Arsenic speciation in the dispersible colloidal fraction of soils from a mine-impacted creek

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ABSTRACT

Arsenic and iron speciation in the dispersible colloid fraction (DCF; 10-1000 nm) from an As-rich mine waste pile, sediments of a streambed that collects runoff from waste pile, the

combining asymmetrical-flow field-flow fractionation (AsFIFFF)/inductively-coupled plasma-mass spectrometry (ICP-MS), transmission electron microscopy (TEM) and X-ray absorption (XAS) spectroscopy. Calcium, Fe and As (Fe/As molar ratio~1) were the main components of the DCF from waste pile. TEM/EDS and As and Fe XAS analysis revealed the presence of nanoparticle scorodite in this same DCF, as well as Fe nanoparticles in all samples downstream of the waste pile. Arsenic and Fe XAS showed As(V) adsorbed onto nanoparticulate ferrihydrite in the DCF of downstream samples. Micro-X-ray fluorescence indicated a strong correlation between Fe and As in phyllosilicate/Fe³⁺ (oxi)hydroxide aggregates from the sediment pond. Fractionation analysis showed the mean particle size of the DCF from the streambed sample to be smaller than that of the streambed subsoil and sediment ponds samples. These results show that an important and variable fraction of As may be bound to dispersible colloids that can be released from contaminated soils and transported downstream in natural systems.

1. Introduction

Understanding the release of colloids from soils and sediments, and their association with contaminants, is essential when evaluating pollutant transport processes [1-7]. The *in situ* mobilization and transport of colloids in soils depends on the latter's physico-chemical characteristics (presence of organic matter, clay minerals, pH, ionic strength, etc.), and the reigning hydrodynamic conditions (flow velocity and soil saturation) [8, 9]. Once a colloid has been mobilized, its transport is controlled by its size and stability in solution, i.e., its tendency to aggregate. Aggregation is controlled mainly by the balance of attractive and repulsive forces between particles [10]. The presence in solution of ions of opposite charge to those on the surface of a colloid, and an increment in the ionic strength of the soil solution and/or any runoff, increases aggregation, while the surface coating of colloids with organic matter enhances colloid stability [11]. Colloids can

strongly bind metals and other pollutants in soils and aquifers. In soils and sediments impacted by mining wastes, the mobility of As and other metals is affected by the release and transport of nanoparticles from the soils and As-colloid adsorption phenomena.

The characterization of natural colloids requires the use of fractionation and analytical techniques that minimize sample perturbation. One option is asymmetrical-flow field-flow fractionation (AsFIFFF), in which colloids are separated according to their diffusion against a flow-field perpendicular to a carrier flow [12, 13]. The AsFIFFF has been used couple to inductively-coupled plasma-mass spectrometry (ICP–MS) to determine the elemental composition of colloids and their particle size distribution [12, 14, 15]. This allows the relationship between trace metal(oids) concentrations and colloid particle size to be established. However, elemental analysis alone provides no information about the molecular-scale chemical association of metal(oids) and colloids, which determines the potential bioavailability and health impacts of dispersed contaminants, and helps predict metal-colloid stability.

Synchrotron X-ray methods have been used to characterize natural colloids and their association with As in mine systems. Slowey et al. [16] described the transport of As(V) when adsorbed onto colloidal ferrihydrite and jarosite in columns packed with mine tailings. Zanker et al. [17] showed that mine wastes contained As within nanometer jarosite-like particles. Additionally, AsFIFFF/ICP-MS has revealed colloid-bound As in abandoned mine tailings [7], while selective sequential extraction, high resolution ICP-MS and transmission electron microscopy (TEM) [18] have revealed nanoparticles sequestered by metal-contaminated mine sediments.

In this work, the dispersible colloid fractions (DCFs) (10-1000 nm) of a mine waste pile and its adjacent sediments and soils were examined to determine their elemental and mineral composition as a function of colloid size. The As and Fe speciation was also

examined, as was the partitioning of As and companion metals between the DCF and the fraction of their total amount that remained dissolved. Understanding the relationship between the composition of natural colloids, and soils and sediments properties, as well as the colloid-contaminant association, is crucial in contaminant transport studies.

2. Materials and methods

2.1. Sample collection and description

Samples were collected from an abandoned smelting factory in Guadalix de la Sierra (Madrid, Spain) where arsenopyrite encapsulated in quartz was mined and processed for wolfram extraction during the Second World War (Fig. 1). Arsenic-rich residues were dumped nearby and pose a public health problem [19]. Four types of sample were collected: (1) samples (0-10 cm depth) from the main waste pile (WP) [19] (dumped on the soil surface); (2) sediments from the bed of a small stream originating at the WP that collects runoff (samples RB2 at 17 m from the WP and at 0-5 cm depth , and RB at 26 m from WP and at 0-10 cm depth); (3) the streambed subsoil (SS) (at 26 m from the WP and at 10-20 cm depth of), and (4), the sediment from a downstream pond (SP) (at 58 m from the WP and at a depth of 0-5 cm) that collects runoff from the stream (Fig. 1).

Characterization methods are described in the Electronic Annex (EA).

2.2. Dispersible colloid fraction: preparation and pre-fractionation

The maximum amount (mg kg^{-1} soil) of potentially releasable colloids from the different samples was termed dispersible colloid fraction (DCF). The DCF was extracted from all samples based on a protocol described elsewhere [13] with modifications (Fig. 2). Preparation and pre-fractionation methods are given in EA.

2.3. Colloid characterization

2.3.1. AsFIFFF-ICP-MS

The distribution of particle size and the concentration of associated metal(oid)s in the <1000 nm fraction was determined by AsFIFFF-ICP-MS (see Table EA-2 for operating conditions).

In AsFIFFF, a surfactant (SDS, 0.01% w/v) adjusted to pH 4.5 (close to the original pH) was used as a carrier solution for the <1000 nm fraction from the WP, RB2, RB and SS samples; for the SP sample it was adjusted to pH 6.5. The carrier was degassed by an on-line vacuum degasser prior to use. Sample loops of 20 and 100 μ L were used throughout depending on the element concentrations detected [20]. Colloid sizes and calibration standards; (details in EA) were detected using a UV-vis diode array detector (Shimadzu). On-line multi-element quantification was performed using an ELAN DRC-e ICP-MS (Perkin Elmer). The samples were introduced into the ICP-MS using a glass concentric slurry nebulizer and a cyclonic spray chamber (Glass Expansion). An internal standard solution of 50 ng mL⁻¹ Rh (Merck) was pumped into the mobile phase at 0.3 ml min⁻¹ for correction of instrumental drift. ICP-MS data acquisition and recovery calculation details are in Table EA-3.

2.3.2. Element concentrations

The element concentrations of the DCF of each sample were analyzed using an OPTIMA 4300DV ICP-optical emission spectrometer (ICP-OES) (Perkin-Elmer) after microwave digestion with HF+HNO₃+HCl followed by H₃BO₃. The DFs (<10 nm fractions) were analyzed using an ELAN DRC-e ICP-MS spectrometer (Perkin Elmer).

The total carbon concentration in the DCF was determined by combustion using a 2400 Series II CHNS/O Elemental Analyzer (Perkin Elmer). The mass retained on the ultrafiltration membranes was determined gravimetrically.

2.3.3. Transmission electron microscopy

Aliquots of the <1000 nm fraction from the WP, RB and SS were examined using a CM200FEG transmission electron microscope (TEM) (Philips,) (See EA).

2.3.4. Microfocused synchrotron X-ray fluorescence

Chemical mapping was performed on the <1000 nm SP fraction using synchrotron microfocused X-ray fluorescence (μ XRF) at the Stanford Synchrotron Radiation Lightsource (SSRL) laboratory (on Beamline 2-3) (See EA).

2.3.5. Arsenic and iron X-ray absorption spectroscopy

Arsenic and Fe K-edge spectra of DCF samples, and of a reference DCF sample of As adsorbed onto ferrihydrite (termed As(V)_Fh_coll; see EA for details), were collected at the European Synchrotron Radiation Facility (ESRF; 6 GeV, 100 mA) (bending-magnet BM25A Beamline). Methods are described in EA. Spectra were analyzed using Athena software [21] for linear combination fits, and EXAFSPAK software [22] for shell-by-shell fits. Data collection and analysis are in EA.

3. Results

3.1. DCF composition and size distribution

Table 1 shows element concentrations of the DCF of the different samples. Figure 3 shows their relative molar proportions. Calcium was the major element ($3.5 \text{ mol kg coll}^{-1}$) of the DCF of the WP sample (WP_{DCF}), followed by As and Fe with a Fe/As mole ratio ~ 1 . Iron and Al were the major elements in RB2_{DCF} , RB_{DCF} and SS_{DCF} . Carbon accounted for 39% of the element composition in SP_{DCF} , and Al 48% (Fig. 3). The RB_{DCF} had the highest Fe concentration of all samples while the SS_{DCF} had the highest Al concentration. The RB_{DCF} and SP_{DCF} had slightly lower (and similar) Al concentrations. The RB_{DCF} had the highest Fe/Al molar ratio, followed by RB2_{DCF} , SP_{DCF} and SS_{DCF} .

The As concentration fell with distance from the WP; indeed, a large difference in As concentration was seen between the WP_{DCF} ($0.25 \text{ mol kg coll}^{-1}$) and the RB2_{DCF} (0.08 mol

kg coll⁻¹), falling further for the RB_{2DCF}, RB_{DCF}, SS_{DCF} and SP_{DCF} (Fig. 1). An increase in the Fe/As molar ratio was observed from the WP to the SP positions (Table 2).

Calcium represented 12% of the elemental composition of the RB_{2DCF} but less than 2% of that of the RB_{DCF}, SS_{DCF} and SP_{DCF} (Fig. 3). Lead was only detected in WP_{DCF}; Cu and Zn were below the detection limit. The SS_{DCF} showed the highest Cu concentration of the downstream samples (0.05 mol kg⁻¹) (SS_{DCF} > RB_{DCF} > SP_{DCF}), while the RB_{2DCF} showed the highest Zn concentration (0.01 mol kg⁻¹) (RB_{2DCF} > RB_{DCF} > SS_{DCF} > SP_{DCF}).

Figure 4 shows the AsFIFFF-ICP-MS fractograms for the RB, SS and SP <1000 nm fractions. Given the low colloid mass (per mass of bulk sample) of the WP_{DCF} and RB_{2DCF} (2634 mg kg⁻¹ and 840 mg kg⁻¹ respectively), and the high conductivity of the WP suspension (Table EA-1) no reliable fractograms were obtained. The <1000 nm fractions had different colloid size distributions but similar Al, Ca, Fe, As, Cu, Zn and Pb concentration distributions. The <1000 nm fraction of RB was characterized by particle size and element concentration maxima at ~30 nm; the maximum element concentration was also associated with this particle size (Fig. 4a). The single-peak element concentration suggests particle homogeneity. For the <1000 nm fraction of the SS sample, two maxima were observed in the colloid size distribution, at 55 and 175 nm (Fig. 4b). The SP fractogram showed a wide distribution with a broad maximum between 55 and 100 nm (Fig. 4c).

3.2. TEM-EDX and μ XRF

Particulate scorodite (~80 nm in diameter) was observed and identified by TEM-EDX in the WP_{DCF} (Fig. 5a). In the RB_{2DCF}, TEM-EDX showed particle aggregates of <50 nm and high concentrations of Si, Al and Fe, suggestive of clay minerals and Fe hydroxides (Fig. 5b). In the RB_{DCF}, 30 nm Fe nanoparticles formed chains or aggregates associated with Si, Ca, Mn and Cu (Fig. 5c, 5d). Iron nanoparticles (10 nm) forming larger

aggregates (~50 nm in diameter) were observed in the SS_{DCF} (Fig. 5e). Arsenic associated with Fe particles in the SS_{DCF} was observed by EDX analysis (data not shown). The SP_{DCF} contained aggregates of small nanoparticles (~10 nm); Fe, Si, Al, Ca, Mg and As were detected by EDX, indicating these aggregates to be heterogeneous. Synchrotron μ XRF maps (mapping area 1x1 μm^2) of the SP_{DCF} indicated a correlation between As and Fe in aggregated nanoparticles (150-250 nm) (Fig. 5g and h).

3.3. Arsenic and iron XAS of colloids

Normalized As XANES of three As reference spectra -natural scorodite [23], As absorbed onto ferrihydrite (As(V)_Fh; As/Fe ratio 0.012) [24], and colloid-extracted As absorbed onto ferrihydrite (<1 μm) (As(V)_Fh_coll; As/Fe ratio 0.09 [this study])- were compared with those of the DCF samples (Fig. 6). The As(V)_Fh and As(V)_Fh_coll reference spectra were similar, although their post-edge spectral features were not identical. The As K-edge XANES spectra of all DCF samples indicated that As was present only as As(V) (absorption maxima 11874.5-11875.5 eV) (Fig. 6). The XANES spectra of all DCF samples, except WP_{DCF}, resembled that of either As(V)_Fh or As(V)_Fh_coll, with small differences associated with a post-edge absorption feature at around 11895 eV (Fig. 6). The LCF of the WP_{DCF} As XANES spectrum indicated a mixture of scorodite (61%) and As(V)_Fh (39%) (Table 2). The XANES spectra of DCFs of the downstream samples were fit best using only the As(V)_Fh reference spectrum (Table 2).

Shell-by-shell quantitative analysis of the WP_{DCF} As EXAFS spectrum indicated a bonding environment for As similar to that of scorodite, with similar coordination numbers and interatomic distances (Table 2, Fig. 6). Fits to RB_{DCF} and SP_{DCF} spectra gave an As-Fe distance of 3.31-3.32 Å, similar to that fit for the As(V)_Fh_coll reference spectrum. For comparison, the fit of As(V)_Fh_coll reference spectrum yielded an As-O first-shell

distance of 1.69 Å ($N_{\text{As-O}}=4$, fixed) and an As-Fe distance of 3.28 Å. This As-Fe distance was shorter than the two As-Fe distances (3.38 and 3.52 Å) obtained from the fit of the reference spectrum of As sorbed to ferrihydrite (As(V)_Fh) (Table 2).

Linear combination fits of Fe XANES spectra showed that the WP_{DCF} was dominated by scorodite (83%) and an Fe(III)-oxide phase (16%) that best matched the As(V)_Fh_coll reference spectrum (Fig. 7, Table 3). The two best-fit components for the RB_{DCF} and SS_{DCF} were smectite (SAz-1) and As(V)_Fh_coll (Fig. 7, Table 3). The SP_{DCF} spectrum was fit best with reference illite (IMT-1 Fe) (60%) and As(V)_Fh_coll (40%) spectra. The RB2_{DCF} spectrum was fit with only the As(V)_Fh_coll spectrum. The reference compounds used in the XANES analysis were also used in LCF of the Fe EXAFS spectra. The EXAFS LCFs overestimated crystalline mineral fractions such as illite compared with amorphous phases such as ferrihydrite because of the stronger second-neighbor backscattering in crystalline materials [25].

3.4. Composition of dispersible colloid and dissolved fractions and bulk sample properties

The bulk WP sample had low pH (3.25), and its main minerals were scorodite, gypsum, quartz and hematite (Table EA-1; Fig. EA-1). Chemical analysis revealed the WP_{DCF} to have high As (1.8 mol kg⁻¹), Fe (3.5 mol kg⁻¹) and Ca (1.1 mol kg⁻¹) contents, (Fig. 3) although these represent only small fractions of the bulk sample contents (<0.04% for As and Fe, and 0.8% for Ca). The Fe/As molar ratio of the WP_{DCF} (Fe/As=0.94) was half that of the bulk WP (1.96). The WP_{DCF} and RB2_{DCF} the smallest colloid masses per mass of bulk sample (Table 1).

The bulk RB2 sample, collected close to the waste pile (Fig. 1), had more acidic pH (3.86) and higher As and Fe concentrations than the RB, SS and SP bulk samples. However, when normalized to the mass of the bulk sample, the As and Fe concentrations of the RB2_{DCF} were lower than in the other downstream samples (0.2 % and 0.07 % of the

total As and Fe contents of the RB2 bulk sample). The bulk RB2 and the RB2_{DCF} had the lowest Ca concentrations. Zinc and Pb concentrations of the RB2, RB, SS and SP bulk samples were similar. The RB2 bulk sample was richer in Cu than in Zn or Pb. Copper concentration increased in the downstream RB and SS bulk samples, but decreased in the SP bulk sample. A similar trend was observed in the DCF of these samples (although no Cu was detected in RB2_{DCF}) (Fig. 8). The bulk RB sample had a higher pH (4.3) and higher organic carbon (OC) content than the bulk RB2 sample (Table EA-1). The total As concentration of the RB2 bulk sample was one order of magnitude greater than that of the RB bulk sample. In contrast, the As concentration per mass of bulk sample in RB_{DCF} was greater than in RB2_{DCF} (Fig. 8). The RB_{DCF} As concentration accounted for more than 35% of the total As in the bulk sample. The XRD pattern of the RB2 and RB bulk samples showed hematite, muscovite, quartz and feldspar to be the primary minerals (Fig. EA-1). The total element composition of the SS bulk sample was similar to that measured for the RB bulk sample (Table EA-1), except that no OC was measured in the SS sample. The SS bulk sample had slightly higher pH (4.5) than the RB bulk sample and similar XRD pattern, although no hematite was detected (Fig. EA-1). The SS_{DCF} had greater colloid mass than the RB_{DCF}, and contained less As and Fe, but more Ca (Fig. 8). The greatest colloid mass per mass of bulk sample was obtained for the SP bulk sample (17644 mg kg⁻¹); the bulk SP (Table EA 1) and SP_{DCF} (Table 1) had the highest C contents and pH (pH= 6.2) of all. The total As concentration of the SP bulk sample (2.3 mmol kg⁻¹) was almost double that of the RB and SS bulk samples (~1.3 mmol kg⁻¹), while the Fe and Ca contents were similar in all three. In contrast, the As and Fe concentrations were lower in the SP_{DCF} than in the RB_{DCF}, and higher than in the SS_{DCF}, while the Ca concentration was lower in the SP_{DCF} than in the RB_{DCF} and SP_{DCF} (Fig. 8). The As concentration of the SS_{DCF} and

SP_{DCF} were 0.12 and 0.24 mmol kg soil⁻¹ respectively, representing ~10 % of the total As concentration of the corresponding bulk samples.

Low As and Fe concentrations were found in all dissolved fractions DFs(<10 nm) (Table EA-5, Fig. 8). The SS_{DF} had the highest As concentration, (0.5% of the total As content of the bulk SS sample). Iron was detected only in the WP_{DF} and RB2_{DF}. The Al concentration was low in all the dissolved fractions. The DF concentrations of Ca, Cu, Zn, and Pb were higher than in the corresponding DCFs (especially with respect to WP and RB2) (Fig. 8). Finally, lower Ca, Cu and Zn concentrations were observed in the RB_{DF}, SS_{DF} and SP_{DF} than in the WP_{DF} and RB2_{DF}.

4. Discussion

4.1. DCF composition and As and Fe speciation

Nanoparticle scorodite was the main As mineral phase in the WP_{DCF}, and it has a local atomic structure similar to that of crystalline scorodite at particle sizes of ~80 nm in diameter). There was no evidence for nanoparticulate scorodite in any other DCF, suggesting dissolution down-gradient of the WP despite its reported low solubility and high stability at pH 3-4 [26].

In the downstream samples, As was mainly associated with Fe(III) oxide phases. The EXAFS spectra showed similar As-Fe interatomic distances in the RB_{DCF} and SP_{DCF} (3.32 Å and 3.31 Å respectively), comparable to that obtained in EXAFS analysis of As(V) adsorbed onto colloidal 2-line ferrihydrite (3.28 Å), but shorter than values obtained in the EXAFS fit of As(V) adsorbed onto bulk 2-line ferrihydrite (fit two Fe shells at 3.38 Å and 3.52 Å) [27]. Differences in the local As(V) bonding environment between these two reference spectra are probably related to differences in their As/Fe molar ratios and the smaller particle size of colloidal ferrihydrite. The greater proportion of Al to Fe in the

SS_{DCF} compared to RB_{DCF} and SP_{DCF} might explain the lack of strong second-neighbor backscattering in the SS_{DCF} spectrum compared to the RB_{DCF} or SP_{DCF} spectra.

The Fe XANES results for the SP_{DCF} suggest a spectral contribution from an Fe-bearing illite-type phase (~60%) rather than a smectite phase in addition to iron oxide-type phases.

The high Al concentration of the DCFs of the downstream samples, and the TEM-EDS observations, indicate the presence of aluminosilicates generally associated with Fe-rich particles. The adsorption capacity of Fe(III) oxides and clay minerals for Ca, Cu, Zn and Pb [28, 29] would explain their presence in the downstream sample DCFs (Fig. 4), although this interaction depends on the pH of the bulk samples (see next section).

The SP_{DCF} had the greatest colloid mass of all. This might be related to its high OC content, which can increase the stability of iron-rich nanoparticles [30]. TEM and μ XRF analysis of SP_{DCF} showed the formation of aggregates with strong Fe/As correlations, supporting the idea that As adsorbs onto the Fe (III) phases, as indicated by As XAS.

4.2. DCF composition and bulk sample properties

The presence of organic matter, circum-neutral pH, and low ionic strength, increase the stability of soil colloids [9, 11]. Thus, the high colloid mass associated with the SP_{DCF} (Table 1) is likely the result of the high pH, high OC content and low ionic strength of the SP bulk sample (Table EA-1). Both the SP and RB bulk samples have similar C contents; however, the higher pH of the former may promote the release of organic matter [31], explaining the higher OC of the SP_{DCF} than the RB_{DCF}. In contrast, the WP_{DCF} and RB2_{DCF} showed the smallest colloid masses, probably related to the acidic pH and undetectable OC content of their bulk samples. This might also be related to the high Ca²⁺ concentration of the WP bulk sample hindering colloid release [32, 33]. The higher Ca²⁺ content of the SS_{DCF} than of the RB_{DCF} or SP_{DCF} might also be associated with the formation of the large aggregates observed (Fig. 5).

Normalized to the bulk sample mass, the higher As concentration of the RB_{DCF} (>35% of the total As in RB) compared to the SS_{DCF} and SP_{DCF} may be related to its smaller colloid size. The specific surface area is related to the particle size and determines the adsorption capacity of colloids [2]. Accordingly, higher As concentrations are expected for samples with smaller particles sizes, such as the RB bulk sample. This trend, however, was not seen for Ca, Cu, Zn or Pb, since their retention on Fe (oxy)hydroxide and clay nanoparticles at the pH of the RB (pH=4.3) is not favored.

The Fe (oxy)hydroxide nanoparticles present in the DCFs may either have formed in the DCF or have been mobilized from the bulk samples. In the SP bulk sample, the precipitation of Fe oxide particles might be associated with its higher pH [31]; Fe solubility decreases with increasing pH [34]. Given the acidic pH of the remaining samples, Fe (oxy)hydroxide and clay mineral particles would originate mostly through their mobilization from the bulk samples. Calcium, Cu, Zn and Pb partitioning between the DCF and DF of the samples might also be affected by pH. In general, samples with lower soil pH (WP and RB2) had DCFs with lower cation concentration, but DF with higher dissolved cation concentration. The opposite behavior was observed in samples which had higher pH, with the exception of Cu in SP, for which higher Cu concentration was observed in the DF than in the DCF.

4.3. Implications for As and metal mobility

Arsenic was present in the DCF of all samples downstream of the WP mostly associated with colloid-size Fe-(oxy)hydroxides. In the corresponding DFs (< 10 nm), low As concentrations were observed. The relative amounts of As bound to colloids varied from 1% to 35% of the total As concentration in the bulk samples, depending on their pH, OC content, ionic strength, and the size distribution of the natural nanoparticles (which determine their surface reactivity [35]). In spite of the differences in these variables, and of

differences in DCF particle sizes, As adsorption onto Fe-(oxy)hydroxides persisted in the DCF of all the downstream samples, indicating the high affinity of As for nanoparticulate Fe-(oxy)hydroxides [36] and their potential mobility. In addition to the concentration of Fe-(oxy)hydroxide nanoparticles and their potential function as As carriers, the transport of trace metals on colloidal particles depends on local water chemistry [1, 35]. Since the extraction of the DCF from the samples was performed *ex situ* using a 1:10 dried bulk sample/solution ratio, results can only be extrapolated to field conditions resulting after rain events following extended dry periods. However, they might represent the potentially removable colloid-bound and dissolved fractions of contaminant elements in natural systems. Further work should include examining the release of colloids *in situ* in seasonally variable environments.

5. Conclusions

This work showed that up to one third of the total As present in bulk samples collected from a mine site and adjacent soils and sediments, was associated with the colloid fraction and very low concentrations were measured in the dissolved fraction (<10 nm). The acidity, OC content and Ca concentration of the samples were closely related to the stability or aggregation of colloids, and thus the particle size distribution. Nanoparticle scorodite was only found in the wastepile samples, which suggest the dissolution of this mineral in downstream samples. The persistent association of As and ferrihydrite in the DCF of samples collected downstream of the WP reflects the high affinity of As for nanosize Fe-(oxy)hydroxides particles irrespective of the pH or OC content, and suggests a potential role of these nanoparticles as As carriers in natural systems. The combination of AsFIFFF-ICP-MS and X-ray absorption spectroscopy provides fundamental information

on the partitioning of contaminants in colloid-size particles, as well as their speciation, that contributes to understanding metal(oid) pollution processes in natural systems.

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FIGURE CAPTIONS

FIGURE 1. Location of the area of study. A: Abandoned processing plant with waste pile in the foreground. B: Plan of sampling locations (WP, RB2, RB, SS, SP).

FIGURE 2. Procedure for fractionation and characterization of DCF and DF extracted from bulk samples.

FIGURE 3. Elemental composition (mol kg^{-1} colloid) of the DCF (10-1000 nm).

FIGURE 4. AsFFF-ICP-MS fractograms for the <1000 nm fractions of the RB, SS and SP samples showing ICP-MS counts per second (cps) as a function of particle size.

FIGURE 5. Transmission electron microscopy and energy dispersive X-ray spectroscopy analysis of colloid fractions. a) Scorodite nanoparticle in WP, b) heteroaggregates (clay minerals and iron particles) in RB2, c) and d) iron nanoparticles and aggregates in RB, e) aggregates of iron nanoparticles in SS, and f) arsenic identified in aggregates of iron nanoparticles and clay minerals in SP, g) and h) synchrotron μ XRF element maps of colloid particles in SP.

FIGURE 6. Arsenic K-edge XANES, EXAFS and Fourier transformations (FT) of DCF from the WP, RB, SS and SP samples (only XANES was performed for RB2). The XANES spectra show the deconvolution of the LCF with the reference scorodite [23] and arsenate adsorbed onto hydrous ferric oxide [As(V)_Fh] [24] (fit results in Table 2). EXAFS were fit using a nonlinear least squares shell-by-shell approach (fitting results in Table EA-6).

FIGURE 7. Iron K-edge XANES, EXAFS and Fourier transformations (FT) of the DCF from the WP, RB2, RB, SS and SP samples. XANES show the deconvolution of the LCF with the reference smectite (SAz-1) (Clay Minerals Society Source Clays Repository), scorodite [23], and the reference As adsorbed onto ferrihydrite (Fh_As(V)_coll) (As/Fe=0.09) (synthetic two-line ferrihydrite prepared as in [37]). The

same reference compounds were used for linear least-squares combination fits for Fe EXAFS. Solid lines are data; dashed lines are fits (fit results in Table 3).

FIGURE 8.Element concentrations (mol kg⁻¹ sample) in the DCFs (10-1000 nm) and DFs (<10 nm).

Table 1. Dispersible colloid fraction (10-1000 nm) properties (mean $\pm$ std dev, n=3)

Sample	WP	RB2	RB	SS	SP
Colloidal mass (mg/ kg sample)	2636 $\pm$ 494	840 $\pm$ 126	7501 $\pm$ 849	4884 $\pm$ 710	17645 $\pm$ 264
As (mol/ kg colloid)	0.25 $\pm$ 0.004	0.08 $\pm$ 0.007	0.07 $\pm$ 0.015	0.02 $\pm$ 0.002	0.01 $\pm$ 0.04
Fe (mol/ kg colloid)	0.27 $\pm$ 0.014	0.57 $\pm$ 0.022	3.97 $\pm$ 0.084	0.96 $\pm$ 0.128	1.08 $\pm$ 2.20
Ca (mol/ kg colloid)	3.55 $\pm$ 1.39	0.30 $\pm$ 0.066	0.04 $\pm$ 0.001	0.15 $\pm$ 0.001	0.09 $\pm$ 0.28
Al (mol/ kg colloid)	b.d.	1.54 $\pm$ 0.076	4.27 $\pm$ 0.078	6.57 $\pm$ 0.07	4.25 $\pm$ 3.99
Cu (mol/ kg colloid)	b.d	b.d	0.02 $\pm$ 0.000	0.05 $\pm$ 0.002	2.7 $\times 10^{-3}$ $\pm$ 0.01
Zn (mol/ kg colloid)	b.d.	0.01 $\pm 5 \times 10^{-4}$	6.9 $\times 10^{-3}$ $\pm 1 \times 10^{-4}$	5.5 $\times 10^{-3}$ $\pm 5 \times 10^{-5}$	2.1 $\times 10^{-3}$ $\pm 6 \times 10^{-3}$
Pb (mol/ kg colloid)	5.3 $\times 10^{-3}$ $\pm 1 \times 10^{-4}$	b.d.	b.d.	b.d.	b.d.
C (mol/ kg colloid)	0.67 $\pm$ 0.002	--	0.7 $\pm$ 0.002	0.6 $\pm$ 0.0092	3.49 $\pm$ 0.02

b.d.: below detection limit; --: not detected

Table 2: Arsenic X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) fits results.

Sample	Molar As/Fe	XANES (%) ^a	As EXAFS ^b					XRD ^c	
			A-B ^d	N	R (Å)	σ^2 (Å ²)	ΔE_o (Å)	χ^2	N R (Å)
WP	0.88	a. 61.3 b. 38.7 ^e	As-O	4.0 ^f	1.69	0.0027 ^f	-0.66	3.26	
			MS ^g	1.0	3.07/	0.0050/			
			As-Fe	3.7 ^f	3.37	0.0062			
			As-As	0.8 ^f	4.22	0.0079			
			As-As	1.9 ^f	4.93	0.0089			
RB2	0.16	100.3 ^h							
RB	0.016	94.5 ^h	As-O	4.0	1.68 ^c	0.0023 ^f	-1.3	1.37	
			MS ^g	1.0	3.06/	0.0035/			
			As-Fe	1.9 ^f	3.32 ^f	0.006			
SS	0.027	101.0 ^h	As-O	4.0	1.69 ^f	0.0024 ^f	-0.56	3.7	
			MS ^g	1.0	3.06/	0.0032/			
			As-Fe	0.6 ^f	3.40 ^f	0.006			
SP	0.013	108.3 ^h	As-O	4.0 ^f	1.69 ^f	0.0028	-1.09	1.36	
			MS ^g	1.0	3.06/	0.0035/			
			As-Fe	1.2 ^f	3.31 ^f	0.006			
Scorodite ⁱ	1		As-O	4.0	1.69 ^f	0.0027 ^f	1.3	1.85	4 1.67-1.69
			MS ^g	1.0	3.07/	0.0050/			2 3.06
			As-Fe	4.0	3.37 ^f	0.0062 ^f			4 3.37-3.39
			As-As	1.0	4.20 ^f	0.0079 ^f			1 4.22
			As-As	2.0	4.91 ^f	0.0089 ^f			2 4.91

		As-As	4.0	5.73 ^f	0.0076 ^f		4	5.46-5.65
As(V)_Fh ^j	0.012	As-O	4.0 ^f	1.68	0.0023	-2.4	1.44	
		MS ^g	1.0	3.06/	0.0035/			
		As-Fe	1.7	3.38	0.006 ^f			
		As-Fe	0.8	3.52	0.006 ^f			
As(V)_Fh_coll ^k	0.09	As-O	4.0	1.69	0.0033 ^f	-0.99	1.07	
		MS ^g	1.0	3.06/	0.0064/			
		As-Fe	1.2 ^f	3.28 ^f	0.006			

^aLinear combination fit results for arsenic XANES (fitting range 11850-12000).

^bResults of As EXAFS shell-by-shell fits for reference compounds and colloids.

^cCrystallographic distances from Xu et al. [38].

^dA-B is the absorber-backscatterer pair; N is the number of backscattering atoms at distance (R); σ^2 (Debye Waller term) is the absorber-backscatterer mean-square relative displacement; ΔE_0 is the energy shift in the least-squares fit; χ^2 is a reduced least-squares goodness-of-fit parameter $(=(F\text{-factor})/(\#\text{points} - \#\text{variables}))$; scale factor (S^2_0) fixed at 1.

^eFraction corresponded to (a.) scorodite (spectrum from Savage et al.[23], and (b.) arsenate sorbed to hydrous ferric oxide (As(V)_Fh); spectrum from Root et al. [24] and refit in Helmhart et al.[27].

^fParameter allowed to vary during the fitting; / parameter linked to the parameter immediately above in the fitting.

^gSpectrum fit with multiple scattering path that is a composite of 6 triangular paths (O→O→As).

^hFraction corresponded to Arsenate sorbed to hydrous ferric oxide (As(V)_Fh) (%) spectrum from Root et al. [24] and refit in Helmhart et al. [27].

ⁱNatural scorodite (FeAsO₄·2H₂O) spectrum from Savage et al.[23].

^jArsenate sorbed to hydrous ferric oxide (As(V)_Fh); spectrum from Root et al. [24] and refit in Helmhart et al. [27].

^kArsenate sorbed to colloidal hydrous ferric oxide (As(V)_Fh_coll) from this study.

Table 3: Linear combination fit results for iron X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS)

Sample	Fitting range	Scorodite (%) ^b	ΔE_V	As_Fh_coll (%) ^c	ΔE_V	Smectite (%) ^d	ΔE_V	Illite (%) ^e	ΔE_V	Total (%)	red. χ^{2f}
<i>Fe</i> XANES (eV)											
WP	7105-7160	82.6 ; 3.4 ^g	0.03	16.4 ; 16.6 ^g	0.2					99	0.000058
RB2	7105-7160			100	0.2					100	0.000050
RB	7105-7160			62.3 ; 60.2 ^g	0.39	41.2 ; 39.7 ^g	-0.2			103	0.000147
SS	7105-7160			44.6 ; 43.3 ^g	0.02	58.3 ; 56.6 ^g	-0.09			103	0.000139
SP	7105-7160			39.3 ; 39.5 ^g	0.04			59.7 ; 60 ^g	-0.45	99	0.000093
Sample	Fitting range	Scorodite (%) ^b		As_Fh_coll (%) ^c		Smectite (%) ^d		Illite (%) ^e		Total (%)	red. χ^{2f}
<i>Fe</i> EXAFS k ($\text{\AA}^{-1}$)											
WP	2-11	81.9 ; 68.8 ^g		37.9 ; 31.06 ^g						119	0.45
RB2	2-11			103.3 ; 100 ^g						103	0.40
RB	2-11			32 ; 41.2 ^g		45.6 ; 58.7 ^g				78	0.50
SS	2-11			34.0 ; 42 ^g		47 ; 58 ^g				81	0.30
SP	2-11			25.2 ; 27 ^g				68.1 ; 73 ^g		93	0.93

^bFit with natural scorodite spectrum from Savage et al. [23] /and fit in this study (Table EA-7).

^cFit with As(V)_Fh_coll spectrum synthesized and analyzed in this study (Fig. 7, Table 9).

^dFit with reference smectite (SAz-1), Clay Minerals Society reference mineral previously analyzed by O'Day et al. [25]

^eFit with reference illite (IMt-1), Clay Minerals Society reference mineral previously analyzed by O'Day et al. [25]

^fGoodness-of fit reported as reduced χ^2 calculated as three times the estimated standard deviation for each component from the linear least-squares fit.

^gRecalculated to Total 100%