

Impact of Redox Conditions on Arsenic Mobilization from Tailings in a Wetland with Neutral Drainage

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More than 80 years of silver mining in the Cobalt area (Ontario, Canada) has led to widespread contamination of water with arsenic. The objective of this study was to determine the impact of changes in redox conditions on the stability of As in samples collected from a tailings wetland in the historic mining camp. Dissolved metal concentrations were monitored while tailings samples (~ 1300 mg of As kg^{-1} , pH 7.4) were subjected to 30 days of reduction. Reoxidation of the samples was accomplished by air drying. The As oxidation states in the original, reduced, and reoxidized samples were determined using X-ray absorption spectroscopy (XAS). Arsenic speciation was affected by changes in redox conditions, resulting in rapid mobilization of As during reduction. Glucose input had a significant impact on the dissolution and speciation of As, suggesting that the As transformation was microbially mediated. When carbon was not limiting, the combination of reducing conditions and lower pH favored the formation of As(–I) species.

Introduction

Before stringent environmental regulations were introduced across Canada in the late 1970s for mining developments, mine wastes were often disposed of in low-lying areas including water courses adjacent to mills. This haphazard way of managing mine wastes led to extensive metal contamination in many historic mining camps (1, 2). In Cobalt (Ontario), 85 years of silver mining (1904–1989) with poor mine waste management has resulted in widespread As contamination of surface and groundwaters (1). The total dissolved As concentrations in many surface waters range from 11 to 20 000 $\mu\text{g L}^{-1}$, exceeding the water quality criteria for drinking (25 $\mu\text{g L}^{-1}$) and sustaining aquatic life (5 $\mu\text{g L}^{-1}$) by orders of magnitude.

Silver in the Cobalt region commonly occurs in close association with various arsenides (notably safflorite, skutterudite, loellingite, rammelsbergite, and nickeline) and sulfarsenides (cobaltite, gersdorffite, arsenopyrite, and glaucodot) in carbonate–chlorite–quartz veins (3). Over the years, 18 mills operated in the Cobalt mining camp. In addition to subaerial disposal in local valleys, significant amounts of tailings were discharged into local lakes, partially converting them into wetlands. cursory assessments of available water monitoring data indicated that the discharged tailings were not inert with respect to As mobilization (1, 4). Kwong et al. (4) documented the geochemistry and mineralogy of tailings

in a large wetland (the Farr Creek wetland) located in North Cobalt. Our study takes a more detailed look at the impact of changes in redox conditions on the mobilization and speciation of As in the tailings.

The studied tailings are dominated by sand-size particles with <10% clay. Mineralogically, quartz, chlorite, feldspar, calcite, dolomite, and mica are the major components, while kaolinite, montmorillonitic mixed-layer clay, and Fe and Mn oxyhydroxides occur in minor to trace amounts. Despite the elevated As concentrations measured in the sediments (1000–1500 mg kg^{-1}), only minimal amounts of safflorite and cobaltite with rare arsenopyrite, gersdorffite, skutterudite, and scorodite have been identified (4). The majority of As appears to occur in a finely dispersed form either as poorly crystalline phases or adsorbed species on other minerals. In the absence of abundant Fe and Mn oxyhydroxides, Al-rich phases (hydroxides, phyllosilicates, and feldspars) and carbonates are known to play a significant role in attenuating As transport (5–9).

Considering the alternating flooding and drying events characteristic of any wetlands, redox conditions and pH are the most important factors that control the stability of As minerals (10). During flooding, reducing conditions might favor As mobilization through (i) direct reduction of sorbed As(V) into As(III) or, more likely, (ii) reductive dissolution of an Fe(III) host, followed by reduction of the released As(V) (10, 11). Reduction of As(V) to As(III) converts the metalloid into a more toxic and mobile form (11), thereby deteriorating the water quality. If a drying phase follows flooding, oxidizing conditions will lead to precipitation of dissolved Fe, Mn, and arsenates/arsenites (12). It is important to identify the chemical species formed because they affect As solubility and vulnerability to redissolution in a subsequent reduction phase (10).

Organic matter is another parameter that can indirectly affect the stability of As minerals by accelerating the onset of anaerobiosis and controlling the reduction rate (13, 14). More specifically, the availability of C can be a limiting factor for microbial activity, which is often the principal cause of oxygen depletion in soils (15, 16). The Farr Creek wetland contains <1% organic C (4), which invariably accumulates at the soil surface (4). Hence, the reduction rate should depend on the tailings layer considered. However, it is not known if the low-C content limits As or Fe reduction and in which layer As mobilization is most important.

We conducted a laboratory experiment to assess how As stability in these tailings was affected by alternating reducing and oxidizing conditions. The specific objectives were to assess the impacts of (i) reduction on the solubilization of As, (ii) soluble C input on the redox state achieved in the intermediate layer during reduction, and (iii) alternating redox conditions on the change in As speciation in the sediments.

Materials and Methods

Field Sampling. Tailings from 15 locations in a wetland area at the confluence of Mill and Farr Creeks in Cobalt were collected in May, 2003. Details on field sampling were reported by Kwong et al. (4). Two to three cores were taken at each location and each profile was subdivided in the field according to three visibly distinct layers. The similar layers were combined to give a composite sample. The samples were quickly sealed in plastic bags and kept in a cooler at 4 °C to prevent changes in oxidation state of the redox-sensitive species (4). In the laboratory, the samples were homogenized in a glovebox and divided into two subsamples: one was

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TABLE 1. Selected Properties^a of the Sediments from the Mill Creek Profile Used for the Redox Study

layer	depth cm	sand g kg ⁻¹	clay g kg ⁻¹	pH	OC g kg ⁻¹	As-w mg kg ⁻¹	total As mg kg ⁻¹	Al _{ox} + Fe _{ox} mmol kg ⁻¹	total Al g kg ⁻¹	total Fe g kg ⁻¹
surface	0–12	802	63	7.37	10.0	28.94	1120	88	75	46
subsurface	12–28	716	80	7.41	10.7	26.98	1480	123	74	47
substratum	>28	847	53	7.51	10.8	15.57	1350	134	75	48

^a As-w: Water-extractable As. OC: Organic carbon determined by dry combustion in a Leco analyzer. Al_{ox}, Fe_{ox}: Oxalate-extractable Al and Fe. Total Al and Fe contents were determined by ICP-AES after digestion of the sediments with HCl, HNO₃, HF, and HClO₄ (4).

directly frozen and the other used for porewater extraction and then freeze-dried for chemical analysis. All samples were stored in N₂-purged Mason jars.

Redox Experiment. The incubation study was carried out on each layer of a profile collected along Mill Creek. Relevant properties of the profile are reported in Table 1.

Reduction. All solutions were prepared with O₂-free distilled water, and all manipulations were carried out in a glovebox. A 3 g subsample of the homogenized, freeze-dried sediment sieved to <2 mm was weighed into a 100 mL serum bottle, and 30 mL of 10 mM KCl was added. For sediments from the intermediate layer, an additional C-enriched treatment (0.5% (w/w) glucose input to the suspension) was included to verify if soluble C input would enhance the reduction threshold achieved in the systems. The bottles were sealed and placed on a rotating shaker for 1 h and then incubated at 23 °C in the dark.

Batches of duplicate subsamples from each type of sediment were destructively sampled at 0 (1 h, 10 mM KCl extraction), 7, 14, and 30 days using a randomized complete block design. The suspensions were transferred into polycarbonate centrifuge tubes and centrifuged at 10 000 rpm (11 950 g) for 10 min. The E_h and pH of the overlying water were recorded, and the suspensions were filtered at 0.45 μm in the glovebox. The residues were freeze-dried and stored in N₂-purged jars for later XAS analysis. The filtrates were analyzed for dissolved metal content.

Reoxidation. After the 30 day reduction, the suspensions from an additional batch of two replicates were transferred into 100 mL beakers in an air-forced hood at room temperature to initiate reoxidation by air drying in the dark.

Solution Analysis. Dissolved As, Ca, Fe, and S in the filtrates were determined by ICP-AES (Varian Vista RL), and Al, Co, Mn, Ni, and Sb were determined by ICP-MS (Elan 6100). Dissolved organic C was determined by infrared detection of CO₂ on a Dohrmann DC-190 carbon analyzer.

Sediment Characterization. *Chemical Analysis.* Water-extractable As in the original samples was obtained by a 2 h DI water extraction of the sediments (1:15 (w/v) sediment to water ratio) (17), followed by ICP-AES, ICP-MS, or both of the leachates. Total As was determined by ICP-AES after microwave sample digestion with aqua regia. Ammonium oxalate extraction was performed on the original, reduced, and reoxidized samples as described in Ross and Wang (18). Extractable As, Al, Fe, and Mn in the oxalate extracts were determined by ICP-AES.

XAS Spectroscopy. XAS spectroscopy at the As K-edge was performed on the treated sediments to investigate changes in solid-phase As speciation. Data were collected at the beamline X-18B of the National Synchrotron Light Source, Brookhaven National Laboratory (Upton, New York). The electron beam energy was 2.58 GeV, and the maximum beam current was 300 mA. The sediments were mounted behind Kapton tape (CHR Industries) in a 380 μm thick Teflon holder and stored in a N₂-purged jar in the dark until analysis. Data for all sediment samples were collected in fluorescence mode with a multielement solid-state germanium detector. Acid-washed Teflon sheets (350–500 μm thickness) were placed between the sample and the 13-element detector to reduce

the background Fe fluorescence signal. Various As reference compounds representing a range in As oxidation state were purchased or obtained from the CANMET mineral collection (Natural Resources Canada, Ottawa). The purity of all reference compounds was checked by XRD. The safflorite sample was a mixture of Ni-rich loellingite-(Fe, Ni, Co)As₂, skutterudite-CoAs₃, and clinasafflorite-CoAs₂. The elemental As standard was later found to be partly oxidized at the time of data collection (60% elemental As/40% As₂O₃) and is referred to hereafter as “elemental As (ox)”. All reference materials were diluted in boron nitride (BN) to a concentration yielding an edge step of 1 in transmission mode and mounted behind Kapton tape in acrylic plexiglass holders. Data were collected in transmission mode using ion chambers. Data for As adsorbed on 2-line ferrihydrite at a molar Fe/As ratio of 100 (pH 7.5) were collected as a moist paste in fluorescence mode.

The energy scale for each sample scan was calibrated to the As K-edge determined as the first inflection point at 11 867 eV in the spectra for elemental As collected in transmission mode simultaneously with sample data. X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data were processed using WinXAS 2.33 (20). Baseline correction and XANES normalization were performed by fitting respectively a linear regression in the preedge region and in the postedge section typically chosen between 170 and 700 eV. Background removal for the EXAFS spectra ($\chi(k)$ data) was done using a cubic spline fit over a wavevector range between 1.60 and 13.50 Å⁻¹. Both end points were selected at the inflection point of a peak (21). The $\chi(k)$ data were cube weighted (k^3) for fitting analysis.

Fitting of EXAFS Spectra. The $\chi(k) \cdot k^3$ spectra were modeled using principal component analysis (PCA), target transformation, and least-squares linear combination fitting (LCF) (22, 23). PCA was first performed on the dataset composed of all 15 $\chi(k) \cdot k^3$ spectra of the Mill Creek profile (3 depths, various redox treatments). The IND empirical function, retained to define the number of significant components (24), reached a minimum at $n = 3$. The first three main components explained 85.4% of the total variation observed in the initial dataset and were used for target transformation. The SPOIL values were used as the goodness-of-fit criterion. SPOIL values of <3 define acceptable standards, values of between 3 and 6 represent marginal standards, and values of >6 are not acceptable targets (24).

LCF was done using in-house programs running on Scilab 2.6 (23). The $\chi(k) \cdot k^3$ spectra were fitted over the k range of 2.7–12.5 Å⁻¹. Shorter k ranges (2.7–11 and 2.7–10 Å⁻¹) were tested to confirm the stability of the fitting results (Table A, Supporting Information). No constraint for the weighting factors to sum to 1 or to be positive was imposed during fitting. Energy offset parameters were kept negligible (<±0.2 Å⁻¹). χ^2 values and the sum of fractions before normalization were adopted as goodness-of-fit criteria. In addition, fits were considered unacceptable when the weighting factors were negative.

Results

Change in Solution Chemistry during Reduction. Characteristics of the Mill Creek samples (Table 1) were similar to

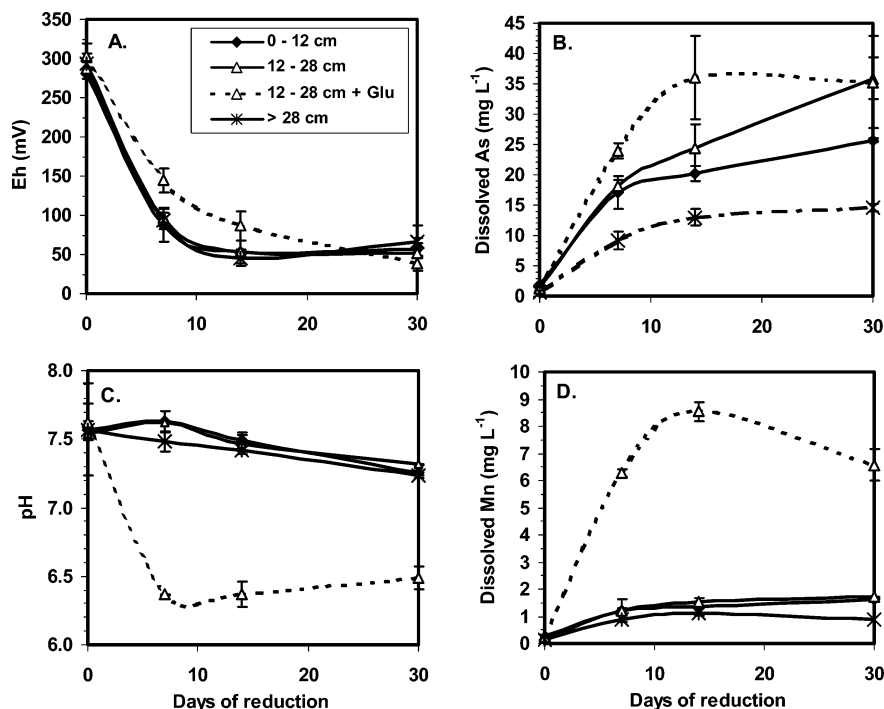


FIGURE 1. Evolution of E_h , pH, dissolved As, and dissolved Mn concentration in the leachates of Mill Creek sediments from different layers during the reduction phase of the experiment (error bars = standard deviation).

those reported previously (4). During the reduction experiment, the E_h of all suspensions dropped rapidly from 250–300 mV on day 0 to ~100 mV by day 7 and stabilized at ~50 mV by day 14 until the end of reduction (Figure 1A). For all three layers, reducing conditions led to an increase in dissolved As (Figure 1B). The input of glucose enhanced the As dissolution rate in the intermediate layer: dissolved As peaked at 36.1 mg L⁻¹ by day 14, whereas the corresponding nonamended sample reached that value on day 30. The sediment from the bottom layer (>28 cm) showed the lowest increase in dissolved As, reaching a maximum of 14.6 mg L⁻¹ by day 30. The glucose input had a significant impact on the suspension pH, which dropped by 1.2 units compared to a decrease of 0.2 unit in the nonamended samples (Figure 1C). In parallel with the marked pH decrease, dissolved Mn on day 30 was seven times greater in the glucose-amended than in the nonamended samples (Figure 1D). A marked increase in dissolved Ca, Co, Fe, and Ni concentrations was also observed in the glucose-amended system (Table B, Supporting Information).

Impact of Redox Treatments on Oxalate-Extractable Metals. Ammonium oxalate extractions were carried out to roughly estimate the impact of reduction and reoxidation on the redox-sensitive and potentially As-sorbing, poorly crystalline phases (i.e., Mn and Fe). In general, poorly crystalline Al, Fe, and Mn oxides represent the main sorbing phase for As (5). In parallel with the increase in dissolved As during reduction, the amount of oxalate-extractable As was significantly lower in the 30 day reduced samples than in the initial samples (Figure A, Supporting Information). The molar ratio of the net amount of oxalate-extractable As/Fe released after 30 days of reduction ranged from 0.5 to 1.5. In comparison, the dissolution of 1 mmol Fe from ferrihydrite saturated with adsorbed As would release ~0.16 mmol of As (maximum sorption capacity ≈ 1500 mmol of As kg⁻¹ of ferrihydrite, pH 7; comparable to that of P; 5, 25). These results suggest that dissolution of poorly crystalline Fe and Mn phases with sorbed As is not the main source of dissolved As.

XAS Speciation of As in the Solid Phase. As K-XANES. For all layers, the alternating redox conditions imposed on the

sediments had a marked impact on the As oxidation state (Figure 2). The main As peak at ~7 eV (relative energy) observed on day 0 is consistent with As(V) species, indicating the dominance of the oxidized species in the samples. A clear shoulder on the low-energy side of this peak at around 2 eV also indicates the presence of reduced As, particularly in the top and bottom layers (Figures 2A and C, respectively). After 30 days of reduction, the peak at ~2 eV noticeably increases, indicating the formation of As(III) species. In the case of the sediments from the top and bottom layers, the short reoxidation forced by the air drying of the samples was sufficient to revert most of this newly formed As(III) to As(V) species (Figures 2A and C). In contrast, the newly formed As(III) in the sediments from the intermediate layer remained unchanged during the reoxidation (Figure 2B). For this layer, the addition of glucose resulted in a lower As oxidation state than that observed in the nonamended system (Figure 3). The overall As oxidation state in the glucose-amended 30 day reduced sample (Day 30 + Glu) was consistent with As(-I) species. Following the reoxidation, the As oxidation state increased from As(-I) to As(III) and reached an oxidation state comparable to that observed in the reduced and reoxidized nonamended sediments.

EXAFS Data. To gain a better insight into the change of As speciation during the treatments, quantitative fitting of the EXAFS $\chi(k)$ spectra was performed on samples from the intermediate layer. The As K-XANES spectra for the Mill Creek samples are dominated by the absorption edge for As(V). For similar tailings, As K-XANES fitting was reported to lack sensitivity in discriminating minor reduced species as only their edges were discernible, while their spectral features above the edge were hidden by the As(V) edge (26). Therefore, the $\chi(k)$ data were chosen over the XANES spectra for quantitative fitting and were investigated with PCA and target analysis. On the basis of this approach, suspected species can be tested individually to determine if their spectral signature explains the structural variation in the sample dataset (22, 24). One requirement of PCA is that the unknown spectrum can be described as a linear sum of the spectral components. This requirement is met with the $\chi(k)$ spectra but not

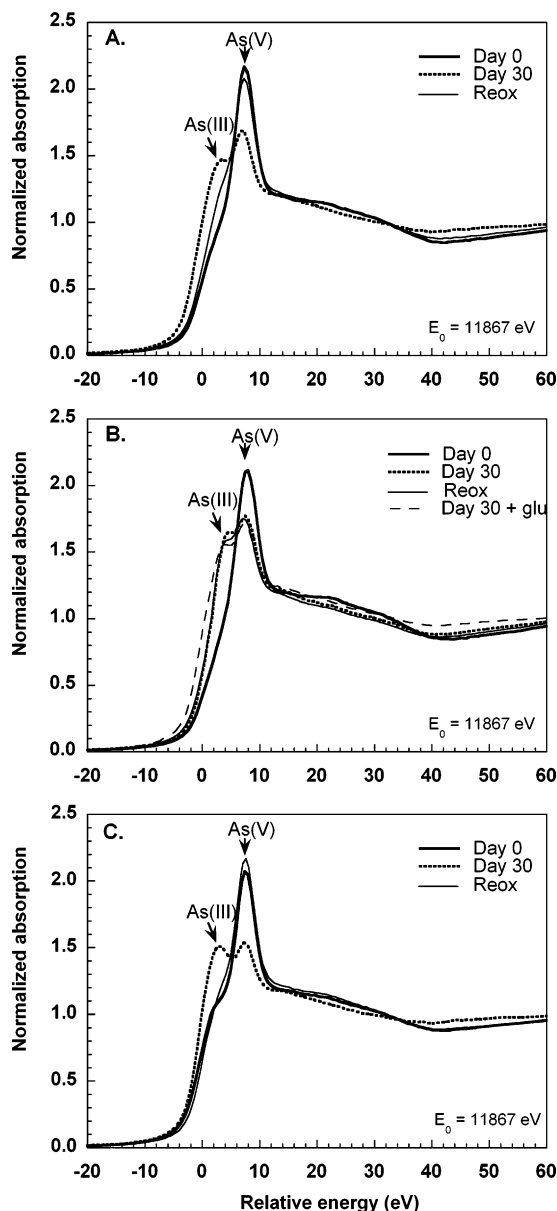


FIGURE 2. As K-XANES spectra for Mill Creek sediment samples showing the change in As speciation with the redox treatments for the (A) surface (0–12 cm), (B) intermediate (12–28 cm), and (C) bottom (> 28 cm) layers.

with the Fourier transformed data (27). Therefore, the fitting analysis was limited to the $\chi(k)$ data and aimed at identifying the combinations of known species that could best explain the unknown spectra.

The target analysis clearly rejected all As sulfide reference species tested (SPOIL values of >6; Table C, Supporting Information). The seven acceptable species with SPOIL values of <6 were used to refine the fitting of each experimental spectrum with least-squares LCF using all possible binary and ternary combinations. The $\chi(k)$ data for the sediments had a high level of noise at energies >10 Å⁻¹. Marginal fits were obtained for three out of five samples (Day 30, Reox, and Reox + Glu; Table 2; Figure 4; Figure B, Supporting Information). For these three samples, the low sum of fractions before normalization (0.64–0.80) indicates that other As species were present but not identified. The best fits were achieved for the samples at day 0 and glucose-amended day 30, with a sum of fractions close to 1. For all five samples, the fitting could not discriminate well the different As(V) species (As₂O₅, adsorbed As(V) on ferrihydrite, calcium

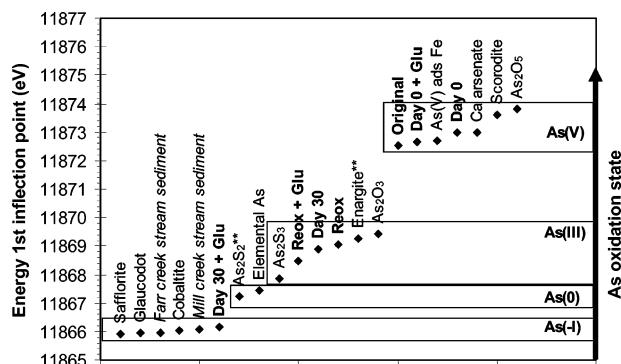


FIGURE 3. As oxidation state for the various treated Mill Creek sediment samples from the intermediate layer (12–28 cm) compared with those of reference As compounds. The arrow serves only as a guide to show the overall trend of an increase in As oxidation state with increasing energy in the first inflection point (first peak, first derivative XANES). Other factors such as the atom species of the nearest neighbors should also be considered before concluding on the As species. (**As occurs as As(V) in enargite, but its association with S reduces the measured binding energy, 40. For As₂S₂, As is slightly more oxidized than As(0), 43.)

arsenate, scorodite). Equally good fits were often obtained by changing one As(V) species with another. For this reason, we report all the equally good fits and the proportion of total As(V) and As(III) obtained in each combination (Table 2).

Despite the limitations encountered in distinguishing specific As(V) species, consistent trends are observed from the fitting analysis. On day 0, an average of 74% of total As occurred as As(V) (Table 2). In agreement with previous SEM-EDX characterization (4), As(-I) species similar to the safflorite reference were present in all samples except for the nonamended reduced sample (Day 30). The safflorite-like species accounts for 15–20% of the total As in the sample on day 0, and a comparable level of As(-I) is detected in the reoxidized sample. Compared to the day 0 sample, the proportion of As(V) species decreases from 74 to 43% after 30 days of reduction, while the proportion of As(III) increases from 12 to 57%. The absence of safflorite-like species in the day 30 unamended sample suggests that this species was not stable under the prevailing conditions. In contrast, up to 40% of As was fitted as safflorite-like species in the glucose-amended reduced sample. In addition to the generation of As(-I), the glucose-amended reduction also led to the formation of intermediate reduced As species best fitted by the elemental As (ox) reference compound [40% As(III) and 60% As(0)]. These intermediate reduced species still persist in the reoxidized sample (Reox + Glu).

Discussion

Impact of Reduction on As Solubilization. Rapid remobilization of As was observed when reducing conditions prevailed. In all layers of the profile, 30 days of reduction resulted in a significant increase in dissolved As and a corresponding decrease in oxalate-extractable As in the solid phase. The relatively high ratio of oxalate-extractable As to Fe released during reduction suggests that the main source of As is the dissolution of primary or secondary As minerals, instead of a Fe-oxyhydroxide host with sorbed As. The dissolution of As after 30 days of reduction was lowest in the bottom layer. There are two possible reasons for this observation. First, compared to the surface layer, a larger proportion of As in the bottom layer already occurs in reduced forms (Figure 2C vs A) that cannot be further reduced under the experimental conditions. Second, the bottom layer is associated in the field with the lowest counts of iron- and sulfate-reducing bacteria (4), which are known to be capable

TABLE 2. Linear Combination Fitting Results Showing the Relative Proportion (normalized to sum = 100) of Each As Standard that Yielded the Best Fits to the Arsenic EXAFS $\chi(k) \cdot k^3$ Spectra for the Mill Creek Samples Intermediate Layer

treatment ^a		GOF ^e (χ^2)	sum of fractions before normalization	percent of total As $\pm$ standard error ^b						percent of total As		
				As ₂ O ₅	adsorbed As(V)	Ca arsenate	scorodite	As ₂ O ₃	elemental As (ox)	safflorite	total As(V) ^c	total As(III) ^c
Day 0	(1)	569	1.07	46 $\pm$ 3			33 ^d $\pm$ 5			21 $\pm$ 4	79	0
	(2)	587	0.99	59 $\pm$ 2				22 $\pm$ 4		19 $\pm$ 4	59	22
	(3)	587	0.96		59 $\pm$ 4		25 ^d $\pm$ 3			15 $\pm$ 4	84	0
	(4)	642	0.82	75 $\pm$ 3				25 $\pm$ 4			75	25
mean											74	12
Day 30	(1)	988	0.64	25 $\pm$ 8			18 $\pm$ 7	57 $\pm$ 6			43	57
	(2)	1001	0.66	43 $\pm$ 3				57 $\pm$ 5			43	57
mean											43	57
Day 30 +Glu	(1)	476	1.14			27 $\pm$ 2			34 $\pm$ 6	39 $\pm$ 4	27	14
	(2)	497	1.11	30 $\pm$ 6					33 $\pm$ 3	39 $\pm$ 4	30	13
	(3)	524	1.02		34 $\pm$ 3				28 $\pm$ 5	38 $\pm$ 4	34	11
	(4)	525	1.05				27 $\pm$ 2		32 $\pm$ 5	41 $\pm$ 4	27	13
mean											30	13
Reox	(1)	507	0.71	49 $\pm$ 2				29 $\pm$ 4		22 $\pm$ 4	49	29
	(2)	508	0.70		54 $\pm$ 3			27 $\pm$ 3		18 $\pm$ 4	54	27
	(3)	528	0.70			48 $\pm$ 3		29 $\pm$ 4		22 $\pm$ 4	48	29
	(4)	597	0.80				30 $\pm$ 2	45 $\pm$ 3		25 $\pm$ 4	30	45
mean											45	32
Reox + Glu		612	0.69				41 $\pm$ 2		45 $\pm$ 6	14 $\pm$ 5	41	18

^a After 1 hour KCl extraction (Day 0), 30 day reduction with (Day 30 + Glu) or without glucose input (Day 30), and after reoxidation of the reduced treatment with (Reox + Glu) or without glucose input (Reox); numbers in parenthesis identify equally good fits obtained for the sample. ^b Percent of total As after normalization to sum = 100% $\pm$ computed standard errors for the linear coefficients. ^c Total As(V) is the sum of As₂O₅, adsorbed As, Ca arsenate, and scorodite. Total As(III) is the sum of As₂O₃ + 40% elemental As (ox), as the latter standard was found to contain 40% As₂O₃. ^d Energy offset parameter for scorodite is 0.3 Å⁻¹, indicating a slightly less good fit than for combination 2. ^e Goodness-of-fit.

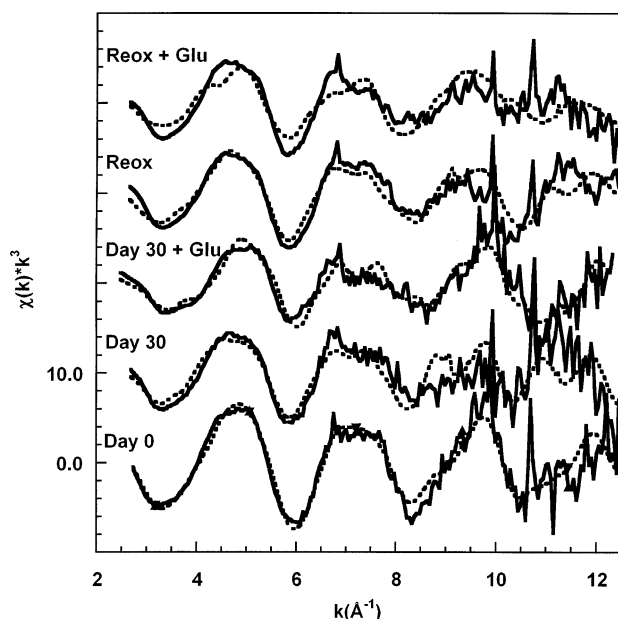


FIGURE 4. Measured (solid line) versus predicted (dotted line) As K-EXAFS $\chi(k) \cdot k^3$ spectra for the intermediate layer of the Mill Creek samples subjected to redox treatments. (Glu = glucose-amended treatment; see Table 2 for fitting parameters. When more than one combination is possible, the fit illustrated is for combination #1, except for Day 0, for which Combination #2 is shown.)

of reducing As (28, 29). The lower counts of these reducing bacteria suggest an a priori smaller potential for microbial reduction of As in this layer.

Impact of Soluble C Input on the System. Glucose input had a marked impact on the dissolution and speciation of As, suggesting that As transformation is microbially mediated in the system. Compared to the corresponding nonamended sample, the input of soluble C sped up the dissolution of As

in the intermediate layer and led to a significant increase in dissolved Fe and Mn. The latter could be partially explained by the concomitant drop in pH of 1.2 units. During the reduction of alkaline soils, the overall impact of chemical reactions is usually the lowering of pH to neutrality because of the accumulation and change in the partial pressure of CO₂ (30). The pH in the nonamended systems showed this typical behavior (Figure 1C). The significant decrease of pH following C input reflects more intense microbial activity in the amended system. During aerobic and anaerobic respiration, the initial step of metabolization of glucose into pyruvic acid generates 2 mol of H⁺ per mole of glucose (30). A range of organic acids is subsequently produced by the anaerobic degradation of pyruvic acid. Therefore, the intense dissolution of As, Fe, and Mn in the glucose-amended suspensions is due to both more intense microbial activity and enhanced chemical dissolution with decreasing pH. These conditions favored the precipitation of As(–I) species in the solid phase as detected by the XAS analyses.

Impact of Alternating Redox Conditions on the As Speciation. The XANES spectra and EXAFS fitting results clearly demonstrate that As in the tailings was quickly reacting to changes in the redox potential of the system. Both the XANES and EXAFS data show that a portion of the As(V) species, dominating in the solid phase on day 0, was transformed after 30 days of reduction to As(III), a more soluble species. Whereas the XANES results show that most of the As(III) was converted back to As(V) after a short reoxidation of the surface and bottom layers, samples from the intermediate layer had a greater proportion of As(III) in the reoxidized than in the initial sample (mean of 32 vs 12%, respectively; Table 2). In addition, compared with the initial samples, the concentration of oxalate-extractable As in the surface and glucose-amended intermediate layer samples significantly decreased after reoxidation (Reox vs Day 0; Figure A, Supporting Information). These results suggest that a small portion of As in the solid phase of our closed system is irreversibly lost to the solution or converted to more soluble

solid species following a full redox cycle. This observation, coupled with the previously discussed lowest As dissolution in the bottom layers, would explain the general depletion of As in the surface layers of the 15 profiles sampled in this wetland (4). In the field, the surface and the intermediate layers are most affected by the water table fluctuation and are thus more prone to As remobilization than the constantly saturated bottom layer.

Although our fitting results do not allow the identification of individual As(V) species, different species most likely co-exist. From SEM-EDX analyses, scorodite is known to occur either separately or rimming liberated grains of skutterudite (4). Scorodite has a low solubility under oxidizing conditions but was shown to dissolve under reducing conditions in slightly acidic flooded soils (31). Similar to our findings, scorodite reduction in flooded soils led to an increase in dissolved Fe and As and the formation of solid-phase As(III) (31).

Another likely sink for As(V) and As(III) in the oxidized system with neutral pH is their sorption on freshly precipitated carbonates and on phyllosilicates (including clays) (7, 10, 12). Reynolds et al. (32) showed that, during reoxidation of flooded soil amended with phosphate, arsenopyrite was destroyed, As(III) persisted and was retained on freshly precipitated Fe (hydr)oxides. On the basis of the results of oxalate extraction and mineralogical characterization done on the Cobalt tailings, Al rather than Fe minerals would be the dominant sorbents (4). However, given the low percentage of clays in the tailings (<10%), adsorbed As species should not represent an important sink. If the oxalate-extractable Al + Fe content is considered as a rough indicator of As adsorption (33, 34), this sink would even be less significant in the surface layer than in the substratum layer (Table 1).

The solution chemistry of the glucose-amended reduced Mill Creek system on day 30 does not support sulfide formation. The E_h on day 30 was 39 mV, more in line with the Fe reduction threshold (~50 to 120 mV at pH 7) than sulfate reduction (~150 mV at pH 7; 30, 35). In addition, the solution had high dissolved Fe compared to S (molar ratio of dissolved As/Fe/S = 17:10:1), suggesting that any sulfide present in solution would preferentially be scavenged by reactive Fe rather than As (36). On the other hand, the increase in dissolved Co and Ni in the glucose-amended reduced treatment would favor the saturation of a safflorite-like arsenide. While the precipitation of As sulfide minerals, such as orpiment (As_2S_3) and realgar (As_2S_2), is often reported as the main sink for As under reducing, acidic, and sulfur-rich conditions (10, 12, 37), As sulfide species are more soluble under neutral to basic pH conditions (10, 38). For the Farr Creek wetland characterized by neutral drainage and low total S content, our results suggest that sulfides are not a major sink for As during reduction. However, this does not preclude the possible, yet marginal, formation of As sulfides under field conditions. Some rare occurrence of framboidal pyrite was observed in the surface Mill Creek samples during the field study (4), indicating that microbial SO_4^{2-} reduction was intense enough in microsites to form metal sulfides when soluble C is not limiting. Framboidal pyrite has been reported to be a preferential site for As sorption (36) and for cobaltite precipitation in some ore deposits (39). Nevertheless, the results of our redox study suggest that formation of arsenide species may be more prominent in this system for attenuating As transport. Given that the safflorite-like phase was detected only in the glucose-amended treatment, its formation may be microbially mediated.

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Supporting Information Available

Tables showing the stability test for the best fitting results obtained using shorter k ranges, the change in dissolved S, Ca, Co, Fe, and Ni concentrations with days of reduction for each layer of the Mill Creek profile, the arsenic reference compounds selected in the study and results from target transformation. Figures showing the oxalate-extractable As concentration in each layer of the Mill Creek sediments at the beginning and end of the reduction phase (day 0 and 30) and following the reoxidation phase, and the As K-EXAFS spectra for selected As reference compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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