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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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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 ± 0.02 μg L^{-1}; $n = 14$) and 2015 (0.16 ± 0.02 μg 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 ± 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 μg L^{-1}), which was most likely present in the form of dissolved organic colloids.

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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

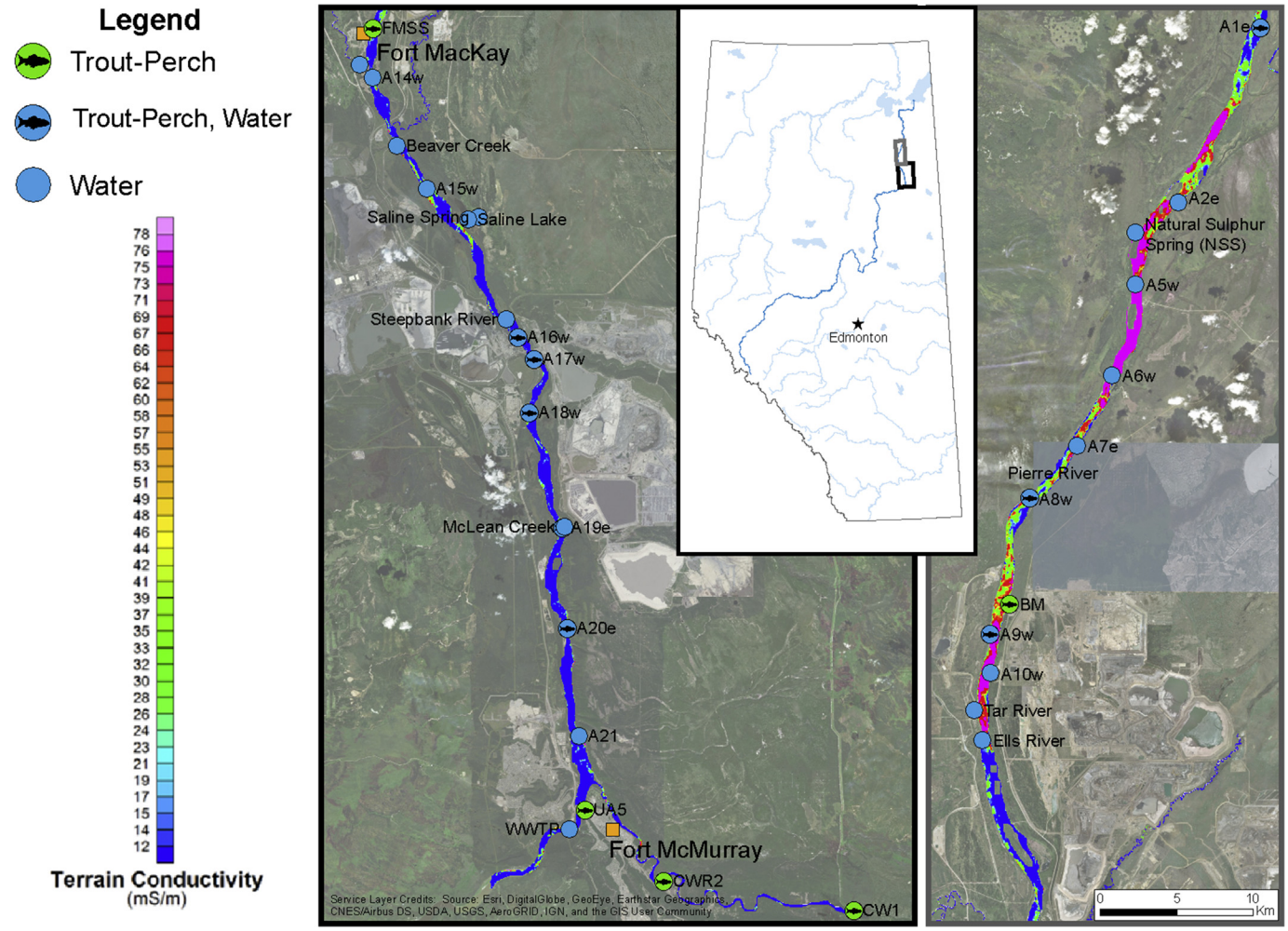

Fig. 1. Map of the study area and sampling locations during the 2014 (water samples and Trout-perch) and 2015 (water samples only) sampling campaigns. Map begins at the bottom of the left panel and continues from the bottom of the right panel. Water sampling locations for Pierre River and McKay River 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

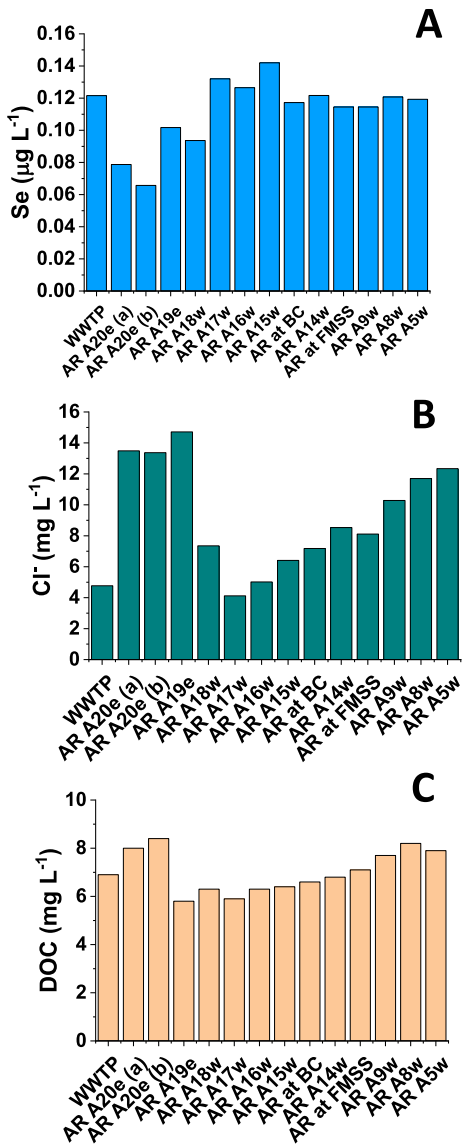

Fig. 2. Concentrations of dissolved (<0.45 µm) Se (Panel A), Cl^- (Panel B) and DOC (Panel C) in the main-stem of the Athabasca River during 2014. Sites are listed from left to right in order from upstream to downstream, with the area of greatest industrial activity located between sites A18w and A9w. Site duplicates are denoted with (a) or (b) and were collected 3 days apart.

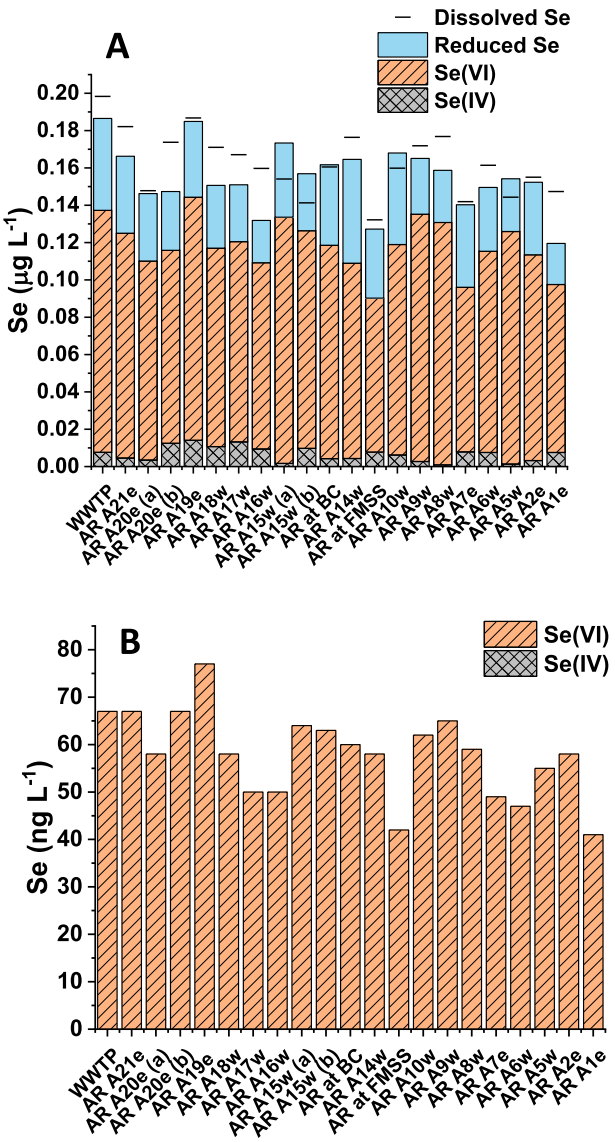

Fig. 3. Selenium speciation in Athabasca River water (2015) using SSHG (Panel A) and IC-ICP-MS (Panel B). Sites are listed from left to right in order from upstream to downstream, with the area of greatest industrial activity located between sites A18w and A9w. Site duplicates were collected 8 and 3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

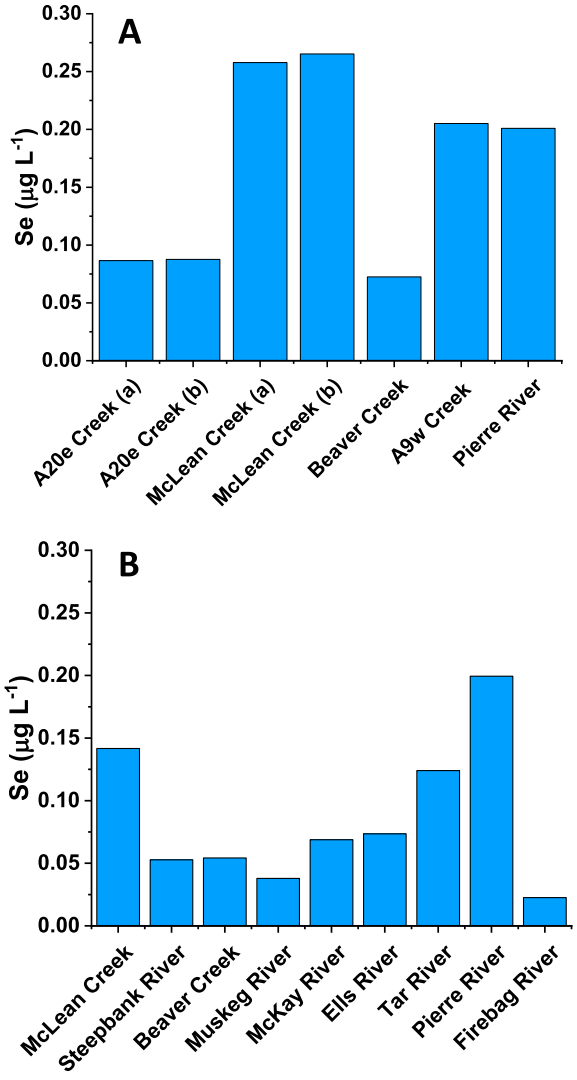

Fig. 4. Concentrations of dissolved (<0.45 µm) Se in selected tributaries along the Athabasca River in 2014 (Panel A) and 2015 (Panel B). Site duplicates are denoted with (a) or (b) and were collected approximately 1 h apart.

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 $0.11 \pm 0.015\ \mu g\ L^{-1}$. Concentrations of Se(IV) were close to, or below the LOD for HG-AFS ($0.012\ \mu g\ L^{-1}$) 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 $0.058 \pm 0.009\ \mu g\ L^{-1}$. 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 $2.2 \pm 0.4\ mg\ kg^{-1}$ ($n = 34$) 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 ($1.1 \pm 0.96\ mg\ kg^{-1}$; 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

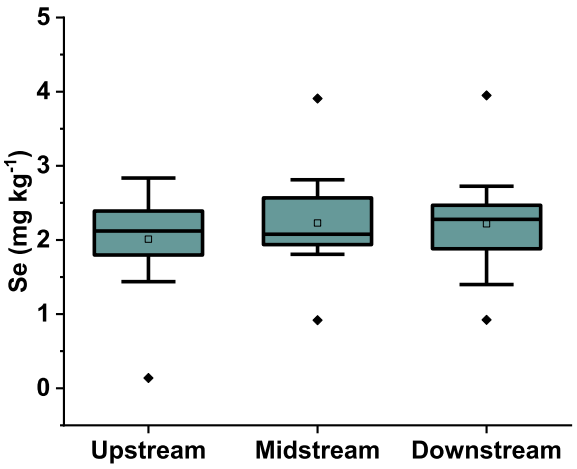

Fig. 5. Selenium concentration (dry-weight) in muscle tissue of Trout-perch collected from the lower Athabasca River ($n = 34$). No significant difference ($p > 0.05$) was observed in Se concentration from fish collected upstream (reference), midstream (industrial) or downstream (saline groundwater).

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 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).

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.

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