

Spatial and Temporal Variability of Arsenic Solid-State Speciation in Historically Lead Arsenate Contaminated Soils

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The arsenic (As) solid-state speciation (i.e., oxidation state, precipitates, and adsorption complexes) is one of the most important factors controlling dissolved As concentrations at As contaminated sites. In this case study, two representative subsurface samples (i.e., oxidized and semi-reduced sites) from former lead arsenate contaminated soils in the northeastern United States were chosen to investigate the effects of aging on As retention mechanisms using multiscale spectroscopic techniques. X-ray powder diffraction (XRD), synchrotron based microfocused (μ) XRD, in situ μ -synchrotron based X-ray fluorescence spectroscopy (SXRF), and μ -X-ray absorption near edge structure (XANES) spectroscopy were used to compliment the final bulk X-ray absorption spectroscopy (XAS) analyses. In the sample from an oxic area, As is predominantly (~71%) present as As(V) adsorbed onto amorphous iron oxyhydroxides with a residue (~29%) of an original contaminant, schultenite (PbHAsO_4). Contrarily, there is no trace of schultenite in the sample from a semi-reduced area. Approximately 25% of the total As is present as adsorbed phases on amorphous iron oxyhydroxide and amorphous orpiment (As_2S_3). The rest of the fractions (~46%) were identified as As(V)–Ca coprecipitates. This study shows that aging effects can significantly alter the original chemical constituent (schultenite) in soils, resulting in multi and site-specific As solid-state speciation. The variability in spatial and temporal scale may be important in assessing the environmental risk and in developing in situ remediation technologies.

Introduction

Current risk assessment of arsenic (As) in soils and sediments is often based on traditional bulk chemical analyses (e.g., EPA3050 chemical digestion). These methods are useful in measuring the total As levels and operationally defined As extractability in heterogeneous materials. However, such bulk analyses often under- and overestimate As bioavailability

because of the complex reactivity of mixed As solid phases in soil matrices. To accurately predict the desorbability/bioavailability of As in natural materials, an accurate evaluation of As solid-state speciation becomes critical since adsorbed and precipitate phases control the As concentrations in soil solutions. Bulk XAS is a powerful technique for constraining the solid-state speciation of As in soils and sediments (1–3). In many contaminated sediments, however, fine scale heterogeneity can make accurate evaluation of the bulk XAS analyses difficult. In such cases spatially resolved X-ray microbeam techniques can provide additional constraints to accurately interpret the As solid-state speciation.

For example, in the case of a toxic metalloid such as arsenic, detection of residual As(III) phases is extremely important because of the higher toxicity and mobility of As(III) compared to that of As(V). Synchrotron based μ -X-ray fluorescence (μ SXRF) spectroscopy can be used to evaluate both arsenic distribution and abundance through compositional mapping. Spatial resolutions for synchrotron based hard X-ray microprobes are typically on the order of a few micrometers with elemental sensitivities for transitional metals of about 50–100 ng/g (1). Additionally, μ XAS measurements can then be performed at specific positions on the sample based on the elemental distribution data generated by μ SXRF.

In this case study, we utilized a combination of in situ bulk- and μ -XAS, in situ μ SXRF, and ex situ bulk- and μ -XRD to investigate As solid-state speciation in aged lead arsenate contaminated soils. Chemical digestion/extraction was also employed to aid in the interpretation of the XAS analyses. The materials used in this study were collected from sites that had an extensive storage/disposal history of industrial byproducts from sulfuric acid and lead arsenate derived from manufacturing processes. High levels of total aqueous As concentration (>50 $\mu\text{g/L}$) have been detected adjacent to groundwater wells. Therefore, understanding of the distribution and fixation mechanisms of As at these sites is extremely important in risk assessment.

Site History and Environmental Background. Soil samples were collected from a former commodity, specialty, and agricultural chemicals manufacturing site located in the northeastern United States. The specific locations are not provided due to proprietary restriction. During its 96-year history, this plant manufactured and sold an array of products, including inorganic and organic pesticides, sulfuric acid, and white pigment (BaSO_4). Production of inorganic arsenicals such as lead arsenate for many years was the primary source of arsenic contamination of groundwater and soils at the site. Barium in the soil originates from the manufacture of (BaSO_4), which was used as a white pigment in paints and paper. The main source of calcium and sulfur in the soil is waste gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) that was generated from the use of lime to neutralize waste sulfuric acid and to remove sulfate impurities from a major herbicide produced at the site. Over the years, the original tidal meadows at the site were gradually filled in as the plant expanded. However, the exact composition of the fill materials employed over the years is not known.

Materials

Two different sampling “sites A and B” were chosen for the study. Whereas site A is generally under stagnant conditions, site B is exposed to periodic tidal action. The redox potentials of samples collected in the top 4 m of soil were measured using a platinum electrode (4). Values are approximately –33 for A and 275 mV for B, indicating that site A is more reduced

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TABLE 1. Total Metal(Ioid) Digestion and Physicochemical Analyses of As Contaminated Soils from Selected Site A and B as a Function of Depths

sample	rock fragments/ texture	pH _{water}	As	Ba mg kg ⁻¹	Ca mg kg ⁻¹	Cr mg kg ⁻¹	Cu mg kg ⁻¹	Mn mg kg ⁻¹	P mg kg ⁻¹	Pb mg kg ⁻¹	Ti mg kg ⁻¹	S mg kg ⁻¹	Zn %	Al %	Fe %	Si %	OM %
site A (m)	gravel/cobble	6.97	76	5370	8585	87	88	225	1350	120	7255	6030	66	8.62	3.08	17.56	5.23
0–1																	
1–2 ^a	gravel/sand	6.97	76	8804	16820	88	98	399	1730	230	3215	46300	74	2.62	7.70	17.55	3.04
2.5–3.25	gravel/sand	6.45	4	2100	157615	4	5	68	2610	15	445	162000	42	0.20	0.09	1.35	1.99
3.75–4	silty loam	7.05	82	395	27580	57	12	118	1000	90	2980	34300	50	4.27	1.25	16.78	0.23
site B (m)	gravel/cobble	5.36	17	1170	7120	134	120	59	656	792	7700	2610	26	10.10	2.15	17.83	NA
0–1																	
1–1.5	loamy sand	5.09	40	2380	10250	78	69	99	1030	281	7630	3580	94	11.91	1.94	18.15	2.95
1.5–2	loamy sand	6.33	45	69570	3323	105	66	17	1290	89	4725	8500	60	7.84	1.99	12.89	0.85
2.75–4 ^a	silty loam	7.07	284	2280	12680	114	36	113	1210	781	4900	2070	73	7.0	3.14	20.46	2.43

^a The depths in bold letters indicate the samples used for the spectroscopic analyses. Total metal(Ioid) values are significant at the 0.05 probability level.

than site B. Geoprobes were used to collect 3.8 cm diameter cores at 0–4 m depths. The samples were immediately sealed in acetate tube liners. The tubes were kept at ~5 °C in a N₂ filled environment for further chemical and XAS analyses. Samples were separated by different depths in a N₂ filled glovebox for chemical digestion and pH measurements. For acid digestion, core samples were freeze-dried for 72 h and kept at approximately 4 °C prior to further analyses. For spectroscopic analyses, a sample that had the highest As loading (Table1) was chosen from each site (site A: 76 mg/kg; site B: 284 mg/kg).

Methods

Total Metal/Metalloid Analyses. Microwave acid digestion was used to determine the total metal/nutrient analyses (As, Cu, Cr, Mn, P, Pb, S, and Zn) (5). A lithium metaborate fusion method was used for nonvolatile elements (Al, Ba, Ca, Fe, Si, and Ti) (6). All elements were analyzed using inductively coupled plasma atomic emission spectrometry. Ammonium oxalate extraction (7) was employed on selected samples that were analyzed for XAS. Soil pH_{water} (1:1 soil/solution ratio after 24 h of equilibration) was measured in a N₂ filled glovebox. Percent organic matter content was measured using a Walkley-Black method (8).

Bulk X-ray Diffraction Analyses. Freeze-dried soil samples were finely ground and passed through a 0.64 mm sieve. Powder XRD data were collected from 5 to 95° 2 θ with a Philips X-ray powder diffractometer (graphite monochromatized Cu K α radiation, 0.05° 2 θ step size, and 4 s count time per steps). All samples were analyzed as random mounts using the back-packed procedure (9). The detection limit for crystalline phases by bulk XRD analyses is approximately 2% by weight. Mineral identifications were conducted using the JCPDS reference files.

μ SXRF, μ XANES, and μ XRD Analyses. The μ SXRF and ex situ μ XRD measurements of the soil samples were performed at beamline X26A at the National Synchrotron Light Source (Upton, NY). Samples for SXRF compositional mapping (e.g., Zn, Cu, Ni, Fe, Mn, Ti, and Ca) were mounted on high-purity Suprasil quartz slides as thin section for ex situ measurements. For in situ analysis, sediment films were used, which were trapped in 8 μ m Kapton films under N₂ environment. XRF imaging was conducted above the As K α absorption edge (11.88 keV) using a Canberra SL30165 Si(Li) detector.

Once areas of high As abundance were identified, synchrotron microbeam XRD patterns (1024 $\times$ 1024 pixel) were collected in transmission using a Bruker SMART 1500 CCD area detector with exposure times ranging from 300 to 500 s. The detector was calibrated using the Fit2D program (10) against the NIST SRM 674a α -corundum standard. Pattern integration was also done in Fit2D to yield 2 θ vs intensity spectra.

In situ μ XANES measurements were carried out at beamline X26A at the NSLS and at beamline 13-ID/GeoSoilEnviroCARS (GSECARS) (Advanced Photon Source, Argonne, IL). As K edge μ XANES measurements were performed with a beam size of ~10 μ m at X26A and ~100 μ m at GSECARS at regions selected from XRF maps of previous in situ measurements. Spectra were collected up to 50–200 eV above the As K edge absorption energy in fluorescence mode using a Canberra 9-element Ge Array detector. Detailed procedures of μ SXRF, μ XANES, and μ XRD analyses are described in SI(Supporting Information)-1a.

Bulk-XAS Analyses. Bulk extended X-ray absorption fine structure spectroscopy (EXAFS) analyses were performed using beamline X11A at the NSLS. Totals of two to eight XAS spectra were collected in fluorescence mode with a 13 element Ge array detector at room temperature. The XAS data reduction and shell-by-shell fit analysis were performed with the SIXPACK/IFEFFIT interface (11) using the method described in the previous research (12) (see SI-1b in the Supporting Information for detailed XAS analyses). To validate the proposed surface species in the shell-by-shell fit analyses, the coordination number of each species at low-to high-R was correlated to conduct the additional XAS analyses using the following steps. We assumed that amplitude reduction for As–S and/or As–metal(Ioid) shells were contributed from the respective fractions (e.g., $f_{\text{metal(Ioid)}}$ is the fraction of As–metal(Ioid) shells and f_s is the fraction of As–S shell) in each sample. Thus, fixed values of theoretical coordination number (N) for As–As, As–Ca, As–Fe, As–Fe, and As–S shells (e.g., $N_{\text{As–S}} = 3$, $N_{\text{As–Fe}} = 2$), which were estimated based on preliminary fit results of R and postulated surface species, were used during the final fit (Table2). The amplitude reduction factors, S_0^2 , were then defined as $0.9 - (N)f_{\text{each shell}}$, where (N) is the theoretical coordination number for each shell, $f_{\text{each shell}}$ is the respective fraction of each shell, and $1 = \sum f_{\text{each shell}}$.

Results and Discussion

Physicochemical Characterization and Total Metal/Metalloid Analyses. Physicochemical and total metal/metalloid/nutrient analyses are shown in Table 1. Whereas the soil pH is about neutral throughout the entire site A soil profile, pH increases from ~5 to ~7 with increasing depth in the soil profile from site B. The soil fragment and texture of samples at site A were extremely gravelly down to 2–3.25 m from the surface and a silty loam texture was present below 3.75 m. Organic matter content decreased with increasing depth from 5.23 to 0.23%. Similarly, the texture of site B samples was gravel/blocky between 0 and 2.75 m and a silty loam texture was present below 2.75 m. Unlike those from site A, the samples below 2.75 m were rich in organic matter (2.43%). Based on the visual observation of the core materials, the

TABLE 2. Structural Parameters of the Least-Squares Analyses of As K-edge EXAFS Spectra

sample		As–O	As–S	As–Fe	As–Ca/Pb	As–As	E ₀	reduced χ^2/R -factor
sample A	CN	4.16(4)	3 ^a	2 ^a	2 ^a	2 ^a		
	f		0.25 ± 0.1	0.28 ± 0.1	0.46 ± 0.3 ^b	0.46 ± 0.3	10 ± 3.32	24.61/0.0891
	R (Å)	1.71(1)	2.27(3)	3.31(7)	4.06(7) ^b	4.16(2)		
	σ^2 (Å ²)	0.008(3)	0.003 ^a	0.002 ^a	0.002 ^a	0.004(9)		
sample B	CN	4.6(6)		2 ^a	2 ^a	1 ^a		
	f			0.71 ± 0.2	0.29 ± 0.2 ^c	0.29 ± 0.2	6 ± 2.1	26.69/0.0342
	R (Å)	1.693(7)		3.29(2)	3.9(4) ^c	4.02(7)		
	σ^2 (Å ²)	0.0023(9)		0.002 ^a	0.002 ^a	0.002(7)		

CN: coordination number. f: fraction of total species. R: interatomic distance (Å). σ^2 : Debye–Waller factor (Å²). Fit quality confidence limit for parameters: Accuracies for R and CN are ±0.03 Å and ±30%. ^a Fixed parameter. ^b As–Ca shell. ^c As–Pb shell. Theoretical coordination numbers: $N_{As-S} = 3$, $N_{As-Fe} = 2$, $N_{As-Ca} = 2$, $N_{As-Pb} = 2$, and $N_{As-As} = 1$ for sample B and $N_{As-As} = 2$ for sample A.

high OM content <2.75 m is attributed to decomposed plant matter from a former wetland.

The total As at site B fluctuates with increasing depth (Table 1). It has a maximum value (i.e., 284 mg/kg) at a depth of 2.75–4 m. In contrast, the total As levels are almost evenly distributed (~80 mg/kg) throughout the entire profile at site A except for the 2.5–3.25 m layer.

Gypsum mud that was used to fill this particular depth (2.5–3.25 m) may have created a low As contaminated layer (~4 mg/kg). The presence of gypsum at 2.5–3.25 m can be supported by (1) the highest total Ca and S concentrations and (2) the XRD results (not shown).

Overall, both sites are rich in Al, Fe, and Si. This may indicate that metal oxide and aluminosilicate minerals in the soils may serve as sinks for dissolved As (13–18). Based on the ammonium oxalate extractions, sites A (1–2 m) and B (2.75–4 m) samples contained 3254 and 16369 mg/kg of iron, respectively, suggesting the presence of amorphous iron oxyhydroxides-like precipitates. Amorphous iron oxyhydroxide reacts strongly with dissolved As(III and V) (19–21). This may indirectly explain why As is concentrated at the 2.75–4 m depth at site B. Other elements that are present in the soils in significant quantities are Ba, Ca, and S. It is possible that insoluble barium arsenate-like precipitates (22) may be controlling the As(V) solubility over PbHAsO₄ phases which were originally introduced. Elevated Ca and S concentrations from the gypsum disposal might contribute to the formation of As(V) substituted CaSO₄ precipitates. Ca₃(AsO₄)₂ species are reported to be thermodynamically stable complexes in oxidized and alkaline environments (23). In the reduced horizons, As(III) sulfide species, such as orpiment-like precipitates, can be expected. In this study, one depth from each site (2–4 m at site A and 2.75–4 m at site B), where total As was most concentrated, was chosen for detailed spectroscopic studies to understand the As solid-state speciation. They are referred to as sample A and sample B, respectively. Bulk XRD analyses are consistent with quartz as the predominant mineral phase in all samples at site B, followed by albite (K/Na (AlSi₃O₈)), calcite, and hematite (Fe₂O₃). Fragments of bricks mixed with fill materials are probably the source of hematite as evidenced by visual observations. A mixture of three mineral components (barite (BaSO₄), gypsum (CaSO₄), and quartz) was found in all samples at site A.

In Situ μ -SXRF and μ -XANES Analyses. Elemental maps of selected areas of samples A and B are shown in Figure 1 and Figure SI-2 in the Supporting Information (from X26A). Flux normalized fluorescence intensity (fluorescence counts/pA incident X-ray signal) of each element are indicated by color contour bars on the left side of each map. Figures 1 and SI-2 are X-ray fluorescence maps for As, Ba, Ca, and Fe for samples A and B, respectively. Because of the difficulty in precisely quantifying matrix effects for absolute abundance calculations in heterogeneous materials, the SXRF data are

qualitatively interpreted in this section. The circled regions on the maps show where μ XANES spectra were collected. In Figure 1, region 1 shows elevated As counts (as appear in blue to yellow color) that is similarly distributed with Ba, Ca, and Fe. Regions 2 and 3 in the As map do not have elevated As concentrations, and As does not seem to be co-distributed with elements such as Cu, Ni, Zn, Mn, and Ca (XRF maps are not shown). Scatter plots of As K α vs Ba L γ counts and K α counts of Ca, Cu, Fe, Mn, and Zn (Figure SI-3) show that most of the elements (e.g., Ca, Fe, and Cu) display no significant correlation with As, suggesting one particular distinct As–metal species is not dominant at this resolution. Only the As–Zn plot shows a slight correlation in a ray (slope of the scatter plot Zn vs As ~ 0.29 ± 12%).

Arsenic hot spots in sample B are shown in Figure SI-2 as regions 4 and 6. The median counts (indicated in blue) of As seem to be correlated with elevated Fe counts (e.g., region 5). In the scatter plots (Figure SI-4), we did not find any specific correlation between As and Mn, Ca, Fe, Ti, or Cu. While the presence of discrete As mineral phases can be excluded, it is possible that As may be present as adsorbed phases on metal oxides. In the As vs Pb plot, there is a potential correlation in two sets of data with a best fit line (slope ~ 0.86±29%) that is not evident in plots of As vs Mn/Fe.

Based on the elemental maps alone, it is difficult to elucidate As binding mechanisms in heterogeneous soils. However, combined with the final bulk-EXAFS analyses, the information on the elemental correlations assists in suggesting possible As adsorption complexes and/or precipitates. To gain insights on the chemical speciation such as As valence state, μ -XANES analyses were performed on regions 1–6 of the μ -SXRF As maps (Figures 1 and SI-2).

The As absorption edge energy positions provided by XANES provide an average As oxidation state. Whereas the energy position of As(V) sorbed on minerals and As(V) minerals/salts is ≥11874 eV, As(III) adsorption complexes exhibit an energy position of approximately ~11871 eV. When As(III) associates with sulfide (e.g., mineral orpiment (As₂S₃)), the As(III) energy position further decreases to ~11869 eV (2, 24). Based on the absorption edge energy positions, the As valence state and As(III)–S association can be suggested. The μ XANES spectra (normalized to incident beam intensity) of regions 1–6 are shown in Figure 2a. The two vertical dotted lines at ~11.869 and ~11.874 keV indicate As(III)–S and As–(V), respectively. In sample A (regions 1–3 in Figure 1), the single white line peak present in region 1, where As is somewhat associated with Ca, Ba, and Fe, and the absorption edge energy position, indicate a predominant As(V) oxidation state. Region 2 also shows a predominant As(V) valence state. The XANES spectrum from region 3 displays a split white line. Based on the second derivative of the spectrum (data not shown), this is attributed to an assemblage of As(V) (~11.874 keV) and As(III) (~11.869 keV). Arsenite is probably associated with sulfide.

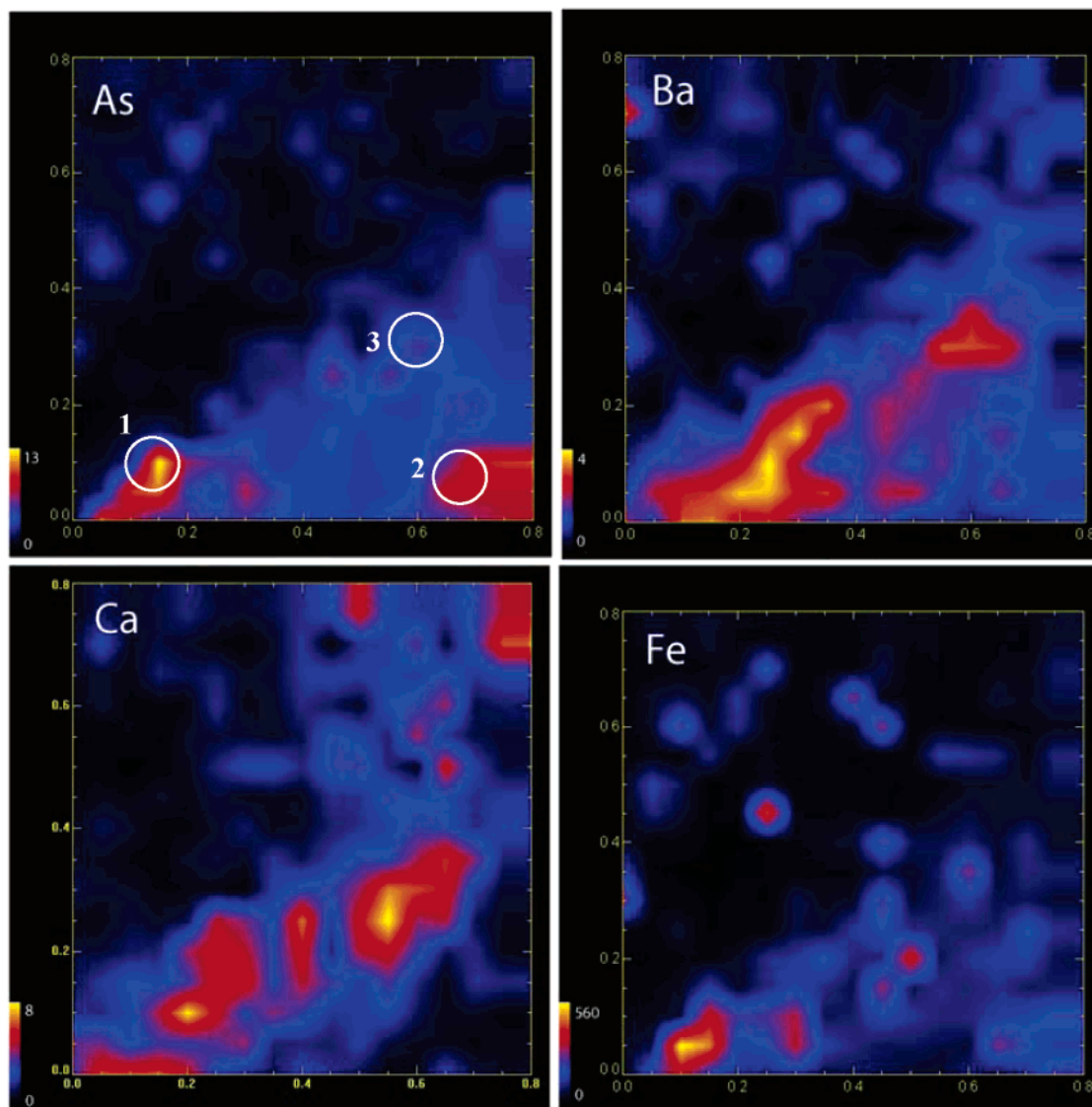


FIGURE 1. In situ μ -SXRF maps of sample A (As K α , Ca K α , Fe K α , and Ba L α). The scale of maps on the x- and y-axis is in millimeters. Fluorescence counts for each element are indicated by color contour bars on the left side of each map, and the intensity of each color is proportional to the amount of the corresponding element. Regions 1, 2, and 3 indicate the area where μ -XANES spectra (Figure 2a) were taken.

In sample B (regions 4–6 in Figure SI-2), the As valence state shows similar differences in valence states between regions. Whereas the As(V) species predominates in regions 4 and 5 where Fe concentrations are elevated, a mixed oxidation state is present in region 6 as evidenced by a wide white line peak (Figure 2a). In region 6, the As(III) absorption energy position is slightly shifted from the vertical dotted line A (~ 11.869 keV) to a higher energy (~ 11.871 keV). This suggests that As(III) is unlikely to be associated with sulfides.

Bulk- and μ -XANES Analyses. Figure SI-5 shows bulk (1×2.5 mm) and μ (~ 100 μ m) XANES spectra for samples A and B (e.g., bulk- and μ -XANES spectra of sample A are denoted as “sample A” and “sample A-1”, respectively). The μ -XANES spectra that are presented here were collected at GSECARS at the APS using similar methods as above, but with a larger beam size ($\sim 100 \times 100$ μ m) than the previous measurements at NSLS. The postedge regions (up to 150 eV) of the As XANES spectra were better resolved. It is clearly observed that the postedge features (11.875–11.920 keV) of the bulk- and μ -XANES spectra of the same sample are different, suggesting a heterogeneous As solid-state speciation. Shoulder features of a wide white line peak in several spectra indicate the presence of multiple oxidation states. In

Figure SI-5, it is clear that As(V) is the predominant valence state in most of the samples except for sample A-4 (as indicated by a vertical dotted line at 11.874 eV). To understand the subtle differences in As valence state, first derivatives of all spectra are shown in Figure SI-5, and they are compared with selected reference spectra (e.g., As(V) sorbed goethite). Although As(V) is the dominant valence state in most of the samples, some samples (samples A-4, A-3, and A) exhibit an inflection point consistent with the mineral orpiment (first derivative peak at 11.869 keV). Furthermore, several spectra (samples B, B-4, and A-2) exhibit an inflection point slightly above 11.869 keV, indicating the presence of other As(III) phases. Overall, we suggest the presence of two significant As valence states in each sample; sample A contains arsenate and As(III) (other than orpiment) and sample B contains orpiment and As(V). The results of multiscale XANES analyses were used to constrain the first shell (e.g., As–O and As–S) in the EXAFS analyses that are discussed below.

Synchrotron Based μ -XRD Analyses. Selected diffractograms of the μ -SXRD measurements on sample B are presented in Figure 2b. The μ -SXRD measurements were taken at As localized areas as determined by μ -SXRF measurements. Due to scatter from the quartz slide, low d

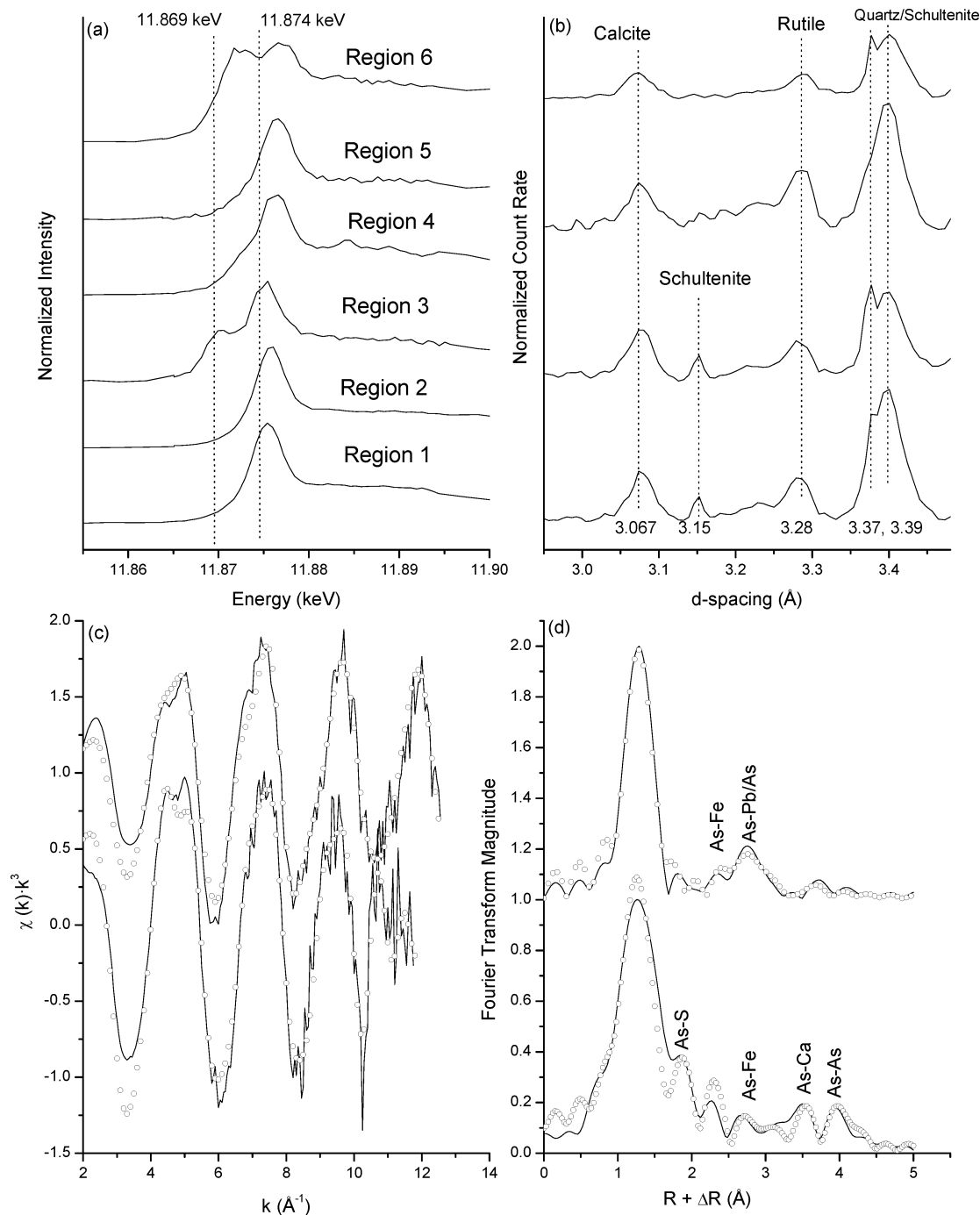


FIGURE 2. (a) Microfocused XANES spectra at region 1–6 of selected areas of the As fluorescence maps shown in Figure 1 and Supporting Information-2. Spectra were collected at beamline X26A. (b) Microfocused SXRD patterns ($\lambda = 0.7598 \text{ \AA}$) of As concentrated areas of sample B. Selected diffractograms show $2.8 \text{ \AA} < d \text{ spacing} < 3.6 \text{ \AA}$. (c) Nonlinear least-squares fits to normalized k^3 -weighted EXAFS spectra of the reference compounds and sample A (bottom) and B (top). Raw data and fits are shown by solid lines and open circles, respectively. See Tables 1 and 2 for fit parameters. (d) Nonlinear least-squares fits to Fourier transforms of the reference compounds and samples A (bottom) and B (top). Raw data and fits are shown in solid lines and open circles, respectively. See Table 2 for the fit parameters.

spacing (< 3) could not be well-resolved. The minerals (calcite, gypsum, barite, and albite) that were identified using bulk XRD were initially considered. Although the peak intensity and d spacing of gypsum, barite, and albite were not identified, a corresponding calcite peak was observed at $3.065 \text{ \AA}$. In addition to calcite, we have identified the presence of rutile and quartz in all 26 diffractograms and schultenite (PbHAsO_4) in about half of the diffractograms.

Bulk-EXAFS Analyses. Bulk EXAFS analyses on natural materials are difficult due to backscattering signals from multi-neighboring atoms. In the case of As contaminated

natural materials, the EXAFS analysis becomes more complex because of the presence of As(III) and As(V) that are possibly coordinated with oxygen or sulfur atoms. To facilitate bulk-EXAFS analysis, the results from the XRD, chemical extraction, SXRF maps, and bulk- and μ -XANES analyses were considered. In this section, radial distances are mainly discussed to elucidate the As solid-state speciation rather than comparing spectral features in $k \text{ (\AA}^{-1}\text{)}$ space. Since the mixed As(III and V) phases are present in the samples, as evidenced from the XANES analyses, the spectral feature comparison between natural samples and reference materials or simu-

lated EXAFS spectra is not effectively used to suggest solid-state speciation. Nonlinear least-squares fits of normalized k^3 -weighted EXAFS and FT spectra of samples A and B are shown in Figure 2c,d. Fit parameters are summarized in Table 2. Interatomic distances that are mentioned in this section are corrected for phase shift (R) and are shown in Table 2 (in units of Å).

Based on the results of bulk- and μ -XANES analyses of sample A, we suggest the presence of As(V) and As(III) sulfide species (orpiment-like) in the sample A. Based on the bulk XRD analyses, calcite, barite, and gypsum are considered as possible adsorbents in addition to common iron oxyhydroxide sinks (e.g., ferrihydrite and hematite). The As–O and As–S distances (1.71 and 2.27 Å) were successfully fit in the first shell, and the fit results are in good agreement with the data reported by other researchers (2, 25, 26). The negligible contribution of two other As–As distances that are present in crystalline orpiment (~ 2.56 and 3.19 Å) (2, 27) is observed in the fit, suggesting that As(III)–sulfide precipitates in sample A are structurally disordered (i.e., amorphous). Helz and co-workers documented the absence of As–As/S backscatters at >2.5 Å in amorphous As(III)–sulfide precipitates (26), and this supports our interpretation. Furthermore, we are able to fit an additional As–Fe distance at ~ 3.3 Å. This distance is commonly seen when As(V) tetrahedral molecules are coordinated on iron octahedral structure in a bidentate binuclear fashion. We have also considered the As–Zn distance at ~ 3.3 Å because (1) the previous SXRF scattered plot indicated a possible As–Zn correlation (Figure SI-3) and (2) the mineral adamite ($\text{Zn}_2\text{AsO}_4(\text{OH})$) contains edge-sharing As(V) coordination on Zn octahedral, resulting in approximately a bond distance of ~ 3.3 Å. We were able to fit the As–Zn distance at 3.33 Å, and the fit quality is near identical to the fit with the As–Fe distance (differences in reduced χ^2 values $\sim 2\%$). Although we cannot exclude the possibility of inner-sphere As(V) coordination on a Zn octahedral structure, it is reasonable to interpret the 3.3 Å backscatters as bidentate binuclear coordination of As(V) on iron oxyhydroxides since the ammonium oxalate extractable Fe (i.e., operationally defined amorphous iron oxyhydroxide fraction) is substantially greater than total Zn (3254 and 74 mg/kg, respectively) (Table 1). The final two shells at >3.5 Å were considered with As–Ba/Ca/As distances. The As–(V)–Ca/Ba interactions were mainly considered based on the results of the SXRF and μ -XANES analyses (Figures 1 and 2a). Two possible As(V)–Ca distances (~ 3.6 and 4.0 Å), which were estimated via XRD/FEFF, can be considered based on the known monodentate corner-sharing and bidentate edge-sharing coordination environments between As tetrahedral and Ca octahedral structures in the minerals, welite- (CaHAsO_4) and conichalcite (CaCuAsO_4) . The best fit is obtained when As–Ca is at 4.06 and As–As is at 4.16 Å. The replacement of these shells with As(V)–Ba single backscatters does not improve the overall fit (i.e., increased reduced χ^2 by $\sim 6\%$). The possible explanation for the presence of As–(V)–Ca/As shells may be due to Ca–As(V) coprecipitates and/or substitution of arsenate into gypsum that is present in large quantities ($>5\%$ by weight). To validate the presence of postulated surface species, coordination numbers of species at low R were correlated with the expected proportions of the species at high R (e.g., As–Ca shell with As–As shell). The results indicate that surface species consist of approximately 25% of amorphous orpiment, 28% adsorbed As(V) on iron oxyhydroxide, 46% of Ca–As(V) coprecipitates, and/or substitution of arsenate into gypsum. The ratio between As(III)–S (25%) and total As(V) species ($28 + 46 = 74\%$) is in good agreement with results of linear combination (LC) of bulk XANES analyses. When two reference XANES spectra (orpiment and As(V) sorbed goethite) were used to fit at 11850 – 11925 eV, the component compositions are 25.2

$\pm 1.2\%$ orpiment and $74.3 \pm 0.98\%$ As(V) species. The results of LC XANES analyses further support the validity of CN correlated XAS analyses.

Sample B contains As(V) with a small fraction of As(III) species, based on the results of the bulk-XANES analyses (Figure SI-5). We initially considered for the first shell fit both As(V)–O (1.69 Å) and As(III)–O (1.77 Å) distances, as reported by other researchers (28, 29). The final results (i.e., As–O at 1.69), however, indicate the presence of predominant As(V)–O distance. E_0 shift values of the first shell fit were used to fit the rest of the shells (2.7 and 3.3 Å when corrected for phase shift). Based on the results of XRD, SXRD, chemical extraction, and SXRF analyses, we speculated (1) albite, hematite, calcite, rutile, quartz, and iron oxides as possible adsorbents, (2) schultenite as a possible As precipitate, and (3) Pb and Ti that are likely to be associated with As. The As–Fe distances seem to give the best fit for the second shells at ~ 3.3 Å as seen in sample A, and the same shell can also be fit with the Ti backscatter. Considering the amounts of ammonium oxalate extractable Fe (1.6% by wt) is significantly greater than the total Ti $\sim 0.49\%$ by weight, it seems reasonable to suggest that ferrihydrite-like precipitates are the predominant adsorbents. In fact, the median fluorescence counts (indicated in blue) of As and Fe in SXRF maps were similarly distributed with each other (e.g., region 5 in Figure SI-2). Several studies (e.g., (2)) have reported As–Fe distances at ~ 3.3 Å that corresponds to the As(V) bidentate binuclear configuration on iron oxyhydroxide surfaces. We were unable to fit with As–Ca distances, suggesting that calcite was not the primary adsorbent for dissolved As(V). We were able to incorporate the As–Pb and As–As distances at >3.9 Å, and this supports the SXRD evidence for schultenite. The As–Pb and As–As distances (3.9 and 4.02 Å, respectively) are close to the values that are estimated by FEFF/XRD calculations (i.e., 3.89 and 4.0 , respectively) (30). As demonstrated in sample A, postulated surface species in the shell-by-shell fit analyses in sample B were further evaluated using the CN correlated XAS analyses. The results show that sample B contains predominantly ($\sim 71\%$) As(V) adsorbed species on iron oxyhydroxide, followed by a residual ($\sim 29\%$) schultenite.

It is important to note that aluminum oxides and phyllosilicate minerals were also considered as potential adsorbents in samples A and B. However, the As–Al/Si shells (3.11 – 3.19 and 2.6 Å, respectively), which corresponds to a As(V) bidentate binuclear configuration on aluminum tetrahedral and silicon tetrahedral, were unable to be incorporated in the fit.

In this study, multiscale spectroscopic techniques (in situ bulk- and μ -XANES, SXRF, and SXRD, and ex situ bulk-XRD) were effectively combined to elucidate the As solid-state speciation in lead arsenate contaminated soils. Decades of contamination and weathering resulted in an alternation of the original As contaminant source (lead arsenate). While sample B from the oxic site predominantly contains As(V) sorbed species on amorphous iron oxyhydroxides with a residual schultenite, sample A from the semi-reduced site had arsenite incorporated species as well as some As(V) sorbed species on the amorphous iron oxyhydroxides. At the semi-reduced site A, we predict that schultenite has undergone reductive dissolution reactions, and dissolved sulfide has contributed to the formation of the amorphous As–S minerals. The dissolution products (dissolved As(III and V)) were influenced by not only the indigenous soil constituents but also the additional dissolved species (e.g., Ca) from lime and gypsum amendments/disposal to form amorphous Ca–As phases. It seems that schultenite has undergone site-specific dissolution reactions (reductive dissolution vs non-reductive dissolution) with time and resulted in heterogeneous As sequestration mechanisms. Traditional bulk chemical digestion and the leachate test could possibly

overestimate the site-specific As solid-state species that significantly control the bioavailability of As in soil solutions. This case study showed the importance of variable As solid-state species at spatial and temporal scales that might be important in risk assessment consideration and in the development of in situ remediation technologies.

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Supporting Information Available

Figure SI-1a: Detailed methodologies for μ SXRF, μ XANES, μ XRD analyses. Figure SI-1b: Bulk-XAS analyses. Figure SI-2: In situ μ -SXRF maps of sample B. Figure SI-3: Scatter plots of fluorescence counts of SXRF maps in Figure 1. Figure SI-4: Scatter plots of fluorescence counts of SXRF maps in Figure SI-2. Figure SI-5: First derivative and normalized arsenic k -edge bulk- and microfocused-XANES spectra. Figure SI-6: Acknowledgments. This material is available free of charge at <http://pubs.acs.org>.

Literature Cited

- Bertsch, P. M.; Hunter, D. B. Application of synchrotron-based X-ray microprobes. *Chem. Rev.* **2001**, *101*, 1809–1842.
- Foster, A. L.; Brown, G. E., Jr.; Tingle, T. N.; Parks, G. A. Quantitative arsenic speciation in mine tailing using X-ray absorption spectroscopy. *Am. Mineral.* **1998**, *83*, 553–568.
- Savage, K. S.; Tingle, T. N.; O'Day, P. A.; Waychunas, G. A.; Bird, D. K. Arsenic speciation in pyrite and secondary weathering phases, Mother Lode Gold District, Tuolumne county, California. *Appl. Geochem.* **2000**, *15*, 1219–1244.
- Rowell, D. L. In *Soil Science: Method and Applications*; John Wiley & Sons: New York, 1994; pp 127–129.
- Amacher, M. C. In *Methods of soil analysis: Chemical methods, Part 3*; Sparks, D. L., Ed.; Soil Science Society of America, Inc.: Madison, WI, 1996; pp 739–768.
- Bertsch, P. M.; Bloom, P. R. In *Method of soil analysis: Part 3-chemical analysis*; Sparks, D. L., Ed.; Soil Science Society of America, Inc.: Madison, WI, 1996; pp 520–522.
- Loeppert, R. H.; Inskeep, W. O. In *Method of soil analysis, Part 3, Chemical methods*; Sparks, D. L., Ed.; Soil Science Society of America, Inc.: Madison, WI, 1996; pp 649–650.
- Nelson, D. W.; Sommers, L. E. In *Methods of soil analysis: Chemical methods, Part 3*; Sparks, D. L., Ed.; SSSA and ASA: Madison, WI, 1996; pp 961–1010.
- Moore, D. M.; R. C. Reynolds, J. *X-ray diffraction and the identification and analysis of clay minerals*, 2nd ed.; Oxford University Press: New York, 1997.
- Hammersley, A. *Fit 2D: Introduction and Overview*; European Synchrotron Radiation Facility: Grenoble Cedex, France, 1997; ESRF97HA02T.
- Webb, S. M. A graphical user interface for XAS analysis using IFEFFIT. *Phys. Scr.* **2005**, 1011–1014.
- Arai, Y.; Sparks, D. L.; Davis, J. A. Effects of dissolved carbonate on arsenate adsorption and surface speciation at the hematite-water interface. *Environ. Sci. Technol.* **2004**, *38*, 817–824.
- Anderson, M. A.; Ferguson, J. F.; Gavis, J. Arsenate adsorption on amorphous aluminum hydroxide. *J. Colloid Interface Sci.* **1976**, *54*, 391–399.
- Fendorf, S. E.; Eick, M. J.; Grossl, P.; Sparks, D. L. Arsenate and chromate retention mechanisms on goethite. 1. Surface structure. *Environ. Sci. Technol.* **1997**, *31*, 315–320.
- Goldberg, S.; Glaubig, R. A. Anion sorption on a calcareous, montmorillonitic soil-arsenic. *Soil Sci. Soc. Am. J.* **1988**, *52*, 1297–1300.
- Lumsdon, D. G.; Fraser, A. R.; Russell, J. D.; Livesey, N. T. New infrared band assignments for the arsenate ion adsorbed on synthetic goethite (α -FeOOH). *J. Soil Sci.* **1984**, *35*, 381–386.
- O'Reilly, S. E.; Strawn, D. G.; Sparks, D. L. Residence time effects on arsenate adsorption/desorption mechanisms on goethite. *Soil Sci. Soc. Am. J.* **2001**, *65*, 67–77.
- Xu, H.; Allard, B.; Grimvall, A. Influence of pH and organic substance on the adsorption of As(V) on geologic materials. *Water, Air, Soil, Pollut.* **1988**, *40*, 293–305.
- Fuller, C. C.; Davis, J. A.; Waychunas, G. A. Surface chemistry of ferrihydrite: Part 2. Kinetics of arsenate adsorption and coprecipitation. *Geochim. Cosmochim. Acta* **1993**, *57*, 2271–2282.
- Jain, A.; Raven, K. P.; Loeppert, R. H. Arsenite and arsenate adsorption on ferrihydrite: surface charge reduction and net OH⁻ release stoichiometry. *Environ. Sci. Technol.* **1999**, *33*, 1179–1184.
- Raven, K. P.; Jain, A.; Loeppert, R. H. Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes. *Environ. Sci. Technol.* **1998**, *32*, 344–349.
- Essington, M. E. Solubility of barium arsenate. *Soil Sci. Soc. Am. Proc.* **1988**, *52*, 1566–1570.
- Sadiq, M.; Zaidi, T. H.; Mian, A. A. Environmental behavior of arsenic in soils: Theoretical. *Water, Air, Soil Pollut.* **1983**, *20*, 1126–1130.
- La Force, M. J.; Hansel, C. M.; Fendorf, S. Arsenic speciation, seasonal transformations, and co-distribution with iron in a mine waste-influenced palustrine emergent wetland. *Environ. Sci. Technol.* **2000**, *34*, 3937–3943.
- Bostick, B. C.; Chen, C.; Fendorf, S. Arsenite retention mechanisms within estuarine sediments of Pescadero, CA. *Environ. Sci. Technol.* **2004**, *38*, 3299–3304.
- Helz, G. R.; Tossell, J. A.; Charnock, J. M.; Patrick, R. A. D.; Vaughan, D. J.; Garner, C. D. Oligomerization in As(III) sulfide solutions: Theoretical constraints and spectroscopic evidence. *Geochim. Cosmochim. Acta* **1995**, *59*, 4591–4604.
- Bostick, B. C.; Fendorf, S. E. Arsenite sorption on troilite(FeS) and pyrite(FeS₂). *Geochim. Cosmochim. Acta* **2003**, *67*, 909–921.
- Arai, Y.; Elzinga, E. J.; Sparks, D. L. X-ray absorption spectroscopic investigation of arsenite and arsenate adsorption at the aluminum oxide-water interface. *J. Colloid Interface Sci.* **2001**, *235*, 80–88.
- Manning, B. A.; Fendorf, S. E.; Goldberg, S. Surface structure and stability of arsenic(III) on goethite: Spectroscopic evidence for Inner-sphere complexes. *Environ. Sci. Technol.* **1998**, *32*, 2383–2388.
- Effenberger, H.; Pertlik, F. Schultenit, PbHAsO₄, und PbHPO₄: Synthesen und Kristallstrukturen nebst einer Diskussion zur Symmetrie. Schultenit, PbHAsO₄, und PbHPO₄; synthesis and crystal structures with a discussion on their symmetry. *Tschermaks Mineral. Petrogr. Mitt.* **1986**, *35*, 157–166.

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