Characterization of colloidal arsenic at two abandoned gold mine sites in Nova Scotia, Canada, using asymmetric flow-field flow fractionation-inductively coupled plasma mass spectrometry

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ABSTRACT

Asymmetric flow-field flow fractionation-inductively-coupled plasma-mass spectrometry was used to determine whether colloidal arsenic (As) exists in soil pore water and soil extract samples at two arsenic-contaminated abandoned gold mines (Montague and Goldenville, Nova Scotia). Colloidal arsenic was found in 12 out of the 80 collected samples (=15%), and was primarily associated with iron (Fe) in the encountered colloids. The molar Fe/As ratios indicate that the colloids in some samples appeared to be discrete iron–arsenic minerals, whereas in other samples, they were more consistent with As-rich iron (oxy)hydroxides. Up to three discrete size fractions of colloidal As were encountered in the samples, with mean colloid diameters between 6 and 14 nm. The pore water samples only contained one size fraction of As-bearing colloids (around 6 nm diameter), while larger As-bearing colloids were only encountered in soil extracts.
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Introduction

Colloids are ubiquitous in the environment and typically composed of inorganic mineral phases, organic biopolymers or microorganisms <1 μm in diameter (Kretzschmar and Schäfer, 2005). Aquatic colloids can be small enough to remain suspended by Brownian motion for long periods of time in the absence of aggregation; *e.g.*, colloids with 10 and 1 nm diameter can remain suspended for >20 and 200 years, respectively (Wilkinson and Lead, 2007). Colloidal material is present in all natural surface, soil pore and ground waters, and is significant for the cycling and transport of contaminants, including metalloids (Kretzschmar and Schäfer, 2005). The presence, stability and mobility of colloids may impact the transport/mobility of and risk associated with contaminants, so failure to distinguish between colloidal and dissolved fractions can lead to inaccurate estimations of contaminant mobility and risk. When assessing the practical importance of colloidal contaminant transport, one must consider (1) the colloidal concentration, including mass concentration and the total number of colloids, (2) the size and shape of the colloids, including size distribution and particle morphology, (3) the colloidal composition, including mineralogy,

elemental makeup and whether it includes organic components and (4) the surface characteristics, including surface charge, area and sorption capacity (Kretzschmar and Schäfer, 2005).

Arsenic, a toxic and carcinogenic metalloid, is ubiquitous in the environment (Dale and Freedman, 1982) due to geogenic occurrence and anthropogenic mobilization (Wang and Mulligan, 2006). Arsenic in natural waters exists predominantly as arsenate, As(V), and arsenite, As(III) (Henke, 2009). Water samples are typically filtered to <0.2 or <0.45 μm, and all of the arsenic in the filtrate is traditionally considered dissolved (Wilkinson and Lead, 2007), despite the fact that truly dissolved As species like As(III) and As(V) are <1 nm. Arsenic species between 1 and 200 (or 450) nm should therefore be considered colloidal rather than truly dissolved (Lesher et al., 2009; Dubascoux et al., 2008). To date, there is very limited evidence of the existence of colloidal arsenic in the environment. A laboratory study on arsenic leaching from mine tailings columns found iron-based colloids to be the primary means of arsenic transport; colloidal mineralogy was determined using X-ray adsorption techniques (Slowey et al., 2007). A second laboratory study investigated the influence of dissolved organic matter (DOM) on arsenate binding to iron (oxy)hydroxides, and found that arsenate binding to organic colloids was small or negligible in the absence of Fe(III), but increased significantly when Fe(III) was present (Bauer and Blodau, 2009). Finally, a field study demonstrated conclusively, using ultrafiltration and extended X-ray absorption fine structure (EXAFS) spectroscopy, that iron-based arsenic colloids exist in a pond receiving acid mine drainage. These arsenic colloids were present at ppm concentrations, had a diameter between 1.3 and 5 nm and accounted for >50% of the total "dissolved" arsenic (Zanker et al., 2002). These results generally confirm the known importance of iron (oxy)hydroxide minerals for arsenic cycling, due to their strong binding interaction (Henke, 2009).

Arsenic background levels in Nova Scotia surface soils are high in comparison to the Canadian soil guideline of 12 mg/kg (Wong et al., 1999), due to glacial transport during the last ice age, resulting in the crushing of mineralized bedrock. Consequently, geogenic arsenic in ground water is also elevated frequently, and many wells in Nova Scotia are naturally contaminated with arsenic (Goodwin et al., 2008) beyond the Canadian drinking water guideline of 10 μg/L (Wong et al., 1999). Additional arsenic contamination problems can arise from historical gold mining activities, which occurred extensively throughout Nova Scotia from the 1860s to the 1940s (Wong et al., 1999). Gold is typically found in quartz veins, which host arsenopyrite (FeAsS), the most common arsenic-bearing mineral (Henke, 2009). After the mining activities ended, approximately three million tonnes of arsenic-rich tailings had been produced, and were deposited on the surface of Nova Scotia mine sites and in local swamps, streams and rivers (Dale and Freedman, 1982).

This study aims to test if colloidal arsenic exists in waters in contact with abandoned gold mine tailings at two sites in Nova Scotia, Canada. Samples were collected at Montague and Goldenville. Since high arsenic concentrations have been found in such waters, concern exists regarding its mobility and the resulting risk. The physical and chemical speciation of arsenic in these waters could have a major influence on its

mobility and (potential) transport from the sites. To determine whether colloidal As species occur at these sites, asymmetric flow-field flow fractionation-inductively-coupled plasma-mass spectrometry (AsFl-FFF-ICP-MS) was used for the first time in this study to characterize arsenic-bearing colloids with respect to their size and elemental composition.

1. Methods and analytical instrumentation

1.1. Sampling sites (Nova Scotia, Canada)

Montague is located on the outskirts of Dartmouth, and is used for recreation purposes. Mining and milling took place from 1863 to 1940 and generated approximately 132,000 tonnes of mine tailings (Dale and Freedman, 1982). Mitchell Brook runs adjacent to the tailings, and tailings materials have been moved over 2 km downstream by it. Goldenville is located in Guysborough County; mining and milling occurred here from 1862 to 1941 and generated approximately 586,000 tonnes of tailings. These tailings occupy an area of 0.25 km² that is adjacent to the former mill sites. Tailings extend more than 8 km along the flood plain of Gegogan Brook (Wong et al., 1999). Maps of the sampling areas are presented in the supplemental information (Appendix A Fig. S1).

1.2. Sample collection and pretreatment

The soils at the two mine sites are strongly disturbed and contain large and variable amounts of weathered tailings materials. Some representative end members, general types of mineralogies produced at the end of the various tailings weathering processes, include calcium-rich tailings at Goldenville, containing on average 0.145% arsenic and 0.47% calcium (Kavalench, 2010), hardpan tailings at Montague, characterized by a large amount of scorodite and low pH, overlain with a layer of hardpan, and containing up to 33% arsenic and 23% iron, with molar ratios ranging from 0.85–1 (DeSisto, 2008), and wetland tailings (reducing; rich in organic matter) at Montague. Samples of these end member types were collected at 10 cm intervals from the surface for the calcium-rich and hardpan tailings, and from 25 and 75 cm depth for the wetland samples. Additional samples, representing mixtures of native soils and weathered tailings materials, were collected at various locations from each mine site.

Eighty samples were collected during four sampling campaigns in May 2009, March 2011, May 2011 and June 2012. The exact sampling locations are shown in the maps in the supplemental information (Appendix A Fig. S1). Surface water samples were collected using 1 L high density polyethylene (HDPE) bottles (Fisher Scientific, Nepean, ON). Pore water samples from the saturated zone (i.e., ground water) of soils were collected using suction PVC lysimeters (Soil Moisture Equipment Corporation, Santa Barbara, CA) and stored in 8 mL HDPE bottles (Fisher Scientific, Nepean, ON) with no headspace. Pore water from the unsaturated zone was extracted from soil samples by filtration. Soil samples were collected using 125 mL HDPE bottles (Fisher Scientific, Nepean, ON) and 50 mL plastic test tubes (Sarstedt, Montreal, QC). From these soil samples, aqueous extracts

were made using 1 g of soil to 10 mL of deionized water. Samples were placed on an end-over-end shaker (GFL, Burgwedel, Germany) for 12 h, and filtered through a 0.2 μm filter (Sarstedt, Montreal, QC) prior to analysis. Time series analyses of selected samples showed that these colloidal suspensions had a tendency to decrease in colloidal As concentration with time, but no statistically significant difference was found over 8 days of storage at room temperature. Therefore, samples were stored at room temperature in the dark after collection/extraction, and analyzed for colloids as quickly as possible, but always within 5 days of collection/extraction.

1.3. Total dissolved element concentration and dissolved arsenic speciation

Total elemental concentrations were determined using the X-2 ICP-MS (Thermo, Bremen, Germany) for ^{25}Mg, ^{26}Mg, ^{27}Al, ^{44}Ca, ^{48}Ca, ^{54}Fe, ^{55}Mn, ^{56}Fe and ^{75}As. Samples were diluted in 1% nitric acid (BDH Anstar VWR, Radnor, PA) prior to analysis. Calibration standards were made using a 1 ppm working solution (SCP Science, Baie D'Urfe, QC). TMDA-61 (Environment Canada, Burlington, ON) is fortified Lake Ontario water and was used as a certified reference material. An internal standard mixture was used to monitor ICP-MS drift. Arsenic speciation was determined using ion chromatography with ICP-MS (IC-ICP-MS) according to Wallschläger and Stadey (2007).

1.4. AsFl-FFF-ICP-MS

Colloids were separated using AsFl-FFF coupled in series to a UV detector (Post Nova Analytics, Landsberg, Germany) and an X-2 ICP-MS (Thermo, Bremen, Germany) for elemental quantitation and characterization using the parameters in Table 1. Field flow fractionation (FFF) is a technique which separates particles based on size. Separation occurs when a "field" is applied at 90° to a sample moving through a thin channel in a mobile phase exhibiting laminar flow characteristics. There are a number of different types of FFF, which use a variety of fields (Schimpf et al., 2000). In asymmetric flow-FFF (AsFl-FFF), a cross-flow is applied perpendicularly to the main flow, which is down the channel. This cross-flow is the field causing the separation of the sample components. The key component to separation in AsFl-FFF is the focusing step. In this portion of the separation, a focus flow is injected into the channel between the inlet flow and the end of the channel, such that part of it moves towards the inlet and part towards the detector. The focus flow and the tip flow meet under what is known as the focus location, where the sample constituents are held in place and separated vertically based on particle size. Two elution steps were used, one with a cross flow to maintain separation and one without a cross flow to elute any larger colloids remaining in the channel.

The sample was introduced to the ICP-MS using a Meinhard TR-30-C3 nebuliser (Meinhard, Santa Ana, CA). The sample injection loop was cleaned between injections using three rinses with 0.1 M sodium hydroxide, followed by three rinses with Milli-Q water, to prevent carryover of colloids from one sample into the next. Samples were diluted with

Table 1 – Asymmetric flow-filed flow fractionation-inductively-coupled plasma-mass spectrometry (AsFl-FFF-ICP-MS) operating parameters and detection limits.

FFF parameters	
Injection volume	100 μL
Focus step (0–7 min)	
Injection flow rate	0.4 mL/min
Cross flow	2 mL/min
Focus flow	2.1 mL/min
Tip flow	0.5 mL/min
(overall channel flow)	
Elution step	
Tip flow	0.5 mL/min
Cross flow: 7–48 min	2.0 mL/min
Cross flow: 48–63 min	0 mL/min
Channel	
Membrane	10 kDa regenerated cellulose amphiphilic
Spacer	350 μm
Eluent	MilliQ water (not pH adjusted)
ICP-MS parameters	
Isotopes measured FFF	^{25}Mg, ^{26}Mg, ^{27}Al, ^{44}Ca, ^{46}Ti, ^{47}Ti, ^{48}Ca, ^{54}Fe, ^{55}Mn, ^{56}Fe and ^{75}As, ^{115}In, ^{126}Te, ^{103}Rh (as internal standards)
Collision gas	5% hydrogen/95% helium
Collision gas flow	6 mL/min
Dwell time	100 ms
(all measurements)	
Radiofrequency power	1500 W
Nebuliser flow	0.9–1.0 L/min
FFF colloidal peak detection limits (μg/L)	
Arsenic	9
Aluminum	2
Iron	7
Manganese	0.3

deionized water, as necessary, prior to analysis, to facilitate removal of dissolved As species during the focusing step (see below). This was done to ensure that the level of dissolved arsenic was below the amount which the focusing step could remove. This dilution changed neither colloid size nor colloid concentration, as shown with replicate analyses of soil extracts at different dilutions.

The presence of high concentrations of dissolved As species (mostly arsenate) in the investigated samples was a major challenge in the development of a method for the determination of colloidal As, because they yielded signals in the fractograms, despite the fact that they should theoretically pass through the membrane during the focusing step. Dissolved As concentrations up to 2000 μg/L were encountered, and with sufficiently large cross flow rates and long focusing times, these concentrations of dissolved As species could be removed from the samples during the focusing step. However, this made the focusing step unreasonably long, compared to the subsequent separation. Therefore, a practical compromise was made to remove dissolved As species only up to concentrations of 200 μg/L, which necessitated appropriate dilution of the samples prior to analysis. This approach worked well in synthetic solutions under the conditions shown in Table 1; however, in some natural samples, peaks

were observed in the fractograms at the time corresponding to "dissolved As", despite being appropriately diluted. In the same samples, other dissolved elements, such as Fe, Al, Mn, Ca and Mg were removed completely during the focusing step, indicating that the problem may be related to the anionic character of the predominant inorganic As species, arsenate. This suggests that either some constituents of the matrix prevented the dissolved As species from passing through the membrane, or that there were small (just above 2 nm) As-bearing colloids present in those samples. Due to our inability to distinguish between these two possibilities analytically, such signals were ignored in the subsequent discussion of colloidal As fractions in the studied samples.

For online quantitation of colloidal elements, a Rheodyne valve (IDEX Health and Science, WA) placed after the FFF channel and two mixed standard solutions (SCP Science, Baie D'Urfe, QC) containing 50 or 100 μg/L of As, Fe, Al, Ca, Mg and Mn were injected sequentially, in triplicate, after the final elution step of the FFF separation to generate two-point calibration curves. The isotopes that were monitored are shown in Table 1. Under the chosen ICP-MS measurement conditions, carbon and sulfur cannot be determined, and were thus neglected in this study.

With an FFF separation/elution time >1 hr, ICP-MS stability during the separation was a potential concern, so it was monitored by continuously adding an internal standard containing 5 μg/L of indium, rhodium and tellurium (SCP Science, Baie D'Urfe, QC) after the FFF channel *via* a peristaltic pump. Instrumental drift was not detected over the course of an individual FFF-ICP-MS run, and changes in the ionization in the plasma were not detected when colloids or nanoparticles entered the plasma. As complete ionization of intact colloids may be a challenge, the ionization efficiency was tested using 20 nm iron oxyhydroxide nanoparticles (Nanochemonics, Wise, VA), which is similar to the colloids encountered in this study. When the iron nanoparticles were injected directly into the plasma under the used FFF-ICP-MS detection conditions, and compared to nitric acid digested solutions, quantitative ionization was achieved. Offline quantification of FFF fractions collected from real samples was not possible because after digestion, the sample had to be diluted such that the concentrations of the elements were below the detection limit of the ICP-MS.

1.5. Colloidal diameter determination

The diameter of the colloids was calculated from first principles using the Stokes (Eq. (1)) and Einstein (Eq. (2)) equations (Schimpf et al., 2000). The diffusion coefficient was calculated using the relationship described by Qureshi and Kok (2010):

$$D_i = (w^2/6t_r) \ln (1 + F_c/F_{out}) \qquad (1)$$

where, w (μm) is the thickness of the spacer, D_i (cm²/sec) is the diffusion coefficient, t_r (min) is the retention time, F_c (mL/min) is the cross flow and F_{out} (mL/min) is the detector flow. The hydrodynamic radius was then determined using:

$$r = kT/6\pi\eta D_i \qquad (2)$$

where, k is Boltzmann's constant, T (K) is the absolute temperature and η is the viscosity of the carrier solution (Schimpf et al., 2000). Retention time (t_r) was determined at the peak maximum by subtracting focus time and dead time, and was used to calculate the "mean" diameter of the colloids detected. The results of this particle size determination method were confirmed by analyzing gold nanoparticles of known diameters, 5 and 20 nm (BB International, Cardiff, Wales); the "calculated" diameters of these standards were 6 and 17 nm, respectively. Additionally, for some samples, particle size was determined both from first principles and *via* calibration using the gold nanoparticle standards; the obtained results agreed well, indicating no systematic bias in the particle size determination.

2. Results and discussion

2.1. AsFl-FFF-ICP-MS method characterization

Many FFF separations use "normal" regenerated cellulose membranes (RCMs), which possess a negative charge. For this project, however, we postulated (correctly, as shown below) that colloidal iron (oxy)hydroxide minerals would be an important potential binding partner for As species, particularly since the As speciation analyses revealed that most of the analyzed waters contained predominantly As(V) in the dissolved fraction. Since these minerals are positively charged at pH 3.5–8 (Buffle et al., 1998), an amphiphilic RCM was used to minimize interaction with the iron-based colloids. An alternate approach to reducing colloid/membrane interactions (*via* competition) would be using a mobile phase with high salt content, but we opted against this potential solution, since it is well known that colloids can change particle size as a function of salinity. Due to the lack of applicable standard As colloids, such effects could not be accounted for, so we decided to use deionized water as the mobile phase instead. Likewise, the lack of appropriate known colloidal As standards, combined with the presence of high concentrations of dissolved As species, made it impossible to determine colloidal As recovery across the FFF channel, so the quantitative results generated in this study were used and interpreted with caution, as it cannot be ruled out that significant and variable fractions of the As-bearing colloids were lost during transport through the FFF channel (=along the membrane).

Ampiphilic RCMs are only available down to a nominal molecular weight cutoff of 10 kDa (2 nm pore size), so the lower limit of particle sizes separated here is *ca.* 2 nm. Consequently, colloids <2 nm diameter may be (partially) lost through the membrane during the focusing step. There are reports that As forms such small colloids, consisting of either minerals, such as orpiment (Wilkinson and Lead, 2007), or of complexes with DOM (Bauer and Blodau, 2009), which is often <2 nm (Buffle et al., 1998). In the latter, it is suggested that As may be bonded to DOM *via* Mn^{2+} or Fe^{3+} as bridging cations (Ahuja, 2008), which are both abundant at the studied mine sites. Therefore, it is conceivable that small As-bearing colloids may have gone undetected in our experiments. In one sample (Mont 2-1 oxic), we observed an As signal in the size range around 2 nm, which showed a lack of accompanying

elements in the FFF-ICP-MS analyses, compared to the corresponding FFF-UV signal, which may hint at the presence of an ICP-MS-undetectable element, such as (organic) carbon, as the major colloidal constituent in this As fraction. However, due to the uncertainty surrounding the completeness of the removal of dissolved As species in natural samples (see below), this explanation is only speculative.

The upper limit of positive particle size separation for the optimized method was calculated to be 32 nm, using the Stokes–Einstein equation (see above). By eliminating the cross flow for the last 15 min, any colloids >32 nm remaining in the channel elute, which was confirmed with a 100 nm gold nanoparticle standard. So, the separation range for this FFF method is 2–32 nm, with unresolved elution of particles between 32 and 100 nm. However, no arsenic containing colloids >32 nm were observed in any of the measured samples.

Using the optimized method (Table 1), baseline resolution ($R = \Delta t_r/w_{avg} = 1.5$, with w_{avg} being the average peak width) was achieved between gold nanoparticles of 5 and 20 nm diameter. Resolution is poorer for natural colloids, because they have a wider size range than manufactured nanoparticles. To estimate the minimum particle size difference required to distinguish qualitatively between two different colloidal fractions of equal abundance by our FFF method, we compared two approaches. First, we calculated (based on the colloidal As peak shape in Fig. 1) that in order to achieve $R = 0.75$ (resolution at 70% peak height), a second colloidal size fraction would need to be 6 nm larger ($\Delta t_r = 7$ min) than the observed colloids to be noticed. For the second approach, we determined the reproducibility of particle size determination for a soil extract ($n = 11$ over six days, which is within the stability period of these colloids, as mentioned above); the average mean particle size was 10 ± 2 nm (maximum deviation). Assuming that both colloidal arsenic fractions have the same uncertainty for their particle size estimate, they would need to differ by at least 4 nm to be visually distinguished reliably. Using the median result between approaches 1 and 2,
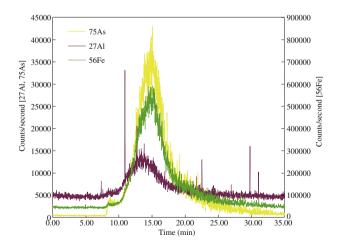
we therefore conclude that in order to be observed separately, two colloidal fractions will have to differ in average diameter by about 5 nm ($\Delta t_r = 6.25$ min).

Due to the lack of a colloidal As standards, detection limits for colloidal elements separated by FFF were determined by an indirect approach. Firstly, ICP-MS detection limits were determined from the signal of the lowest quantification standard *versus* the background. To compensate for the broadness of the FFF peaks relative to the quantification peaks, the ratio of peak area to peak height was then determined for both quantification peaks and FFF peaks. The compensation factor (=ratio for the quantification peak divided by the ratio for the FFF peak; ~22 for arsenic) was then multiplied by the ICP-MS detection limit (0.4 μg/L for arsenic) to provide a detection limit for FFF peaks (~9 μg/L for arsenic).

2.2. Characterization of colloidal arsenic

Combining the four separate sampling events, a total of 80 samples were analyzed for colloidal arsenic. Of these samples, 12 samples contained detectable amounts of colloidal arsenic; data for three of these samples were lost due to computer problems, so Table 2 only shows the results for the characterization of colloidal As in nine samples. Arsenic-bearing colloids were only detected in samples collected at the surface of the soils/tailings (within the top 10 cm), presumably because weathering rates are highest here. The measured concentrations of colloidal arsenic ranged from 20 to 200 μg/L, corresponding to 5%–20% of the total dissolved As concentrations, but acknowledging the potential problems associated with the quantification of these colloids with respect to unknown recovery across the FFF channel, these concentrations and fractions may be underestimated. In the only other field study that provided conclusive evidence of colloidal arsenic, arsenic colloids were determined to account for upwards of 50% of the total arsenic concentration in acid mine drainage from a mine near Freiberg, Germany (Zanker et al., 2002). The total concentration of colloids present in those samples was much higher than in this study, presumably explaining the higher colloidal arsenic fraction encountered.

In all cases, colloidal As coincided perfectly with Fe in the fractograms, suggesting the presence of mixed As-Fe colloids. Other elements, specifically Al and Mn, were sometimes found in the colloidal form as well, but didn't always match up perfectly with the As–Fe colloids. An example of this is presented in Fig. 1, which shows an offset between the peak maxima, as well as different peak shapes, for As/Fe *vs.* Al, suggesting that colloidal Al was not primarily physically associated with colloidal As and Fe.

Eight samples (only six shown in Table 2) contained only one visible peak in their fractograms; for the other four samples (only three shown in Table 2), multiple unresolved peaks were observed, indicating the presence of several discrete colloidal As/Fe fractions. Fig. 2 shows an example of a sample with three distinct colloidal As fractions, which was the maximum number of peaks observed. The remaining As fractograms are shown in the supplemental material for completeness. The pore water samples contained the smallest colloids (*ca.* 6 nm), and only one colloidal As fraction. Multiple and larger (up to 14 nm) colloidal As fractions were

Fig. 1 – AsFl-FFF-ICP-MS fractogram of a pore water sample from Goldenville mine (sample GV 1-2; collected 2011). AsFl-FFF-ICP-MS: asymmetric flow-field flow fractionation-inductively-coupled plasma-mass spectrometry.

Table 2 – Physical and chemical characterization of As-bearing colloids detected in mine tailings. The corresponding As fractograms are shown in Appendix A. Supplementary data and in Figs. 1 and 2.

Sample	Type	Colloidal As (µg/L)	Colloidal Fe (µg/L)	Molar Fe/As ratio	Mean colloidal size (nm)
MT upper tailings	Pore water	75	250	4.5	8.5
GV 1-2	Pore water	165	400	3.2	6.2
MT 2-1 oxic	Pore water	215	200	1.2	6.4
MT 2-2 oxic	Pore water	210	205	1.3	5.6
MT 1	Soil extract	23	113	6.6	13.5
MT 3	Soil extract	199	436	2.9	7.2 + 12.7
MT 4	Soil extract	89	300	4.5	7.0 + 11.4
MT 8	Soil extract	141	297	2.8	5.8 + 8.5 + 12.3
MT 12	Soil extract	18	60	4.5	14.2

observed in the soil extracts, which is consistent with the idea that smaller colloids are more mobile and therefore occur naturally in the pore waters, while larger colloids have a lower tendency to be in the suspended state.

The molar ratio of iron to arsenic in the colloids ranged from 1 to 7 (Table 2). In samples with multiple colloidal As fractions, each one contained Fe, but the Fe/As ratios could not be determined for each fraction, due to incomplete separation. For the samples with only one peak, these Fe/As ratios can be interpreted geochemically by comparison to the general tailings mineralogy at Montague and Goldenville (Walker et al., 2009). These authors showed that the most dominant mineral hosts of arsenic were the discrete ferric arsenates scorodite ($FeAsO_4 \cdot 2H_2O$) and kankite ($FeAsO_4 \cdot 3.5H_2O$), as well as amorphous and poorly crystalline ferric arsenates, referred to as hydrous ferric arsenate (HFA). The measured iron to arsenic ratios were typically one for kankite, close to one for scorodite (with a range of 0.94–1.14), and consistently greater than one for HFA (range 1.1–3). The increased Fe/As ratio in HFA, compared to scorodite and kankite, may be due to surface weathering of ferric arsenate yielding iron oxyhydroxides (Robins, 1987). The Fe/As ratios of several colloidal As-Fe fractions (Table 2) are consistent with HFA, therefore suggesting that the colloids in these samples represent weathered ferric arsenate minerals.

Walker et al. (2009) showed furthermore that As-laden iron oxyhydroxides at these sites had even higher Fe/As ratios (range from 3 to 30) and that goethite was among the most co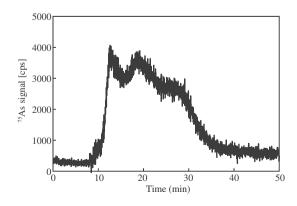mmonly observed iron oxyhydroxide minerals at these locations. The colloidal As fractions in the remaining samples in Table 2 had Fe/As ratios consistent with this kind of material, suggesting that they were native iron colloids, to which large amounts of As have been adsorbed. This matches reports indicating that iron oxyhydroxides, unlike intact arsenic iron minerals, are important for and effective at adsorbing arsenic species from solution (Henke, 2009).

The elemental composition and size of the colloids determined here matches qualitatively those of colloids isolated from Mitchell Brook, the stream running along the tailings at Montague, by tangential flow filtration (Andrew Gault, Queen's University, unpublished data), potential evidence of the transport of As-bearing colloids from the contaminated soils/tailings into the surrounding aquatic environment. While synchrotron-based micro-XRD has been used successfully to identify discrete As–Fe mineral particles, similar to the minerals found in the bulk material at the sites (Walker et al., 2009), in both the tailings and airborne dust at the two study sites (Jamieson et al., 2011), such attempts were unsuccessful for colloidal material isolated from the waters at the sites, presumably due to the comparably low particle concentrations encountered. Therefore, there is no further direct evidence for the proposed mineralogical nature of the encountered As–Fe colloids, other than their stoichiometric Fe/As ratios relative to those encountered in the bulk material.

In comparison to the results from the only other previous field study on As-bearing colloids (Zanker et al., 2002) the colloids encountered here are larger and have a different chemical composition. At the comparison site near Freiberg, Germany, the As-bearing colloids had a size range of 1.3–5 nm, and consisted mostly of As-substituted jarosite, a ferric sulfate mineral. These differences are likely due to the fact that the German site was primarily characterized as an acid mine drainage environment, so the lower pH (compared to many parts of the Montague and Goldenville ecosystems) and associated extensive sulfur oxidation presumably explain the mineralogical differences between the colloidal As–Fe fractions.

2.3. Relevance of arsenic-bearing colloids at Goldenville and Montague

Colloidal arsenic was only detected in 15% of the samples analyzed. Given the low frequency of colloidal arsenic detected in the soils/tailings, it can be concluded that arsenic in the pore/ground waters exists primarily in the truly dissolved state,

Fig. 2 – Colloidal arsenic fractions in a soil extract from Montague mine (sample MT 8; collected 2012).

rather than in association with colloids. There are a number of potential reasons why colloidal arsenic was not encountered more frequently, but due to the limited scope of this initial study, we cannot make any conclusive statements about their validity, so they are presented here to outline potential follow up studies (be it at these study sites, or elsewhere). First, observation of colloidal As (or lack thereof) may be tied to specific hydrological conditions: during dry periods, there may not be enough mobilization from the solid phase, while during very wet periods, the concentrations of colloidal As may be too low for detection by FFF-ICP-MS, due to dilution. Second, the pH/redox conditions in large parts of the study area may not be favorable for the formation/ stability of As–Fe colloids; for example, the scorodite-rich regions may be acidic enough to dissolve iron (oxy)hydroxide minerals, or the wetland regions may be too reducing to allow the presence of insoluble Fe(III) minerals. Third, our data suggest that colloidal As is found only near the soil/tailings surface, possibly due to increased weathering and erosion in this horizon. Not knowing this beforehand, we collected many samples deeper in the soil/tailings profile, which may have biased the frequency with which colloidal As was observed low. Future studies will have to test if colloidal As is more prevalent than our study suggests, when the experimental design of the study is adapted to these open questions.

In those samples where As-bearing colloids were found, they accounted only for between 5%–20% of the total dissolved arsenic concentration, albeit with a caveat that the analytical results could be biased low, due to unknown recovery of the colloids across the FFF channel. Given that colloidal arsenic (determined by different analytical methods) accounted for upwards of 50% of the total arsenic concentration in acid mine drainage from a mine near Freiberg, Germany (Zanker et al., 2002) it is certainly desirable to undertake further FFF-ICP-MS method development studies to determine if the recovery of As-bearing colloids during the separation is low, and if so, how those problems could be addressed. On the other hand, if the observed differences with respect to the relative proportions of colloidal and dissolved As are real, then it will be worthwhile investigating under what conditions (e.g., hydrological or geochemical) colloidal As predominates. Ultimately, the question of whether a colloidal As fraction, be it a major or a minor fraction of the total "dissolved" As concentration, is significant, depends more on the environmental fate of this colloidal fraction: if it is mobile and bioavailable, it may not be evaluated very differently from dissolved As species, but if it is much less mobile and/or bioavailable, that may lead to an overall reduction in risk potential.

In this regard, our study provides a few hints about the potential mobility of As-bearing colloids in the subsurface environment, albeit no conclusive evidence. The size of the observed colloidal As fractions (6–14 nm) suggests that these colloids will be quite mobile in the studied soils/tailings, which were classified as loamy sand with approximately 50% porosity (Lowell Yellowhorn, Trent University, unpublished data). The theoretical settling time of these colloids from solution, calculated from Stokes' law, is on the order of 15–30 years. By comparison, the ground water flow at Montague was estimated to be on the order of hundreds of meters per year (Stephanie DeSisto, Queen's University, unpublished data), suggesting that colloids can be transported for many kilometers in the subsurface environment. This is in line with the observation of colloidal As in Mitchell Brook (Andrew Gault, Queen's University, unpublished data), the surface water body ultimately receiving the subsurface flow.

On the flip side, the observed As-containing colloids are largely constituted of iron minerals, which tend to have a positive surface charge at circumneutral pH (Buffle et al., 1998; Robins, 1987). By contrast, the tailings are predominantly composed of silicate minerals, which are negatively charged at neutral pH (pK_a = 1.8). Therefore, the mobility of Fe-based colloids in this environment should be reduced by electrostatic attraction to the bulk solid phase. Furthermore, arsenate, the main dissolved As species encountered, will readily sorb to the positively charged surface of Fe colloids at circumneutral pH (Beker et al., 2010) which could lead to additional removal of As from the dissolved phase onto immobilized colloids. Due to these conflicting hypotheses, further research is needed to fully understand the role of colloid-facilitated arsenic transport, in mining-impacted environments and elsewhere.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.10.009.

REFERENCES

Ahuja, S., 2008. Arsenic Contamination of Groundwater: Mechanisms, Analysis and Remediation. Wiley, Hoboken, New Jersey, USA.

Bauer, M., Blodau, C., 2009. Arsenic distribution in the dissovled, collodial and particulate size fraction of experimental solutions rich in dissolved organic matter and ferric iron. Geochim. Cosmochim. Acta 73, 529–542.

Beker, U., Cumbal, L., Duranoglu, D., Kucuk, I., Sengupta, A.K., 2010. Preparation of Fe oxide nanoparticles for environmental applications: arsenic removal. Environ. Geochem. Health 32 (4), 291–296.

Buffle, J., Wilkinson, K.J., Stoll, S., Filella, M., Zhang, J.W., 1998. A generalized description of aquatic colloidal interactions: the three-colloidal component approach. Environ. Sci. Technol. 32 (19), 2887–2899.

Dale, J.M., Freedman, B., 1982. Arsenic pollution associated with tailings at an abandoned gold mine in Halifax County, Nova Scotia. Proc. Nova Scotia Inst. Sci. 32, 337–349.

DeSisto, S.L., 2008. Dynamic Arsenic Cycling in Scorodite-bearing Hardpan Cements, Montague Gold Mines, Nova Scotia. MSc thesis. Queen's University, Kingston Ontario, Canada.

Dubascoux, S., Le Hecho, I., Gautier, M.P., Lespes, G., 2008. On-line and off-line quantification of trace elements associated to colloids by As-Fl-FFF and ICP-MS. Talanta 77 (1), 60–65.

Goodwin, T.A., Parsons, M.B., Taylor, R.B., 2008. Environmental geology of halifax and surrounds. EdGEO Field Excursion. Guidebook Vol. 20–21.

Henke, K. (Ed.), 2009. Arsenic Environmental Chemistry, Health Threats and Waste Treatment. Wiley, Chichester, UK.

Jamieson, H.E., Walker, S.R., Andrade, C.F., Wrye, L.A., Rasmussen, P.E., Lanzirotti, A., Parsons, M.B., 2011. Identification and characterization of arsenic and metal compounds in contaminated soil, and house dust using synchrotron-based microanalysis. Hum. Ecol. Risk Assess. 17, 1292–1309.

Kavalench, J.L., 2010. Effects of Tailings Mineralogy and Infiltration Water Chemistry on Arsenic Release from Historic Gold Mine Tailings. MSc thesis. Queen's University, Kingston, Ontario, Canada.

Kretzschmar, R., Schäfer, T., 2005. Metal retention and transport on colloidal particles in the environment. Elements 1 (4), 205–210.

Lesher, E.K., Ranville, J.F., Honeyman, B.D., 2009. Analysis of pH dependent uranium(VI) sorption to nanoparticulate hematite by flow field-flow fractionation-inductively coupled plasma mass spectrometry. Environ. Sci. Technol. 43 (14), 5403–5409.

Qureshi, R.N., Kok, W.T., 2010. Optimization of asymmetrical flow field flow fractionation (AF4). LC-GC Europe 23 (1), 18–25.

Robins, R., 1987. Solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$: discussion. Am. Mineral. 72, 842–844.

Schimpf, P.L., Caldwell, K., Giddings, J.C., 2000. Field Flow Fractionation Handbook. Wiley, New York.

Slowey, A.J., Johnson, S.B., Newville, M., Brown Jr., G.E., 2007. Speciation and colloid transport of arsenic from mine tailings. Appl. Geochem. 22, 1884–1898.

Walker, S.R., Parsons, M.B., Jamieson, H.E., Lanzirotti, A., 2009. Arsenic mineralogy of near-surface tailings and soils: influences on arsenic mobility and bioaccesibility in the Nova Scotia gold mining districts. Can. Mineral. 47 (3), 533–556.

Wallschläger, D., Stadey, C.J., 2007. Determination of (oxy)thioarsenates in sulfidic waters. Anal. Chem. 79 (10), 3873–3880.

Wang, S., Mulligan, C.N., 2006. Occurrence of arsenic contamination in Canada: sources, behavior and distribution. Sci. Total Environ. 366 (2–3), 701–721.

Wilkinson, K.J., Lead, J.R. (Eds.), 2007. Environmental Colloids and Particles — Behaviour, Separation and Characterisation. John Wiley & Sons, Chichester, UK .

Wong, H.K.T., Gauthier, A., Nriagu, J.O., 1999. Dispersion and toxicity of metals from abandoned gold mine tailings at Goldenville, Nova Scotia, Canada. Sci. Total Environ. 228 (1), 35–47.

Zanker, H., Moll, H., Richter, W., Brendler, V., Hennig, C., Reich, T., Kluge, A., Huttig, G., 2002. The colloid chemistry of acid rock drainage solution from an abandoned Zn–Pb–Ag mine. Appl. Geochem. 17 (5), 633–648.