Contents lists available at ScienceDirect

Science of the Total Environment





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Bioaccumulation of Tl in otoliths of Trout-perch (*Percopsis omiscomaycus*) from the Athabasca River, upstream and downstream of bitumen mining and upgrading*



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HIGHLIGHTS

- Concentrations of trace elements were determined in fish otoliths using ICP-QMS.
- Compared to river water, Tl shows the greatest enrichment of any element.
- Thallium dissolved in the Athabasca River is at natural, background levels.
- The enrichment of Tl in the fish otoliths is a natural process.
- There is no significant difference in enrichment upstream or downstream of industry.

ARTICLE INFO

Article history: Received 11 June 2018 Received in revised form 21 September 2018 Accepted 24 September 2018 Available online 27 September 2018

Editor: Filip M.G. Tack

Keywords: Thallium Trout-perch Otoliths Athabasca River Bituminous sands

GRAPHICAL ABSTRACT



ABSTRACT

It has been suggested that open pit mining and upgrading of bitumen in northern Alberta releases TI and other potentially toxic elements to the Athabasca River and its watershed. We examined TI and other trace elements in otoliths of Trout-perch (*Percopsis omiscomaycus*), a non-migratory fish species, collected along the Athabasca River. Otoliths were analyzed using ICP-QMS, following acid digestion, in the metal-free, ultraclean SWAMP laboratory. Compared to their average abundance in the dissolved (<0.45 µm) fraction of Athabasca River, TI showed the greatest enrichment in otoliths of any of the trace elements, with enrichments decreasing in the order TI, Sr, Mn, Zn, Ba, Th, Ni, Rb, Fe, Al, Cr, Ni, Cu, Pb, Co, Li, Y, V, and Mo. Normalizing TI in the otoliths to the concentrations of lithophile elements such as Li, Rb, Al or Y in the same tissue reveals average enrichments of 177, 22, 19 and 190 times, respectively, relative to the corresponding ratios in the water. None of the element concentrations (TI, Li, Rb, Al, Y) or ratios were significantly greater downstream of industry compared to upstream. This natural bioaccumulation of TI most likely reflects the similarity in geochemical and biological properties of TI⁺ and K⁺.

☆ The authors declare no competing financial interest
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Summary of main findings: Thallium is enriched in fish otoliths, relative to the chemical composition of the river, to the same degree both upstream and downstream of industry.

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1. Introduction

Based upon snowpack sampling, it was suggested that open pit mining and upgrading of bitumen in northern Alberta "releases the 13 elements considered priority pollutants (PPE) under the Environmental Protection Agency's Clean Water Act, via air, soil and water, to the Athabasca River and its watershed" (Kelly et al., 2010, PNAS 107:16178, line 1). The priority pollutants listed by Kelly et al. (2010) refer to Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl and Zn. The appearance of Tl on this list of elements of concern is especially disconcerting, as it is more toxic to humans than either Cd, Hg or Pb (Peter and Viraraghavan, 2005). Subsequent studies of precipitation in the area have further extended the list of elements of concern to many other trace metals and metalloids (Bari et al., 2014; Guéguen et al., 2016). Fish is an important component of the traditional diet of First Nations communities in northern Alberta, and concerns about fish health (Tetreault et al., 2003; Schwalb et al., 2015; Arens et al., 2017; Parrott et al., 2018) as well as fish taste (Barona et al., 2011) are of particular importance. Concerns have also been expressed about impacts of trace elements on other aquatic organisms including invertebrate communities (Gerner et al., 2017) and mussels (Pilote et al., 2018). Examination of existing, long-term monitoring data revealed elevated concentrations of Al and Cu in the Athabasca River during periods of episodic acidification (pH < 6.5) at snowmelt (Fiera (Biological Consulting Ltd), 2013). Recently it was suggested that Tl and other trace elements are similarly affected (Alexander et al., 2017).

As part of a multi-disciplinary study on the physics, chemistry, and biology of groundwater-surface interactions in the lower reaches of the Athabasca River, we collected Trout-perch (Percopsis omiscomaycus) to explore its use as a biomonitor of potentially toxic trace elements; early work had suggested that this fish could be used as a sentinel species for studying environmental change in this watershed (Spafford, 1999). Also known as the Sand Minnow, and with features resembling both the trout and the perch (Kocovsky et al., 2014), this small fish (typically not >10 cm long) is non-migratory (Natureserve, 2013), providing an opportunity to use the fish to indicate water quality conditions at discrete locations along the river. Here, we examine the trace element chemistry of otoliths, the small, primarily calcium carbonate (aragonite) structures that form extracellularly within the inner ear of the fish (Degens et al., 1969; Campana, 1999). Otoliths are metabolically inert so that otolith material is not reabsorbed after deposition, and formation occurs continually in concentric layers of proteins and calcium carbonate about the nucleus (Campana and Neilson, 1985). Because of these characteristics, some trace elements, primarily those that are non-essential to fish, have been found to reflect environmental levels (Milton and Chenery, 2001; Arslan and Secor, 2005; Halden and Friedrich, 2008; Friedrich and Halden, 2010, 2011; Arnold et al., 2015; Thomas et al., 2017).

2. Materials and methods

2.1. Study sites

Trout-perch (*Percopsis omiscomaycus*) were collected from 12 sites on the Athabasca and 2 sites on the Clearwater Rivers during October of 2014. Fish harvest locations were based on an earlier geophysical survey of terrain conductivity: this had identified zones of elevated conductivity which are thought to reflect inputs of saline groundwaters of natural and/or industrial origin which occur commonly along the Athabasca River between Fort McMurray and the Firebag River (Gibson et al., 2011). While the fish collection was taking place, a water sampling campaign was underway at the same sites on the river, with much of the trace element data already published (Cuss et al., 2018; Donner et al., 2017; Javed et al., 2017; Shotyk et al., 2017a).

2.2. Field collection

Trout-perch were collected using a 20 ft Smith-Root electrofishing boat (Model SR-20H) equipped with a 7.5 GPP electrofishing system by conducting multiple transects of approximately 1 km in length starting from the site locations shown in Fig. 1. The GPS coordinates of the sites are provided in the Supporting information (SI Table 1). Along with fish sampling, water temperature, turbidity, conductivity and pH were measured. Trout-perch were euthanized in accordance with an approved animal care protocol (AUP00001111), frozen at -20 °C, and shipped back to the University of Alberta for processing.

2.3. Sample preparation

For work on trace elements, 56 Trout-perch were defrosted in the lab, then measured for fork length and weight. Sagittal otoliths were extracted, cleaned with deionized water, and allowed to air dry overnight. No tumors were found in any of the fish. All subsequent sample handling and analysis was undertaken in the metal-free, ultraclean SWAMP lab, within polypropylene, Class 100 clean air cabinets (including the autosampler for the ICP-MS), using procedures similar to those described elsewhere (Shotyk et al., 2017a) for the study of trace elements in the dissolved fraction of the Athabasca River. After weighing, otolith samples were transferred to acid-cleaned, 4 ml PFA (perfluoroalkoxy alkane) tubes, then 200 µl of concentrated nitric acid was added and allowed to react for 30 min. The acid employed was distilled twice using sub-boiling distillation in high purity quartz (Duopur, MLS, Leutkirch, Germany). After adding 800 µl of DI/RO water (18.2 M Ω · cm; Milli-Q Element, Millipore, USA), the samples were further diluted to contain 1 mg/ml, then analyzed using ICP-MS.

2.4. Analysis of trace elements using ICP-MS

Samples were analyzed using a quadrupole ICP-MS (ICAPQc, Thermo Fisher Scientific, Waltham MA, USA) in Kinetic Energy Discrimination mode, with helium (He) as the collision gas. Stock standard solutions were purchased from Spex CertiPrep (Metuchen, NJ, USA). Multielement solutions (1 & 2A) as well as single element solutions (Mo, Bi, Re & Sb) were diluted as appropriate to create the calibration curves. A linear regression was confirmed for all selected isotopes ($R^2 > 0.99$). Indium-115 was used as the internal standard, with instrument parameters of 80 sweeps and 30 ms dwell time for all isotopes.

2.5. Limits of detection, accuracy, and precision

The limits of detection (LODs) for trace elements in otoliths were based on the daily instrument response (cps) to diluent blanks (2% HNO₃). For each isotope, the LOD was calculated using the average instrument response (cps) from 5 blank replicates plus 3 times the associated standard deviation. The mass/volume LODs were converted to mass/mass LODs by applying the sample dilution factor. The LODs obtained (μ g/kg) were Al, 480; Ba, 3.1; Co, 0.7; Cr, 2.1; Cu, 15; Fe, 230; Li, 1.1; Mn, 3.2; Ni, 17; Pb, 0.2; Rb, 0.9; Sr, 5.1; Tl, 0.6; V, 1.6; Y, 0.2; Zn, 210.



Fig. 1. Trout-perch sampling locations on the Athabasca River during the autumn 2014 campaign, in relation to the terrain conductivity of the main stem of the river. Terrain conductivity data from Gibson et al. (2011). Water samples collected at the same time, at the same locations, from a second boat, were analyzed for dissolved trace metals as described elsewhere (Shotyk et al., 2017a).

The accuracy of the trace element determinations was assessed using two certified, standard reference materials: 1) GSR-6 Limestone (Institute of Geophysical and Geochemical Prospection (IGGE), Ministry of Geology, China) and 2) NIST 1640a, Trace Elements in Natural Water (National Institute of Standards and Technology, MD, USA). Measured TI concentrations were 84% of the certified values in GSR-6 and 98 and 95% of their certified values in NIST 1640a. We note that our value for TI in GSR-6 (0.30 mg/kg) is closer to the value recently proposed for TI in this material (0.34 mg/kg) by Hu and Gao (2008) than the original, certified value (0.36 mg/kg). After removing the outliers (Supporting Information), the average concentrations of TI in otoliths from all sites (17 \pm 5 μ g/kg) are 28 times above the corresponding LOD.

3. Results

3.1. Trace elements in otoliths compared to Athabasca River

The elements which were determined in the otoliths are shown in order of decreasing abundance, spanning more than five orders of magnitude (Fig. 2a). The average concentrations of these elements in the dissolved (<0.45 μ m) fraction of the Athabasca River (Shotyk et al., 2017a) are also shown in order of decreasing abundance (Fig. 2b), again, spanning more than five orders of magnitude. When the ratio of element concentrations in the otoliths is compared to the corresponding concentrations in the river, it becomes clear that Tl is enriched more than any other element (Fig. 2c). Given that Tl has no known physiological function (Fraústo da Silva and Williams, 2001), is one of the most toxic trace metals (Peter and Viraraghavan, 2005), and despite the fact that divalent metal cations are preferentially incorporated into

otolith structures compared to monovalent cations (Melancon et al., 2005, 2008), the Tl enrichment is remarkable.

3.2. Spatial variation in the relative abundance Tl

Concentrations of Tl in otoliths along the transect are shown in Fig. 3a. Statistical analyses of the data (Supporting information) show that Tl concentrations in fish downstream from industry (BM, A8, A5 and A1) are not significantly greater than those from sites upstream of industry (sites UA5, A20 and A19). Moreover, the concentration of Tl in the otoliths was not significantly correlated with fork length, weight of fish or weight of otolith (Spearman's rho, 0.27); further,normalizing the Tl concentrations to the metrics for fish size/age did not change the lack of significant difference from upstream to downstream. The variation in Tl concentrations (Fig. 3a) in the otoliths along the transect may reflect differences in natural inputs from tributary streams, including variations in the amounts and proportions of fine grained sediment, organic matter, or ferric hydroxide (Cuss et al., 2018), or differences in groundwater inputs. Geochemically, Tl behaves similarly to K and Rb (Ahrens, 1948; Shaw, 1952; Brooks and Ahrens, 1961). Potassium-bearing silicates such as potassium feldspar and biotite, both common rock-forming minerals, are enriched in TI: up to 3.3 and 7.4 mg/kg (Heinrichs et al., 1980), compared to 0.9 mg/kg in the Upper Continental Crust (Rudnick and Gao, 2014). In addition, Tl is strongly adsorbed onto clay minerals such as illite (Wick et al., 2018). Variations in metal concentrations in otoliths might also reflect physiological differences among the fish themselves including age, sex, and health (Lin et al., 2001; Canli and Atli, 2003; Gantner et al., 2009). Rather than focus exclusively on concentrations, we normalized Tl



Fig. 2. A) Trace elements (μ g/kg) in otoliths of Trout-perch, listed in order of decreasing abundance (this study). B) Trace elements (ng/l) in the dissolved fraction of the Athabasca River (Shotyk et al., 2017a). C) Ratio of trace element concentrations in Trout-perch to Athabasca River (dissolved fraction).

concentrations to an independent element, to help identify the extent of enrichment or depletion, relative to the composition of the river. Normalizing trace metal concentrations to a reference element is an approach commonly used in geochemistry to quantify enrichments and depletions of trace elements, relative to some reference state, including studies of soils (Nesbitt et al., 1980), sediments (Förstner and Wittmann, 1989), peat (Shotyk et al., 2001) and atmospheric aerosols (Rahn, 1976). The justification for this procedure, as well as advantages and disadvantages of various reference elements, is discussed in detail in those publications.

Here, we elected to normalize Tl to Rb, for several reasons. First, like Tl, Rb is a non-essential trace element (Fraústo da Silva and Williams, 2001) and should be unaffected directly by physiological processes. Second, unlike Tl which is a chalcophile element (Nriagu, 1998) whose geochemical cycle has been considerably modified by human activities (Pacyna and Pacyna, 2001; Karbowska, 2016), Rb is a lithophile element and its concentrations in environmental media should mainly reflect natural inputs. Third, assuming that Tl in the Athabasca River is mainly in the form of Tl (I), the ionic radii of Tl (149 pm) and Rb (149 pm) are identical (Emsley, 1998). Finally, Rb was measured in the fish otoliths (Fig. 3b) as well as the dissolved fraction of the Athabasca River, so an internally consistent, high quality data set is available for both elements. The spatial variation in Tl/Rb (Fig. 3c) shows no significant difference between downstream and upstream values (Supporting information).

3.3. Enrichment of Tl in fish otoliths

The average abundance of Tl and Rb in the otoliths $(17.0 \pm 4.5 \text{ and } 230 \pm 68 \text{ µg/kg}$, respectively) yields a Tl/Rb ratio of 7.4×10^{-2} . Compared to the average Tl/Rb ratio in the dissolved fraction of the Athabasca River (3.4×10^{-3}) , the otoliths are enriched in Tl, relative to Rb, by a factor of 22 times. Rubidium, however, may accumulate in fish



Fig. 3. A) Box-whisker plots showing median, minimum, and maximum concentrations of Tl (μ g/kg) in otoliths of Trout-perch, along with upper and lower quartiles. B) Rb (μ g/kg). C) Tl/Rb ratio. The direction of river flow is from left to right, and the numbers in brackets (e.g. 3/3) refer to the number of samples > LOD, versus the total number of samples per site.

due to its chemical similarity to K (Patterson and Settle, 1977; Campbell et al., 2005). Also, it has been suggested that Rb may even be essential to some animals (Anke and Angelow, 1995). Thus, the enrichment factor calculation using Rb as reference element may underestimate the true extent of Tl accumulation. The other monovalent cation that could be used to estimate the accumulation of Tl is Li; like Rb, Li has no known physiological function. Lithium concentrations in fish otoliths along the transect are shown in Fig. 4a, and the Tl/Li ratios in Fig. 4b. Using the average concentration of Li in the otoliths (0.23 μ g/g) as well as that dissolved in the Athabasca River (7.1 μ g/l), we obtain an average Tl enrichment in the otoliths of 177 times.

4. Discussion

4.1. Selection of reference element for calculating enrichments and depletions

Calculating the enrichment of Tl in otoliths relative to river water, using either Rb or Li as reference element, implicitly assumes that Tl in the Athabasca River is predominantly in the form of Tl (I). The rationale for this assumption lies in the thermodynamic stability of Tl (I) versus Tl (III) in aqueous solutions: Tl (III) occupies an extremely small stability field (Pourbaix, 1966), and only predominates under oxidizing conditions that are either extremely acidic ie pH values <1 (Vink, 1993) or alkaline (Vink, 1998) ie pH > 9 (Lin and Nriagu, 1998). The pH



Fig. 4. A) Box-whisker plots showing median, minimum, and maximum concentrations of Li (µg/kg) in otoliths of Trout-perch, along with upper and lower quartiles. B) Tl/Li ratio. (Direction of river flow is from left to right).

of the Athabasca River varies seasonally, but it lies within the range 6.8 to 8.5 (Fiera, 2013). Within this pH range, therefore, even at the highest possible redox potentials, Tl should exist predominantly in the form of Tl⁺. Also, speciation studies of Tl in river waters receiving drainage from an abandoned Pb—Zn mine in France (Casiot et al., 2011) showed that >98% of the dissolved Tl was in the form of Tl (I).

Although Tl (I) should be the dominant species in the Athabasca River, studies of the redox state speciation of Tl in Lake Michigan (Lin and Nriagu, 1999) showed that ca. 2/3 of the dissolved Tl is in the form of Tl (III). Ignoring the important detail noted by Lin and Nriagu (1999) that

much of the Tl (III) may be colloidal, we should at least consider the possibility that the dominant form of Tl in the Athabasca River may be Tl (III). Support for this consideration comes from an independent study which also found that Tl (III) was the predominant species in Great Lakes surface waters, and attributed this to bacterial oxidation of Tl (I) (Twining et al., 2003). In a recent study of stream water in a region of acid mine drainage in Italy, both Tl (I) and Tl (III) were found to be important oxidation states of Tl (Campanella et al., 2017). Assuming that Tl (III) is the dominant form of dissolved Tl in the Athabasca River, it would be more reasonable to normalize the Tl concentrations to those of a trivalent cation such as Al or Y. The concentrations of Al and Y in fish otoliths along the transect, along with the Tl/Al and Tl/Y ratios, are shown in Fig. 5. Using Al as reference element for Tl, we obtain an average enrichment in the otoliths of 19 times. However, we note that the average Al/Y ratio in the fish otoliths exceeds that of the river by a factor of 9 times (data not shown) which means that normalizing to Al, like normalizing to Rb, may underestimate the extent of enrichment of Tl. Using Y as the reference element for Tl normalization, we obtain an average enrichment factor of 190 times. Yttrium concentrations (Fig. 5c) are clearly elevated in fish otoliths sampled from the industrial sector of the river (midstream locations, ie those sites from A18 to A9), yielding anomalously low Tl/Y ratios (Fig. 5d). The reason for the anomaly is unclear, and it is surprising, given the conservative behavior of Y during the weathering cycle.

Regardless of the reference element selected (Al, Li, Rb or Y), Tl is certainly enriched in the otoliths, relative to river water, by between 19 and 190 times, a phenomenon that can best be described as "bioaccumulation" (Mackay et al., 2018). While bioaccumulation of Tl in aquatic microorganisms is well known (Twiss et al., 2004; Hassler et al., 2007; Turner and Furniss, 2012; Turner et al., 2013; Pavoni et al., 2017), we wish to emphasize that Tl is enriched in the fish otoliths, relative to composition of the river, to a greater degree than any of the other trace elements we have studied.

4.2. Enrichments and depletions of trace elements in otoliths, versus river water

The occurrence of trace metals in fish otoliths has been lucidly described by Geffen et al. (1998) as "the result of a series of complex



Fig. 5. A) Box-whisker plots showing median, minimum, and maximum concentrations of Al (µg/kg) in otoliths of Trout-perch, along with upper and lower quartiles. B) Tl/Al ratio. C) Y (µg/kg). D) Tl/Y ratio.

interactions, starting with the concentration of the element in the environment, its bioavailability, the physiological state of the fish, the mechanism of different fish species for metal detoxification, the growth rate of individual fish, and the affinity of the Ca carbonate otolith for the metal". To pass from the environment to the otolith, an element must be transferred across several key physiological interfaces, with the mechanisms along the way having been described as a series of barriers or filters, each of which may influence the concentration of the element available for passage to the otolith (Sturrock et al., 2014). Despite all of the obstacles facing a potentially toxic element such as Tl, not only is Tl enriched in Trout-perch otoliths, it appears to be more enriched than in the case of marine fishes. For example, Tl concentrations in otoliths of coastal marine fishes are far lower than the Trout-perch (17.0 \pm 4.5 μ g/kg): Winter Flounder, 1.1 \pm 0.9 μ g/kg; Striped Bass, 2.1 \pm 1.1 μ g/kg; Spotted Hake, 2.8 \pm 0.8 μ g/kg (Arslan, 2005). At the same time, Tl concentrations in seawater range from 12 to 16 ng/kg (Flegal and Patterson, 1985) which are well above the levels found in the Athabasca River (average concentration 2.8 ng/l; Shotyk et al., 2017a). Thus, the concentration ratios of Tl in fish otoliths/water are approximately 40 times greater in the case of the Athabasca River compared to seawater. We note further that K concentrations in seawater (380 mg/l, according to Chester, 2009) are much greater than in the Athabasca River (1.3 \pm 0.1 mg/l; Shotyk et al., 2017a). Thus, the K/Tl ratio in seawater exceeds that of the Athabasca River by approximately 58 times. It is well known that the Tl⁺ is the only ion that approaches K⁺ in respect to mobility through the K⁺ ion channel of cell membranes (Fraústo da Silva and Williams, 2001). It seems reasonable to suspect that fish in the Athabasca River contain relatively more Tl in their otoliths (approximately 40 times, compared to marine fishes) because of the relative abundance of Tl⁺ to K⁺ in freshwaters. Other workers have noted the importance K⁺ in determining the toxicity of Tl⁺, and have even suggested that water quality guidelines for Tl should consider K concentrations (Twiss et al., 2004; Hassler et al., 2007).

While it is commonly assumed that uptake of non-essential trace elements is passive, and that uptake is proportional to ambient concentrations, the enrichment of Tl in the Trout-perch otoliths, relative to the Athabasca River, suggest that physiological processes are involved. It has been suggested that the abundance of elements such as Tl in fish otoliths are very low because elements such as these have no biological utility to the fish and are therefore not assimilated sufficiently to influence the levels in otoliths (Arslan, 2005). Relative to the composition of the Athabasca River, however, our data suggests that Tl is more enriched than any other trace element (Fig. 2c).

Of the trace elements studied here, only two are enriched in the otoliths, relative to the dissolved fraction of the Athabasca River: Al and Tl. At this time, there does not appear to be enough data in the literature to decide whether or not Al and Tl are enriched in fish otoliths generally. Given that the enrichments of Al and Tl in the fish otoliths are found throughout the transect, both upstream as well as downstream of industry, and given that dissolved concentrations of Al and Tl in the Athabasca River are comparable to other rivers (Shotyk et al., 2017a), we suspect that Al and Tl may be enriched in fish otoliths collected from other aquatic ecosystems.

4.3. Toxicity of Tl and its environmental significance

Thallium is toxic to aquatic organisms (Pickard et al., 2001; Ralph and Twiss, 2002; Lan and Lin, 2005; Bozcaarmutlu, 2007; Turner and Furniss, 2012; Rickwood et al., 2015; Tatsi et al., 2015), but LC_{50} values for *Daphnia magna* and Rainbow Trout (*Oncorhynchus mykiss*) are above 1 mg/l (Pickard et al., 2001) which is consistent with pioneering work on the toxicity of Tl to these organisms (Nehring, 1962-1963). In Canada, the current Canadian Council for Ministers of the Environment (CCME) Guideline for the Protection of Aquatic Life is 0.8 µg/l (CCME), and this is based on total, not dissolved concentrations. The average concentration of total Tl during the 2014 and 2015 Athabasca River

campaigns was $0.01 \pm 0.0 \,\mu\text{g/l}$ which is 80 times less than the CCME Guideline value. As noted earlier, the average concentration of dissolved Tl in the Athabasca River, during the 2014 autumn sampling campaign when flows are at their lowest and groundwater inputs at their greatest, was 2.8 ng/l (Shotyk et al., 2017a): this is well below the values reported for Lake Michigan and Lake Huron, and comparable to those of Lake Superior (Lin and Nriagu, 1999); in fact, it is within a factor of five of Tl concentrations in pristine groundwater from carbonate terrains (Shotyk et al., 2010) and similar to the median value (2 ng/l) reported for Tl in bottled waters worldwide (Krachler and Shotyk, 2009). For context, dissolved Tl in the Athabasca River, upstream and downstream of industry, is below the average value of 4.5 ng/l reported for "clean rivers" and less than one-half of the global average river water value of 6.6 ng/l (Nielsen et al., 2005). In other words, it is important to emphasize that, while Tl is certainly a potentially toxic heavy metal, its occurrence in the Athabasca River, downstream of industry as well as upstream, is at natural, background values.

4.4. Anthropogenic emissions of Tl to the environment

Thallium is a chalcophile element, and as such is commonly enriched in metal sulphides (Nriagu, 1998). In consequence, base metals mining and refining (Zitko, 1975) coal combustion (Cheam et al., 2000) and cement production (Ewers, 1988) are all potentially important sources of anthropogenic Tl to the environment (Couture et al., 2011; Karbowska, 2016). Acidic drainage waters in abandoned lead-zinc mining regions commonly yield elevated Tl concentrations (Belzile and Chen, 2017), including districts in Canada (Zitko et al., 1975), China (Liu et al., 2016), England (Turner and Furniss, 2012; Turner et al., 2013; Tatsi and Turner, 2014), Italy (Pavoni et al., 2017), Poland (Lis et al., 2003) and Spain (Martín et al., 2004). For example, in the vicinity of Tl-bearing pyrites in Tuscany, acidic drainage waters (pH 1.5 to 2.0) typically contain 200 to 1000 µg/l (Campanella et al., 2016); these exceed the CCME Guideline for Tl by hundreds of times.

4.5. Anthropogenic emissions of Tl from bitumen mining and upgrading?

Lead-zinc ores contain up to 90 mg/kg of Tl (Liu et al., 2016). In contrast, the concentration of Tl in the Athabasca Bituminous Sands (ABS) is only 0.09 mg/kg (Bicalho et al., 2017) which is an order of magnitude less than its abundance in the Upper Continental Crust (0.9 mg/kg, according to Rudnick and Gao, 2014). Moreover, >90% of the Tl in the ABS is found in the mineral (i.e. "sand") fraction (Bicalho et al., 2017). Given the abundance of carbonate alkalinity in the Athabasca River which maintains the pH in the range 7 to 8 (Fiera, 2013), combined with the fact that silicate mineral dissolution rates are at their minimum in this pH range (Sverdrup and Warfvinge, 1988), there appears to be very limited potential for mobilization of Tl to the aquatic environment. Our data for Tl in the Athabasca River (Shotyk et al., 2017a), and Troutperch otoliths (this study), upstream and downstream of industry, is consistent with this suggestion. Moreover, these findings for Tl in water and fish are consistent with the absence of contemporary atmospheric contamination by Tl recorded by Sphagnum moss from ombrotrophic (ie rain-fed) peat bogs in the vicinity of the open pit bitumen mines and upgraders (Shotyk et al., 2014, 2016), and the peat bog evidence of decades of declining atmospheric Tl contamination (Shotyk et al., 2017b). Despite the very low concentrations of Tl dissolved in the Athabasca River, upstream and downstream of industry, fish otoliths are certainly enriched in this potentially toxic element. Clearly, any study of human impacts on the environmental geochemical cycling of this element, must duly consider its natural bioaccumulation.

Acknowledgements

We gratefully acknowledge funding for this project provided jointly by AB Innovates (AI) contract number: 2083, with special thanks to Brett Purdy and John Zhou, and the Canadian Oil Sands Innovation Alliance (COSIA), with special thanks to John Brogly. We are grateful to our Co-Pls Jon Fennell, Jonathan Martin, and Tariq Siddique for their help in designing this study. The SWAMP lab was created through the munificent support of the University of Alberta, the Faculty of Agricultural, Life and Environmental Sciences and Alberta Environment and Parks. The Canada Foundation for Innovation contract number: 28641 together with Alberta Enterprise and Advanced Education contract number: RCP-12-047-SEG provided generous equipment grants. We are grateful to Bryan Maitland for assistance in the field, to Tracy Gartner and Karen Lund for administrative and laboratory support and to Rick Pelletier for the location map. Finally, we thank the reviewers for their helpful comments.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.scitotenv.2018.09.318.

References

- Ahrens, L., 1948. The unique association of thallium and rubidium in minerals. J. Geol. 56 (6), 578–590.
- 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. https://doi.org/10.1016/j.scitotenv.2017.04.207.
- Anke, M., Angelow, L., 1995. Rubidium in the food chain. Fresenius J. Anal. Chem. 352, 236–239. https://doi.org/10.1007/BF00322334.
- 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. https://doi.org/10.1002/etc.3735.
- Arnold, M.C., Friedrich, L.A., Lindberg, T.T., Ross, M., Halden, N.M., Bernhardt, E., Palace, V.P., Di Giulio, R.T., 2015. Microchemical analysis of selenium in otoliths of two West Virginia fishes captured near mountaintop removal coal mining operations. Environ. Toxicol. Chem. 34 (5), 1039–1044. https://doi.org/10.1002/etc.2885.
- Arslan, Z., 2005. Analysis of fish otoliths by electrothermal vaporization inductively coupled plasma mass spectrometry: aspects of precipitating otolith calcium with hydrofluoric acid for trace element determination. Talanta 65 (5), 1326–1334. https://doi.org/10.1016/j.talanta.2004.09.009.
- Arslan, Z., Secor, D.H., 2005. Analysis of trace transition elements and heavy metals in fish otoliths as tracers of habitat use by American eels in the Hudson River estuary. Estuaries 28 (3), 382–393. https://doi.org/10.1007/BF02693921.
- Bari, M.A., Kindzierski, W.B., Cho, S., 2014. A wintertime investigation of atmospheric deposition of metals and polycyclic aromatic hydrocarbons in the Athabasca oil sands region, Canada. Sci. Total Environ. 485-486, 180–192. https://doi.org/10.1016/j. scitotenv.2014.03.088.
- Barona, B., Young, R.F., Fedorak, P.M., Wismer, W.V., 2011. Blinded taste panel evaluations to determine if fish from near the oil sands are preferred less than fish from other locations in Alberta, Canada. Environ. Sci. Technol. 45, 1730–1736. https://doi.org/ 10.1021/es103359f.
- Belzile, N., Chen, Y.W., 2017. Thallium in the environment: a critical review focused on natural waters, soils, sediments and airborne particles. Appl. Geochem. 84, 218–243. https://doi.org/10.1016/j.apgeochem.2017.06.013.
- 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. https://doi. org/10.1016/j.fuel.2017.05.095.
- Bozcaarmutlu, A., 2007. Mechanism of inhibition of purified leaping mullet (*Liza saliens*) NADPH-cytochrome P450 reductase by toxic metals: aluminum and thallium. Mol. Toxicol. 21 (6), 340–347. https://doi.org/10.1002/jbt.20200.
- Brooks, R., Ahrens, L.H., 1961. Some observations on the distribution of thallium, cadmium and bismuth in silicate rocks and the significance of covaleney on their degree of association with other elements. Geochim. Cosmochim. Acta 23, 100–115.
- Campana, S.E., 1999. Chemistry and composition of fish otoliths: pathways, mechanisms and applications. Mar. Ecol. Prog. Ser. 188, 263–297. https://doi.org/10.3354/ meps188263.
- Campana, S.E., Neilson, J.D., 1985. Microstructure of fish otoliths. Can. J. Fish. Aquat. Sci. 42, 1014–1032. https://doi.org/10.1139/f85-127.
- Campanella, B., Onor, M., D'Ulivo, A., Giannecchini, R., D'Orazio, M., Petrini, R., Bramanti, E., 2016. Human exposure to thallium through tap water: a study from Valdicastello Carducci and Pietrasanta (northern Tuscany, Italy). Sci. Total Environ. 548–549, 33–42. https://doi.org/10.1016/j.scitotenv.2016.01.010.
- Campanella, B., Casiot, C., Onor, M., Perotti, M., Petrini, R., Bramanti, E., 2017. Thallium release from acid mine drainages: speciation in river and tap water from Valdicastello mining district (northwest Tuscany). Talanta 171, 255–261. https://doi.org/10.1016/j. talanta.2017.05.009.

- Campbell, L.M., Fisk, A.T., Wang, X., Köck, G., Muir, D.C., 2005. Evidence for biomagnification of rubidium in freshwater and marine food webs. Can. J. Fish. Aquat. Sci. 62, 1161–1167. https://doi.org/10.1139/f05-027.
- Canli, M., Atli, G., 2003. The relationships between heavy metals (Cd, Cr, Cu, Fe, Pb, Zn) levels and the size of six Mediterranean fish species. Environ. Pollut. 121, 129–136. https://doi.org/10.1016/S0269-7491(02)00194-X.
- Casiot, C., Egal, M., Bruneel, O., Verma, N., Parmentier, M., Elbaz-Poulichet, F., 2011. Predominance of aqueous Tl(1) species in the river system downstream from the abandoned Carnoulés mine (Southern France). Environ. Sci. Technol. 45 (6), 2056–2064. https://doi.org/10.1021/es102064r.
- Cheam, C., Garbai, G., Lechner, J., Rajkumar, J., 2000. Local impacts of coal mines and power plants. Water Qual. Res. J. Can. 35 (4), 581–607.
- Chester, R., 2009. Marine Geochemistry. 2nd ed. Blackwell Sciences, Oxford, U.K.
- Couture, P., Fortin, C., Hare, L., Lapointe, D., Pitre, D., 2011. Critical review of thallium in aquatic ecosystems. Research Report (R1272). INRS, Water, Land and Environment Center, Quebec.
- Cuss, C.W., Donner, M.W., Grant-Weaver, I., Noernberg, T., Pelletier, R., Sinnatamby, R.N., Shotyk, W., 2018. Measuring the distribution of trace elements amongst dissolved colloidal species as a fingerprint for the contribution of tributaries to large boreal rivers. Sci. Tot. Environ. 642, 1242–1252. https://doi.org/10.1016/j. scitotenv.2018.06.099.
- Degens, E.T., Deuser, W.G., Hardrich, R.L., 1969. Molecular structure and composition of fish otoliths. Mar. Biol. 2, 105–113.
- 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. https://doi.org/10.1016/ j.envpol.2017.02.004.
- Emsley, J., 1998. The Elements. 3rd ed. Clarendon Press, Oxford, U.K.
- Ewers, U., 1988. Environmental exposure to thallium. Sci. Total Environ. 71, 285-292.
- Fiera (Biological Consulting Ltd), 2013. State of the watershed report phase 3: water quantity and basic water quality in the Athabasca Watershed. Report (1234) Prepared for the Athabasca Watershed Council; Hinton, Alberta.
- Flegal, A.R., Patterson, C.C., 1985. Thallium concentrations in seawater. Mar. Chem. 15, 327–331.
- Förstner, U., Wittmann, G.T.W., 1989. Metal Pollution in the Aquatic Environment. New York, Springer-Verlag, Berlin.
- Fraústo da Silva, J.J.R., Williams, R.J.P., 2001. The Biological Chemistry of the Elements: The Inorganic Chemistry of Life. 2nd ed. Oxford University Press.
- Friedrich, L.A., Halden, N.M., 2010. Determining exposure history of northern pike and walleye to tailings effluence using trace metal uptake in otoliths. Environ. Sci. Technol. 44, 1551–1558. https://doi.org/10.1021/es903261q.
- Friedrich, L.A., Halden, N.M., 2011. Laser ablation inductively coupled plasma mass spectrometric analyses of base metals in Arctic char (*Salvelinus alpinus*) otoliths collected from a flooded base metal mine. Environ. Sci. Technol. 45, 4256–4261. https://doi. org/10.1021/es1040514.
- Gantner, N., Power, M., Babluk, J.A., Reist, J.D., Kock, 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.
- Geffen, A.J., Pearce, J.G., Perkins, W.T., 1998. Metal concentrations in fish otoliths in relation to body composition after laboratory exposure to mercury and lead. Mar. Ecol. Prog. Ser. 165, 235–245. https://doi.org/10.3354/meps165235.
- Gerner, N.V., Koné, M., Ross, M.S., Pereira, A., Ulrich, A.C., Martin, J.W., Liess, M., 2017. Stream invertebrate community structure at Canadian oil sands development is linked to concentration of bitumen-derived contaminants. Sci. Total Environ. 575, 1005–1013. https://doi.org/10.1016/j.scitotenv.2016.09.169.
- Gibson, J., Birks, S., Moncur, M., Yi, Y., Tattrie, K., Jasechko, S., Richardson, K., Eby, P., 2011. Isotopic and Geochemical Tracers for Fingerprinting Process – Affected Waters in the Oils Sands Industry: A Pilot Study. Oil Sands Research and Information Network (OSRIN), University of Alberta, School of Energy and Environment, Edmonton, Alberta, Canada.
- Guéguen, C., Cuss, C.W., Cho, S., 2016. Snowpack deposition of trace elements in the Athabasca oil sands region, Canada. Chemosphere 153, 447–454. https://doi.org/ 10.1016/j.chemosphere.2016.03.020.
- Halden, N.M., Friedrich, L.A., 2008. Trace-element distributions in fish otoliths: natural markers of life histories, environmental conditions and exposure to tailings effluence. Mineral. Mag. 72 (2), 593–605. https://doi.org/10.1180/minmag.2008.072.2.593.
- Hassler, C.S., Chafin, R.D., Klinger, M.B., Twiss, M.R., 2007. Application of the biotic ligand model to explain potassium interaction with thallium uptake and toxicity to plankton. Environ. Toxicol. Chem. 26 (6), 1139–1145. https://doi.org/ 10.1897/06-315R.1.
- Heinrichs, H., Schulz-Dobrick, B., Wedepohl, K.H., 1980. Terrestrial geochemistry of Cd, Bi, Tl, Pb, Zn and Rb. Geochim. Cosmochim. Acta 44, 1519–1533.
- Hu, Z., Gao, S., 2008. Upper crustal abundances of trace elements: a revision and update. Chem. Geol. 253, 205–221. https://doi.org/10.1016/j.chemgeo.2008.05.010.
- 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), 1–11. https://doi.org/ 10.1038/srep43622.
- Karbowska, B., 2016. Presence of thallium in the environment: sources of contaminations, distribution and monitoring methods. Environ. Monit. Assess. 188 (11), 640. https:// doi.org/10.1007/s10661-016-5647-y.
- Kelly, E.N., Schindler, D.W., Hodgson, 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. https://doi.org/10.1073/pnas.1008754107.

Kocovsky, P.M., Stoneman, A.T., Kraus, R.T., 2014. Ecology and population status of Troutperch (*Percopsis omiscomaycus*) in western Lake Erie. J. Great Lakes Res. 40, 208–214. https://doi.org/10.1016/j.jglr.2013.09.004.

Krachler, M., Shotyk, W., 2009. Trace and ultratrace metals in bottled waters: survey of sources worldwide and comparison with refillable metal bottles. Sci. Total Environ. 407, 1089–1096.

Lan, C.H., Lin, T.S., 2005. Acute toxicity of trivalent thallium compounds to Daphnia magna. Ecotoxicol. Environ. Saf. 61, 432–435. https://doi.org/10.1016/j.ecoenv.2004.12.021.

Lin, T.-S., Nriagu, J.O., 1998. Speciation of thallium in natural waters. In: Nriagu, J.O. (Ed.), Thallium in the Environment. John Wiley and Sons, NY, pp. 31–43.

- Lin, T.S., Nriagu, J.O., 1999. Thallium speciation in the Great Lakes. Environ. Sci. Technol. 33, 3394–3397. https://doi.org/10.1021/es9810960.
- Lin, T.S., Nriagu, J., Wang, X.Q., 2001. Thallium concentration in lake trout from Lake Michigan. Bull. Environ. Contam. Toxicol. 67 (6), 921–925. https://doi.org/10.1007/ s001280209.
- Lis, J., Pasieczna, A., Karbowska, B., Zembrzuski, W., Lukaszewski, Z., 2003. Thallium in soils and stream sediments of a Zn-Pb mining and smelting area. Environ. Sci. Technol. 37, 4569–4572. https://doi.org/10.1021/es0346936.
- Liu, J., Wang, J., Chen, Y., Xie, X., Qi, J., Lippold, H., Luo, D., Wang, C., Su, L., He, L., et al., 2016. Thallium transformation and partitioning during Pb-Zn smelting and environmental implications. Environ. Pollut. 212, 77–89. https://doi.org/10.1016/j. envpol.2016.01.046.
- MacKay, D., Celsie, A.K.D., Powell, D.E., Parnis, J.M., 2018. Bioconcentration, bioaccumulation, biomagnification and trophic magnification: a modelling perspective. Environ. Sci.: Processes Impacts https://doi.org/10.1039/C7EM00485K.
- Martín, F., García, I., Dorronsoro, C., Simón, M., Aguilar, J., Ortíz, I., Fernández, E., Fernández, J., 2004. Thallium behavior in soils polluted by pyrite tailings (Aznalcóllar, Spain). Soil Sediment Contam. 13, 25–36. https://doi.org/10.1080/10588330490269769.
- Sediment Contam. 13, 25–36. https://doi.org/10.1080/10588330490269769.
 Melancon, S., Fryer, B.J., Ludsin, S.A., Gagnon, J.E., Yang, Z., 2005. Effects of crystal structure on the uptake of metals by lake trout (*Salvelinus namaycush*) otoliths. Can. J. Fish. Aquat. Sci. 62, 2609–2619. https://doi.org/10.1139/f05-161.
- Melancon, S., Fryer, B.J., Gagnon, J.E., Ludsin, S.A., 2008. Mineralogical approaches to the study of biomineralization in fish otoliths. Mineral. Mag. 72 (2), 627–637. https:// doi.org/10.1180/minmag.2008.072.2.627.
- Milton, D.A., Chenery, S.R., 2001. Sources and uptake of trace metals in otoliths of juvenile barramundi (*Lates calcarifer*). J. Exp. Mar. Biol. Ecol. 264, 47–65. https://doi.org/ 10.1016/S0022-0981(01)00301-X.
- Natureserve, 2013. Percopsis omiscomaycus. The IUCN Red List of Threatened Species 2013: e.T202613A18236961. https://doi.org/10.2305/IUCN.UK.2013-1.RLTS. T202613A18236961.en (Downloaded on 22 November 2017).
- Nehring, D., 1962-1963. Untersuchungen über die toxikologische Wirkung von Thallium-Ionen auf Fische und Firschnährtiere. Zeitschrift für Fischerei. Vol. XI (7,8).
- Nesbitt, H.W., M, G., Price, R.C., 1980. Chemical processes affecting alkalis and alkaline earths during continental weathering. Geochim. Cosmochim. Acta 44 (11), 1659–1666. https://doi.org/10.1016/0016-7037(80)90218-5.
- Nielsen, S.G., Rehkämper, M., Porcelli, D., Andersson, P., Halliday, A.N., Swarzenski, P.W., Latkoczy, C., Günther, D., 2005. Thallium isotope composition of the upper continental crust and rivers - an investigation of the continental sources of dissolved marine thallium. Geochim. Cosmochim. Acta 19 (8), 2007–2019. https://doi.org/10.1016/j. gca.2004.10.025.
- Nriagu, J.O., 1998. In: Nriagu, J.O. (Ed.), Thallium in the Environment. Wiley & Sons, New York.
- 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 (4), 269–298. https://doi.org/10.1139/er-9-4-269.
- Parrott, J.L., Marentette, J.R., Hewitt, L.M., McMaster, M.E., Gillis, P.L., Norwood, W.P., Kirk, J.L., Peru, K.M., Headley, J.V., Wang, Z., et al., 2018. Meltwater from snow contaminated by oil sands emissions is toxic to larval fish, but not spring river water. Sci. Total Environ. 625, 264–274. https://doi.org/10.1016/j.scitotenv.2017.12.284.
- Patterson, C., Settle, D., 1977. Comparative distributions of alkalies, alkaline earths and lead among major tissues of the tuna *Thunnus alalunga*. Mar. Biol. 39 (3), 289–295. https://doi.org/10.1007/BF00391003.
- Pavoni, E., Petranich, E., Adami, G., Baracchini, E., Crosera, M., Emili, A., Lenaz, D., Higueras, P., Covelli, S., 2017. Bioaccumulation of thallium and other trace metals in *Biscutella laevigata* nearby a decommissioned zinc-lead mine (Northeastern Italian Alps). J. Environ. Manag. 186, 214–224. https://doi.org/10.1016/j.jenvman.2016.07.022.
- Peter, A.L.J., Viraraghavan, T., 2005. Thallium: a review of public health and environmental concerns. Environ. Int. 31 (4), 493–501. https://doi.org/10.1016/j.envint.2004.09.003.
- Pickard, J., Yang, R., Duncan, B., McDevitt, C.A., Eickhoff, C., 2001. Acute and sublethal toxicity of thallium to aquatic organisms. Bull. Environ. Contam. Toxicol. 66, 94–101. https://doi.org/10.1007/s001280000210.
- Pilote, M., André, C., Turcotte, P., 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. https://doi.org/10.1016/j.scitotenv.2017.08.023.
- Pourbaix, M., 1966. Atlas of Electrochemical Equilibria in Aqueous Solutions. Pergamon Press, Oxford.
- Rahn, K.A., 1976. The Chemical Composition of the Atmospheric Aerosol. Technical Report. Graduate School of Oceanography, University of Rhode Island, Kingston, R.I. USA.
- Ralph, L., Twiss, M.R., 2002. Comparative toxicity of thallium(I), thallium(II), and cadmium(II) to the unicellular alga Chlorella isolated from Lake Erie. Bull. Environ. Contam. Toxicol. 68, 261–268. https://doi.org/10.1007/s001280247.
- Rickwood, C.J., King, M., Huntsman-Mapila, P., 2015. Assessing the fate and toxicity of thallium I and thallium III to three aquatic organisms. Ecotoxicol. Environ. Saf. 115, 300–308. https://doi.org/10.1016/j.ecoenv.2014.12.024.
- Rudnick, R.L., Gao, S., 2014. Composition of the continental crust. In: Holland, H., Turekian, K. (Eds.), Treatise on Geochemistry. Elsevier.

- Schwalb, A.N., Alexander, A.C., Paul, A.J., Cottenie, K., Rasmussen, J.B., 2015. Changes in migratory fish communities and their health, hydrology, and water chemistry in rivers of the Athabasca oil sands region: a review of historical and current data. Environ. Rev. 23 (2), 133–150. https://doi.org/10.1139/er-2014-0065.
- Shaw, D.M., 1952. The geochemistry of thallium. Geochim. Cosmochim. Acta 2 (2), 118–154. https://doi.org/10.1016/0016-7037(52)90003-3.
- 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 12,370⁻¹⁴C yr BP. Geochim. Cosmochim. Acta 65 (14), 2337–2360. https://doi. org/10.1016/S0016-7037(01)00586-5.
- Shotyk, W., Krachler, M., Aeschbach-Hertig, W., Hillier, S., Zheng, J.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. https://doi.org/10.1039/b909723f.
- Shotyk, W., Belland, R., Duke, J., Kempter, H., Krachler, M., Noernberg, T., Pelletier, R., Vile, M.A., Wieder, K., Zaccone, C., et al., 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. https://doi. org/10.1021/es503751v.
- 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. https://doi.org/10.1016/j.envint.2016.03.018.
- Shotyk, W., Bicalho, B., Cuss, C.W., Donner, M.W., Grant-Weaver, J., Haas-Neill, S., Javed, M.B., Krachler, M., Noemberg, T., Pelletier, R., et al., 2017a. 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. https://doi.org/ 10.1016/j.scitotenv.2016.12.012.
- Shotyk, W., Appleby, P.G., Bicalho, B., Davies, L.J., Froese, D., Grant-Weaver, I., Magnan, G., Mullan-Boudreau, G., Noernberg, T., Pelletier, R., et al., 2017b. Peat bogs document decades of declining atmospheric contamination by trace metals in the Athabasca Bituminous Sands region. Environ. Sci. Technol. 51, 6237–6249. https://doi.org/ 10.1021/acs.est.6b04909.
- Spafford, M.D., 1999. Trout-perch Percopsis omiscomaycus (Walbaum) and Lake Chub Couesius plumbeus (Agassiz), as Sentinel Monitoring Species in the Athabasca River, Alberta. University of Alberta, Edmonton, Alberta, Canada.
- Sturrock, A.M., Trueman, C.N., Milton, J.A., Waring, C.P., Cooper, M.J., Hunter, E., 2014. Physiological influences can outweigh environmental signals in otolith microchemistry research. Mar. Ecol. Prog. Ser. 500, 245–264. https://doi.org/ 10.3354/meps10699.
- Sverdrup, H., Warfvinge, P., 1988. Weathering of primary silicate minerals in the natural soil environment in relation to a chemical weathering model. Water Air Soil Pollut. 38 (3–4), 387–408.
- Tatsi, K., Turner, A., 2014. Distributions and concentrations of thallium in surface waters of a region impacted by historical metal mining (Cornwall, UK). Sci. Total Environ. 473–474, 139–146. https://doi.org/10.1016/j.scitotenv.2013.12.003.
- Tatsi, K., Turner, A., Handy, R.D., Shaw, B.J., 2015. The acute toxicity of thallium to freshwater organisms: implications for risk assessment. Sci. Total Environ. 536, 382–390. https://doi.org/10.1016/j.scitotenv.2015.06.069.
- Tetreault, G.R., McMaster, M.E., Dixon, D.G., Parrott, J.L., 2003. Using reproductive endpoints in small forage fish species to evaluate the effects of Athabasca Oil Sands activities. Environ. Toxicol. Chem. 22 (11), 2775–2782. https://doi.org/10.1897/03-7.
- Thomas, O.R.B., Ganio, K., Roberts, B.R., Swearer, S.E., 2017. Trace element–protein interactions in endolymph from the inner ear of fish: implications for environmental reconstructions using fish otolith chemistry. Metallomics 9 (3), 239–249. https://doi. org/10.1039/C6MT00189K.
- Turner, A., Furniss, O., 2012. An evaluation of the toxicity and bioaccumulation of thallium in the coastal marine environment using the macroalga, *Ulva lactuca*. Mar. Pollut. Bull. 64 (12), 2720–2724. https://doi.org/10.1016/j.marpolbul.2012.09.023.
- Turner, A., Turner, D., Braungardt, C., 2013. Biomonitoring of thallium availability in two estuaries of Southwest England. Mar. Pollut. Bull. 69, 172–177. https://doi.org/ 10.1016/j.marpolbul.2013.01.030.
- Twining, B.S., Twiss, M.R., Fisher, N.S., 2003. Oxidation of thallium by freshwater plankton communities. Environ. Sci. Technol. 37, 2720–2726. https://doi.org/10.1021/ es026145i.
- Twiss, M.R., Twining, B.S., Fisher, N.S., 2004. Bioconcentration of inorganic and organic thallium by freshwater phytoplankton. Environ. Toxicol. Chem. 23 (4), 968–973. https://doi.org/10.1897/02-643.
- Vink, B.W., 1993. The behaviour of thallium in the (sub) surface environment in terms of Eh and pH. Chem. Geol. 109, 119–123. https://doi.org/10.1016/0009-2541(93) 90065-Q.
- Vink, B.W., 1998. Thallium in the (sub)surface environment: its mobility in terms of Eh and pH. In: Nriagu, J.O. (Ed.), Thallium in the Environment. John Wiley and Sons, NY, pp. 45–58.
- Wick, S., Baeyens, B., Fernandes, M.M., Voegelin, A., 2018. Thallium adsorption onto illite. Environ. Sci. Technol. 52, 571–580.
- Zitko, V., 1975. Toxicity and pollution potential of thallium. Sci. Total Environ. 4, 185–192. https://doi.org/10.1016/0048-9697(75)90039-X.
- Zitko, V., Carson, W.V., Carson, W.G., 1975. Thallium: occurrence in the environment and toxicity to fish. Bull. Environ. Contam. Toxicol. 13 (1), 23–30. https://doi.org/10.1007/ BF01684859.