumulative variance between elements could largely be accounted for by V, Ni, S and Se [5,10]. That study [12] suggested that, since V, Ni and S are all known to be present mainly in the form of organic compounds, it is likely that Se also exists in an organic form in conventional crude oil. As convincing as their data is for conventional crude oil (n = 86), the results were less conclusive for the ABS samples (n = 2); also, the authors experienced challenges in separating entrained fine mineral material from the bitumen in the ore. Combining earlier analyses and arguments [12] with the results obtained from the current study, the data available to date supports the hypothesis that Se is also part of the organic fraction of the ABS, and is not due to entrained mineral particles. Some additional support for this claim is also found in an independent study of bitumen [44] that included 1 sample from the ABS region (see Table 4 for comparison).

4.3. Relevance to the environment in northern Alberta

Mining and upgrading of bitumen in northern Alberta releases S to the environment in both the gaseous as well as particulate phases [56,57], but emissions of Se have received far less attention. To understand the potential for Se to be released to the environment during bitumen mining, upgrading and refining, whether the concerns are emissions to the air, soil, or water, requires an understanding of the abundance and distribution Se in the bitumen versus mineral fractions of the ABS. It is evident from the results presented here that unlike other potentially toxic chalcophile trace elements (Ag, As, Bi, Cd, Cu, Pb, Sb, Tl and Zn), which are found almost exclusively in the mineral fraction [17], Se is hosted predominantly in the bitumen fraction of the ABS. These other trace elements are expected to be bound within stable mineral structures and should experience limited mobility during industrial processing of the ABS. In contrast, there are several possible sources of Se release to the environment in northern Alberta.

Generally, most of the Se should be in bitumen separated from the ABS during the initial recovery and froth clean-up stages. When the collected bitumen is eventually heated during primary upgrading (430–550 °C for coking, < 460 °C for hydroconversion), or further treated to reduce levels of S, nitrogen and oxygen in secondary upgrading, there is then potential for Se partition into the gas phase or be collected as a waste by-product [47]. Selenium may become residually enriched in the produced petroleum coke (petcoke), which is currently being stored primarily as massive stockpiles or added to tailings ponds; some operators also use petcoke as a source of fuel or as a material in land reclamation [47]. Petcoke has recently generated interest when it was determined to be the predominant source of polycyclic aromatic hydrocarbons (PAHs) in the ABS region [58]. Due to the high S content of bitumen, there are also engineered technologies in-place to lower the S content of upgraded bitumen and reduce airborne emission of SO_2 and related compounds. The reduction of S in recovered oil is achieved by the Claus process, where reduced S compounds (H_2S) are oxidized and elemental S is produced. The dry S material is stored in large stockpiles and could be a repository of Se. Unlike natural deposits of elemental S, which are commonly enriched in Se (up to 682 mg/kg), the Se contents of diverse examples of elemental sulphur obtained from industrial processing were below the limit of detection [59]. The limit of detection in that study employing neutron activation analysis was 1 mg/kg [59], which is well above the average value of Se in bitumen reported here (Fig. 2). The second S-related removal process is flue-gas desulphurization (FGD), which takes place in stacks and removes SO_2 with $Ca(OH)_2$ to produce gypsum ($CaSO_4{\cdot}2H_2O$) as an end product [47]. The majority of gypsum is landfilled, thereby limiting its relevance as a potential source of Se to the environment in the ABS region; however, some is used as an amendment to increase the rate of tailings densification (composite/consolidated tailings) [47]. Of the two S removal processes, the latter seems likely to be more relevant for Se because the FGD systems are in-place to remove gaseous by-products of combustion. The applications of FGD systems in coal combustion are known for their potential to also remove Se (e.g., SeO_2) simultaneously [38]. Given the potential effectiveness of FGD systems to also capture Se from stack gases, the Se content (and speciation) in both produced gypsum and petcoke should be considered before its widespread use as an amendment in reclamation. Clearly, more work is required to fully understand the sources and sinks of Se during the industrial processing of bitumen, the chemical forms in which Se is emitted and their potential impact to environmental receptors.

5. Conclusions

The extraction and analysis of bitumen and mineral fractions of ores from the ABS region has revealed that Se is located predominantly in the bitumen fraction. Selenium abundance in bitumen correlates positively with S, but further study is required to determine if it exhibits similar behavior during industrial processing, especially upgrading and refining. Despite its low abundance in bitumen relative to other fossil fuels, it should be given specific attention in environmental monitoring programs and reclamation projects due to the scale and increasing rate of oil production in the ABS region. Those measurements will require strict attention to the unique analytical challenges posed by Se, including the need for the low limits of detection necessary to provide meaningful information on its abundance in environmental media.

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References

[1] Larter SR, Head IM. Oil sands and heavy oil: origin and exploitation. Elements 2014;10:277–83. http://dx.doi.org/10.2113/gselements.10.4.277.
[2] Garven G. A hydrogeological model for the formation of the giant oil sands deposits

of the western Canada sedimentary basin. Am J Sci 1989;289:105–66.

[3] Alberta Energy Regulator. ST98:2017 Alberta's Energy Reserves & Supply/Demand. Outlook, http://www1.aer.ca/st98/data/executive_summary/ST98-2017_Executive_Summary.pdf; 2017 [accessed 12.19.2017].

[4] Mossop GD. Geology of the Athabasca oil sands. Science 1980;207:145–52.

[5] Hitchon B, Filby RH. Use of trace elements for classification of crude oils into families – example from Alberta, Canada. Am Assoc Pet Geologists Bull 1984;68:838–49.

[6] Beach LK, Shewmaker JE. The nature of vanadium in petroleum. Ind Eng Chem 1957;49:1157–64.

[7] Champlin JBF, Dunning HN. A geochemical investigation of the Athabasca bituminous sands. Econ Geol 1960;55:797–804.

[8] Addison PA, Puckett KJ. Deposition of atmospheric pollutants as measured by lichen element content in the Athabasca oil sands area. Can J Bot 1980;58:2323–34. http://dx.doi.org/10.1139/b80-269.

[9] Hargesheimer EE, Apps MJ, Malhotra SS. Determination of vanadium in jack pine needles using neutron activation analysis. Environ Technol Lett 1980;1:273–82. http://dx.doi.org/10.1080/09593338009383977.

[10] Hitchon B, Filby R, Shah K. Geochemistry of trace elements in crude oils, Alberta, Canada. In: Yen T, editor. The role of trace metals in petroleum, Ann Arbor, MI: 1975, p. 111–21.

[11] Jacobs FS, Filby RH. Solvent extraction of oil-sand components for determination of trace elements by neutron activation analysis. Anal Chem 1983;55:74–7. http://dx.doi.org/10.1021/ac00252a021.

[12] Hitchon B, Filby RH. Geochemical studies – 1. Trace elements in Alberta crude oils. Alberta Research Council Open File Report: 1983.

[13] Scott J, Collins GA, Hodgson G. Trace metals in the McMurray oil sands and other cretaceous reservoirs of Alberta. Can Min Metall 1954;57:34–40.

[14] Schindler DW. Water quality issues in the oil sands region of the lower Athabasca River, Alberta. Geosci Canada 2013;40:202–14.

[15] Kelly EN, Schindler DW, Hodson PV, Short JW, Radmanovich R, Nielsen CC. Oil sands development contributes elements toxic at low concentrations to the Athabasca River and its tributaries. Proc Natl Acad Sci USA 2010;107:16178–83. http://dx.doi.org/10.1073/pnas.1008754107.

[16] Schindler D. Tar sands need solid science. Nature 2010;468:499–501.

[17] Bicalho B, Grant-Weaver I, Sinn C, Donner MW, Woodland S, Pearson G, et al. Determination of ultratrace (< 0.1 mg/kg) elements in Athabasca Bituminous Sands mineral and bitumen fractions using inductively coupled plasma sector field mass spectrometry (ICP-SFMS). Fuel 2017;206:248–57. doi: 10.1016/j.fuel.2017.05.095.

[18] Goldschmidt VM. The principles of distribution of chemical elements in minerals and rocks. J Chem Soc 1937:655–73. http://dx.doi.org/10.1039/jr9370000655.

[19] Selby D. Direct radiometric dating of hydrocarbon deposits using rhenium-osmium isotopes. Science 2005;308:1293–5. http://dx.doi.org/10.1126/science.1111081.

[20] White AF, Dubrovsky NM. Chemical oxidation–reduction controls on selenium mobility in groundwater systems. In: Frankenberger WT, Benson S, editors. Selenium in the environment. New York: Marcel Dekker Inc; 1994. p. 185–221.

[21] Rayman MP. The importance of selenium to human health. Lancet 2000;356:233–41. http://dx.doi.org/10.1016/S0140-6736(00)02490-9.

[22] Navarro-Alarcon M, Cabrera-Vique C. Selenium in food and the human body: a review. Sci Total Environ 2008;400:115–41. http://dx.doi.org/10.1016/j.scitotenv.2008.06.024.

[23] Hamilton SJ. Review of selenium toxicity in the aquatic food chain. Sci Total Environ 2004;326:1–31. http://dx.doi.org/10.1016/j.scitotenv.2004.01.019.

[24] Hamilton SJ. Review of residue-based selenium toxicity thresholds for freshwater fish. Ecotoxicol Environ Saf 2003;56:201–10. http://dx.doi.org/10.1016/S0147-6513(02)00091-X.

[25] Hamilton SJ. Rationale for a tissue-based selenium criterion for aquatic life. Aquat Toxicol 2002;57:85–100. http://dx.doi.org/10.1016/S0166-445X(01)00262-4.

[26] Lemly DA. Pathology of selenium poisoning in fish. In: Frankenberger WJ, Engberg R, editors. Environmental chemistry of selenium, 1998, p. 281–96.

[27] Ohlendorf HM, Hothem RL, Bunck CM, Marois KC. Bioaccumulation of selenium in birds at Kesterson reservoir, California. Arch Environ Contam Toxicol 1990;19:495–507. http://dx.doi.org/10.1007/BF01059067.

[28] Outridge PM, Scheuhammer AM, Fox GA, Braune BM, White LM, Gregorich LJ, et al. An assessment of the potential hazards of environmental selenium for Canadian water birds. Environ Rev 1999;7:81–96. http://dx.doi.org/10.1139/er-7-2-81.

[29] Cutter GA, San Diego-McGlone MLC. Temporal variability of selenium fluxes in San Francisco Bay. Sci Total Environ 1990;97(98):235–50. http://dx.doi.org/10.1016/0048-9697(90)90243-N.

[30] Nriagu JO, Wong HK. Selenium pollution of lakes near the smelters at Sudbury, Ontario. Nature 1983;301:55–7. http://dx.doi.org/10.1038/301055a0.

[31] Mosher BW, Duce RA. A global atmospheric selenium budget. J Geophys Res 1987;92:13289–98. http://dx.doi.org/10.1029/JD092iD11p13289.

[32] Nriagu JO, Pacyna JM. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 1988;333:134–9.

[33] Pacyna JM, Pacyna EG. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environ Rev 2001;9:269–98. http://dx.doi.org/10.1139/a01-012.

[34] Rahn KA. The chemical composition of the atmospheric aerosol. Technical Report, Graduate School of Oceanography, University of Rhode Island, Kinston, R.I., USA: 1976.

[35] Andren AW, Klein DH, Talmi Y. Selenium in coal-fired steam plant emissions. Environ Sci Technol 1975;9:856–8.

[36] Shendrikar AD, Ensor DS, Cowent SJ, Woffindei GJ. Size-dependent penetration of trace elements through a utility baghouse. Atmos Environ 1983;17:1411–21.

[37] Petrov PK, Charters JW, Wallschläger D. Identification and determination of selenosulfate and selenocyanate in flue gas desulfurization waters. Environ Sci Technol 2012;46:1716–23. http://dx.doi.org/10.1021/es202529w.

[38] Senior CL, Tyree CA, Meeks ND, Acharya C, McCain JD, Cushing KM. Selenium partitioning and removal across a wet FGD scrubber at a coal-fired power plant. Envrion Sci Technol 2015;49:14376–82.

[39] Pettine M, McDonald TJ, Sohn M, Anquandah GAK, Zboril R, Sharma VK. A critical review of selenium analysis in natural water samples. Trends Environ Anal Chem 2015;5:1–7. http://dx.doi.org/10.1016/j.teac.2015.01.001.

[40] B'Hymer C, Caruso JA. Selenium speciation analysis using inductively coupled plasma-mass spectrometry. J Chromatogr A 2006;1114:1–20. http://dx.doi.org/10.1016/j.chroma.2006.02.063.

[41] Jackson BP, Liba A, Nelson J. Advantages of reaction cell ICP-MS on doubly charged interferences for arsenic and selenium analysis in foods. J Anal At Spectrom 2015;30:1179–83. http://dx.doi.org/10.1039/c4ja00310a.

[42] Lum T, Leung KS. Strategies to overcome spectral interference in ICP-MS detection. J Anal At Spectrom 2016;31:1078–88. http://dx.doi.org/10.1039/C5JA00497G.

[43] Jervis RE, Richard Ho KL, Tiefenbach B. Trace impurities in Canadian oil-sands, coals and petroleum products and their fate during extraction, up-grading and combustion. J Radioanal Chem 1982;71:225–41. http://dx.doi.org/10.1007/BF02516152.

[44] Hosterman JW, Meyer RF, Palmer CA, Doughten MW, Anders DE. Chemistry and mineralogy of natural bitumens and heavy oils and their reservoir rocks from the United States, Canada, Trinidad and Tobago, and Venezuela. U.S Geological Survey Circular 1047: 1990.

[45] Takamura K. Microscopic structure of Athabasca oil sand. Can J Chem Eng 1982;60:538–45.

[46] Innes ED, Fear JVD. Canada's first commercial tar sands development. In: 7th World Petrol Congr Proc 1967; 3:633–643.

[47] Gosselin P, Hrudey SE, Naeth MA, Plourde A, Therrien R, Van Der Kraak G, et al. Environmental and health impacts of Canada's oil sands industry. Ottawa: Royal Society of Canada; 2010.

[48] Riley JL. Laboratory methods for testing peat – Ontario Peatland Inventory Project. Open File Report 5572. Ontario Geological Survey, Toronto. http://www.geologyontario.mndm.gov.on.ca/mndmfiles/pub/data/imaging/OFR5572/OFR5572.pdf; 1986 [accessed 12.27.2017].

[49] Jia B. Distribution of oil sands formation water in bitumen froth Thesis Edmonton: University of Alberta; 2010.

[50] Rudnick RL, Gao S. The composition of the continental crust. In: Holland H, Turekian K, editors. Treatise on geochemistry, vol. 1, Oxford: Elsevier-Pergamon; 2003. doi: 10.1016/B0-08-043751-6/03016-4.

[51] Pollock SM, Goodarzi F, Riediger CL. Mineralogical and elemental variation of coal from Alberta, Canada: an example from the No. 2 seam, Genesee mine. Int J Coal Geol 2000;43:259–86. http://dx.doi.org/10.1016/S0166-5162(99)00063-4.

[52] Berrow M, Ure A. Geological materials and soils. In: Inhat M, editor. Occurrence and distribution of selenium. Boca Raton, Florida: CRC Press; 1989. p. 213–42.

[53] Young TF, Finley K, Adams WJ, Besser J, Hopkins WD, Jolley D, et al. What you need to know about selenium. In: Chapman PM, Adams WJ, Brooks ML, Delos CG, Luoma SN, Maher WA, editors. Ecological assessment of selenium in the aquatic environment. New York: CRC Press; 2010. p. 7–36.

[54] Orr WL. Sulfur in heavy oils, oil sands and oil shales. Oil Sand Oil Shale Chem New York, Verlag Chemie 1978:223–43.

[55] Shi Q, Pan N, Liu P, Chung KH, Zhao SQ, Zhang YH, et al. Molecular characterization of sulfur compounds in Venezuela crude oil and its SARA fractions by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. Energy Fuels 2010;24:5089–96. http://dx.doi.org/10.1021/Ef100904k.

[56] Wieder RK, Vile MA, Scott KD, Albright CM, McMillen KJ, Vitt DH, et al. Differential effects of high atmospheric N and S deposition on bog plant/lichen tissue and porewater chemistry across the Athabasca oil sands region. Environ Sci Technol 2016;50:12630–40. http://dx.doi.org/10.1021/acs.est.6b03109.

[57] Mullan-Boudreau G, Belland R, Devito K, Noernberg T, Pelletier R, Shotyk W. *Sphagnum* moss as an indicator of contemporary rates of atmospheric dust deposition in the Athabasca bituminous sands region. Environ Sci Technol 2017;51:7422–31. http://dx.doi.org/10.1021/acs.est.6b06195.

[58] Zhang Y, Shotyk W, Zaccone C, Noernberg T, Pelletier R, Bicalho B, et al. Airborne petcoke dust is a major source of polycyclic aromatic hydrocarbons in the Athabasca oil sands region. Environ Sci Technol 2016;50:1711–20. http://dx.doi.org/10.1021/acs.est.5b05092.

[59] Steudel R, Strauss EM, Papavassiliou M, Brätter P, Gatschke W. Selenium content of naturally occurring elemental sulfur, of industrially produced sulfur and of the mineral selensulfur. Phosphorus Sulfur 1986;29:17–21.

[60] Bowen. Environmental chemistry of the elements. London; New York: Academic Press; 1979.

[61] Nriagu JO. Global cycling of selenium. In: Inhat M, editor. Occurrence and distribution of selenium. Boca Raton, Florida: CRC Press; 1989. p. 327–40.

[62] Government of Alberta. The micronutrient and trace element status of forty-three soil quality benchmark sites in Alberta: results and summary, http://www1.agric.gov.ab.ca/$department/deptdocs.nsf/all/aesa8885; 2004 [accessed 12.19.2017].

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ARTICLE

A rapid and sensitive IC-ICP-MS method for determining selenium speciation in natural waters

Mark W. Donner and Tariq Siddique

Abstract: Selenium (Se) is an element monitored by water quality agencies worldwide. The challenge of assessing its presence in aquatic systems is its low concentrations (parts per trillion) and the need for determining its chemical speciation. A method was developed using an ion chromatograph (IC) paired with a quadrupole inductively coupled plasma mass spectrometer (ICP-MS) equipped with a hydrogen reaction cell to provide analysts with a rapid and sensitive method to measure Se speciation with suitable accuracy and precision. The Se species selenite (Se^{IV}) and selenate (Se^{VI}) were separated within a 5 min span using dilute nitric acid as a mobile phase in a step-wise gradient (50–400 mmol L^{-1}) and quantified using ^{80}Se isotope that yielded low limits of detection (<10 ng L^{-1}). Spectral interference from plasma generated diatomic argon ions ($^{40}Ar_2^+$; $m/z = 80$) on ^{80}Se was eliminated by hydrogen gas (H_2) in the reaction cell. Polyatomic $^{79}Br^1H^+$ ($m/z = 80$) did not interfere with ^{80}Se for quantification of common aquatic Se species (Se^{VI} and Se^{IV}) due to different column retention times. Two organic species (methylselenocysteine and selenomethionine) commonly found in aquatic and terrestrial plant tissues were also tested to rule out possible chromatographic interference and explore the potential application to biological samples. Urban rainwater and Canadian river water samples were analyzed for Se species to demonstrate the applicability of the method. Owing to its ability to rapidly determine Se species in water samples at environmentally relevant concentrations, the method may be useful for monitoring agencies to routinely measure Se species in freshwater aquatic systems.

Key words: selenium, chemical speciation, water monitoring, ion chromatography.

Résumé : Le sélénium (Se) est un élément qui fait l'objet d'une surveillance par les organismes responsables de la qualité de l'eau partout dans le monde. Il est difficile d'évaluer sa présence dans les systèmes aquatiques, car, d'une part, les concentrations sont faibles (parties par billion) et, d'autre part, il faut établir sa spéciation. Nous avons mis au point une méthode faisant appel à la chromatographie par échange d'ions couplée à un spectromètre de masse à plasma à couplage inductif (ICP-MS) doté d'une cellule à hydrogène afin d'offrir aux analystes une méthode rapide et sensible qui permet d'établir la spéciation du Se avec une exactitude et une précision adéquates. Nous avons séparé les espèces sélénites (SeIV) et sélénates (SeVI) dans un laps de temps de 5 minutes en utilisant un gradient séquentiel (50–400 mmol L^{-1}) d'acide nitrique dilué comme phase mobile, et nous avons quantifié ces espèces de Se à l'aide de l'isotope ^{80}Se, lequel a permis d'atteindre de faibles limites de détections (<10 ng L^{-1}). L'interférence causée par les ions d'argon diatomique générés dans le plasma ($^{40}Ar_2^+$; $m/z = 80$) dans le spectre du ^{80}Se a été éliminée par l'hydrogène gazeux (H_2) dans la cellule à hydrogène. Étant donné les différences de temps de rétention des ions polyatomiques de $^{79}Br^1H^+$ ($m/z = 80$) sur la colonne, ces derniers n'ont pas causé d'interférence à la quantification du ^{80}Se dans les espèces de Se communément présentes en milieu aquatique (SeVI et SeIV). Nous avons également testé deux espèces organiques (la méthylsélénocystéine et la sélénométhionine) communément présentes dans les tissues de plantes aquatiques et terrestres afin d'exclure une éventuelle interférence chromatographique et d'explorer la possibilité d'appliquer la méthode à des échantillons biologiques. Nous avons analysé les espèces de Se dans des échantillons d'eau de pluie en milieu urbain et des échantillons d'eau d'une rivière au Canada pour démontrer l'applicabilité de la méthode. Cette méthode, grâce à la capacité qu'elle offre d'analyser rapidement les espèces de Se dans des échantillons d'eau à des concentrations représentatives de la réalité environnementale, pourrait être utile aux organismes de surveillance pour analyser de manière systématique les espèces de Se dans les systèmes aquatiques d'eau douce. [Traduit par la Rédaction]

Mots-clés : sélénium, spéciation chimique, surveillance de la qualité de l'eau, chromatographie par échanges d'ions.

Introduction

The chemistry of selenium (Se) in the environment has long captured the interest of researchers from a variety of disciplines. Given that it is an essential trace element for humans and animals[1] and is also sometimes an environmental toxin,[2] understanding the complex behavior of Se in environmental systems is of great importance. Depending on biogeochemical processes and redox conditions, Se can exist in a variety of oxidation states (–II, –I, 0, IV, VI) with greater mobility at higher redox potentials.[3] Owing to its ability to bio-accumulate in the food chain, Se concentrations in water deemed harmful to aquatic life are low relative to other elements (e.g., Fe, Mo, Zn, Cu) essential to life.[2,4] Surface water (oxic to suboxic environments) where Se concentrations exceed guideline values (typically ≥1 μg L^{-1}) are generally attributed to a direct geologic or anthropogenic Se source, with the resulting predominant forms being the oxyanions selenite (SeO_3^{-2} or Se^{IV}), and selenate (SeO_4^{2-} or Se^{VI}).[5,6] Reports of other inorganic and organic forms, in addition to the ubiquitous Se^{IV} and Se^{VI}, have been described in aquatic systems that are biolog-

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ically productive or impacted by industrial effluents (e.g., natural organic matter containing Se, Se-NOM; selenocyanate, $SeCN^-$).[6,7] Selenium species are also known to differ with respect to bioavailability.[8] Therefore, the fundamental challenge to understand Se in the aquatic environment is the low concentration combined with the need to understand its chemical speciation.

Numerous methods have been developed to determine Se species,[9,10] with the bulk of conventional methods utilizing the hydride forming ability of Se^{IV}. Following the pioneering work of Cutter,[11,12] a large portion of Se speciation analyses of water are based on a selective sequential hydride generation (SSHG) approach.[6] That technique takes advantage of the fact that only Se^{IV} forms a hydride; therefore, samples can be analyzed directly for Se^{IV} and then chemically altered through online or offline oxidation and reduction reactions to obtain Se^{VI} and reduced Se species by difference.

The SSHG method is a first step towards the chemical speciation and has some advantages. (*i*) It can be used to incorporate colloidal and particulate Se,[13] (*ii*) it is effective for saline waters (e.g., sea water) to bypass chromatographic interferences, and (*iii*) when coupled with appropriate detection technique such as atomic fluorescence, it has excellent sensitivity, even at low concentrations (limit of detection (LOD), typically <10 ng L^{-1}). Modifications to this method have also been made to limit bias resulting from the decomposition of organo-Se molecules during heat-acid reflux,[14] but there is still considerable potential for large errors to be made when determining speciation by difference.[6] SSHG procedures also call for large quantities of sample with considerable time and effort to perform the necessary redox reactions, with each step and sample type requiring detailed quality control. Fundamentally, the greatest disadvantage of any version of the SSHG approach is the inability to identify species within the “reduced Se” (primarily organic) fraction.

Ion chromatography (IC) coupled with inductively coupled plasma mass spectrometry (ICP-MS) is a powerful analytical tool that has been used successfully for identifying a wide variety of Se containing compounds based on their retention times.[15–17] For Se analyses, however, conventional quadrupole ICP-MS operation suffers from inadequate sensitivity for concentrations typical of natural waters. This is due to the high ionization potential of Se in the plasma, as well as isobaric and polyatomic interferences.[9,18] Selenium has six stable isotopes (^{74}Se, 0.87%; ^{76}Se, 9.02%; ^{77}Se, 0.58%; ^{78}Se, 23.52%; ^{80}Se, 49.82%; ^{82}Se, 9.19%), which adds complexity to the analysis.[19] The greatest sensitivity is achieved by monitoring the most abundant isotope (^{80}Se); however, the use of argon (Ar) gas in ICP-MS operation results in the dimer $^{40}Ar_2^+$ ($m/z = 80$) interference.[9,20] Using a reaction gas such as hydrogen (H_2) or methane (CH_4) eliminates the interference by $^{40}Ar_2^+$ and greatly increases sensitivity by reliably quantifying ^{80}Se.[20]

Although using a chromatographic approach offers greater detail to identify the species that are present, methods for coupling these instruments and achieving the necessary detection limits (parts per trillion or lower) for natural waters are still limited in the literature and may not be practical for routine monitoring due to long run times. Adequate sensitivity is achievable with ICP-MS, but appropriate mobile and stationary phases must also be considered. To provide analysts with a rapid and sensitive method for Se speciation in freshwater, we tested the use of dilute nitric acid (HNO_3) as a mobile phase. This offers some advantages to other mobile phases with basic or near-neutral pH, as follows: (*i*) it prevents precipitation of iron (Fe) and aluminum (Al) (hydr)-oxides in samples taken from acidic[21] or anoxic waters,[22] (*ii*) it eliminates the need for salt or organic solvent-based eluents that can also be undesirable for interfacing IC with ICP-MS, thus improving detection limits, as well as reducing maintenance costs,[23] and (*iii*) HNO_3 is already commonly used for ICP-MS analyses and can be distilled and purified to the extent necessary to achieve the desired background concentrations (blank values).

Experimental

Chemicals and reagents

To prepare standard solutions for selenium speciation, Se compounds were purchased from Sigma-Aldrich and dissolved in high purity (18.2 Ω cm) water (Barnstead Nanopure, Thermo Scientific). Individual stock solutions had concentrations of 2000 mg L^{-1} for sodium selenite (Se^{IV}; 99%; Cat. #S3876) and sodium selenate decahydrate (Se^{VI}; 99.999% — trace metal basis; Cat. #450294), whereas organic Se species were prepared with a concentration of 500 mg L^{-1} using seleno-DL-methionine (SeMet; ≥99%; Cat. #S3876) and Se-(methyl)selenocysteine hydrochloride (MeSeCys; ≥95%; Cat. #M6680). Working standards (20 to 400 ng L^{-1}) were prepared daily from the stock solutions by diluting with high purity water inside a HEPA filtered clean air cabinet. Mass calibration standard solutions for total Se analysis were prepared by diluting SPEX CertiPrep Instrument Calibration Standard 2 (100 mg Se L^{-1} stock) with high purity water and acidifying final calibration solutions (0.1 to 2 μg L^{-1}) to 1% HNO_3. A multi-element Internal Standard 1 was also diluted from its original concentration (10 mg L^{-1}) to 2 μg L^{-1} with high purity water and acidified to 1% HNO_3.

TraceMetal grade HNO_3 purchased from Fisher Scientific (Cat. #A509P212) was used to prepare the mobile phase and acidify solutions analyzed for total concentration of Se. Hydrochloric acid (HCl) used for preserving samples and determining blank values was either TraceSELECT (Sigma-Aldrich, Cat. #72787) or Optim (Fisher Scientific, Cat. #A466-500) HCl.

Instrument setup for Se speciation and total Se analysis

A high performance ion chromatograph (HPIC; Thermo Scientific Dionex ICS-5000$^+$) equipped with a Dionex IonPac AS7 anion exchange column (inner diameter, 4 mm; length, 250 mm) and AG7 guard column (inner diameter, 4 mm; length, 50 mm) was used to separate different Se species. The system included a single gradient pump, temperature-controlled oven module, degasser, and AS-AP auto-sampler equipped with a 25 μL sample loop. The mobile phase was prepared in a stepwise concentration gradient as follows: 0–2 min (50 mmol L^{-1} HNO_3), 2–4 min (400 mmol L^{-1} HNO_3), and 4–5 min (50 mmol L^{-1} HNO_3). It is important to note that the potential corrosion of metallic parts by a dilute HNO_3 mobile phase is not problematic in this system due to the use of PEEK (polyetheretherketone) instead of steel, thus allowing for a “metal-free” flow path. This IC system was connected to a single quadrupole ICP-MS (iCap Q, Thermo Scientific) operated in CRC (chemical reaction cell) mode. After passing through the column, the mobile phase was introduced to the ICP-MS at a fixed flow rate (1.0 mL min^{-1}) through a MicroFlow PFA-LC zero dead volume nebulizer into a quartz cyclonic spray chamber cooled to ~3 °C. Peak areas of Se species were integrated using Dionex Chromeleon 7 software.

Preliminary work for the chromatographic conditions presented above is also described by Javed.[24] Two important modifications were made to that method and are as follows: (*i*) the flow rate of the mobile phase was kept constant (1 mL min^{-1}) to keep the optimized aerosol size and introduction rate consistent with tuned parameters and (*ii*) H_2 gas was used as a reaction gas in place of He (collision gas) in the pressurized cell to enable the accurate quantification of ^{80}Se. The flow rate of H_2 was adjusted until low background signals were achieved for ^{80}Se, without any substantial loss of sensitivity. The isotopes ^{77}Se and ^{78}Se were monitored during analysis to compare differences in the accuracy and precision and to assess the role of relevant polyatomic interferences such as $^{79}Br^1H^+$ (see Results and discussion).

The same ICP-MS was used for total Se analyses; however in this case, the instrument was equipped with a CETAC ASX-520 autosampler and PFA-ST MicroFlow Nebulizer. Total Se in water samples (described below) was determined under kinetic energy discrimination (KED) mode with He as a collision gas. Quantifica-

Table 1. Parameters and conditions for IC-ICP-MS and ICP-MS operations.

Parameter	Optimized setting
IC-ICP-MS	
Radio frequency power (W)	1548
Ar flow rate (L min^{-1})	0.8
H_2 flow rate (mL min^{-1})	9
Dwell time (s)	0.1 (Se)
Eluent flow rate (mL min^{-1})	1.0
Mobile phase A	50 mmol L^{-1} HNO_3
Mobile phase B	400 mmol L^{-1} HNO_3
Gradient program	0–2 min 100% A; 2–4 min 100% B; 4–5 min 100% A
Wash volume (μL)	250
Column temperature (°C)	30
ICP-MS	
Skimmer cone	Ni
Sample cone	Ni/Cu
Dwell time (s)	0.2 (Se); 0.02 (Sc); 0.01 (In); 0.01 (Ho)
Auxiliary gas flow rate	0.8 (L min^{-1})
He flow rate	5.0 (mL min^{-1})

tion was based on the average of three main runs with 25 sweeps using ^{78}Se. The internal standard solution was introduced continuously online through a PEEK T-mixing piece. Scandium (Sc), indium (In), and holmium (Ho) from the internal standard solution were monitored and used to account for any instrumental drift on the basis of interpolation. Corrections made by software to account instrument drift were minor, with no substantial changes in the internal standard observed during analyses (~±10%). Gases (Ar, He, H_2) used for (IC)-ICP-MS analysis were of ultra-high purity (Praxair, purity 5.0). A summary of relevant operating information for both total Se and Se speciation is provided in Table 1.

Quality control and method validation

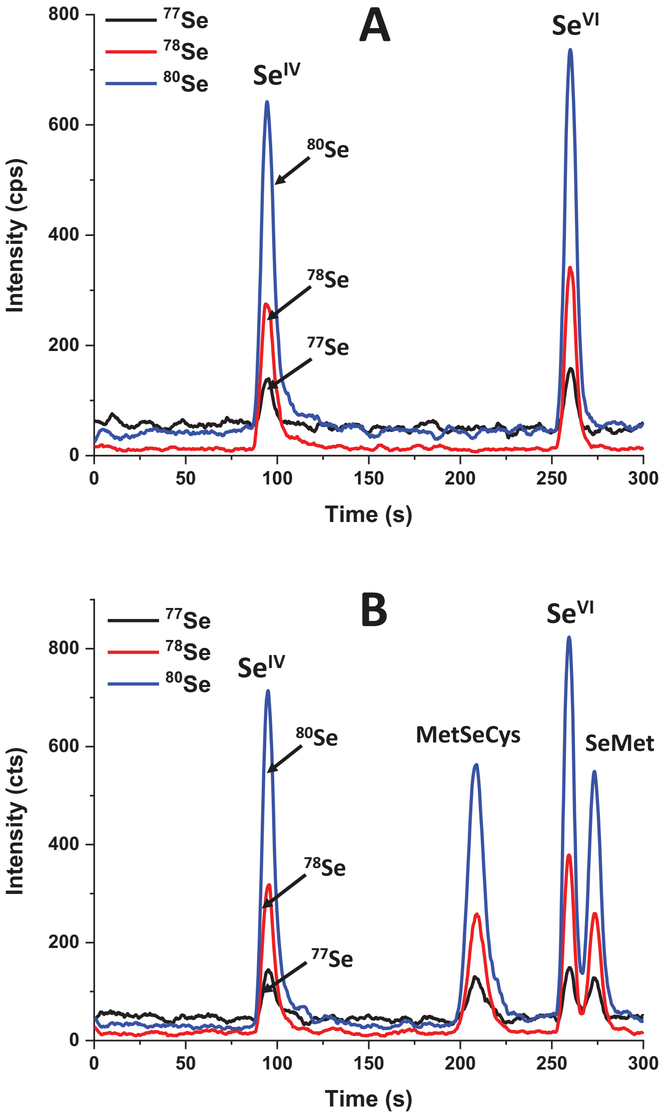
Method accuracy for Se speciation and total Se concentrations was evaluated by analyzing certified standard reference material (SRM; NIST 1640a: Trace Elements in Natural Water; Se = 20.13 ± 0.17 μg L^{-1}), whereas precision was assessed by analyzing samples in triplicate. For routine ICP-MS quality control, instrument blanks (1% HNO_3) and check standards were used. Multiple blanks containing either high purity water only or a dilute mixture of HCl and high purity water (~0.8% HCl) were also included to identify any possible contamination and evaluate spectral interference related to the increased chloride concentration from HCl. To further study any interconversion of Se species during separation in the IC or potential chromatographic interferences (e.g., competition from competing ions), an acidified river water sample was also chosen and spiked with Se^{IV} and Se^{VI}.

As an additional method for verification of Se^{IV} and Se^{VI}, acidified blank (~0.8% HCl) samples (n = 3) were spiked with Se^{IV} and analyzed using both IC-ICP-MS and HG-AFS. Details for HG-AFS analysis are provided in the Supplementary data. Briefly, samples spiked at 200 ng Se^{IV} L^{-1} were acidified with HCl to 3.6 mol L^{-1}, diluted (5× dilution), and analyzed directly with a PS Analytical 10.055 (Millennium Excalibur) HG-AFS system. During the online chemical reduction with sodium borohydride, only Se^{IV} is capable of forming a gaseous hydride, and therefore, any Se signal is the result of Se^{IV} in the sample.

Method application: river and rainwater sampling

The method was applied to natural water samples collected from three different rivers and one sample of urban rainwater. The purpose was to demonstrate the applicability of the method on chemically diverse natural waters containing low concentrations of Se. The determined chemical speciation is compared with the total concentrations and with the results available in the literature where different Se speciation methods have been applied to similar water types (e.g., snow, rain, river water).[10]

Fig. 1. Peak resolution of Se species and the sensitivity difference of measured isotopes. Chromatogram A represents a standard solution containing 200 ng L^{-1} each of Se^{IV} and Se^{VI}; chromatogram B represents a standard solution containing 200 ng L^{-1} of each Se species. Both standards were prepared using high purity water without any acidification of solutions. Chromatography method uses a Dionex IonPac AS7 anion exchange column (4 mm ID, 250 mm length, 10 μm particles size) and AG7 guard column (inner diameter, 4 mm; length, 50 mm) at 30 °C, with 1 mL min^{-1} flow rate and 25 μL sample injection. [Colour online.]



For river water, samples from the shore of the North Saskatchewan River in the city of Edmonton, (Alberta, Canada) were collected in June 2016. Four samples were syringe filtered into polypropylene (PP) centrifuge tubes (15 mL) on-site using 30 mL all plastic syringes (Thermo Scientific, Cat. #S7510) and 0.22 μm polytetrafluoroethylene (PTFE) disk filters (Thermo Scientific; 30 mm; Cat. #033911E). Samples were analyzed on the same day; samples for chemical speciation of Se (n = 3) were analyzed directly (i.e., filtered only) without any further treatment, whereas the sample (n = 1) for total Se was acidified with HNO_3 (1% v/v) before analysis. A water sample was also collected from the shore

Table 2. Comparison of method accuracy, precision, and sensitivity between isotopes for each of the studied species.

Speciation	Calibration linear coefficient	LOD (ng L^{-1})	LOQ (ng L^{-1})	Recovery of 20 ng L^{-1} standard (n = 5)	Recovery of 50 ng L^{-1} standard (n = 5)	Instrument sensitivity (cts) at 200 ng L^{-1}
^{77}Se						
Se^{IV}	0.961	24	110	**11 (±8)**	**33 (±12)**	1056
MetSeCys	0.967	41	100	**2 (±5)**	**11 (±16)**	1050
Se^{VI}	0.984	10	149	**ND**	**28 (±12)**	620
SeMet	0.970	38	147	**6 (±8)**	**20 (±16)**	498
^{78}Se						
Se^{IV}	1.000	9	28	18 (±3)	52 (±7)	2462
MetSeCys	0.996	20	64	**6 (±4)**	39 (±6)	2697
Se^{VI}	0.999	3	23	18 (±2)	54 (±5)	2192
SeMet	0.996	12	36	**20 (±8)**	44 (±3)	1586
^{80}Se						
Se^{IV}	0.997	4	14	21 (±3)	49 (±7)	5354
MetSeCys	0.999	5	12	21 (±3)	51 (±2)	5868
Se^{VI}	0.999	4	15	20 (±3)	49 (±4)	4673
SeMet	0.998	9	38	18 (±4)	46 (±4)	3154

Note: LOD, limit of detection; LOQ, limit of quantification; ND, not detected. Standard deviations for measurements are shown in parentheses. Bold values indicate analyses with >20% relative standard deviation.

of Maligne River, Jasper National Park, Alberta, Canada, and was immediately syringe filtered using 30 mL plastic syringes (see above) and 0.45 μm PTFE disk filters (Thermo Scientific™; 30 mm; Cat. #03-391-1C) into 125 mL acid-cleaned fluorinated polyethylene (FLPE) bottle containing 1 mL of HCl as preservative. The sample was stored at ~4 °C until analysis was performed. The Athabasca River in northern Alberta, Canada was also sampled in October 2015. Water sample collection and handling used the same materials and procedure as described above for Maligne River but were collected from the bow of a small boat anchored in the middle of the river. This sample is unique in that it was collected relatively close to the large surface mines of the Athabasca bituminous (oil) sands.

Urban rainwater was collected in an acid-cleaned 125 mL borosilicate glass bottle (Wheaton; 219815) with Teflon lined lid during a rain event at the University of Alberta, Edmonton, on 30 June 2016. The sample was immediately filtered (0.22 μm) using a 30 mL plastic syringe (see above) and PTFE disk filters into three separate vials for analysis on the same day (<30 min from collection). Only a small portion of the original sample was saved for Se speciation analysis and total Se was not analyzed.

Results and discussion

Peak resolution of Se species and differences in isotopic sensitivity with corresponding detection limits

Inorganic Se species (Se^{IV} and Se^{VI}) maintained excellent peak shape and resolution at low concentrations when a standard solution containing inorganic Se species (200 ng L^{-1}) was injected into the IC-ICP-MS (Fig. 1A). Similar to the behavior of arsenite (As^{III}) in a method using a HNO_3 mobile phase and AS7 column for arsenic speciation,[22] the low mobile phase pH and acid dissociation constant of Se^{IV} (pKa$_1$ = 2.46)[25] explains its quick movement through the column with little retention. Selenate required a stronger HNO_3 eluent concentration (400 mmol L^{-1}) to elute in a suitable amount of time. An additional 60 s of run time using 50 mmol L^{-1} HNO_3 mobile phase was added following the elution of Se^{VI} to re-condition the column and prepare for the next sample. After adequate separation and sensitivity was achieved for the inorganic Se species, the method was thoroughly tested for potential interferences (see below). Because the predominant species in aquatic systems tend to be Se^{IV} and Se^{VI}, the method was optimized for those species. However, to evaluate its performance in samples that contain organo-Se species, two selenoamino acids (SeMet and MeSeCys) were also tested. This is important because Se^{IV} is passing through the column with little interaction with the stationary phase (presumably in the void volume) and an analytical artefact is plausible if there are other Se species that do not interact with the stationary phase. With recent evidence of organo-Se species in ultra-trace quantities in biologically productive waters,[26,27] two selenoamino acids (SeMet and MeSeCys) were also tested using the same instrumental conditions. Although effective for the oxyanions Se^{IV} and Se^{VI}, the analysis of selenoamino acids by ion exchange chromatography is significantly more challenging; this is in part due to the zwitterionic nature of amino acids. For example, at the low pH (<2) of mobile phase used here, SeMet would be present as positively charged cation[16,28] and may not be suitable for analysis with an anionic exchange column. However, despite being developed as a strong anion exchange column for polyvalent species,[29] the IonPac AG7 and AS7 are known for both cation and anion exchange capability due to a sulfonic surface coating and an outer layer of submicron anion-exchange MicroBeads with alkyl quaternary ammonium functional groups;[30] this is in addition to other retention mechanisms such as molecule and stationary phase polarity, as the stationary phase is hydrophobic. With these processes in mind, simultaneous determination of cationic and anionic Se species using this setup was deemed possible.

The results showed that SeMet and MeSeCys had a relatively high affinity for the stationary phase and eluted in a short time (<5 min) with consistent peak shapes and good separation (Fig. 1B); however, baseline separation between Se^{VI} and SeMet was not obtained. In an attempt to gain additional resolution between Se^{VI} and SeMet, the eluent strength was decreased to 300 mmol L^{-1} and then to 100 mmol L^{-1}. These manipulations did not yield greater peak resolution and instead showed increased retention times and produced an undesirable peak shape compared with the desired Gaussian peak shape (data not shown). Analysis of calibration standards with different concentrations yielded consistent but considerable differences in sensitivity for all species among the three measured isotopes, with the ranking of most sensitive to least sensitive being ^{80}Se > ^{78}Se > ^{77}Se (see Fig. 1 for example). The difference in signal intensity of ^{80}Se from ^{77}Se and ^{78}Se was approximately two and five times, respectively (Table 2). As mentioned above, this sensitivity was directly related to the natural abundance of each isotope. The LOD and limit of quantification (LOQ) were also calculated based on 3 and 10 times the standard deviation of eight blanks ($n = 8$), respectively. These values were assessed experimentally by analyzing a 20 ng $\mathrm{L^{-1}}$ and a 50 ng $\mathrm{L^{-1}}$ standard five times each. Overall, the accuracy and precision of the measured standards were representative of the calculated LODs and LOQs (Table 2). Between the three isotopes, ^{80}Se had the lowest overall LODs and produced excellent accuracy and precision at 20 and 50 ng $\mathrm{L^{-1}}$ concentrations. Isotope ^{78}Se also produced good overall results and is beneficial to include in the Se analysis for critically evaluating the data for potential interferences (see below). Due to the relatively poor results of ^{77}Se, this isotope will not be discussed in detail; however, it is still useful in the data evaluation stages to distinguish Se from interferences.

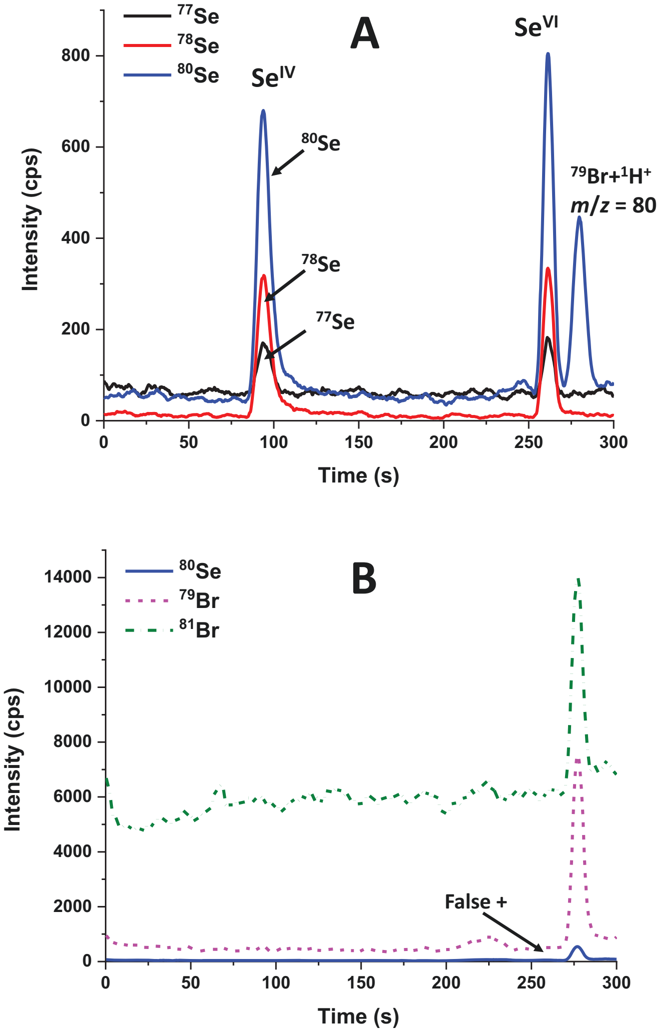
The importance of using a reaction cell gas ($\mathrm{H_2}$) is further highlighted by an observed increase in sensitivity compared with the previous method that utilized He collision cell performed on the same IC-ICP-MS.[24] Using reaction gas and the method described here, the sensitivity was approximately 28 000 and 24 000 cps $\mathrm{ppb^{-1}}$ for $\mathrm{Se^{IV}}$ and $\mathrm{Se^{VI}}$, respectively. Using He as a collision gas (and ^{78}Se for quantification), the sensitivity was approximately 1400 and 800 cps $\mathrm{ppb^{-1}}$ for $\mathrm{Se^{IV}}$ and $\mathrm{Se^{VI}}$, respectively.[24]

Bromine interference and influence of HCl preservation on Se species determination

Arguably one of the most critical challenges to overcome when using $\mathrm{H_2}$ in a reaction cell of ICP-MS for Se measurements is the polyatomic interferences created by samples containing bromine (Br). Hydrogen gas reacts to form $^{79}\mathrm{Br}^{1}\mathrm{H}^{+}$ ($m/z = 80$) and $^{81}\mathrm{Br}^{1}\mathrm{H}^{+}$ ($m/z = 82$), and these polyatomic ions overlap with the commonly measured ^{80}Se and ^{82}Se isotopes. In this study, we observed the interference caused by $^{79}\mathrm{Br}^{1}\mathrm{H}^{+}$ on ^{80}Se; however, because Br (presumably as ionic bromide; $\mathrm{Br^{-}}$) was effectively separated from three of the species in question, there was no influence on the results (Fig. 2). SeMet quantified using ^{80}Se was an exception to this, as it was observed to elute at approximately the same time as $\mathrm{Br^{-}}$; therefore, ^{78}Se must be used for accurate quantification of SeMet. If the extremely high sensitivity offered by ^{80}Se is critical for the application, the use of deuterium ($\mathrm{D_2}$) in place of $\mathrm{H_2}$ as the reaction gas has been successful in overcoming the Br interference[31] and might be a suitable alternative in this method as well. Silver cartridges are commonly used for removing unwanted $\mathrm{Cl^{-}}$, $\mathrm{Br^{-}}$, and $\mathrm{I^{-}}$ from samples but should not be used in this particular scenario, as it has been reported that these cartridges remove SeMet along with other halogen ions.[26]

The potential influence of HCl on this method was also evaluated for two main reasons: (*i*) it has been described as a preservative (in addition to refrigerated storage) used to stabilize $\mathrm{Se^{IV}}$ and $\mathrm{Se^{VI}}$ in water samples[32] and (*ii*) it is known to contain trace amounts of Br. To test the potential influence from Br contamination, a solution of high purity water and HCl (TraceMetal grade) was analyzed (final HCl concentration ~0.8%). This concentration was chosen because it maintains a pH < 2 required for preserving a wide variety of samples and is also appropriate for reliable ICP-MS analysis. Even with the high purity acid, Br contamination was evident from $\mathrm{Br^{-}}$ peaks (Supplementary Fig. 2A) and is enough to affect quantification of SeMet using ^{80}Se. The effect of HCl used to acidify water containing $\mathrm{Se^{IV}}$ and $\mathrm{Se^{VI}}$ speciation was assessed by adding the same proportion of HCl (~0.8%). The change in sample pH did not affect retention times of either species and $\mathrm{Br^{-}}$ eluted after $\mathrm{Se^{VI}}$, without interfering with $\mathrm{Se^{VI}}$ (Supplementary Fig. 2B). Based on these results, it is confirmed that HCl does not impact the analysis of $\mathrm{Se^{IV}}$ or $\mathrm{Se^{VI}}$, and samples preserved with ≤0.8% HCl can be analyzed reliably using this method for $\mathrm{Se^{IV}}$ or $\mathrm{Se^{VI}}$ determination.

Fig. 2. The potential influence of bromine (Br) and HCl on Se quantification. Chromatogram A represents a solution of high purity water and HCl (acidified to ~0.8%). Two isotopes of Br were monitored to confirm that Br (presumably as ionic $\mathrm{Br^{-}}$) was present in HCl, and due to $\mathrm{H_2}$ reaction with ^{79}Br, the resulting $^{79}\mathrm{Br}^{1}\mathrm{H}^{+}$ is responsible for the observed artefact of ^{80}Se. Chromatogram B represents a standard solution (200 ng $\mathrm{L^{-1}}$ each of $\mathrm{Se^{IV}}$ and $\mathrm{Se^{VI}}$) prepared using high purity water and acidified with HCl. The results indicate that the $\mathrm{Br^{-}}$ peak does not interfere with $\mathrm{Se^{VI}}$ and the acidification of the solution has no influence on $\mathrm{Se^{IV}}$ and $\mathrm{Se^{VI}}$ retention times. [Colour online.]



Method validation

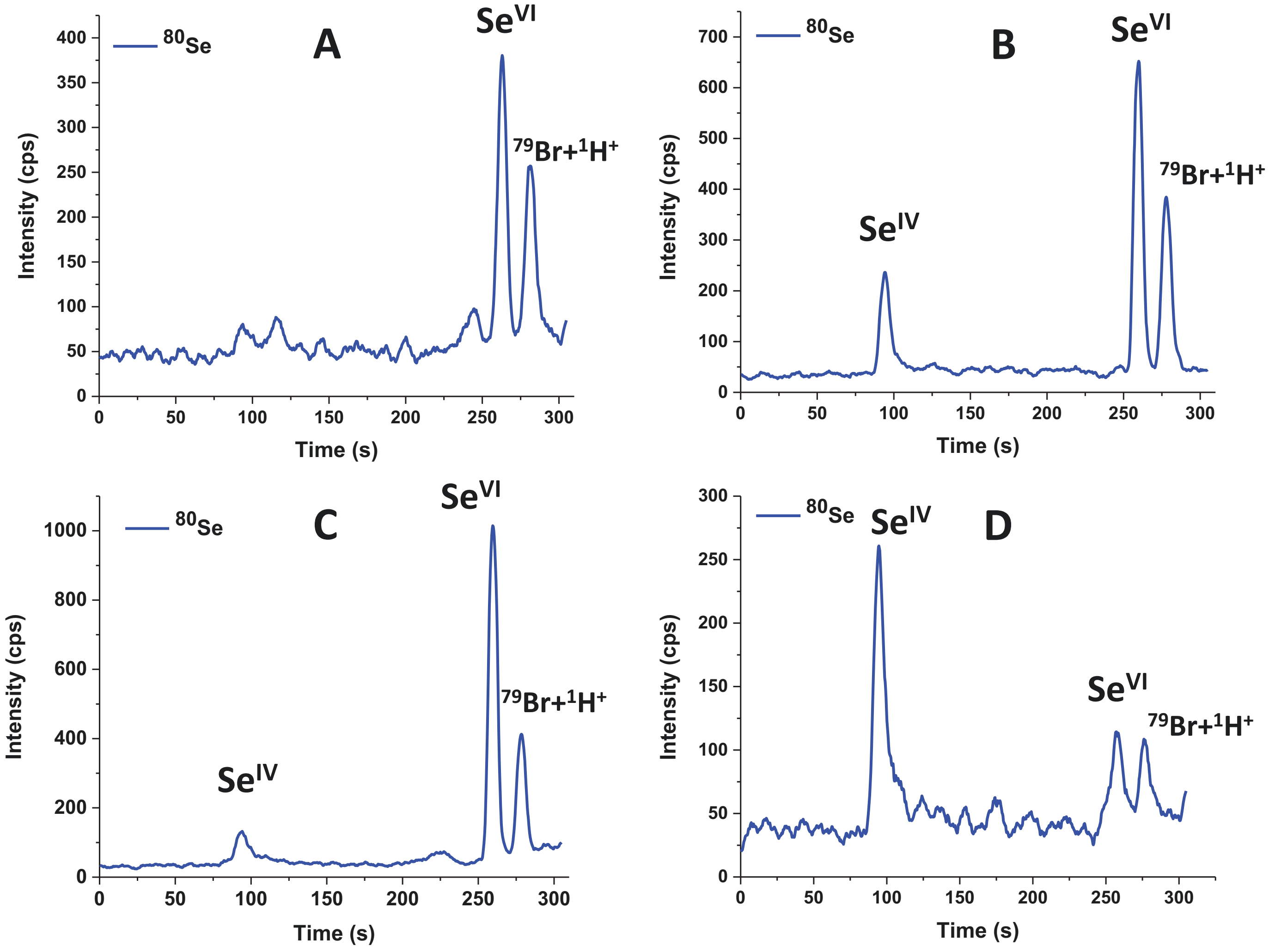
The accuracy of measurements was partially determined by measuring certified standard reference material NIST 1640a (Trace Elements in Natural Water; Se = 20.13 ± 0.17 μg $\mathrm{L^{-1}}$) because there are currently no certified standard reference water samples for Se species. The SRM was diluted 50 times prior to analysis to bring the concentration into the range of the calibration standards. It was found that all measurable Se was present as $\mathrm{Se^{IV}}$ and the recovery for every measurement was within 10% of the certified total Se value. An independent method check of triplicate samples containing 200 ng $\mathrm{L^{-1}}$ of $\mathrm{Se^{IV}}$ measured by IC-ICP-MS and HG-AFS also yielded no observable difference (Supplementary Fig. S1). To evaluate the recovery of spiked Se species from a natural water sample, an aliquot of the Athabasca River water (deemed to be the most chemically complex of the river samples) was spiked with 100 ng $\mathrm{L^{-1}}$ of $\mathrm{Se^{IV}}$ and $\mathrm{Se^{VI}}$. Full recovery (>96%) was obtained for both species and repeatability of triplicate measurements had <3% RSD (Table 3). Accuracy of total Se measurements was assessed using NIST 1640a (diluted 50 times). Full

Table 3. Method validation using standard reference water and spiked river water.

Water type	Analysis	No. of measurements (*n*)	Certified or expected value (μg L^{-1})	Measured value	Recovery (%)	Relative standard deviation (%)
NIST 1640a	Speciation	4	20.13 (±0.17)	20.35	101	5.7
Se(IV) spike	Speciation	3	0.100	0.099	99	2.5
Se(VI) spike	Speciation	3	0.177	0.170	96	2.6
NIST 1640a	Total	1	20.13 (±0.17)	20.20	100	NA

Note: Results are based on quantification of ^{80}Se. Athabasca River water was spiked with Se^{IV} and Se^{VI}. NIST 1640a is used as an indicator of method accuracy for speciation by comparing sum of species with certified total concentration. Spiked solutions diluted the original sample by 5%. NA, not available.

Fig. 3. General depiction of Se speciation in river and rainwater samples obtained using the developed method. Chromatograms represent (A) Athabasca River, (B) North Saskatchewan River, (C) Maligne River, and (D) urban rainwater. A false Se peak was expected in chromatograms A and C due to preservation with HCl, but trace Br was still detected in un-acidified samples (B and D). See Table 4 for the corresponding concentrations. [Colour online.]



details for all quality assurance and quality control are provided in Table 3.

Se speciation in natural waters

Water samples from three rivers and one rain event were used to evaluate the method. Figure 3 displays the Se speciation in those water samples, with each river having slightly different proportions of Se^{IV} and Se^{VI} relative to the total Se. Compared with the North Saskatchewan River (261 ng L^{-1}) and the Athabasca River (187 ng L^{-1}; Table 4), Maligne River contained the highest concentration of total Se (314 ng L^{-1}) and the most Se^{VI}. This observation is most likely a reflection of the local geology, as well as input from snow melt, which has been found to contain predominantly Se^{VI}.[33–35]

The sum of inorganic species (Se^{IV} and Se^{VI}) accounted for most of the Se dissolved in North Saskatchewan River water (77%) and the Maligne River water (88%), but in the Athabasca River water, there was no detectable Se^{IV} and Se^{VI} was only 43% of the total Se (Table 4). The differences in proportion of inorganic Se could be related to the natural organic matter (NOM) content of the waters and the known ability of complex organic structures to incorpo-

Table 4. Total Se and its chemical species in natural water samples.

Water type	GPS location	No. of samples (n)	Se^{IV} (ng L^{-1})	SeMetCys (ng L^{-1})	Se^{VI} (ng L^{-1})	SeMet (ng L^{-1})	Total Se (ng L^{-1})	Sum of species relative to total (%)
Maligne River	52.921591–118.016796	1	24	ND	252	ND	314	88
Athabasca River	56.8971667–111.419116	1	<LOD	ND	77	ND	187	43
North Saskatchewan River	53.529857–113.517937	3	45 (±6)	ND	155 (±55)	ND	261	77
Edmonton rain	53.526103–113.523896	3	72 (±5)	ND	24 (±5)	ND	NA	NA

Note: Results for chemical speciation were quantified using ^{80}Se and total Se analysis was ^{78}Se. ND, not detected; NA, not available; LOD, limit of detection. Standard deviations for measurements are shown in parentheses.

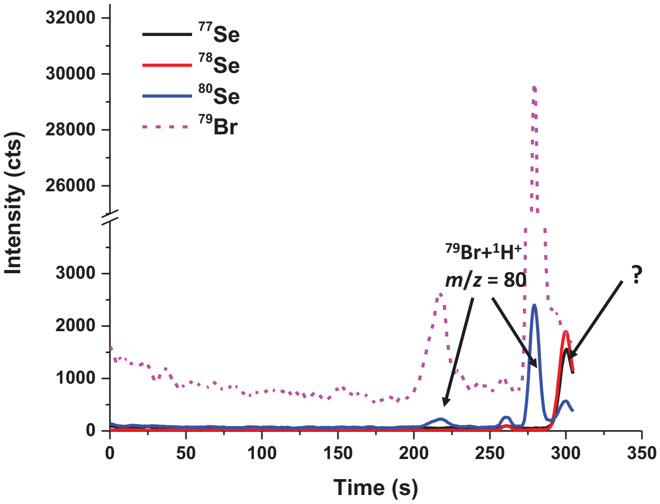
rate Se.[6] Dominated by snow melt, the Maligne River likely contains low concentrations of NOM, whereas the Athabasca River is well known for its complex dissolved organic matter consisting of humic material, as well as bitumen derived compounds from bituminous sand outcrops.[36,37]

Rainwater was selected for analysis using this method because concentrations are usually low, and therefore, it requires the level of sensitivity demonstrated here. Moreover, because Se speciation in rainwater has been documented using various analytical techniques, it offers some additional insight into performance relative to other methods using a similar matrix. Unlike snow, Se^{IV} is commonly the predominant oxidation state in rainwater.[11,33,34,38] The results for rainwater from Edmonton (Table 4) yielded similar chemical speciation results as those obtained by others that also employed a chromatography based Se speciation approach.[38] Rainwater (n = 3) from Edmonton contained 72 ± 5 ng L^{-1} Se^{IV} and 24 ± 5 ng L^{-1} Se^{VI}, whereas Seattle rain (n = 3) contained 59.4 ± 2.6 ng L^{-1} Se^{IV} and 16 ± 0.4 ng L^{-1} Se^{VI}.[38]

Method limitations

The method was found to be effective for water samples with a very simple matrix (low salinity and NOM concentrations), but its performance with more complex matrices was not critically evaluated. A comprehensive study is necessary to fully evaluate the effect of competing ions (e.g., sulfate) and any necessary sample clean-up steps. This would help expand its application toward samples with greater ionic strength such as seawater or industrial effluents. There is also an inherent disadvantage associated with using a low pH mobile phase on water samples containing abundant colloidal (i.e., <0.45 μm) organic and mineral particles. A more representative determination of the chemical speciation of Se (or other elements) requires methods of collection and analyses, including selection of the mobile phase, to mimic as closely as possible the environmental conditions at the time of sampling. Mobile phases used in chromatography typically are not tuned for site-specific parameters (e.g., pH, ionic strength), so there are risks of potential changes to the colloids such as partial dissolution, desorption, or dissociation. Therefore, a combination of other techniques for Se speciation such as asymmetrical flow-field flow fractionation[39] would be worth investigating. To this point, we offer an example from some preliminary work on Se speciation in surface water of a peat bog in northern Saskatchewan, situated near a flooded uranium mine (Fig. 4). The total concentration of Se was 140 ng L^{-1}, with 40 ng L^{-1} Se^{VI} and no detectable Se^{IV}. As in the case of the Athabasca River, the form(s) of the unidentified Se fraction in these waters remains unknown; however, given the complex chemistry and array of organic compounds present in peat bog water, it may be possible that a significant portion of the Se was incorporated into NOM.

Fig. 4. Selenium speciation of chemically complex peat bog surface water. A signal response from all three Se isotopes appear at 300 s, which suggests that it is Se being detected, but ^{80}Se signal had the lowest response, and therefore, it is likely that a different spectral interference is at play here. A second Br peak was also observed (~225 s), possibly indicating the presence of another form or column artifact due to the very high concentration of Br^{-}. [Colour online.]



Conclusions

The purpose of this study was to develop a method that can quickly analyze Se species in natural water samples with high sensitivity using a dilute HNO_3 acid mobile phase. Although originally intended for Se^{IV} and Se^{VI}, it was also found to be effective for at least two organic species and, therefore, may also have applications for studying biological (e.g., plant or animal tissue) samples. The use of an acidic mobile phase may also be useful for anoxic groundwater or sediment pore water samples that require acid preservation to prevent the precipitation of Fe (hydr)-oxides. When coupled with single quadrupole ICP-MS using hydrogen in the reaction cell, the method has excellent sensitivity and allows for accurate and precise measurements below 50 ng Se L^{-1}. Given the simple mobile phase, low cost of consumables and rapid elution and detection of species of interest, this method will be a useful analytical option for monitoring agencies tasked with routinely determining Se speciation in freshwater environments.

Supplementary data

Supplementary data are available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2017-0637.

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References

(1) Rayman, M. P. *Lancet* **2000**, *356*, 233. doi:10.1016/S0140-6736(00)02490-9.
(2) Hamilton, S. J. *Sci. Total Environ.* **2004**, *326*, 1. doi:10.1016/j.scitotenv.2004.01.019.
(3) Winkel, L. H. E.; Vriens, B.; Jones, G. D.; Schneider, L. S.; Pilon-Smits, E.; Bañuelos, G. S. *Nutrients* **2015**, *7*, 4199. doi:10.3390/nu7064199.
(4) Hamilton, S. J. *Aquat. Toxicol.* **2002**, *57*, 85. doi:10.1016/S0166-445X(01)00262-4.
(5) Maher, W.; Roach, A.; Doblin, M.; Fan, T.; Foster, S.; Garrett, R.; Möller, G.; Oram, L.; Wallschläger, D. In *Ecological Assessment of Selenium in the Aquatic Environment*; Chapman, P. M., Adams, W. J., Brooks, M. L., Delos, C. G., Luoma, S. N., Maher, W. A., Ohlendorf, H. M., Presser, T. S., Shaw, D. P., Eds.; CRC Pres: Boca Raton, Fla., 2010; pp. 47–91.
(6) Wallschläger D.; Feldmann, J. In *Organometallics in the Environment and Toxicology: Metal Ions in Life Sciences*; Sigel, A., Sigel, H., Sigel, R. K. O., Eds.; RSC Publishing: Cambridge, UK, 2010; pp. 319–364. doi:10.1039/9781849730822-00319.
(7) Fernández-Martínez, A.; Charlet, L. *Rev. Environ. Sci. Biotechnol.* **2009**, *8*, 81. doi:10.1007/s11157-009-9145-3.
(8) Riedel, G. F.; Ferrier, D. P.; Sanders, J. G. *Water, Air, Soil Pollut.* **1991**, *57–58*, 23. doi:10.1007/BF00282865.
(9) Pettine, M.; McDonald, T. J.; Sohn, M.; Anquandah, G. A. K.; Zboril, R.; Sharma, V. K. *Trends Environ. Anal. Chem.* **2015**, *5*, 1. doi:10.1016/j.teac.2015.01.001.
(10) Conde, J. E.; Sanz Alaejos, M. *Chem. Rev.* **1997**, *97*, 1979. doi:10.1021/cr960100g.
(11) Cutter, G. A. *Anal. Chim. Acta* **1978**, *98*, 59. doi:10.1016/S0003-2670(01)83238-4.
(12) Cutter, G. A. *Science* **1982**, *217*, 829. doi:10.1126/science.217.4562.829.
(13) Cutter, G. A. *Anal. Chem.* **1985**, *57*, 2951. doi:10.1021/ac00291a045.
(14) Chen, Y.-W.; Zhou, M.-D.; Tong, J.; Belzile, N. *Anal. Chim. Acta* **2005**, *545*, 142. doi:10.1016/j.aca.2005.02.079.
(15) Kölbl, G.; Kalcher, K.; Irgolic, K. J.; Magee, R. J. *Appl. Organomet. Chem.* **1993**, *7*, 443. doi:10.1002/aoc.590070704.
(16) Pedersen, G. A.; Larsen, E. H. *Fresenius' J. Anal. Chem.* **1997**, *358*, 591. doi:10.1007/s002160050475.
(17) Bird, S. M.; Ge, H.; Uden, P. C.; Tyson, J. F.; Block, E.; Denoyer, E. *J. Chromatogr. A* **1997**, *789*, 349. doi:10.1016/S0021-9673(97)00657-2.
(18) Lum, T.-S.; Leung, K. S.-Y. *J. Anal. At. Spectrom.* **2016**, *31*, 1078. doi:10.1039/C5JA00497G.
(19) Haygarth, P. M. In *Selenium in the Environment*; Frankenberger, W. T., Jr., Benson, S., Eds.; Marcel Dekker: New York, 1994; pp. 1–27.
(20) B'Hymer, C.; Caruso, J. A. *J. Chromatogr. A* **2006**, *1114*, 1. doi:10.1016/j.chroma.2006.02.063.
(21) Floor, G. H.; Iglesías, M.; Román-Ross, G.; Corvini, P. F. X.; Lenz, M. *Chemosphere* **2011**, *84*, 1664. doi:10.1016/j.chemosphere.2011.05.006.
(22) Gorny, J.; Dumoulin, D.; Lesven, L.; Noiriel, C.; Madé, B.; Billon, G. *J. Anal. At. Spectrom.* **2015**, *30*, 1562. doi:10.1039/C5JA00095E.
(23) Wang, W.; Chen, Z.; Davey, D. E.; Naidu, R. *J. Liq. Chromatogr. Relat. Technol.* **2010**, *33*, 1151. doi:10.1080/10826076.2010.484363.
(24) Javed, M. B. Ph.D. Thesis, University of Alberta, Edmonton, Alta., 2015.
(25) Li, H.-F.; McGrath, S. P.; Zhao, F.-J. *New Phytol.* **2008**, *178*, 92. doi:10.1111/j.1469-8137.2007.02343.x.
(26) Leblanc, K. L.; Ruzicka, J.; Wallschläger, D. *Anal. Bioanal. Chem.* **2016**, *408*, 1033. doi:10.1007/s00216-015-9124-1.
(27) Leblanc, K. L.; Wallschläger, D. *Environ. Sci. Technol.* **2016**, *50*, 6164. doi:10.1021/acs.est.5b05315.
(28) Potin-Gautier, M.; Boucharat, C.; Astruc, A.; Astruc, M. *Appl. Organomet. Chem.* **1993**, *7*, 593. doi:10.1002/aoc.590070720.
(29) Weiss, J. *Handbook of Ion Chromatography*; Wiley-VCH: Weinheim, Germany, 2004; Vol. 1, pp. 63, 182, and 528.
(30) Xing, L.; Beauchemin, D. *J. Anal. At. Spectrom.* **2010**, *25*, 1046. doi:10.1039/c004699j.
(31) Ogra, Y.; Ishiwata, K.; Suzuki, K. T. *Anal. Chim. Acta* **2005**, *554*, 123. doi:10.1016/j.aca.2005.08.021.
(32) Cutter, G. A. In *Occurrence and Distribution of Selenium*; Ihnat, M., Ed.; CRC Press: Boca Raton, Fla, 1989; pp. 243–262.
(33) Wang, D.; Alfthan, G.; Aro, A. *Environ. Sci. Technol.* **1994**, *28*, 383. doi:10.1021/es00052a007.
(34) Alfthan, G.; Wang, D.; Aro, A.; Soveri, J. *Sci. Total Environ.* **1995**, *162*, 93. doi:10.1016/0048-9697(95)04436-5.
(35) Papoff, P.; Bocci, F.; Lanza, F. *Microchem. J.* **1998**, *59*, 50. doi:10.1006/mchj.1998.1564.
(36) Headley, J. V.; Barrow, M. P.; Peru, K. M.; Fahlman, B.; Frank, R. A.; Bickerton, G.; McMaster, M. E.; Parrott, J.; Hewitt, L. M. *Rapid Commun. Mass Spectrom.* **2011**, *25*, 1899. doi:10.1002/rcm.5062.
(37) Ross, M. S.; Pereira, A. S.; Fennell, J.; Davies, M.; Johnson, J.; Sliva, L.; Martin, J. W. *Environ. Sci. Technol.* **2012**, *46*, 12796. doi:10.1021/es303432u.
(38) Wallschläger, D.; London, J. *J. Anal. At. Spectrom.* **2004**, *19*, 1119. doi:10.1039/B401616E.
(39) Cuss, C. W.; Grant-Weaver, I.; Shotyk, W. *Anal. Chem.* **2017**, *89*, 8027. doi:10.1021/acs.analchem.7b01427.

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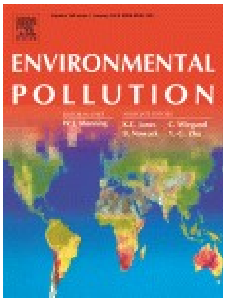

Title: Selenium in surface waters of the lower Athabasca River watershed: Chemical speciation and implications for aquatic life

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Selenium in surface waters of the lower Athabasca River watershed: Chemical speciation and implications for aquatic life[☆]

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Fish tissue

ABSTRACT

Selenium in the lower Athabasca River (Alberta, Canada) is of concern due to potential inputs from the weathering of shallow bitumen deposits and emissions from nearby surface mines and upgraders. Understanding the source of this Se, however, is complicated by contributions from naturally saline groundwater and organic matter-rich tributaries. As part of a two-year multi-disciplinary study to assess natural and anthropogenic inputs, Se and its chemical speciation were determined in water samples collected along a ~125 km transect of the Athabasca River and associated tributaries. Selenium was also determined in the muscle of Trout-perch (*Percopsis omiscomaycus*), a non-migratory fish species, that were sampled from selected locations. Dissolved (<0.45 µm) Se in the Athabasca River was consistently low in 2014 ($0.11 \pm 0.02\ \mu g\ L^{-1}$; $n = 14$) and 2015 ($0.16 \pm 0.02\ \mu g\ L^{-1}$; $n = 21$), with no observable increase from upstream to downstream. Selenate was the predominant inorganic form (~$60\ ng\ L^{-1}$) and selenite was below detection limits at most locations. The average concentration of Se in Trout-perch muscle was $2.2 \pm 0.4\ mg\ kg^{-1}$ ($n = 34$), and no significant difference ($p > 0.05$) was observed between upstream and midstream (industrial) or downstream reaches. Tributary waters contained very low concentrations of Se (typically $< 0.1\ \mu g\ L^{-1}$), which was most likely present in the form of dissolved organic colloids.

1. Introduction

Selenium (Se) is often referred to paradoxically as an “essential toxin” because of its role as either a critical micronutrient, or as a harmful contaminant (Lenz and Lens, 2009). The distinction between toxic or beneficial depends on the form of selenium (chemical speciation) and its concentration (Young et al., 2010). The environmental chemistry of selenium is similar to that of sulphur, as they share similar oxidation states (−II, 0, IV, VI) and form analogous biomolecules. Selenium in the aquatic environment requires special attention due to its ability to bioaccumulate and promote teratogenic effects on organisms at higher trophic levels such as waterfowl and fish (Ohlendorf et al., 1986, 1990). Selenium in oxic surface water is often present as selenite [SeO_3^{2-}; Se(IV)] and selenate [SeO_4^{2-}; Se(VI)]. However, many other forms of Se exist in aquatic environments due to chemical and biological processes, such as reduced selenides [Se (-II)], discrete biomolecules (e.g., amino acids), non-discrete organo-Se compounds (e.g., bound with natural organic matter) as well as volatile gaseous species (e.g., dimethyl selenide) (Wallschläger and Feldmann, 2010). The environmental cycling of Se has some unique and important considerations compared to other potentially toxic trace metals and metalloids (e.g., As, Ag, Cd, Pb, Tl). One critical difference is that the organic forms of Se are the most bioavailable, with diet being the primary route of exposure (Young et al., 2010).

Predicting whether Se is a problem or could become a threat to aquatic organisms in the future, requires knowledge of the local and regional environmental setting, particularly as it relates to hydrology and geology (Outridge et al., 1999). For example, Se bioaccumulation is typically lower in lotic systems (flowing water) than lentic systems (stagnant water), where there is greater biological cycling and production of organo-Se (Hillwalker et al., 2006; Simmons and Wallschläger, 2005). The unique and complex behavior of Se in the aquatic environment is further reflected by

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inconsistent environmental guidelines around the world (Luoma, 2009). It is widely accepted that the concentration of Se in fish tissue is a more reliable measure of exposure and potential ecological effects than the concentration in water, however concentration thresholds have also been the focus of considerable research and debate (e.g., Chapman, 2007; Deforest et al., 1999; Hamilton, 2002). In 2016, the United States Environmental Protection Agency (US EPA) issued a new aquatic guideline for Se that prioritizes a fish tissue-based criterion (muscle or gonads) over water-based criteria (US EPA, 2016). If data for fish tissue is not available then guideline values for dissolved Se concentrations in water take precedence, and differ for lotic (3.1 $\mu g\,L^{-1}$) and lentic systems (1.5 $\mu g\,L^{-1}$) (US EPA, 2016).

The surface mining and upgrading of bituminous sands along the lower Athabasca River in northeastern Alberta, Canada, have provoked concerns about environmental contamination by potentially toxic trace elements such as Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl and Zn (Kelly et al., 2010). The inclusion of Se on this list requires extra attention given the importance of fish in the diet of local First Nations communities, and the toxic effects observed in fish exposed to high concentrations (Lemly, 1998). A study of historical water quality data (1972–2010) in rivers near bitumen mining indicated that 'dissolved' (presumably < 0.45 μm by filtration) Se concentrations were elevated due to construction and other activities related to early bitumen production (Alexander and Chambers, 2016). A similar data analysis based on a 25-year record (1989–2014) of water quality in rivers near mining and upgraders found that concentrations of Se and 11 other potentially toxic trace elements were elevated during snow melt due to greater acid deposition (Alexander et al., 2017). Other contemporary studies of trace element concentrations in the Athabasca River either did not include Se (Conly et al., 2007; Donner et al., 2017; Guéguen et al., 2011; Javed et al., 2017; Shotyk et al., 2017; Zhu and Guéguen, 2016), or did not label it an element of concern (Pilote et al., 2018). Moreover, there have been no studies of the chemical speciation of Se in the Athabasca River, and there is no published data for Se in fish from this river.

An inherent challenge in assessing water quality in the lower Athabasca River is distinguishing natural and anthropogenic inputs (e.g., Shotyk et al., 2017; Sun et al., 2017). Although there is considerable industrial activity related to surface mining and bitumen upgrading, quantifying the contribution of trace elements from industrial activities is complicated by large inputs of dissolved organic matter (DOM), iron oxyhydroxides and associated trace elements from the surrounding boreal forest and peatlands (Cuss et al., 2018), high salinity groundwater (Ellis and Jasechko, 2018; Gibson et al., 2013) and bitumen-derived compounds from the weathering of bituminous sands (Ross et al., 2012; Sun et al., 2017). A recent study of trace metals in the dissolved (<0.45 μm) fraction of Athabasca River water found that the concentrations of four trace metals increased significantly from upstream to downstream of bitumen mines and upgraders: V, Ni, Mo and Re (Shotyk et al., 2017). These elements are enriched in bitumen (Bicalho et al., 2017; Goldschmidt, 1937; Selby, 2005), whereas many other potentially toxic elements are contained almost exclusively within the mineral fraction (e.g., As, Ag, Pb, Sb, Tl, etc.). Recently, however, determination of Se in mineral and bitumen fractions of Athabasca bituminous sands (ABS) showed that Se was predominantly (ca. 80%) contained in the bitumen fraction (Donner et al., 2018). Therefore, aquatic organisms in the Athabasca River may be exposed to naturally elevated concentrations of Se due to the weathering of bitumen-laden banks, with potentially greater exposure downstream from open-pit bitumen mines and upgrading facilities.

The two objectives of this study were to: i) Measure the concentration and chemical speciation of Se in Athabasca River surface water, upstream, alongside and downstream of bitumen mining and upgrading, and ii) Evaluate the potential impact of Se on aquatic life based on concentrations in the muscle tissue of Trout-perch (*Percopsis omiscomaycus*). Trout-perch are small fish that do not migrate far from a single area (Gibbons et al., 1998), and have been promoted as a valuable sentinel species for the Athabasca River watershed (Spafford, 1999). Water samples from the Athabasca River and tributaries were also collected to determine concentrations in the dissolved (<0.45 μm) phase and the major chemical species.

2. Methods

2.1. Water sampling from lower Athabasca River watershed

Water sampling was conducted in October 2014 and 2015 as part of a large multi-disciplinary study of groundwater-surface water interactions in the lower Athabasca River watershed. Samples were collected in the autumn when water levels are typically at their lowest and the contribution of groundwater is greatest. In 2014, samples were collected from 13 sites on the Athabasca River and five associated tributaries. In 2015, 19 sites were sampled along the Athabasca River and nine in tributaries. Field duplicates were collected at various locations in both years to assess sampling reproducibility. As an independent check, dissolved Se concentrations were also determined in two additional bottles collected at the same time, but designated for a suite of trace metal analyses (Shotyk et al., 2017). A comparison of data for additional bottles is provided in Fig. S1. A map denoting all sampling locations for water samples (2014, 2015) and Trout-perch (see below) is provided in Fig. 1. Detailed information about the GPS coordinates for all surface water sampling locations can be found elsewhere (Donner et al., 2017; Shotyk et al., 2017). Water samples were collected from the Athabasca River (main-stem) at a depth of approximately 30 cm, off the bow of a small boat anchored approximately 80 m from shore. Tributary samples were collected midway from each bank in an area of ample flow, near to their confluence with the Athabasca River but upstream of the mixing zone. A detailed description of materials and methods for bottle cleaning and sampling is provided elsewhere (Donner et al., 2017). All sample bottles (low-density polyethylene or fluorinated high-density polyethylene), syringes (polypropylene), and filters (polytetrafluoroethylene) were precleaned in acid and individually packaged in two re-sealable plastic bags. Water was immediately filtered (0.45 μm) into a bottle containing HCl as preservative (OptimaGrade™; 0.8% v/v) and transported in a cooler containing ice packs. Analyses for dissolved (<0.45 μm) Se and its speciation were conducted using the same water samples as for As published previously (Donner et al., 2017).

A large suite of samples were collected at each site to analyze a variety of parameters, including: dissolved (<0.45 μm) trace metals (Shotyk et al., 2017), Pb speciation (Javed et al., 2017), naphthenic acids (Sun et al., 2017), speciation of colloidal forms of trace elements (Cuss et al., 2018), dissolved organic matter (DOM) quality and quantity (Cuss et al., in review) and As speciation (Donner et al., 2017). The concentrations of major cations, anions, dissolved organic carbon (DOC) and other water quality parameters are also presented in Shotyk et al. (2017) for the 2014 sampling campaign. Methods and data for DOC determined in 2015 samples is available elsewhere (Cuss et al., in review) and unpublished data for Cl^- in 2015 samples is presented here.

2.2. Fish collection and handling

Trout-perch were collected in October of 2014 from 11 locations

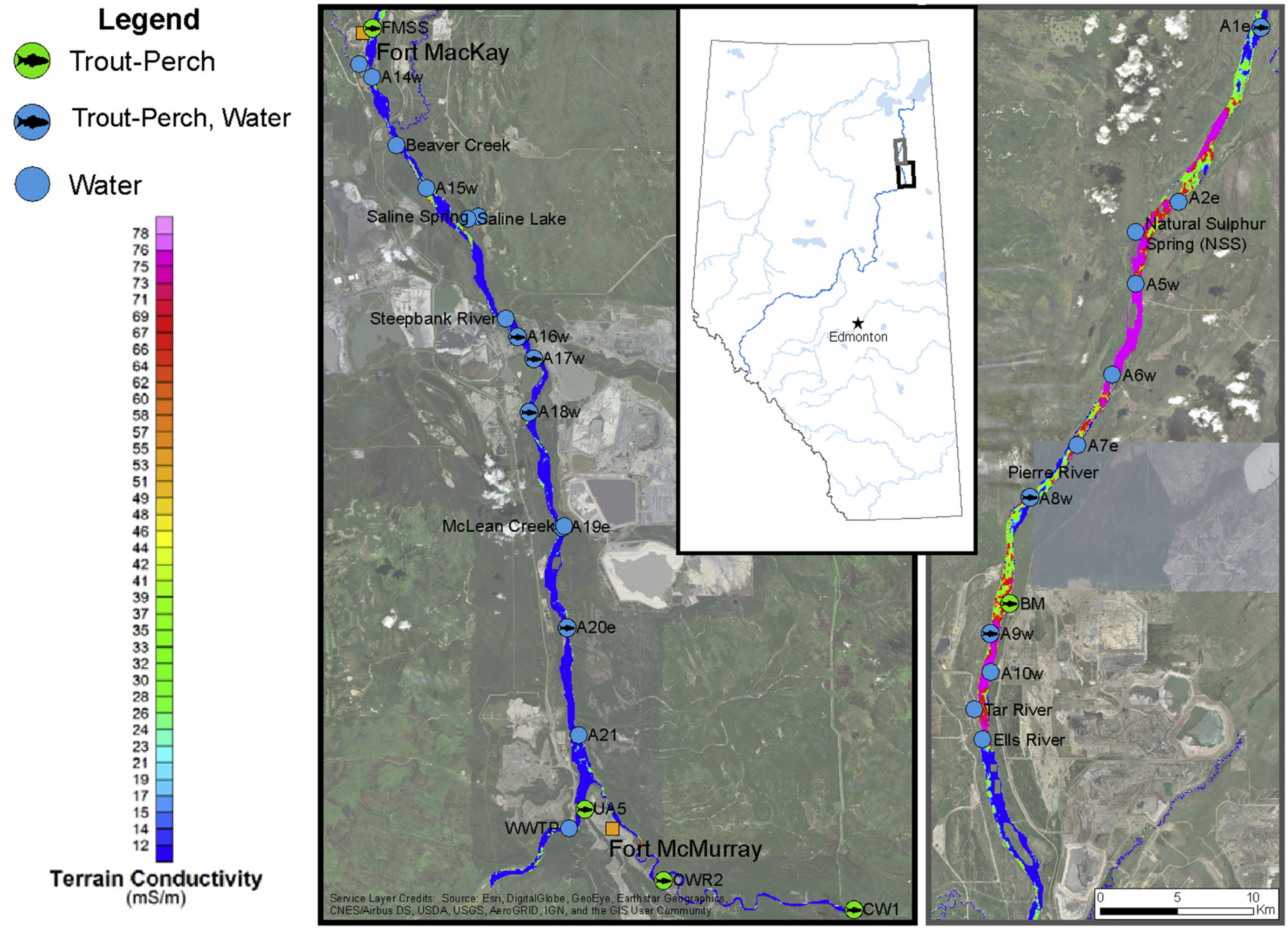

Fig. 1. Map of the study area and sampling locations during the 2014 (water samples and Trout-perch) and 2015 (water samples only) sampling campaigns. Map begins at the bottom of the left panel and continues from the bottom of the right panel. Water sampling locations for Pierre River and McKay River are hidden from view and some minor adjustments of site labels were applied for greater clarity (see Supplementary Info for exact coordinates). Data for lower terrain conductivity mapping were taken from Gibson et al. (2013).

on the Athabasca River and two on the Clearwater River, with the furthest site (CWR2) being approximately 30 km upstream of its confluence with the Athabasca River. The GPS coordinates for Trout-perch collection sites are available in Table S1. Sampling was conducted in coordination with the water sampling teams to ensure comparable results between the biological and chemical components. A Smith-Root 7.5 Generator Powered Pulsator electrofisher (designed for low to very high conductivity water) was operated from a 20 ft boat that travelled along multiple transects (ca. 1 km each) at each site. Transects began at the indicated site location (Fig. 1) and were conducted parallel to the bank; the distance from shore was dependent on channel morphology and varied between sites. Fish were removed using handheld nets and euthanized in accordance with animal care protocol AUP00001111. Fish were kept in cooler boxes and transferred to freezers at the end of each day.

The weight and fork length of 56 Trout-perch were measured in the laboratory. Muscle tissue samples were obtained from above the lateral line in the dorsal portion, excluding bone and skin tissues. Samples were then air-dried for at least 48 h inside an exhausted (class-100) clean-air cabinet, housed in the ultraclean, metal-free SWAMP facility (Soil Water Air Manure Plants) at the University of Alberta. Dried samples were acid-digested in a mixture of double-distilled nitric acid (3 mL) and tetrafluoroboric acid (0.1 mL) using a high pressure microwave (ULTRAclave, MLS, Leutkirch, Germany). After cooling, the liquid digestate was diluted to a total volume of 10 mL with MilliQ water (18.2 MΩ•cm; MilliporeSigma, Massachusetts, USA) and stored under refrigeration until analysis.

2.3. Determination of dissolved selenium

Concentrations of dissolved Se were determined using a single quadrupole inductively coupled plasma mass spectrometer (ICP-MS; iCAP-Q Thermo Scientific) operating in kinetic energy discrimination mode, with He collision gas (0.05s dwell time; 120 sweeps). External mass calibration solutions were prepared using SPEX CertiPrep Instrument Calibration Standard 2. Minor instrument drift was accounted for using a multi-element internal standard (Multi-element Internal Standard 1; 1 $\mu g\,L^{-1}$) added continuously on-line through a mixing tee. Concentrations were quantified using ^{78}Se and presented as the average value of three main runs. A blank sample was analyzed after approximately every 10 samples, in addition to a standard reference material (SRM), NIST 1640a Trace Elements in Natural Water; $[Se] = 20.13 \pm 0.17\ \mu g\,L^{-1}$. The average recoveries of NIST 1640a for analyses in 2014 and 2015 were 94.9 and 98.2%, respectively.

Dissolved Se was also determined in water samples using hydride generation atomic fluorescence spectroscopy (HG-AFS). Selenium analysis by HG-AFS first requires a pre-reduction step to reduce any Se(VI) to Se(IV), as only Se(IV) will form a hydride when reduced by sodium tetraborate under acidic conditions (Sánchez-Rodas et al., 2010). To accomplish this, 10 mL of sample was combined with 15 mL of HCl, heated at 90 °C for 60 min in a microwave digestion unit (MARS, CEM Corporation, USA), and diluted with MilliQ water. Owing to the presence of undissolved or reduced Se forms in water samples, an additional 1 mL of HNO_3 was added to enhance oxidizing power and the program was extended to 90 min. The use of high purity HNO_3 (Optima™ HNO_3 or double-distilled TraceGrade HNO_3) was necessary to obtain suitable blank values.

2.4. Determination of selenium speciation

Unfortunately, the extremely low concentrations of Se in water samples obtained in 2014 precluded reliable speciation using the methods and instruments that were available. Two analytical techniques capable of measuring low concentrations of Se species were established and applied to samples collected in 2015: sequential selenium hydride generation (SSHG) using HG-AFS and ion chromatography paired with ICP-MS (IC-ICP-MS) (Donner and Siddique, 2018). The focus of these methods was to obtain data for the most commonly expected forms, Se(VI) and Se(IV). Sequential selenium hydride generation takes advantage of the ability of Se(IV) to form a hydride, and the inability of other species present to convert into a gaseous state; this can then be used to determine fractions of selenium present in a water sample. There are several variations of the SSHG (e.g., Chen et al., 2005; Cutter, 1978) and the approach herein was based on three treatments for separating total Se into three fractions:

i) Analysis of samples without pre-reduction = Se(IV)
ii) Microwave heating with HCl = Se(IV) + Se(VI)
iii) Microwave heating with HNO_3 and HCl = $\sum Se_{dissolved}$

The concentration of Se(VI) was obtained as the difference between Se(IV)+Se(VI) and Se(IV), and the difference between $\sum Se_{dissolved}$ and Se(IV)+Se(VI) was considered the “reduced Se” fraction. The latter is often referred to as “organo-Se”, but this term is imprecise as it does not include reduced inorganic Se compounds that have been found in aquatic systems and wastewaters, such as selenocynate ($SeCN^-$) (Wallschläger and Feldmann, 2010). Importantly, SSHG has some limitations that can produce significant artefacts and misleading results. For example, organo-Se compounds can decompose during the heat-acid reflux step applied to reduce Se(VI) to Se(IV), thereby giving an artificially high concentration of Se(VI) in waters rich in organic matter (Chen et al., 2005). Therefore, SSHG provides broader fractions of Se compounds and does not provide positive identification of individual forms. However, there are advantages to using it in a complementary analytical role. In particular it has an excellent limit of detection (typically ~10 ng L^{-1}), includes of Se-bearing colloids and provides an independent confirmation of analyses performed using ICP-MS. In each sequential step, multiple QC samples were included to ensure the complete reduction (or oxidation then subsequent reduction) of Se in samples. This included spiking 100 ng L^{-1} of Se(IV) or Se(VI) into a sample of Athabasca River water or tributary water. The solutions used for spiking were diluted from 2000 mg L^{-1} stock solutions of sodium selenate decahydrate (99.999% trace metal basis; Sigma Aldrich) and sodium selenite (99%; Sigma Aldrich), which were of a different source than that used to prepare the external calibration (Fluka Analytical; TraceCERT®). The average recovery of spiked samples compared to the expected value was 112 ± 5% (n = 4). NIST 1640a was also determined during analyses (108 ± 5% recovery; n = 2).

To compare with results obtained by SSHG, water samples from 2015 were also analyzed using an IC-ICP-MS method for determining Se(IV) and Se(VI) in natural freshwaters (Donner and Siddique, 2018). Briefly, the system consisted of the same quadrupole ICP-MS as described above, operated in chemical reaction cell mode using H_2 as a reaction gas instead of He as a collision gas. The use of H_2 allowed for the quantification of the more abundant ^{80}Se isotope by eliminating the interfering dimer $^{40}Ar_2^+$ (m/z = 80). To separate Se(VI) and Se(IV), a high performance IC (Thermo Scientific Dionex ICS-5000$^+$) with a Dionex IonPac AS7 anion exchange column and guard column was used. The mobile phase was dilute nitric acid delivered in a step-wise concentration gradient: 0–2 min (50 mM HNO_3), 2–4 min (400 mM HNO_3) and 4–5 min (50 mM HNO_3).

2.5. Selenium in fish muscle tissue

Acid digests of Trout-perch muscle tissue, SRMs, and digestion blanks were analyzed for total Se using both ICP-MS and HG-AFS. For HG-AFS analysis, 1 mL of digestate was combined with 9 mL of MilliQ water and 15 mL of HCl. Samples were pre-reduced for 60 min using the same heating procedure as described above for Se(VI) reduction and brought to a volume of 50 mL using MilliQ water before analysis using HG-AFS. Instrument operating conditions and calibration solutions were the same as those used to measure total Se in acid-digests of bitumen samples (Donner et al., 2018). Concentrations were derived from an 8-point linear calibration (0.02–4 μg L^{-1}) and reported as an average of duplicate injections (<2% RSD). Each digestion batch contained a minimum of three blanks and triplicates of two different SRMs (n = 6): NIST 1566b (Oyster Tissue; [Se] = 2.06 mg kg^{-1}) and NIST 1577c (Bovine Liver; [Se] = 2.031 mg kg^{-1}). The same digests were measured using ICP-MS after a 50x dilution with MilliQ water using the operating conditions described above. Quality control results for SRMs analyzed by HG-AFS and ICP-MS are provided in Fig. S2.

2.6. Data analysis

Selenium data from fish muscle was grouped into three categories based on their location on the Athabasca River relative to industrial activity: upstream, midstream (area of industrial activity) and downstream. Normality was assessed using Lilliefors test, following the removal of outliers ($n = 5$), determined as values > 3x the mean absolute deviation. A Student's *t*-test (one-tailed) was applied to test for significant differences ($p < 0.05$) between Se concentrations in the tissue of Trout-perch collected upstream of industrial activity, compared to the midstream and downstream reaches. Data analyses were performed using MatLab R2017a and Origin graphing software. Selenium data generated using ICP-MS yielded slightly better average recoveries of SRMs (NIST 1566b = 116%; NIST 1577c = 109%) and was chosen as the primary data source to be represented in the main text. Raw data from both instruments are provided in Table S2 (Clearwater River) and S3 (Athabasca River).

3. Results

3.1. Dissolved selenium in Athabasca River water and tributaries

The average concentration of dissolved (i.e., <0.45 μm fraction) Se in the main stem of the Athabasca River in 2014 was 0.11 ± 0.02 μg L^{-1} (n = 14) and 0.16 ± 0.02 μg L^{-1} (n = 21) in 2015 (Figs. 2A and 3A). Concentrations of Se were relatively consistent

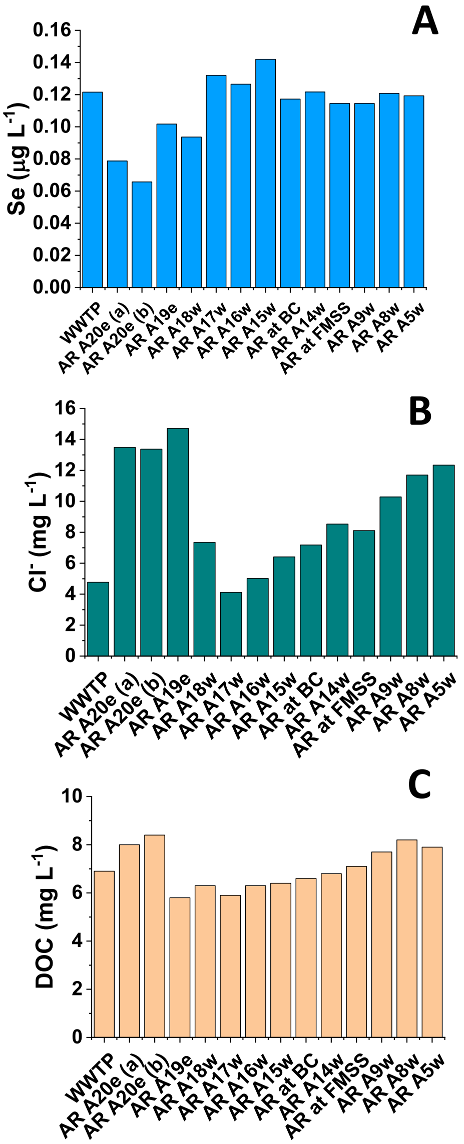

Fig. 2. Concentrations of dissolved (<0.45 µm) Se (Panel A), Cl⁻ (Panel B) and DOC (Panel C) in the main-stem of the Athabasca River during 2014. Sites are listed from left to right in order from upstream to downstream, with the area of greatest industrial activity located between sites A18w and A9w. Site duplicates are denoted with (a) or (b) and were collected 3 days apart.

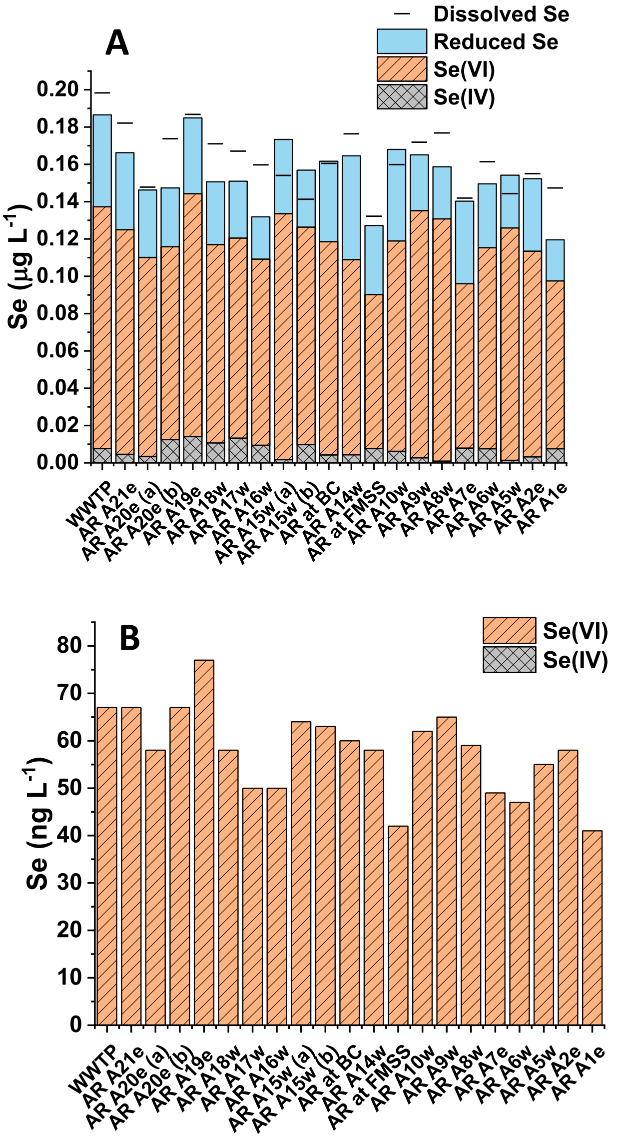

Fig. 3. Selenium speciation in Athabasca River water (2015) using SSHG (Panel A) and IC-ICP-MS (Panel B). Sites are listed from left to right in order from upstream to downstream, with the area of greatest industrial activity located between sites A18w and A9w. Site duplicates were collected 8 and 3 days apart for A20e and A15, respectively.

upstream to downstream, despite greater concentrations of Cl⁻ and dissolved organic carbon (DOC) (Fig. 2B and C). Higher Cl⁻ concentrations indicate greater influence from saline groundwater. In 2014, Se concentrations were lower at site A20e (Fig. 2A), whereas concentrations of Cl⁻ and DOC at this site were elevated relative to other sections of the river (Fig. 2B and C, respectively). This pattern is most likely the result of the Athabasca River mixing with the Clearwater River, which enters approximately 1.5 km upstream of site A20e (Fig. 1). Due to the low-flow conditions and substantial channelling, samples were collected from the eastern portion of the river and so were likely subject to greater influence by the Clearwater River. In 2015, when water levels were noticeably higher, a similar pattern of Cl⁻ concentrations was observed (Fig. S3B) but Se (Fig. 3A) and DOC concentrations were more consistent. (Fig. S3A).

Concentrations of dissolved Se in tributaries were generally lower than the Athabasca River (0.02–0.27 µg L^{-1}). Of the tributaries studied, two were previously identified as potentially receiving oil sands process affected water (OSPW) from industrial activity: Beaver Creek and McLean Creek (Ross et al., 2012; Sun et al., 2017). The Se concentrations in these two tributaries were similar to the Athabasca River and other tributaries (Fig. 4). The extremely low concentrations (<100 ng L^{-1}) observed in some tributaries (e.g., Steepbank River, Ells River, McKay River and Beaver Creek) are remarkable given the significant amount of exposure to surrounding industrial activity and natural erosion of bitumen outcrops. The concentration of Se in the Athabasca River and tributaries were also well below the US EPA guideline value for lotic systems (3.1 µg L^{-1}; US EPA, 2016) and are comparable to estimates of background dissolved Se concentrations for undisturbed surface waters (0.07–0.19 µg L^{-1}; Luoma and Rainbow, 2008) and global rivers (0.060 µg L^{-1}; Nriagu, 1989). Unfortunately, dissolved concentrations cannot be compared to guidelines described by the Canadian Council of Ministers of the Environment (CCME) for the protection of aquatic life, as the Se guideline value (1 µg L^{-1}) is based on total concentrations (i.e., bulk, unfiltered water; CCME,

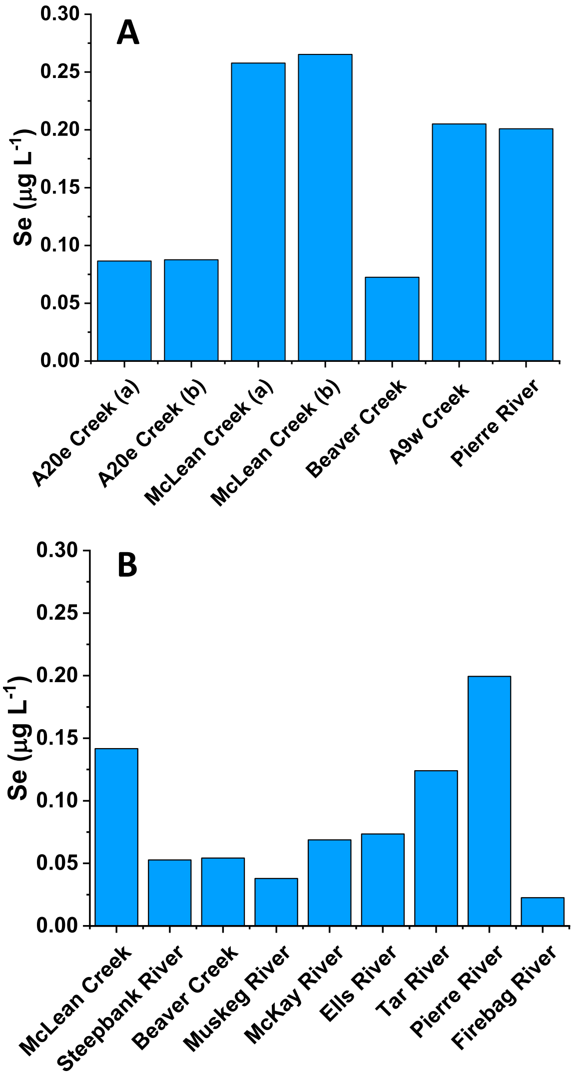

Fig. 4. Concentrations of dissolved (<0.45 µm) Se in selected tributaries along the Athabasca River in 2014 (Panel A) and 2015 (Panel B). Site duplicates are denoted with (a) or (b) and were collected approximately 1 h apart.

1987).

3.2. Selenium speciation in Athabasca River water and tributaries

The average concentration of Se(VI) in the Athabasca River determined using SSHG was 0.11 ± 0.015 µg L^{-1}. Concentrations of Se(IV) were close to, or below the LOD for HG-AFS (0.012 µg L^{-1}) and could not be quantified reliably (Fig. 3A). Only after samples were oxidized using HNO_3, full recovery of Se was obtained, as compared to analysis with ICP-MS (Fig. 3A), suggesting that a portion of the Se was neither Se(VI) nor Se(IV). Similar to dissolved concentrations, no increasing trend was observed upstream to downstream, failing to indicate inputs from oil sands mining or natural saline groundwater. Analysis using IC-ICP-MS revealed a very similar concentration profile (Fig. 3B), but suggested an even lower proportion of Se(IV) and Se(VI), as concentrations of Se(IV) were below the limit of quantification (LOQ; 14 ng L^{-1}) and the average concentration of Se(VI) was only 0.058 ± 0.009 µg L^{-1}. This discrepancy is likely a reflection of the differences between analytical methods, as the strong acid and heat required by SSHG may have promoted decomposition of Se-bearing molecules/colloids that were neither Se(VI) nor Se(IV). This was further revealed by the analysis of water from tributaries, where dissolved concentrations were extremely low (~100–300 ng L^{-1}), and Se speciation analysis by IC-ICP-MS did not yield concentrations above the LOQ. The results for tributary waters analyzed using SSHG were considered unreliable given that the waters contained extremely low concentrations of Se but abundant colloidal material (Cuss et al., 2018). To further study this issue, tributary waters were analyzed twice using SSHG: once with the microwave temperature programmed for 90 °C (as described above), and again with the temperature at 110 °C. Even this slight change in temperature promoted the generation of higher concentrations of Se during HG-AFS analysis, highlighting the uncertainty associated with analyzing low concentrations of Se in colloid-rich water (Fig. S4). Clearly, more work is required to understand both the chemical form and behavior of Se in the <0.45 µm fraction.

3.3. Selenium concentrations in Trout-perch muscle

The average concentration of Se in muscle of Trout-perch harvested from the Athabasca River was 2.2 ± 0.4 mg kg^{-1} ($n = 34$) and the concentration in upstream fish was not significantly higher ($p > 0.05$) than those from the midstream or downstream reaches (Fig. 5). The results for Se measurements in acid-digests by ICP-MS and HG-AFS were in good agreement (Table S3) and the outcome of the statistical analysis was the same. Greater variability in the concentrations of Se in the muscle tissue of Trout-perch from the Clearwater River, together with the low number of samples ($n = 5$), prevented a detailed assessment (Table S2); however, Se concentrations in Trout-perch from the Clearwater River were comparable to those collected from Athabasca River (1.1 ± 0.96 mg kg^{-1}; 0.08–2.2 mg kg^{-1}). To assess the potential influence of fish size or age as a factor controlling Se concentrations in muscle tissue, Trout-perch fork length and total weights were compared to Se concentrations. However, no significant correlation was observed between Se concentrations and either parameter ($p > 0.05$; Figs. S5 and S6). Selenium concentrations in Trout-perch muscle were also below guidelines issued by the US EPA (11.3 mg kg^{-1}) and the British Columbia Ministry of Environment (interim value of 4 mg kg^{-1}; BC MoE, 2014); Canadian Federal (CCME) tissue guidelines for Se have not been established. Although Se uptake by fish and other aquatic organisms involves a number of interrelated and site specific

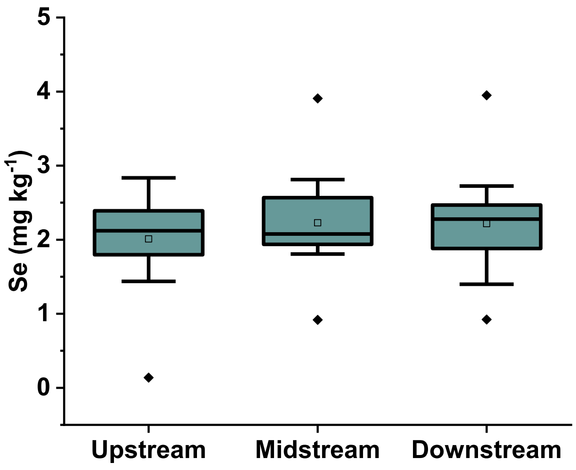

Fig. 5. Selenium concentration (dry-weight) in muscle tissue of Trout-perch collected from the lower Athabasca River ($n = 34$). No significant difference ($p > 0.05$) was observed in Se concentration from fish collected upstream (reference), midstream (industrial) or downstream (saline groundwater).

factors (see Discussion), the enrichment of Se in fish muscle relative to Athabasca River water (~2000 μg/kg versus ~0.2 μg/kg) speaks to the ability of aquatic organisms to accumulate Se. The natural enrichment of Se in fish relative to water is a reminder that measuring the concentration of Se in water is inadequate for determining its ecological implications.

4. Discussion

4.1. Se in the lower Athabasca River watershed

Previous assertions that Se is more abundant in Athabasca River water downstream of bitumen mining and upgrading (Kelly et al., 2010) have led to considerable public concern regarding fish and human health. However, that conclusion was based on limited data, with all values for the dissolved phase below detection limits and only one sample (downstream) containing a quantifiable amount of total Se (Kelly et al., 2010). The instrumentation and methods applied here yielded much lower limits of detection and failed to reveal evidence of increased Se concentrations in the Athabasca River due to bitumen mining and upgrading. Moreover, Se inputs to the Athabasca River from natural bitumen erosion and saline groundwater did not appear to pose an ecological threat. As the purpose of this study was to distinguish between these different sources and assess their relevance, sampling was purposely conducted under base-flow conditions. Additional studies are underway to assess the atmospheric deposition of Se from ABS mining and upgrading, as well as seasonal changes in trace element concentrations in the Athabasca River.

As a cautionary remark, the potential for Se contamination from bitumen processing still requires careful monitoring due to its enrichment in bitumen (Donner et al., 2018) and a general lack of knowledge regarding its fate in upgrading and refining processes. For example, in 2006, a major bitumen upgrading and refining facility near Edmonton (Alberta) discovered elevated concentrations (up to 600 $\mu g\ L^{-1}$) of Se in their effluent that was being discharged to the North Saskatchewan River (BC MoE, 2014). Since the problem was found, measures were taken to successfully reduce Se loadings by 80%; apparently, however, sediment and biota immediately downstream still showed elevated Se concentrations (BC MoE, 2014).

4.2. Colloidal versus truly dissolved Se species

Broadly defined as particles that have a length between 1 nm and 1 μm in at least one dimension, the colloidal phase is often incorrectly equated with the "dissolved" fraction, which is operationally defined as the material that passes through a 0.45 μm membrane (Filella, 2007). Colloids are composed of an array of inorganic (e.g., Fe oxyhydroxides, Mn oxides, carbonate minerals, clays) and organic (e.g., humic substances and fulvic acids) particles, and are known for their considerable influence on trace element speciation, transport and bioavailability (Lead and Wilkinson, 2007). Selenium can be transported as part of the colloidal fraction by way of reversible surface adsorption, incorporation during mineral formation or through biological uptake into tissue. The uptake rates and strength of bonding can differ greatly depending on the speciation of dissolved Se, as selenate and selenite display remarkably different behavior. With respect to adsorption, selenate anions are highly mobile under oxidizing conditions and retained primarily through weak bonding mechanisms such as outer-sphere complexation or attraction in the diffuse swarm (Fernández-Martínez and Charlet, 2009; Hayes et al., 1987; Zhang and Sparks, 1990; Sposito, 1995). Conversely, selenite mobility is strongly influenced by adsorption phenomena and displays a much higher affinity for reactive sites on particle surfaces (Fernández-Martínez and Charlet, 2009), particularly −OH bonds on common Fe minerals (Hayes et al., 1987; Zhang and Sparks, 1990), functional groups in DOM (Bruggeman et al., 2007), or ternary complexes of Fe-DOM constituents (Gustafsson and Johnsson, 1994; Martin et al., 2017; Peel et al., 2017). Selenite is also considerably more bioavailable than Se(VI) and is rapidly sequestered by phytoplankton and other base-level consumers, as well as being used for dissimilatory reduction by sediment dwelling microorganisms (Luoma and Rainbow, 2008). Therefore, unless a major anthropogenic source exists, Se(VI) tends to predominate in oxic surface waters and a larger proportion of "organo-Se" (either incorporated, surface-bound, or as a true biomolecule) is observed in organic-rich waters (Zhang and Moore, 1996).

This general description of biogeochemical behavior is consistent with the results of Se speciation observed in the Athabasca River. Tributaries drain massive areas of boreal forest and peatlands, and deliver large amounts of DOM and Fe to the Athabasca River. A recent study of trace element speciation using asymmetrical flow field-flow fraction coupled to ICP-MS determined that both the concentration and proportion of trace elements (As, Co, Fe, Mn, Pb, U, Zn) bound to natural colloids increased due to inputs from these tributaries, and the concentrations of small, mainly ionic, forms of As, Ba, Mo, and U decreased upstream-downstream, suggesting binding and removal from the dissolved phase (Cuss et al., 2018). The input of DOM and Fe rich material to the Athabasca River could therefore be a primary factor governing the low concentrations of Se(IV). While Se was not included in the list of elements studied by Cuss et al., 2018, dissolved As (also present in water as oxyanions) had the strongest correlation with DOC, which was consistent with observations of its redox-state speciation in a companion study (Donner et al., 2017).

With large fluctuations in suspended particles and wetland material combined with considerable inputs of Fe and organic matter from tributaries, understanding the bioavailability and bioaccessibility of Se as it relates to natural or anthropogenic inputs is challenging and illustrates the need for biological indicators. Indeed, measuring the total (particulate + dissolved) Se concentrations provides additional detail, but Se must be present in the dissolved phase to enter the food chain via uptake by microflora − the transfer rates of Se associated with particulates to higher-level organisms are not well defined and vary depending on their composition (Hodson et al., 2010). In other words, assessing whether suspended particulate matter is a relevant dietary source of Se requires knowledge of its composition (ranging from algae to clay minerals), which cannot be obtained by digesting a bulk water sample and measuring total Se. The same issue exists for the colloidal phase; despite knowing that a significant portion of Se < 0.45μm is likely colloidal, little information can be inferred regarding its bioaccessibility.

4.3. Selenium in Trout-perch

The concentration and bioaccumulation of Se in fish tissue varies with a number of site specific factors, making it difficult to compare with other species of fish or the same species in different habitats (Stewart et al., 2010). Even within the same watershed, fish have seasonal migration routes or are capable of foraging over long distances. Therefore, comparisons of Se concentrations in fish collected from different areas in a river may not be reliable. For that reason, a comparison of Trout-perch in the same water body is a valuable and more reliable indicator of Se exposure, as their lack of migration increases the chances of identifying specific inputs. Unlike elements such as Hg, Cs, and Tl, fish age (excluding juveniles) and trophic position are not considered highly relevant factors for the bioaccumulation of Se (Gantner et al., 2009). Fish size has been linked to Se concentrations, but due to dietary changes at specific times in the life-cycle and not simply due to age or size alone (Stewart et al., 2010). This is consistent with the lack of relationship observed here between Se concentrations in Trout-perch muscle and fork length. Due to these important differences between species and habitat, it is challenging to compare the present results with data for fish from other areas. A study of the biological impacts of bitumen derived contaminants found that the average concentration of Se in the liver of white sucker (*Catostomus commersonii*) in the Muskeg River was 0.87 mg kg^{-1} ($n = 6$; Arens et al., 2017). Unfortunately, the Se data in that study was compared only to white sucker sampled from a nearby reference lake (lentic system), wherein the processes governing the biogeochemical cycling and hence exposure to and uptake of Se likely differ compared to fish from the lotic system in the Muskeg River. For perspective, the results of a nationwide study (541 sites) of river and stream health in the United States of America conducted in 2008 and 2009 revealed that fish species commonly consumed by humans had a median Se concentration of 1.90 mg kg^{-1} (wet-weight; USEPA, 2016).

The presence of Se in aquatic systems is of interest both due to its potential toxicity, and its role as an essential micronutrient. However, what has not yet been discussed with respect to its presence in the Athabasca River is its potential role in mitigating the toxicity of other potentially toxic metals (Ikemoto et al., 2004; Levander and Argrett, 1969; Magos et al., 2008; Morris, 2015; Sørmo et al., 2011). Selenium is well known for its antagonistic relationship with Hg in animal tissue, limiting toxic effects through the formation of highly stable mercury selenides (Hg—S) (Khan and Wang, 2009; Sørmo et al., 2011). Given concern regarding Hg emissions from the mining and upgrading of ABS (Kirk et al., 2014; Willis et al., 2018), an assessment of the biological relevance of Hg in aquatic organisms in the lower Athabasca River should include information about Se. A good example of this comes from a study of Se contaminated lakes near the metal smelters in Sudbury, Canada, where fish (walleye, *Sander vitreus* and yellow perch, *Perca flavescens*) were harvested from a series of lakes varying in distance from the smelters (Chen et al., 2001). It was found that the concentrations of Se and Hg in fish muscle tissue had a significant, inverse correlation, suggesting that the high input of Se to lakes from smelting had an antagonistic effect on Hg concentrations (Chen et al., 2001).

5. Conclusions

Surface water samples collected from the Athabasca River and tributaries in 2014 and 2015 failed to reveal elevated concentrations of Se either due to naturally saline groundwater inputs or emissions from bitumen surface mining and upgrading in the ABS region. Similarly, no significant increase ($p < 0.05$) in the Se concentration of muscle tissue in Trout-perch was observed for regions near-industry or downstream of industry compared to upstream. Despite the enrichment of Se in the bitumen (organic) fraction of ABS, concentrations in the Athabasca River and Trout-perch muscle were consistently low and do not suggest Se contamination by ABS mining and upgrading activities.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2018.09.067.

References

Alexander, D.A., Chambers, D.P., 2016. Assessment of seven Canadian Rivers in relation to stages in oil sands industrial development, 1972 to 2010. Environ. Rev. 24 (4), 484–494.

Alexander, A.C., Chambers, P.A., Jeffries, D.S., 2017. Episodic acidification of 5 rivers in Canada's oil sands during snowmelt: a 25-year record. Sci. Total Environ. 599–600, 739–749.

Arens, C.J., Arens, J.C., Hogan, N.S., Kavanagh, R.J., Berrue, F., Van Der Kraak, G.J., van den Heuvel, M.R., 2017. Population impacts in white sucker (*Catostomus commersonii*) exposed to oil sands-derived contaminants in the Athabasca River. Environ. Toxicol. Chem. 36 (8), 2058–2067.

Bicalho, B., Grant-Weaver, I., Sinn, C., Donner, M.W., Woodland, S., Pearson, G., Larter, S., Duke, J., Shotyk, W., 2017. Determination of ultratrace (<0.1 mg/kg) elements in Athabasca Bituminous Sands mineral and bitumen fractions using inductively coupled plasma sector field mass spectrometry (ICP-SFMS). Fuel 206, 248–257.

Bruggeman, C., Maes, A., Vancluysen, J., 2007. The interaction of dissolved Boom Clay and Gorleben humic substances with selenium oxyanions (selenite and selenate). Appl. Geochem. 22, 1371–1379.

CCME, 1999. Canadian Environmental Quality Guidelines. Canadian Council of Ministers of the Environment. Environment Canada, Hull, Quebec. Accessed at. http://st-ts.ccme.ca/en/index.html?lang=en&factsheet=197#aql_fresh_date.

Chapman, P.M., 2007. Selenium thresholds for fish from cold freshwaters. Hum. Ecol. Risk Assess. 13, 20–24.

Chen, Y.-W., Belzile, N., Gunn, J.M., 2001. Antagonistic effect of selenium on mercury assimilation by fish populations near Sudbury metal smelters? Limnol. Oceanogr. 46 (7), 1814–1818.

Chen, Y.-W., Zhou, X.-L., Tong, J., Truong, Y., Belzile, N., 2005. Photochemical behavior of inorganic and organic selenium compounds in various aqueous solutions. Anal. Chim. Acta 545 (2), 149–157.

Conly, F.M., Crosley, R.W., Headley, J.V., Quagraine, E.K., 2007. Assessment of metals in bed and suspended sediments in tributaries of the lower Athabasca River. J. Environ. Sci. Health 42 (8), 1021–1028.

Cuss, C.W., Donner, M.W., Grant-Weaver, I., Noernberg, T., Pelletier, R., Sinnatamby, R.N., Shotyk, W., 2018. Fingerprinting sources of trace elements in aquatic systems by measuring their distribution amongst colloidal species. Sci. Total Environ. 642, 1242–1251.

Cuss, C.W., Donner, M.W., Noernberg, T., Pellletier, R., Shotyk, W. Disentangling the seasonal and source-based variation of dissolved organic matter quality in a large river and its source waters using EEM-PARAFAC-SOM. J. Geophys. Res. Biogeosci. (In review).

Cutter, G.A., 1978. Species determination of selenium in natural waters. Anal. Chim. Acta 98 (1), 59–66.

Deforest, D.K., Brix, K.V., Adams, W.J., 1999. Critical review of proposed residue-based selenium toxicity thresholds for freshwater. Hum. Ecol. Risk Assess. 5 (6), 1187–1228.

Donner, M.W., Siddique, T., 2018. A rapid and sensitive IC-ICP-MS method for determining selenium speciation in natural waters. Can. J. Chem. https://doi.org/10.1139/cjc-2017-0637 (in press).

Donner, M.W., Javed, M.B., Shotyk, W., Francesconi, K.A., Siddique, T., 2017. Arsenic speciation in the lower Athabasca River watershed: a geochemical investigation of the dissolved and particulate phases. Environ. Pollut. 224, 265–274.

Donner, M.W., Bicalho, B., Sinn, C., Shotyk, W., 2018. Selenium and sulphur in Athabasca bituminous sands mineral and bitumen fractions. Fuel 224, 718–725.

Ellis, J., Jasechko, S., 2018. Formation waters discharge to rivers near oil sands projects. Hydrol. Process. 32 (4), 533–549.

Fernández-Martínez, A., Charlet, L., 2009. Selenium environmental cycling and bioavailability: a structural chemist point of view. Rev. Environ. Sci. Biotechnol. 8 (1), 81–110.

Filella, M., 2007. Colloidal properties of submicron particles in natural waters. In: Wilkinson, K.J., Lead, J.R. (Eds.), Environmental Colloids and Particles Behaviour, Separation and Characterisation. John Wiley & Sons, Ltd, England, pp. 17–93.

Gantner, N., Power, M., Babaluk, J.A., Reist, J.D., Köck, G., Lockhart, L.W., Solomon, K.R., Muir, D.C.G., 2009. Temporal trends of mercury, cesium, potassium, selenium, and thallium in Arctic Char (*Salvelinus alpinus*) from Lake Hazen, Nunavut, Canada: effects of trophic position, size, and age. Environ. Toxicol. Chem. 28 (2), 254–263.

Gibbons, W.N., Munkittrick, K.R., McMaster, M.E., Taylor, W.D., 1998. Monitoring aquatic environments receiving industrial effluents using small fish species 2: comparison between responses of trout-perch (*percopsis omiscomaycus*) and white sucker (*catostomus commersoni*) downstream of a pulp mill. Environ. Toxicol. Chem. 17 (11), 2238–2245.

Gibson, J.J., Fennell, J., Birks, S.J., Yi, Y., Moncur, M.C., Hansen, B., Jasechko, S., 2013. Evidence of discharging saline formation water to the Athabasca River in the oil sands mining region, Northern Alberta. Can. J. Earth Sci. 50 (12), 1244–1257.

Goldschmidt, V.M., 1937. The principles of distribution of chemical elements in minerals and rocks. J. Chem. Soc. 655–673.

Guéguen, C., Clarisse, O., Perroud, A., McDonald, A., 2011. Chemical speciation and partitioning of trace metals (Cd, Co, Cu, Ni, Pb) in the lower Athabasca river and its tributaries (Alberta, Canada). J. Environ. Monit. 13 (10), 2865–2872.

Gustafsson, J.P., Johnsson, L., 1994. The association between selenium and humic substances in forested ecosystems—Laboratory Evidence. Appl. Organomet. Chem. 8, 141–147.

Hamilton, S.J., 2002. Rationale for a tissue-based selenium criterion for aquatic life. Aquat. Toxicol. 57, 85–100.

Hayes, K.F., Roe, A.L., Brown Jr., G.E., Hodgson, K.O., Leckie, J.O., Parks, G.A., 1987. In Situ x-ray absorption study of surface complexes: selenium oxyanions on α-FeOOH. Science 238 (4828), 783–786.

Hillwalker, W.E., Jepson, P.C., Anderson, K.A., 2006. Selenium accumulation patterns in lotic and lentic aquatic systems. Sci. Total Environ. 366, 367–379.

Hodson, P.V., Reash, R.J., Canton, S.P., Campbell, P.V., Delos, C.G., Faribrother, A., Hitt, N.P., Miller, L.L., Ohlendorf, H.M., 2010. Selenium risk characterization. In: Chapman, P.M., Adam s, W.J., Brooks, M.L., Delos, C.G., Luoma, S.N., Maher, W.A., Ohlendorf, H.M., Presser, T.S., Shaw, D.P. (Eds.), Ecological Assessment of Selenium in the Aquatic Environment. CRC Press, Taylor & Francis Group, Boca Raton, pp. 233–256.

Ikemoto, T., Kunito, T., Tanaka, H., Baba, N., Miyazaki, N., Tanabe, S., 2004. Detoxification mechanism of heavy metals in marine mammals and seabirds: interaction of selenium with mercury, silver, copper, zinc, and cadmium in liver. Arch. Environ. Contam. Toxicol. 47, 402–413.

Javed, M.B., Cuss, C.W., Grant-Weaver, I., Shotyk, W., 2017. Size-resolved Pb distribution in the Athabasca River shows snowmelt in the bituminous sands region an insignificant source of dissolved Pb. Sci. Rep. 7, 43622.

Kelly, E.N., Schindler, D.W., Hodson, P.V., Short, J.W., Radmanovich, R., Nielsen, C.C., 2010. Oil sands development contributes elements toxic at low concentrations to the Athabasca River and its tributaries. Proc. Natl. Acad. Sci. U.S.A. 107 (37), 16178–16183.

Khan, M.A.K., Wang, F., 2009. Mercury—selenium compounds and their toxicological significance: toward a molecular understanding of the mercury—selenium antagonism. Environ. Toxicol. Chem. 28 (8), 1567–1577.

Kirk, J.L., Muir, D.C.G., Gleason, A., Wang, X., Lawson, G., Frank, R.A., Lehnherr, I., Wrona, F., 2014. Atmospheric deposition of mercury and methylmercury to landscapes and waterbodies of the Athabasca Oil Sands Region. Environ. Sci. Technol. 48, 7374–7383.

Lead, J.R., Wilkinson, K.J., 2007. Environmental colloids and particles: current knowledge and future developments. In: Wilkinson, K.J., Lead, J.R. (Eds.), Environmental Colloids and Particles Behaviour, Separation and Characterisation. John Wiley & Sons, Ltd, England, pp. 1–15.

Lemly, D.A., 1998. Pathology of selenium poisoning in fish. In: Frankenberger Jr., W.T., Engberg, R.A. (Eds.), Environmental Chemistry of Selenium. Marcel Dekker, Inc., New York, NY, pp. 281–296.

Lenz, M., Lens, P.N.L., 2009. The essential toxin: the changing perception of selenium in environmental sciences. Sci. Total Environ. 407 (12), 3620–3633.

Levander, O.A., Argrett, L.C., 1969. Effects of arsenic, mercury, thallium, and lead on selenium metabolism in rats. Toxicol. Appl. Pharmacol. 14, 308–314.

Luoma, S.N., 2009. Emerging opportunities in management of selenium contamination. Environ. Sci. Technol. 43, 8483–8487.

Luoma, S.N., Rainbow, P.S., 2008. Selenium: dietary exposure, trophic transfer and food web effects. In: Metal Contamination in Aquatic Environments: Science and Lateral Management. Cambridge University Press, New York, NY, p. 573p.

Magos, L., Webb, M., Clarkson, T.W., 2008. The interactions of selenium with cadmium and mercury. Crit. Rev. Toxicol. 8 (1), 1–42.

Martin, D.P., Seiter, J.M., Lafferty, B.J., Bednar, A.J., 2017. Exploring the ability of cations to facilitate binding between inorganic oxyanions and humic acid. Chemosphere 166, 192–196.

BC MoE, 2014. British Columbia Ministry of Environment. Ambient Water Quality Guidelines for Selenium Technical Report Update. Accessed at: https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/wqgs-wqos/approved-wqgs/bc_moe_se_wqg.pdf.

Morris, D.L., 2015. Chemistry and activity of selenium dioxide and selenite ions. In: Preedy, V.R. (Ed.), Selenium: Chemistry, Analysis, Function and Effects. The Royal Society of Chemistry, Cambridge, UK, pp. 65–80.

Nriagu, J.O., 1989. Global cycling of selenium. In: Inhat, M. (Ed.), Occurrence and Distribution of Selenium. CRC Press, Boca Raton, Florida, pp. 327–340.

Ohlendorf, H.M., Hoffman, D.J., Saiki, M.K., Aldrich, T.W., 1986. Embryonic mortality and abnormalities of aquatic birds: apparent impacts of selenium from irrigation drainwater. Sci. Total Environ. 52 (1–2), 49–63.

Ohlendorf, H.M., Hothem, R.L., Bunck, C.M., Marois, K.C., 1990. Bioaccumulation of selenium in birds at Kesterson Reservoir, California. Arch. Environ. Contam. Toxicol. 19 (4), 495–507.

Outridge, P.M., Scheuhammer, A.M., Fox, G.A., Braune, B.M., White, L.M., Gregorich, L.J., Keddy, C., 1999. An assessment of the potential hazards of environmental selenium for Canadian water birds. Environ. Rev. 7 (2), 81–96.

Peel, H.R., Martin, D.P., Bednar, A.J., 2017. Extraction and characterization of ternary complexes between natural organic matter, cations, and oxyanions from a natural soil. Chemosphere 176, 125–130.

Pilote, M., Turcotte, A.C., Gagné, F., Gagnon, C., 2018. Metal bioaccumulation and biomarkers of effects in caged mussels exposed in the Athabasca oil sands area. Sci. Total Environ. 610–611, 377–390.

Ross, M.S., Pereira, A.D.S., Fennell, J., Davies, M., Johnson, J., Sliva, L., Martin, J.W., 2012. Quantitative and qualitative analysis of naphthenic acids in natural waters surrounding the canadian oil sands industry. Environ. Sci. Technol. 46 (23), 12796–12805.

Sánchez-Rodas, D., Corns, W.T., Chen, B., Stockwell, P.B., 2010. Atomic fluorsecence spectrometry: a suitable detection technique in speciation studies for arsenic, selenium, antimony and mercury. J. Anal. At. Spectrom. 25, 933–946.

Selby, D., 2005. Direct radiometric dating of hydrocarbon deposits using rhenium-osmium isotopes. Science 308 (5726), 1293–1295.

Shotyk, W., Bicalho, B., Cuss, C.W., Donner, M.W., Grant-Weaver, I., Haas-Neill, S., Javed, M.B., Krachler, M., Noernberg, T., Pelletier, R., Zaccone, C., 2017. Trace metals in the dissolved fraction (< 0.45 μm) of the lower Athabasca River: analytical challenges and environmental implications. Sci. Total Environ. 580, 660–669.

Simmons, D.B.D., Wallschläger, D., 2005. A critical review of the biogeochemistry and ecotoxicology in lotic and lentic environments. Environ. Toxicol. Chem. 24 (6), 1331–1343.

Sørmo, E.G., Ciesielski, T.M., Øverjordet, I.B., Lierhagen, S., Eggen, G.S., Berg, T., Jenssen, B.M., 2011. Selenium moderates mercury toxicity in free-ranging freshwater fish. Environ. Sci. Technol. 45 (15), 6561–6566.

Spafford, M.D., 1999. Trout-perch *Percopsis Omiscomaycus* (Walbaum) and Lake Chub Couesius Plumbeus (Agassiz), as Sentinel Monitoring Species in the Athabasca River, Alberta. Thesis. University of Alberta, Edmonton, Alberta.

Sposito, G., 1995. Adsorption as a problem in coordination chemistry: the concept of the surface complex. In: Huang, C.P., O'Melia, C.R., Morgan, J.J. (Eds.), Aquatic Chemistry Interfacial and Interspecies Processes. American Chemical Society, Washington, DC, pp. 33–57.

Stewart, R., Grosell, M., Buchwalter, D., Fisher, N., Luoma, S., Mathews, T., Orr, P., Wang, W.-X., 2010. Bioaccumulation and trophic transfer of selenium. In: Chapman, P.M., Adam s, W.J., Brooks, M.L., Delos, C.G., Luoma, S.N., Maher, W.A., Ohlendorf, H.M., Presser, T.S., Shaw, D.P. (Eds.), Ecological Assessment of Selenium in the Aquatic Environment. CRC Press, Taylor & Francis Group, Boca Raton, pp. 93–139.

Sun, C., Shotyk, W., Cuss, C.W., Donner, M.W., Fennell, J., Javed, M., Noernberg, T., Poesch, M., Pelletier, R., Sinnatamby, N., Siddique, T., Martin, J.W., 2017. Characterization of naphthenic acids and other dissolved organics in natural water from the Athabasca Oil Sands Region, Canada. Environ. Sci. Technol. 51 (17), 9524–9532.

USEPA, 2016. Aquatic Life Ambient Water Quality Criterion for Selenium – Freshwater. United States Environmental Protection Agency. https://www.epa.gov/sites/production/files/2016-07/documents/aquatic_life_awqc_for_selenium_-_freshwater_2016.pdf.

Wallschläger, D., Feldmann, J., 2010. Formation, occurrence, significance, and analysis of organoselenium and organotellurium compounds in the environment. In: Sigel, A., Sigel, H., Sigel, R.K.O.((Eds.), Organometallics in Environment and Toxicology: Metal Ions in Life Sciences. Royal Society of Chemistry, Cambridge, UK, pp. 319–364.

Willis, C.E., Kirk, J.L., Louis, V.L.S., Lehnherr, I., Ariya, P.A., Rangel-Alvarado, R.B., 2018. Sources of methylmercury to snowpacks of the Alberta Oil Sands Region: a study of in situ methylation and particulates. Environ. Sci. Technol. 52, 531–540.

Young, T.G., Finley, K., Adams, W.J., Besser, J., Hopkins, W.D., Jolley, D., McNaughton, E., Presser, T.S., Shaw, P., Unrine, J., 2010. What you need to know about selenium. In: Chapman, P.M., Adam s, W.J., Brooks, M.L., Delos, C.G., Luoma, S.N., Maher, W.A., Ohlendorf, H.M., Presser, T.S., Shaw, D.P. (Eds.), Ecological Assessment of Selenium in the Aquatic Environment. CRC Press, Taylor & Francis Group, Boca Raton, pp. 7–46.

Zhang, Y., Moore, J.N., 1996. Selenium fractionation and speciation in a wetland system. Environ. Sci. Technol. 30, 2613–2619.

Zhang, P., Sparks, D.L., 1990. Kinetics of selenate and selenite adsorption/desorption at the goethite/water Interface. Environ. Sci. Technol. 24 (12), 1848–1856.

Zhu, Y., Guéguen, C., 2016. Evaluation of free/labile concentrations of trace metals in Athabasca oil sands region streams (Alberta, Canada) using diffusive gradient in thin films and a thermodynamic equilibrium model. Environ. Pollut. 219, 1140–1147.