

Arsenic speciation in surface waters and lake sediments in an abandoned mine site and field observations of arsenic eco-toxicity

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ABSTRACT

The region of Cobalt in Ontario, Canada has been affected by arsenic (As) and trace metals contamination since the early twentieth century due to unconfined dumping of high As-containing tailings. The concentrations of total dissolved As in lakes and streams have exceeded Canadian drinking water quality guidelines. The present study was focused on the examination of conditions that could influence chemical transformations of As(III) to As(V) and As speciation in lakes and stream waters and sediment of this area, as toxicity and mobility differ between different forms of As. Laboratory results showed that the stability of As(III) is strongly influenced by temperature, light, the presence of nitrate and chloride and by pH. The study shows that although total As concentrations were relatively high in the water samples collected in the area, As(V) was the predominant species in almost all water samples, and the most toxic form of As (III) was low, often < 1% of total dissolved. The concentrations of total and bioavailable As in sediment/tailing core samples of two studied lakes varied greatly with the depth and sampling sites, but the extracted form was generally in a lower proportion (< 35%). Iron oxides and organic matter likely play an important role in As transformation and mobilization in the sediment. Field observations showed a partial recovery of the two lakes where the ecosystem has adapted to the tailings. The presence of fish communities in both high As-containing lake invites the questions on whether As (III) should be a more appropriate parameter than total As in eco-toxicity and environmental assessments.

1. Introduction

The trace metalloid arsenic (As) is introduced in the environment through various natural processes and anthropogenic inputs (Smedley and Kinniburgh, 2002). Arsenic is a multi-chemical valence element and is actively involved in many biogeochemical processes. In soil and sediment, As geochemistry is very often controlled or strongly influenced by iron and manganese oxides and a variety of aluminosilicates through adsorption processes in oxic systems (e.g. Belzile and Tessier, 1990; Root et al., 2007). Once environmental conditions changed from oxidizing to reducing environments, iron and manganese oxides can be transformed to dissolved species such as Fe^{2+} and Mn^{2+} , thus releasing As previously adsorbed on the surface of these oxides. Under such sub-oxic or anoxic conditions, the reduction of arsenate can occur and the As mobility should be dominantly controlled by formation of sulfide minerals (Belzile, 1988; O'Day et al., 2004; Couture et al., 2010).

Both arsenate (As(V) or AsO_4^{3-}) and arsenite (As(III) or AsO_3^{3-}) are protonated oxyanions in natural aquatic conditions. Their level of protonation is pH dependent. Under oxygenated conditions and $\text{pH} < 2$, As(V) dominates and exists as fully protonated H_3AsO_4 ; at

$\text{pH} 2.2\text{--}6.9$ and oxygenated conditions, As is present mainly as H_2AsO_4^- ; at $\text{pH} 6.9\text{--}11.5$, as HAsO_4^{2-} and when $\text{pH} \geq 11.5$, it exists as the fully deprotonated species of AsO_4^{3-} . Under moderately reducing conditions, As(III) should be the dominant form. At $\text{pH} < 9.2$, arsenite is fully protonated as the neutral H_3AsO_3 ; at $\text{pH} 9.2\text{--}12$, as H_2AsO_3^- , and at $\text{pH} > 12$, as HAsO_3^{2-} (Smedley and Kinniburgh, 2002; Lu and Zhu, 2011). Because its neutral electrical charge at $\text{pH} < 9.2$ – a pH range for most natural water samples, this property can be used to separate As(III) from the charged As(V) in speciation work. The pH of an aqueous system also strongly influences the adsorption capacity of Fe–Mn oxides and other adsorbents containing $\equiv\text{S-OH}$ functional groups based on its influence on the surface charge of these types of solid phases.

According to thermodynamic calculations, arsenite is unstable under oxidizing conditions and will be converted to arsenate in most natural systems (Oscarson et al., 1980; DeVitre et al., 1991). In presence of sunlight, the conversion of arsenite to arsenate is usually followed by the adsorption of arsenate on the iron and manganese oxides (Hug et al., 2001; Bhandari et al., 2011, 2012). The adsorption on a solid phase makes As less mobile and less available for organisms. Arsenate

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can also be reduced to arsenite, and this can occur abiotically (absence of bacteria) in presence of dissolved sulfide (HS^-) and possibly Fe (II). It could also lead to the immobilization of the reduced form via the (co)-precipitation with sulfide (e.g. arsenopyrite - FeAsS , cobaltite - $(\text{Co, Fe})\text{AsS}$, orpiment As_2S_3 , etc.) or via the adsorption on other metal sulfides such as pyrite (Belzile and Lebel, 1986; Belzile, 1988). When sulfides are exposed to oxygen, the As-bearing minerals could be oxidized and As be mobilized from its mineral form.

Both the oxidation of arsenite to arsenate and the reduction of arsenate to arsenite can also be mediated by bacteria and microorganisms also involving iron (e.g. Huang, 2014; Campbell et al., 2006). For instance, the presence of bacteria and microorganisms also play a role in the As redox cycle in soil and sediment (Zeng et al., 2018), and some volatile methylated As compounds can escape from soil, sediment and water bodies into the atmosphere (Mudhoo et al., 2011a).

Not only the geochemical processes of As are complicated, but the toxic effects of As species also differ greatly and are sometimes contradictory. In general, inorganic As is more toxic than organic As species, As(V) is less toxic than As(III), and methylated As(V) species are less toxic than methylated As(III) species. For instance, Petrick et al. (2000) summarized the results of three cytotoxicity assays (LDH, K(+) and XTT) and presented an order of toxicity in Chang human hepatocytes as: monomethylarsonous acid, MMA(III) > inorganic As(III) > inorganic As(V) > monomethylarsenic acid, MMA(V) = dimethylarsenic acid, DMA(V). Naranmandura et al. (2007) proposed that the lethal concentration (LC_{50}) to human cells follow an order of 571, 843, 5.46, and 2.16 μM for inorganic As(V), dimethyl As(V), inorganic As(III) and dimethyl As(III), respectively. The high toxicity of As(III) compounds is related to their high affinity for sulfhydryl groups (e.g. -SH) in biological binding sites of plants and animals (Sharma and Sohn, 2009), whereas inorganic As(V) has been found no specific affinity to sulfhydryl groups (Suzuki et al., 2008). A more comprehensive review on As behavior in environment and its remediation can be found in a review by Sharma and Sohn (2009).

The current study was carried in the region of Cobalt (latitudes $47^{\circ}20'14''\text{N}$ – $47^{\circ}27'30''\text{N}$ and longitudes $79^{\circ}45'22''\text{W}$ – $79^{\circ}35'34''\text{W}$) located at about 500 km north of Toronto. It was named after the discovery of this element in 1884. In 1903, silver was discovered in the ores of this region. It soon became the largest silver producer in the world in 1908. At the start of World War I, there were > 100 mining companies operating in this region. Until 1960's and the reduction of mining activity in the region, the quantity of silver extracted from the mines in Cobalt had reached around 420 million ounces (Cobalt municipality website, n.d.).

The ores of this region are dominated by native silver, cobalt and nickel arsenides, sulphide-arsenides, sulpho-arsenites, antimonides and sulpho-antimonites. Sulpho-bismuthites and their secondary alteration ores occur in predominant carbonate gangue (Reid et al., 1924). Due to the lack of environmental regulations and general industry understanding of the processes leading to element leaching in the earlier mining activities in the area, tailings containing high concentrations of various polluting elements, particularly As, were disposed at locations of low-lying areas within a radius of 6 km of the township of Cobalt (Dumaresq, 1993). As a result, surrounding water and soil systems became highly contaminated by As. A few earlier studies have reported the contamination of As in this region (Percival et al., 2004; Dumaresq, 1993), but these works were mostly focused on a geological perspective. Over the years, field observations and recent studies by governmental agencies and mining companies (e.g. MNDMF, 2010) in the Cobalt area have demonstrated the presence of aquatic life (aquatic plants, benthos and fish) in lakes and streams despite the concentrations of As exceeding water quality criteria.

The current study was designed to look more specifically at investigating on As speciation in water and at estimating the solubility and mobility of As in lake sediments. For logistic reasons, the emphasis of the work was put on a sector of the watershed where streams are

flowing toward Lake Timiskaming and on the recently added sediments of two lakes that have received important tailing discharges in the previous century. A controlled laboratory study was also designed to better understand the factors that may influence the stability of As(III) and its oxidation to As(V). Based on obtained data and field observations, better parameters can be used to estimate the eco-toxicity of As in an aquatic system.

2. Materials and methods

2.1. Water sampling and chemical speciation

Water samples (23) were collected ~5 cm below the surface of the creeks or ~60 cm below the surface of the lakes in acid pre-cleaned dark glass bottles (250 mL). Surface water samples were collected in July 2012. The surface water samples were taken from Sasaginaga (Sas), Crosswise (Cr) and Farr Wetland (Farr) creeks and two lakes, Cobalt and Crosswise. Cobalt Lake, which was densely surrounded by mining activities, has received approximately 300,000 tons of tailings covering depths around 10–11.5 m in some sections of the lake. Crosswise Lake was a repository of tailings from 1908 to 1970 and its length was shortened by ~300 m due to this practice. Sasaginaga Lake, located northwest of the Cobalt Catchment and at the edge of most mining and milling sites, was not filled with tailings. The Sasaginaga Creek and Crosswise Creek are converging before flowing into the Crosswise wetland (Dumaresq, 1993). Fig. 1 shows a watershed map of the studied region that indicates the sites of the closed mills and sampling locations of this study.

For As speciation work (Ke et al., 2000; USGS, 2002; Watts et al., 2010), a volume of ~35 mL of the water sample was syringe-filtered through a 0.45 μm Millipore membrane with the first 1–2 mL filtrate being rejected. This filtrate was then subdivided into three fractions. In Fraction 1, a volume of ~13 mL was passed through a pre-activated SAX cartridge (6-cc 500 mg from Agilent) with 15.0 mL of 50% (v/v) methanol, followed by rinsing with 15.0 mL of deionized water. Once again, the first 2 mL of eluate was rejected and the rest was collected in a clean 50 mL Falcon tube. Because the surface of SAX resin is positively charged, it retains only the negatively charged As(V) (in mixed forms of H_2AsO_4^- and HASO_4^{2-} in a pH range of 4–9) and allows the uncharged As(III) (in form of H_3AsO_3 in pH range < 7) to flow out of the cartridge non-retained. The As directly measured in this eluate (without pre-reduction) is named as As^{III} . The As(V) adsorbed by SAX cartridge was eluted from the cartridge by 15.00 mL of 1.0 M HCl, as at this high H^+ concentration, H_2AsO_4^- and HASO_4^{2-} will be fully protonated to neutral H_3AsO_4 . The As measured after pre-reduction in this elute was named As^{V} . In Fraction 2, a volume of ~13 mL of the filtrate was converted to As(III) by adding KI for the determination of total inorganic As(V) + As(III), named $\text{As}^{\text{III}+\text{V}}$. The remaining filtrate of ~9 mL, Fraction 3, was acidified with 16 M HNO_3 to make it a 3.5% (v/v) nitric acid matrix. It was then submitted to a microwave digestion (Milestone Ethos 1600, from 20 to 130 °C in 10 min, held at 130 °C for 15 min) to mineralize As attached to organic matter or complexed. After the digestion, KI was added and the As measured in this fraction is named as As^{Tot} . Arsenic associated with dissolved organic matter, named As^{DOM} , was obtained by subtraction between As^{Tot} and $\text{As}^{\text{III}+\text{V}}$. Recovery of As species varied between 94 and 105%.

All field samples were stored in dark and refrigerated conditions after collection. Filtrations for As(III) and As(V) separation were accomplished in absence of daylight and within 12 h after sampling. The determination of As in water was completed within 48 h after sampling. To estimate analytical variations, multiple analysis was performed with some randomly selected samples. In contact with sodium borohydride (NaBH_4), As(III) is readily reduced to gaseous arsine (AsH_3), which can be atomized in a miniature H_2 flame and determined by atomic fluorescence spectrometry. This is a very sensitive method, called hydride generation – atomic fluorescence spectrometry (HG – AFS, PSA 10.055

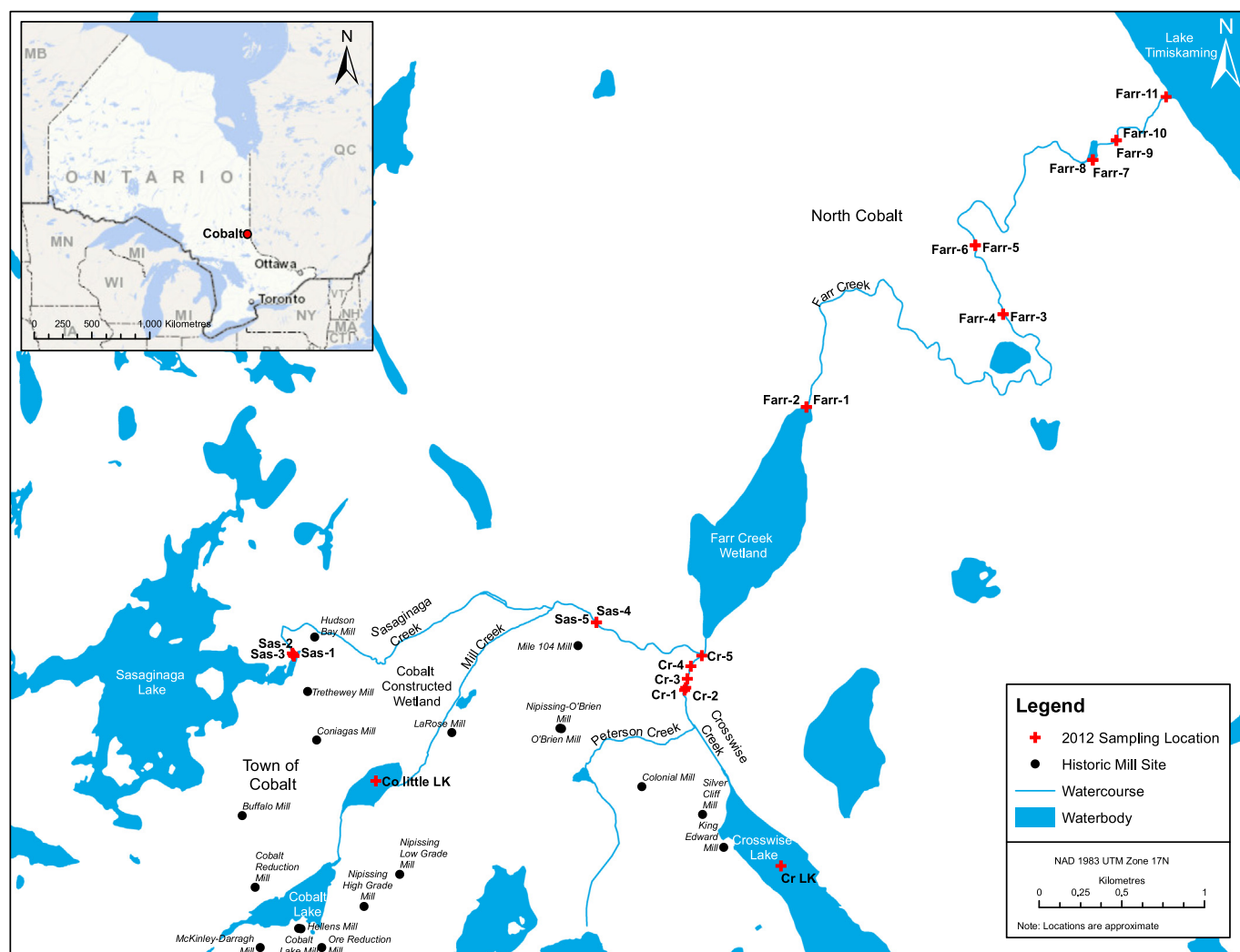


Fig. 1. Watershed map of the studied area and sites of water and sediment sampling (red crosses). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Millennium Excalibur). However, this reaction can barely occur with As (V). To determine As (V), it is necessary to convert it first to As (III) by KI in an aqueous medium containing 3.6% (w/v) KI – 3.0 M HCl for 30 min at around 23 °C; HCl in the medium is used to produce H₂ gas for the flame. In natural water samples, some As can be associated to organic matter. To determine As associated in this form, it should be first break down to inorganic form under high temperature in presence of a strong oxidant reagent and this process will oxidized As to As(V).

2.2. Sediment sampling, sample preparation and phase speciation

To evaluate the addition of new sediments on discharge tailing, a gravity corer (Tech Ops) was operated manually from a boat to collect sediment from Cobalt and Crosswise lakes (Fig. S1). In Cobalt Lake, three cores with different depths were collected. Core B was located only ~30 m east of Core A. Core C was located near to the exit of the Little Cobalt Lake to the Mill Creek. For Crosswise Lake, it was possible to collect only one long and two short cores. Sediment cores and surface sediments were collected the same as water samples. Multiple attempts were made for the collection of sediment cores at various locations of both lakes. It was a difficult task largely because of the presence of aquatic plants in the lakes as their dense rooting systems made the penetration of the gravity corer nearly impossible. In several cases, only the top layer of sediment samples was collected manually with the core

liner in shallow parts of the lakes.

Cores were brought to the shore to be sub-sampled immediately using a specially designed pneumatic extruder to allow a detailed subdivision of the core. The top of the core were sampled at a resolution of 5 mm per sample followed by 1.0 cm per sample. All solid samples were transferred into clean opaque high-density polyethylene plastic bottles and store on ice until return to the lab where they were freeze-dried (LabConco) and hand ground. The prepared sediment samples were stored in a refrigerator and ready for chemical speciation work.

2.2.1. Total arsenic (As-AR)

A mass of 0.25 g of sample was precisely weighed and placed into a Teflon container, to which 3.0 mL of 16 M HNO₃ and 5.0 mL of 12 M HCl were added. All sediment samples were digested in a microwave system (Milestone Ethos 1600) with a program from 20 to 200 °C in 15 min, held at 200 °C for 20 min and cooled down at room temperature. The digested solution was then filtered through a 0.22 μm Millipore filter, brought to 25.00 mL with deionized water and kept at 4 °C until analysis. Arsenic in this digest was determined after a KI pre-reduction and defined as As in *aqua regia* extraction (As-AR) expressed on a dry weight (dw) basis. Because under such digestion conditions, almost all As in the sediment should be extracted into the solution, therefore it can be considered also as *total arsenic* in the sediment sample.

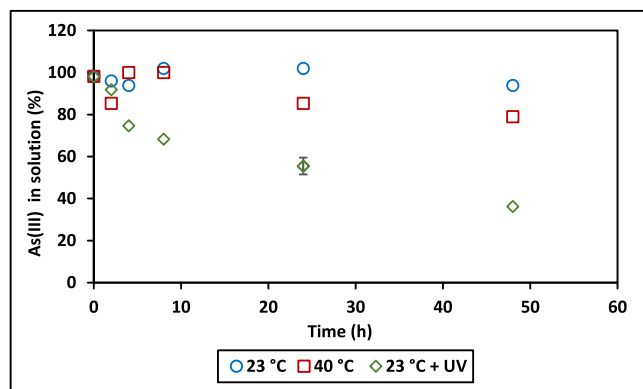


Fig. 2. Stability of As(III) in water at 23 °C and 40 °C under laboratory light (mercury fluorescence bulb) and at 23 °C in presence of a single UV light (230 nm, 8 W). Note: all these solutions contained 3.0×10^{-5} M HCl.

2.2.2. Labile arsenic (As-Ox)

A precisely weighed 0.25 g sediment sample was submitted to an extraction in a solution of 0.2 M ammonium oxalate adjusted to pH 3.25 using a solvent:mass ratio of 25-mL:1-g. The sample was extracted by an arm wrist shaker (120 cycle/min) for 4 h at room temperature. In this extract, As is defined as As in oxalate extraction (As-Ox) dw (Deng et al., 2011). The iron dissolved in this solvent was determined by flame atomic absorption spectrometry (FAAS) and defined as Fe in oxalate extraction (Fe-Ox). As-Ox was also determined after KI pre-reduction. Because As-Ox was extracted with a much weaker chemical reagent and under a room temperature compared to As-AR, the arsenic obtained with this protocol can be considered as *labile arsenic* species adsorbed or co-precipitated with amorphous and low crystalline Fe oxyhydroxides.

For analytical quality control, the certified reference materials (CRM) PACS-2 (NRC, Canada) was digested in *aqua regia* at a frequency of 1 CRM per 15 samples and As in the digests was analyzed along with the samples. Several reagent blanks were also performed during extraction in oxalate and *aqua regia* medium and no reagent contamination was found in either extraction system. The detected As value of PACS-2 was comparable to the certified value of the CRM.

2.3. Laboratory studies on the factors influencing the stability of As(III)

The speciation of As in water samples is based on the different chemical reactivity of different forms of As in water (see 2.1). For stability, the stock reducing reagent 50% (w/v) KI - 10% (w/v) ascorbic acid (to prevent KI oxidation) was freshly prepared and could be stored in a refrigerator for a few days.

The stock solution of 1000 mg/L As(III) in stability studies was prepared by refluxing pure As_2O_3 in a concentrated hydrochloric acid to prevent As(III) oxidation. The HCl concentration was approximately 0.6 M in the final stock solution. When this solution was diluted with deionized water to around 50 μ g/L As(III), the solution contained $\sim 3.0 \times 10^{-5}$ M HCl. Thus, all 50 μ g/L solutions used in this study contained this concentration of HCl as a background matrix.

2.3.1. Stability of As(III) under different temperatures and light exposures

Either laboratory light (common mercury fluorescence bulbs) or a single UV tube (Germicidal Hg lamp, 254 nm, 8 W) was used in this experiment. A series of ~ 50 μ g/L As(III) solutions were subjected to different light or heat exposures (Water bath Isotemp 220 Fisher Scientific); one sample was retrieved at a pre-determined time and As (III) in such a sample was determined without any treatment. The decrease of As(III) in the solution can be regarded as a transformation of As(III) to unmeasurable As(V). To confirm the conversion of As(III) to As(V), an aliquot of the same sample solution was treated with KI solution and the total As was measured. If the signal was found the same

as its initial concentration, it proved that the missing As(III) had been indeed converted to As(V). Quartz containers were used to avoid the absorption of UV light by normal glass material.

2.3.2. Stability of As(III) in the presence of Cl^- and NO_3^-

The study was performed in a series of solutions of ~ 50 μ g/L of As (III) with addition of 1.0% (v/v) HCl (0.12 M) or 1.0% (v/v) HNO_3 (0.15 M). A parallel series of ~ 50 μ g/L of As(III) with addition of 0.1 and 1.0% (w/v) of NaCl (0.017 or 0.17 M Cl^-) or $NaNO_3$ (0.012 or 0.12 M NO_3^-) under laboratory light (common mercury fluorescence bulb) or a UV light tube (peak 254 nm, range 180–315 nm, 8 W) at 23 ± 1 °C. An aliquot solution was taken at set times and the concentration of As(III) and total As in the testing solution were determined as described earlier.

3. Results and discussion

3.1. Factors influencing the stability of As(III)

Under oxic conditions, As(III) is chemically unstable species because it can be transformed to its higher chemical valence form of As(V). Our laboratory simulation work revealed that, when exposing As(III) solution (containing 3.0×10^{-5} M HCl) to a laboratory light (commercial mercury fluorescence bulb) at 23 ± 1 °C, its concentration remained more or less stable within 48 h of observation. However, at 40 ± 1 °C, a noticeable As(III) concentration decrease was observed. The decrease of As(III) became much more prominent when the sample solution was exposed to a UV lamp irradiation (Fig. 2). This transformation (oxidation) of As(III) to As(V) has been confirmed by a 100% recovery of initial As(III) after a KI pre-reduction treatment, proving that a decrease of As concentration was due to formation of non-measurable As(V) by HG-AFS.

A similar test was carried with a 50 μ g/L As(III) solution in presence of additional 1.0% (v/v) HNO_3 ($[NO_3^-] \approx 0.15$ M) and 1% (v/v) HCl ($[Cl^-] \approx 0.12$ M) solutions. Under laboratory light, As(III) present in these acidic matrices appeared stable within 48 h of observation; however, when the solutions were exposed to the UV light, the concentration level of As(III) dropped rapidly in the first 8 h, then remained relatively constant. This suggests that an equilibrium has been reached between the oxidation to As(V) and its reduction to As(III) (Fig. 3). Under UV irradiation, the concentration of As(III) still remained at 34% of its initial concentration after 48 h, indicating that an equilibrium between As oxidation and reduction processes had been reached. However when HCl and HNO_3 were replaced by the addition of 1.0% (w/v) NaCl ($[Cl^-] = 0.17$ M) and 1.0% (w/v) $NaNO_3$ ($[NO_3^-] = 0.12$ M) respectively, As(III) in solution was oxidized

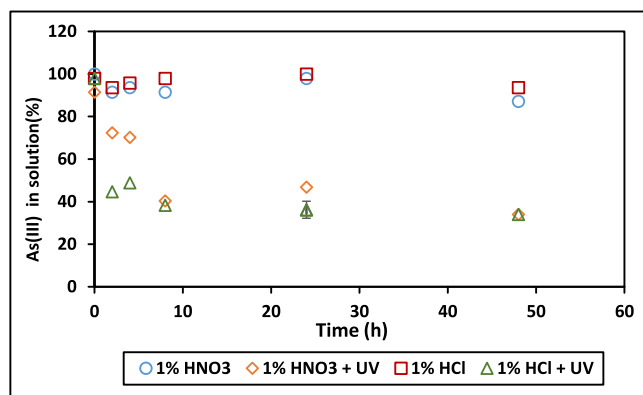


Fig. 3. Stability of As(III) in two types of acidic solutions under laboratory light and in presence of a UV lamp (254 nm, 8 W) at 23 °C. Note: In 1.0% (v/v) HNO_3 , $[NO_3^-] \approx [H^+] \approx 0.15$ M, $[Cl^-] \approx 3.0 \times 10^{-5}$ M; in 1.0% (v/v) HCl, $[Cl^-] \approx [H^+] \approx 0.12$ M.

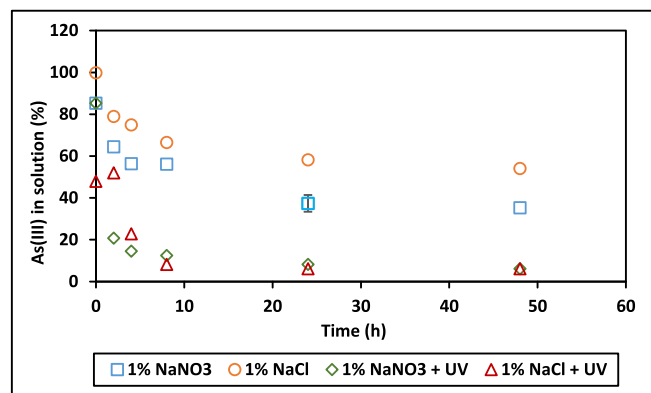


Fig. 4. Stability of As(III) in two types of ionic solutions under laboratory light and in presence of a UV light (254 nm, 8 W) at 23 °C. Note: in 1.0% (w/v) NaNO₃, [NO₃⁻] ≈ 0.12 M, [Cl⁻] ≈ 3.0 × 10⁻⁵ M; in 1.0% (w/v) NaCl, [Cl⁻] ≈ 0.170 M. All solutions contained [H⁺] ≈ 3.0 × 10⁻⁵ M.

quickly even under laboratory light (Fig. 4). The difference between these two systems is that the acidity of the latter was much lower, at only 3.0 × 10⁻⁵ M [H⁺] (or pH 4.52). When a UV light source was introduced, an irreversible oxidation of As(III) to As(V) occurred, whereas in the acidic condition (Fig. 3), an equilibrium between As(III) and As(V) was observed.

When [H⁺] was at a much lower level (≈ 3 × 10⁻⁵ M), the influence of NO₃⁻ and Cl⁻ on the oxidation of As(III) can be noticed when their respective concentrations were as low as 0.015 M and 0.012 M, respectively. The oxidation rate of As(III) to As(V) was accelerated with the concentrations of these anions (Fig. 5). The results also showed that NO₃⁻ likely possesses a higher oxidation capacity than Cl⁻, considering its much lower molar concentration than that of Cl⁻ in the matrix. Considering that the presence of H⁺ can stabilize As(III) and the slight acidic condition in all studied solutions (3.0 × 10⁻⁵ M HCl or pH 4.52), the oxidation effect induced by NO₃⁻ and Cl⁻ should be more pronounced if As(III) was present in a matrix with a pH ≥ 7. Because of the ubiquitous existence of NO₃⁻ and Cl⁻ in natural environmental systems and the slightly alkaline environment of the studied region, their influence on the stability of As(III) could be an important factor to consider.

Contrary to the previous belief, Herndon et al. (2018) have recently shown that sun irradiations at wavelength UV-B (280–320 nm) and UV-C (200–280 nm) do indeed reach the earth's surface, therefore the oxidation of As(III) should be influenced by sunlight. Based on the above studies, some important conclusions can be drawn: (1) UV light

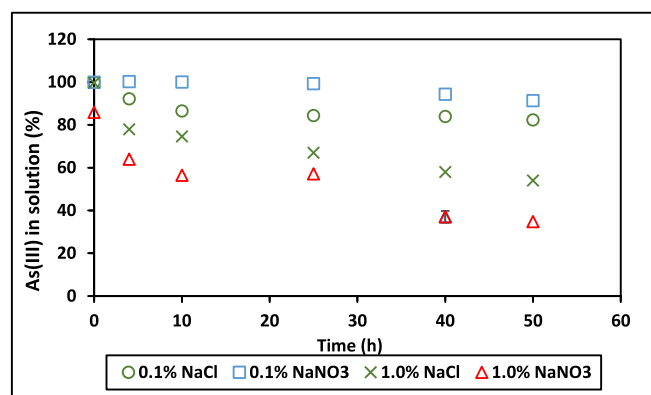


Fig. 5. Influence of NO₃⁻ and Cl⁻ concentration on the stability of As(III), under exposure of the laboratory light at 23 °C in 0.1% and 1.0% NaNO₃ (i.e. [NO₃⁻] ≈ 0.012 M and 0.12 M), or in the 0.1% and 1.0% NaCl (i.e. or [Cl⁻] ≈ 0.017 M and 0.17 M). All solutions contained [H⁺] ≈ 3.0 × 10⁻⁵ M.

Table 1

Arsenic speciation in water samples of the Cobalt area. (Values in parentheses are the percentages of each species in total arsenic).

Name	As ^{Tot} (µg/L)	As ^{III+V} (µg/L)	As ^{III} (µg/L)	As ^V (µg/L)	As ^{DOM} (µg/L)
Sas-1	106.9	87.5	0.9 (0.8)	86.7 (81.1)	19.4 (18.1)
Sas-2	134.1	120.1	22.9 (17.1)	97.2 (72.5)	14.1 (10.5)
Sas-3	100.4	85.5	12.8 (12.7) ^g	62.6 (62.4)	14.9 (14.8)
Sas-4	635.3 ^a	527.7	14.7 (2.3)	514.9 (81.0)	107.6 (16.9)
Sas-5	798.9	600.8	14.0 (1.8)	586.1 (73.4)	198.1 (24.8)
Cr-1	770.1	626.0	2.5 (0.3)	623.5 (81.0)	144.0 (18.7)
Cr-2	709.8	639.4	1.3 (0.2)	638.1 (89.9)	70.4 (9.9)
Cr-3	693.1	658.7	9.2 (1.3)	649.6 (93.7)	34.3 (5.0)
Cr-4	721.6	610.7	0.9 (0.1)	609.8 (84.5)	110.9 (15.4)
Cr-5	775.7	674.3 ^c	1.3 (0.2)	673.0 (86.8)	101.4 (13.1)
Farr-1	235.1	229.9	0.1 (0.1)	229.8 (97.8)	5.2 (2.2)
Farr-2	247.9	232.9	0.9 (0.4)	232.0 (93.6)	15.0 (6.0)
Farr-3	361.3	361.0	0.2 (0.1)	360.7 (99.8)	0.4 (0.1)
Farr-4	365.5	346.9	1.4 (0.4)	345.5 (94.5)	18.6 (5.1)
Farr-5	360.6	352.1	0.0 (0.0)	352.1 (97.7)	8.5 (2.4)
Farr-6	337.8	310.9	1.2 (0.4)	309.7 (91.7)	26.9 (8.0)
Farr-7	434.5	369.8	1.5 (0.3)	368.3 (84.8)	64.7 (14.9)
Farr-8	475.2	400.5	1.6 (0.3)	398.9 (83.9)	74.7 (15.7)
Farr-9	397.8	396.5	2.3 (0.6)	394.2 (99.1)	1.3 (0.3)
Farr-10	436.4	389.7	2.1 (0.5)	387.6 (88.8)	46.7 (10.7)
Farr-11	420.3 ^b	410.1 ^f	2.5 (0.7) ^h	407.6 (97.0)	10.1 (2.4)
Cobalt LK	822.1 ^c	814.7	1.3 (0.2)	813.4 (98.9)	7.4 (0.9)
Crosswise LK	698.1 ^d	644.4	2.3 (0.3)	642.0 (92.0)	53.8 (7.7)

Note: a, b, c, d, e, f, g, h are the standard deviation of at least 3 replicate analysis for each corresponding values, and they were 28.4, 29.2, 39.8, 4.7, 63.5, 13.9, 2.1 and 0.7 µg/L, respectively.

at 180–315 nm is a strong oxidant for As(III); (2) Higher temperature can accelerate the oxidation of As(III); (3) As(III) is more stable in a higher [H⁺] solutions and less stable in neutral and alkaline conditions; (4) Both NO₃⁻ and Cl⁻ can oxidize As(III) and NO₃⁻ is likely a stronger oxidant than Cl⁻ for As(III), and their oxidation strength increases with concentration.

It was noticed that a 1000 mg/L As(III) solution prepared in 0.6 M HCl was found still stable after 70 days when stored in a refrigerator. This is likely due to the high concentration of As(III) and acidity, the absence of light and the low temperature. It should be indicated that the As(III) stock solution should be always prepared in hydrochloric acid rather than in nitric acid.

3.2. Arsenic speciation in surface waters of the Cobalt region

The results of chemical speciation of As in surface water samples are given in Table 1. Total As concentration in collected water samples (As^{Tot}) varied from 107 µg/L in Sasaginaga Creek (Sas-3) to 822 µg/L in Cobalt Lake, which are significantly higher than the value of 25.0 µg/L of the Ontario drinking water quality standards. The relatively low concentration of As^{tot} in the water samples collected close to the exit of Sasaginaga Lake might be explained by its geographic location as a head lake and longer distance from old tailing deposits. However, as Sasaginaga Creek flows away from its source, the As concentration in the water quickly increased. The high concentrations of As^{tot} in both Cobalt and Crosswise lakes are attributed to the presence of tailings in both lakes and the high As background of the region. It is important to note that As^{tot} at the outlet of the Crosswise wetland decreased from its entrance level of ~ 780 µg/L to 240 µg/L, thus representing a ~70% decline of As^{tot} concentration. This gradual decrease of As^{tot} as the creek flows through the wetland suggests that nearly 70% of As^{tot} concentration could be retained by the wetland although some dilution effect along the wetland cannot be excluded. After the wetland, there is still some sources of As that caused an increase of the concentration from 235 to 420 µg/L from Farr-1 to Farr-11 (Fig. 1).

Arsenate, As^V was the dominant As species in all samples, ranging

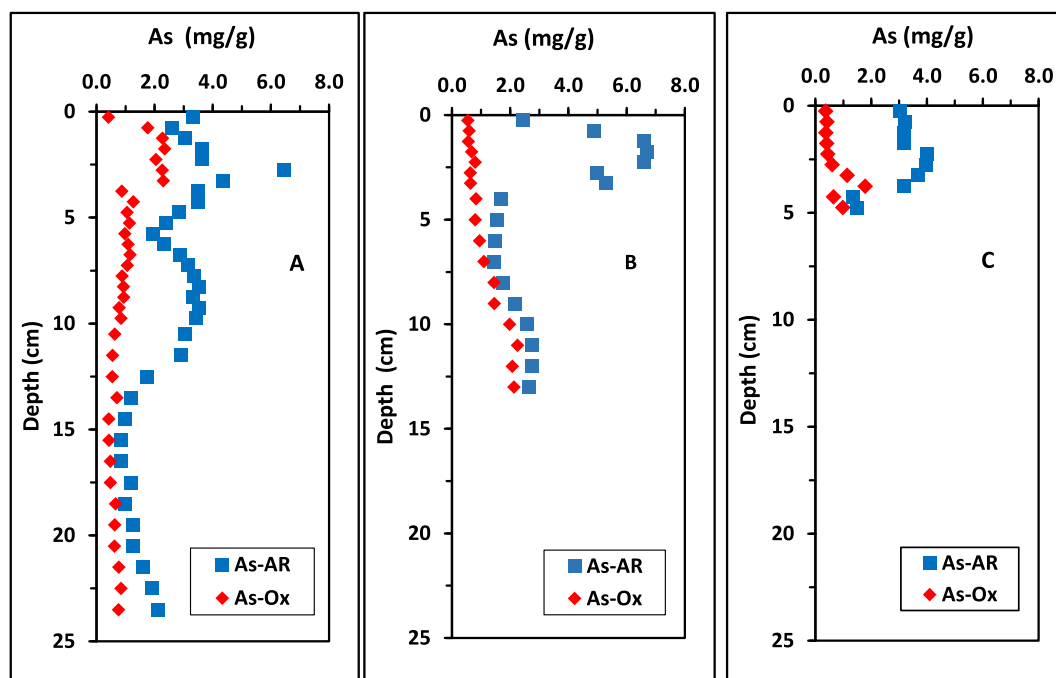


Fig. 6. Depth-distribution of total (As-AR) and labile (As-Ox) arsenic in the sediments of Cobalt Lake. Panels A, B and C are profiles for Cores A, B and C respectively. Error bars presenting $\pm 5\%$ of As concentrations cannot be seen.

from 73 to 99.8%, with an average 88% of the total. The organic-complexed As (As^{DOM}) was the next most abundant As species, ranging from 0.1 to 24.8%, with an average 9.7% of As^{tot} . As^{III} was the least abundant form of As with an average of 0.53% when excluding Sas-2 and Sas-3. The exceptionally high proportion of As^{III} in these two sampling sites (17.1 and 12.7%) could be associated to the particularity of these two locations. Sample Sas-1 was collected at the exit of Sasaginaga Lake, which is about 2 m above the creek and fully exposed to the summer sunlight. Samples Sas-2 and Sas-3, although very close to Sas-1 in distance, were collected in locations with very different environmental conditions where water passes through a flat section of the creek that seems stagnant in tiny pools formed by died tree branches and rocks. The two sampling locations were in a cold, dark and humid zone completely covered by a dense crown of trees, where the sunlight beam could hardly penetrate. The water was light brown in color and rich in decayed organic matter. This may have created reducing conditions for a partial transformation of As(V) to As(III) and less favorable for the oxidation process, as it has been proven in our laboratory study. The exact mechanism of formation of As(III) is not known but it could involve a biotic action.

The fact that the As(V) is a largely dominant species in water samples agrees well with our laboratory results, as a large majority of water samples were collected in fully sun exposed and well oxygenated open areas, a condition favorable for the oxidation of As(III). The presence of particulates iron and manganese oxides in water suspension can also play a catalytic role in the transformation of As(III) to As(V) when exposed to sunlight (Oscarson et al., 1980; DeVitre et al., 1991; Hug et al., 2001; Bhandari et al., 2011, 2012). Several papers also report the bacterial oxidation of As(III) (Santini et al., 2000) under similar environmental conditions. Because the minerals in the region are present in predominant CaCO_3 gangue (Reid et al., 1924), we speculate that a $\text{pH} > 7$ in the lake and creek waters could be another factor that can influence the stability of As(III). Because of its lower toxicity, As(V) is expected to cause less harsh impacts to living species present in this ecosystem (Sharma and Sohn, 2009).

3.3. Arsenic speciation in sediments

Two representative cores collected from Cobalt and Crosswise lakes (Fig. S1) showed a layer of recently formed organic material, indicated by a dark brown color in sharp contrast with the gray tailings below (Tables S1 & S2). This natural sediment layer originated from the lake's watershed and internal biological productivity. The thickness of the fresh sediment layer varied significantly (at some places the tailings could still be seen uncovered), depending on factors, such as the morphology of the lake basin, the presence of currents, the surrounding environment and the productivity of the lakes. A variety of chemical sequential extraction methods are used to estimate the potential mobility and bioavailability of As and other elements in the solid phase of environmental samples (Wenzel et al., 2001; Keon et al., 2001; Omen et al., 2002; Rodriguez et al., 2003). A study on soils of a mining zone (Anawar et al., 2008) reported that As found in the water soluble fraction (As weakly bound to the solid phase) represented 0.0–1.9% of the total, compared to 0.1–3.6% in an acetate buffer fraction (As bound to carbonate), 0.77–77.0% in the hydroxylamine hydrochloride extraction fraction (As bound to amorphous Fe and Mn oxides), and 15.2–75.3% in the oxalate extraction (As bound to low crystalline Fe and Mn oxides). The oxalate buffer is a chemical reagent possessing both reducing and complexation capacity, therefore it can dissolve not only freshly formed iron/manganese oxides, but also those with lower level of crystallinity (Schwertmann and Taylor, 1964; Keon et al., 2001) and carbonate. Thus, As extracted by oxalate would likely not underestimate the amount of potentially reducible and labile As. To simplify the analytical process, we chose to perform only oxalate extraction to represent all possibly reducible and labile As and an *aqua regia* digestion to cover total concentration in sediment samples. It should be indicated that none of the chemical extraction methods is perfectly adapted to the large diversity of samples (soil types, sediment, tailing, etc.) and can accurately analyze all types of As forms. Nevertheless, the sequential extraction can be considered as a useful tool for a better evaluation of environmental impact of a pollutant at trace level than the measurement of its total concentration.

The vertical distribution of total *aqua regia* (As-AR) and oxalate-

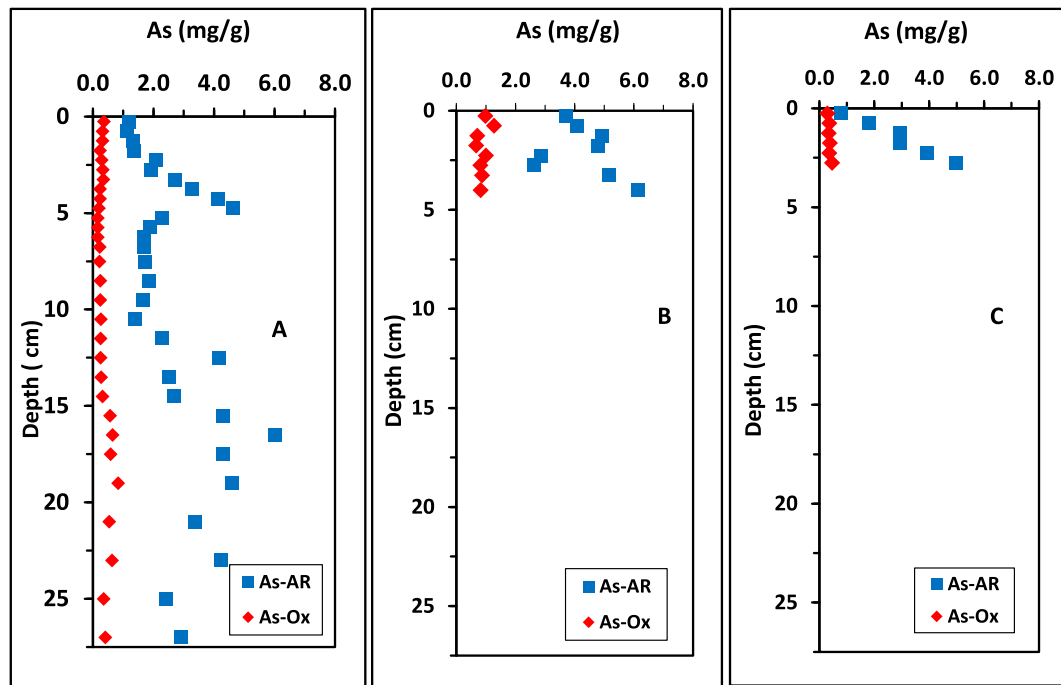


Fig. 7. Depth-distribution of total (As AR) and labile (As Ox) arsenic in the sediments of Crosswise Lake. Panels A, B and C are profiles of Cores A, B and C respectively. Error bars presenting $\pm 5\%$ of As concentrations cannot be seen.

extractable As (As-Ox) in the sediment cores and surface sediments collected from Cobalt Lake are presented in Fig. 6a–c and those taken from Crosswise Lake in Fig. 7a–c. All analytical data, including surface sediments in Cobalt and Crosswise Lakes are given in Supplementary information Tables S2 and S3. In sediment samples of Cobalt Lake, the concentration of total As (As-AR) varied greatly, particularly with depth. For instance, in Cobalt Core A, As-AR varied from a minimum of 0.85 mg/g dw to a maximum of 6.47 mg/g dw, and the labile fraction (As-Ox) from 0.41 to 2.77 mg/g dw, which represents 12 and 75% of total As (Fig. 6 and Table S2). For Crosswise Lake, the variation was similar, from a minimum of 1.13 mg/g to a maximum of 6.01 mg/g for As-AR. The As-Ox fractions in this lake sediment were usually lower than in Cobalt Lake. They varied from 0.16 to 0.84 mg/g in Core A, representing 7% and 18% of total As in the sediment, respectively (Fig. 7 and Table S3). The results show that the fraction of labile As in Crosswise sediment Core A was much lower than in Cobalt sediment Core A.

Double peaks in As-AR were observed in both long sediment core A of Cobalt and Crosswise Lakes, suggesting that disturbed geochemical conditions had occurred in the sediments. Indeed, these cores likely reflect the historical mining activities in this region. As mentioned earlier, due to the lack of environmental regulations in 1907, tailings from surrounding mills were rejected directly into several lakes, including Cobalt and Crosswise. However, these tailings often contained significant amount of un-extracted silver because of their coarse sizes and ineffective concentrating technology. For instance, the old technology could extract only 4.0–4.5 oz., compared 8.0–10.0 oz. of silver per ton of ore with the new technology proceeding fine crushed particles and improved floatation cells. For this reason, tailings in Cobalt and Crosswise Lakes were excavated and re-processed in 1950's to 1960's (Dumaresq, 1993).

Although the labile As (As-Ox) generally represents only a much smaller fraction of total As (As-AR), the As-Ox fraction represents an important percentage at several depths of Core A and Core B of Cobalt sediment. The usage of xanthate, sodium cyanide, potassium amyyl and other chemicals for the silver pre-concentration step was reported historically (Dumaresq, 1993). These chemicals were therefore released

together with the tailings to react with fine mineral particles and eventually affect As mobility. In this period, the mines were operated by many small companies, which frequently changed of ownerships. The applied technologies differed greatly.

It is conceivable that during the periods of tailings rejection and reprocessing, the environmental redox conditions were drastically modified. The formation of concentration peaks of total As could be due to many factors: sources of tailings with different mineral compositions, levels of oxygen to which these tailings were exposed, sizes of particle grains, chemicals and their concentrations used in ore extraction, and so on. When the vertical distributions of total As (As-AR) and oxalate extractable iron (Fe-Ox) are compared, the parallels between these two parameters differ in the cores collected from different sampling sites (Figs. 8a–c and 9a–c). It can be noticed that the total As (As-AR) profiles obtained from the cores A, B and C of Cobalt Lake are reasonably similar to those of Fe-Ox (amorphous and weakly crystallized iron/manganese oxides), i.e. As-AR increasing with Fe-Ox.

There is an abundant literature describing the affinity of As for iron oxides and oxyhydroxides (e.g. Belzile and Tessier, 1990) and the utilization of iron oxide minerals in remediation processes through adsorption (e.g. Sharma and Sohn, 2009; Gallegos-Garcia et al., 2012; Aredes et al., 2013). The presence of Fe, Mn and Al oxides as well as clay minerals is beneficial to limit the mobility and solubility of As under oxidizing conditions (Belzile and Tessier, 1990; DeVitre et al., 1991; Bhandari et al., 2011). The solubility of As under reducing conditions is generally controlled by the formation of As sulfides or adsorption onto amorphous iron sulfides or pyrite (Belzile and Lebel, 1986; Belzile, 1988; Beauchemin and Kwong, 2006). The oxidation of sulfide mineral releases both dissolved Fe^{2+} and oxyanion arsenite (AsO_3^{2-}) or arsenate (AsO_4^{3-}) in porewater. Fe^{2+} would diffuse upward due to the concentration gradient, but it should be quickly oxidized when meeting oxygen to form several types of oxides. The strong adsorption capacity of iron oxides could have served as an adsorbent to accumulate and pre-concentrate As. The decrease of As-AR beneath the peak seems the result from a relocation of As to an upper layer of iron oxide. In the sediment cores collected in Crosswise Lake, the relationships between As-AR and Fe-Ox (Table S3) are not clearly shown (Figs.

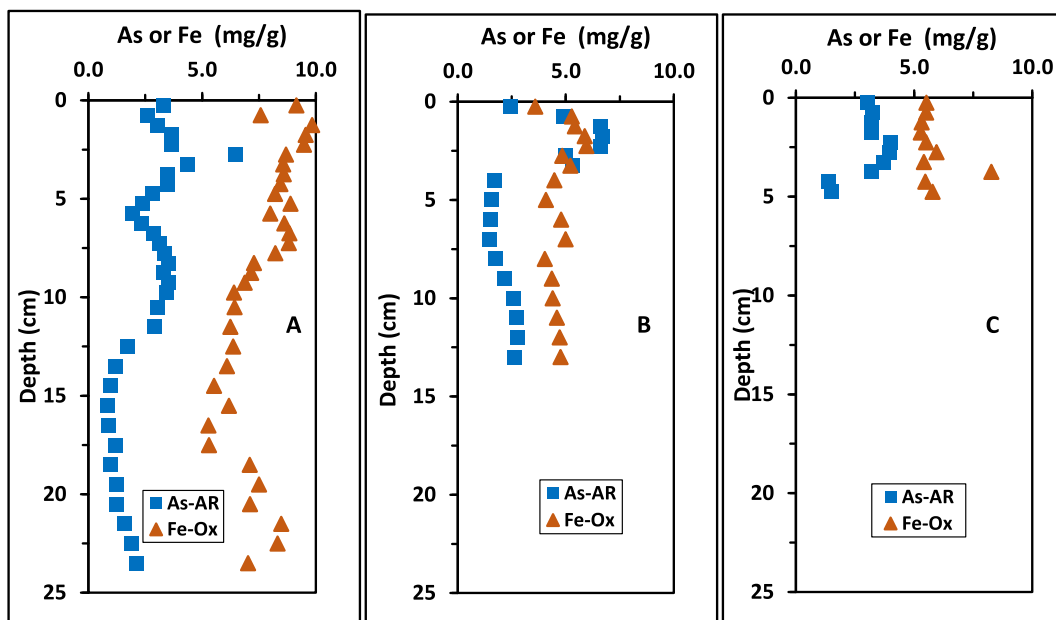


Fig. 8. Depth-distribution of total (As-AR) and oxalate extractable iron (Fe-Ox) in the sediments of Cobalt Lake. Panels A, B and C are profiles for Cores A, B and C respectively.

S2 & S3). When sediments and tailings were disturbed, the geochemical processes were strongly affected. The lack of detailed information on the mining operation makes this type of profile difficult to interpret. It can also be seen that the bioavailable (As-Ox) in Crosswise Lake sediment is generally lower than in Cobalt Lake; this could suggest that the oxidation level of tailings in Cobalt is higher than in Crosswise Lake. The comparison between As-Ox and Fe-Ox in the vertical sediment profiles of Crosswise Lake (Figs. S2 & S3) does not show clear correlation, probably due to the very low fraction of As-Ox in the samples.

Lower concentrations of total As at the top surface of the sediment cores could be related to the presence of new sediments rich in organic matter (Figs. 6 & 7). This new material can originate from exogenous and endogenous sources, and its As concentration is lower in comparison to the underlying tailing layers. The presence of organic matter in

overlying sediments can also induce some reducing conditions that are not favorable to the oxidation of underlying As sulfides, upward migration and diffusion of dissolved As species to the lake.

4. Field observations of Cobalt and Crosswise Lakes

As discussed earlier, the tailings filled lake sediments are remarkably different from one location to another. In the southern section of Crosswise Lake, water is deeper and we observed several shoals of small fish, often 50–80 in a shoal and many as long as 15 cm, swimming between clusters of long and flourishing aquatic grass. In the northern section where it is generally shallow, a large majority of sediment surface was covered by short and dense aquatic plants and their roots. It is similar in Cobalt Lake, where the southern basin is deeper than the

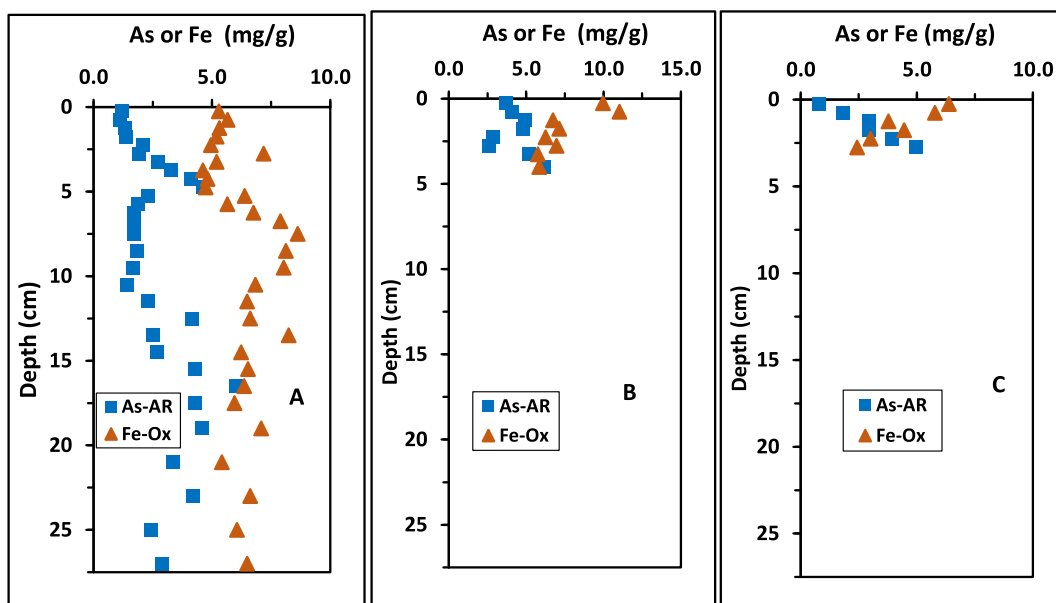


Fig. 9. Depth-distribution of total (As-AR) and oxalate extractable iron (Fe-Ox) in the sediments of Crosswise Lake. Panels A, B and C are profiles for Cores A, B and C respectively.

northern one and is covered by aquatic plants whereas the northern basin is shallow and covered with much shorter aquatic plants. A shoal of 40–50 small fish was also observed in the northern section of Cobalt Lake. Fish community in both Crosswise and Cobalt Lakes can then survive and prosper in water containing As concentration as high as 698 and 822 $\mu\text{g/L}$, respectively but it is important to recall that As^{III} concentrations were much lower at only 2.3 and 1.3 $\mu\text{g/L}$, respectively. It suggests that perhaps As^{III} , rather than total As, should be considered as a more appropriate indicator for environmental risk assessment. However, the size and diversity of fish populations was not assessed.

It was shown in Table 1 that the total As concentration in Crosswise Creek (Cr-5) has dropped by some 70% when the water had flown out of the Crosswise wetland (Farr-1 and Farr-2). This wetland, which was part of the original Crosswise Lake, was formed by the flood of tailings between 1908 and 1970. Nowadays, a large field of cattails and other plants is growing on the tailing site. The cattail field has been reported as early as 1985 in internal reports (e.g. Kelly, 2006; Beauchemin and Kwong, 2006). The lavish growth of plants in such environmental conditions demonstrates high As tolerance and strong capacity to reduce As concentration. Although there are a few studies on phytoremediation of As (Mudhoo et al., 2011b; Vithanage et al., 2012), most of them have been focused on Chinese brake ferns or other plants, and nearly all of them were conducted at small laboratory scale (Raj and Singh, 2015; Salido et al., 2003). In a review paper, Rahman and Hasegawa (2011) listed seven different aquatic plants involved in previous studies but the capacity of cattails was not mentioned. The finding of its strong As resistance and removing capacity directly on cold and wild mining site of the northern hemisphere indicates that cattail could be an excellent candidate for phytoremediation of As in a wide range of weather conditions.

5. Conclusive remarks

The ecotoxicity of As differs widely depending on its chemical forms, and among them, As^{III} is believed to be much more toxic than As^{V} . In our laboratory study, it has been found that the stability of As^{III} is greatly influenced by factors such as heat, light, the presence of NO_3^- and Cl^- at $\text{pH} \geq 7$. The presence of high temperature, sunlight, nitrate and chloride ions neutral pH conditions can make As^{III} to be quickly oxidized to As^{V} . It is suspected that a slightly basic pH could be a favorable condition for As^{III} oxidation. The chemical speciation of the water samples collected in various locations of the mining contaminated region of Cobalt indicates that the great dominant As species was the much less toxic forms of As^{V} , which was followed far behind by organic As. The toxic form of As^{III} is negligible in all these water samples, except in two samples collected in a cool and densely covered forest area with presence of rich organic matter and quasi-stagnant hydrological conditions, which coincides well with the favorable conditions for As^{III} stability found in laboratory conditions.

Arsenic in the sediments of Cobalt and Crosswise lakes is high because both lakes were used as tailing dumping sites historically. A significant layer of natural sediment with rich organic matter has been established since 1988 when the last silver mine was closed this region. A generally low concentration of total As at the top layer of sediment suggests it could have played a crucial role in controlling the mobility of As in tailings. The creation of anoxic conditions that are unfavorable to the oxidation of sulfidic As minerals and their upward diffusion in the sediment can also help. The reprocessing of tailings in both Cobalt and Crosswise lakes was reflected by double peaks of total As, which could be caused by the exposure to sulfide mineral oxidation and subsequent mobilization of As species. The As speciation results shows that labile As (As-Ox) is usually much lower than total As (As-AR) in sediment of both lakes. However, the percentages of possibly mobile As-Ox in Cobalt Lake were higher than in Crosswise Lake. Due to large scales of mining activities and many unknown factors, the geochemical processes occurring in these sediments cannot be interpreted with

certainty. Nevertheless, it is certain that iron oxides play an important role in mobilizing, adsorbing and accumulating As under certain redox conditions in some periods.

Some 30 years after the halt in mining activities, certain forms of life have returned in both lakes and surrounding wetlands and a food chain is establishing. This is likely due to conditions that are favorable to the oxidation of As^{III} and to the addition of new sediments on submerged tailings. A strong As removal capacity of the tailings filled wetland with robustly growing cattails and plants has been observed, which is certainly worth a further study. The field observations shed light on the gradual recovery of this mining contaminated ecosystem. The fact that a fish population, benthos and aquatic plants exist in these high As lakes, invites us to ask whether the concentration of As^{III} , rather than total As, could potentially be a more appropriate parameter in assessing the ecotoxicity of this metalloid. However, although speciation can be a critical factor in evaluating the toxicity of an element, several numerous aspects of such complex affected ecosystems must be considered in an evaluation process.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gexplo.2019.106349>.

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