

Original Paper

Arsenic Speciation in As(III)- and As(V)-Treated Soil Using XANES Spectroscopy

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Abstract. Arsenic (As) is a toxic trace element that occurs naturally in groundwater and soils. Understanding the reactions of arsenite (As(III)) and arsenate (As(V)) with soil and mineral surfaces is critical for predicting the fate and transport of As in the environment and developing better ways to remediate As-contaminated areas. This investigation uses X-ray absorption near edge spectroscopy (XANES) to evaluate the solid phase oxidation state and mineral surface binding sites in three agricultural soil samples from California, USA by fitting linear combinations of XANES spectra derived from several synthetic and well characterized As(III)- and As(V)-treated model compounds (Fe and Al metal hydroxides and aluminosilicate illite clay mineral). The results suggest that As(III) is either partially or completely oxidized to As(V) when reacted with soil in an aqueous, batch reaction. The As(III)-treated Aiken soil was composed of 60% As(III) attached to surfaces similar to lepidocrocite (γ -FeOOH) and 40% As(V) attached to aluminosilicate (illite). The Fallbrook soil completely oxidized As(III) and the product was As(V) adsorbed on Al hydroxide (gibbsite, γ -Al(OH)₃) (62%), illite (16%), and lepidocrocite (γ -FeOOH) (22%). The reaction of As(III) with Wyo soil resulted in 42% As(III) adsorbed on surface similar to goethite and 58% As(V)

adsorbed on lepidocrocite. Arsenic(V) adsorption on soil resulted in stable As(V) surface complexes that were well described by XANES spectra from As(V) adsorption complexes on gibbsite, illite, and lepidocrocite.

Key words: Arsenic; speciation; soil; XANES.

The speciation of arsenic (As) in solids is important due to the environmental health significance of this toxic element. The environmental chemistry of As is complicated by the tendency of the element to exist in multiple oxidation states and phases simultaneously. In aqueous systems, As is present as either the oxidized form arsenate (As(V)) or the reduced form arsenite (As(III)), which is more mobile and toxic than As(V) [1]. In many cases, leaching of As-bearing minerals and transport of As(III) and As(V) in groundwater or surface water results in adsorption, coprecipitation, and/or redox reactions on soil or sediment mineral surfaces. For this reason, detailed knowledge of solution and solid phase speciation of As are both necessary for a complete understanding of the environmental chemistry of As.

Many techniques are available for detection of both As(III) and As(V) in aqueous solution including hydride generation atomic absorption spectrometry (HGAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and ICP-mass

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spectrometry (ICP-MS). In a mixed As(III) + As(V) liquid sample, separation and detection of As(III) and As(V) can be carried out by chromatographic separation followed by continuous, in-line detection. Techniques that combine high performance liquid chromatography (HPLC) with element-specific detection include HPLC-HGAAS, HPLC-ICP-AES, and HPLC-ICP-MS. Modern techniques for As speciation in solution are robust due to (1) unequivocal physical separation of As(III) and As(V) species using a column prior to detection, (2) separation of the analyte from the sample matrix, and (3) highly sensitive and element-specific detection. Aqueous phase speciation of As(III)/(V) has been extensively investigated for trace analysis of natural waters and aqueous extracts of As-contaminated soils [2–5].

Unlike solutions, speciation of As in solids has inherent challenges which are unique to the solid phase. These include (1) determining As speciation *in situ* when more than one As species is present in the sample, (2) the presence of artifacts such as alteration in As speciation during the high energy probing of the sample, and (3) analysis of the resulting As signal in the presence of spectral interferences from other more abundant elements in the solid matrix. Available techniques to analyze As speciation in solids include Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), X-ray fluorescence (XRF), and X-ray absorption spectroscopy (XAS). Of the techniques currently available to analyze the speciation of As in solids, synchrotron-based XAS has become widely accepted as the most applicable to solid samples due to the high energy resolution, intensity, and collimated nature of the synchrotron-based X-ray beam. For structural and electronic analysis of elements having atomic number greater than sodium, the XAS technique is of particular significance because (1) it is an *in situ* measurement (no vacuum is required), (2) amorphous and poorly ordered solids can be probed, (3) redox state of the analyte element can be determined, and (4) element-specific structural information is obtained such as coordination environment and nearest neighbor atoms in the solid matrix. Perhaps the most pressing disadvantage of XAS is the limited availability of competitive beam time for users at synchrotron X-ray sources.

Many investigations have employed XAS for speciation of As in solids including plants and other biological samples [6–8], geological materials and mine tailings [9–13], coal fly ash [14], and zerovalent iron

[15–17]. Arsenic is encountered in geological materials as realgar (AsS), orpiment (As₂S₃), arsenopyrite (FeAsS), scorodite (FeAsO₄ · 2H₂O), and native, elemental As⁰ [9, 11]. Weathering, dissolution, and oxidation of geological materials yields dissolved As(III) and As(V) species which migrate in the aqueous phase as neutral H₃AsO₃ and H₂AsO₄⁻/HAsO₄²⁻ anions, respectively. Dissolved As(III) and As(V) species are known to adsorb strongly on Fe and Al oxide/hydroxide surfaces and can form secondary phases of adsorbed/co-precipitated As in soil, sediment, and groundwater aquifer solids. X-ray absorption spectroscopy is well-suited for the analysis of As speciation in these materials due to the general heterogeneity and poor crystallinity of secondary phases containing As, low As surface coverage on mineral surfaces, and the need to maintain the integrity of the sample (i.e., water content and redox state) during measurement.

In this paper we investigate the use of X-ray absorption near edge spectroscopy (XANES) for solid phase speciation of As(III)/(V) in samples where As(III) and As(V) have been adsorbed on solid surfaces such as synthetic minerals, soil minerals, and whole soil. These materials are representative of contaminated soil, sediment, and aquifer solids that are commonly encountered in the environment. It is important to distinguish between samples prepared by adsorption of As(III) and As(V) on mineral surfaces and geologic materials containing As-bearing mineral phases such as AsS, As₂S₃, or FeAsS where As is present in the unit cell of a bulk mineral. For extensive investigations of As speciation in As-bearing mineral phases, see Savage et al. [9] and Foster et al. [11]. The problems encountered with the investigation of As(III) and As(V) adsorption complexes include heterogeneous oxidation of As(III) and reduction of As(V), mixtures of As(III) and As(V) on individual mineral surfaces, and As(III) and As(V) simultaneously adsorbed on multiple mineral surfaces. The objective of this paper is to investigate the use of XANES to simultaneously analyze the redox state and mineral surface environment of As adsorbed on solid phase environmental samples.

Experimental

Materials

The solid samples analyzed in this study include well-characterized soil, soil minerals, and synthetic Al hydroxides (Al(OH)₃) and

Table 1. Selected properties of three California soils

Measurement	Soil		
	Aiken	Fallbrook	Wyo
pH (1:10 soil:solution)	5.90	7.10	6.77
Clay (%w:w)	47	9.2	16
Al _{CD} (mg kg ⁻¹) ¹	161	540	989
Fe _{CD} (mg kg ⁻¹)	2260	4090	8160
As _{CD} (mg kg ⁻¹)	0.21	0.15	0.45
Al _{ox} (mg kg ⁻¹) ²	207	277	492
Fe _{ox} (mg kg ⁻¹)	309	345	2660

¹ Al_{CD}, Fe_{CD}, and As_{CD} measured in citrate-dithionite extracts.

² Al_{ox} and Fe_{ox} measured in oxalate buffer extracts.

Fe oxyhydroxides (FeOOH) have been previously investigated [18–20]. Three arid-zone soils from California, USA were used in this study and were the <2 mm fractions of Aiken (clay-loam), Fallbrook (sandy-loam), and Wyo (fine-loam). Citrate-dithionite extractable Al, As, and Fe were determined by shaking 4 g of soil in 120 mL of 0.57 M sodium citrate (Na₃C₆H₅O₇ · 5H₂O) and 0.1 M sodium dithionite (Na₂S₂O₄) for 16 h. Amorphous Al and Fe oxides were determined by reacting 4 g of soil in 120 mL of acidified ammonium oxalate buffer (0.175 M (NH₄)₂C₂O₄ + 0.1 M H₂C₂O₄, pH 3.0) for 2 h. The extracts were filtered (0.2 μm membrane) followed by Al and Fe analysis using inductively coupled plasma atomic emission spectrometry (ICP-AES). Arsenic was determined by hydride generation atomic absorption spectrometry as described below. The soil pH, surface area, citrate-dithionite and oxalate extractable Al and Fe data are included in Table 1. Illite (hydrous mica) from Silver Hill, Montana, USA (sample IMt-2) was obtained from the Clay Minerals Society Source Clay Repository (Department of Geology, University of Missouri, Columbia, MO).

Synthetic goethite (α-FeOOH) was prepared by adjusting the pH of 0.2 M Fe(NO₃)₃ solution to 11 with 0.2 M NaOH and storing the suspension at 22 ± 1 °C for 2 d. The suspension was then heated at 90 °C for 16 h and repeatedly rinsed with deionized (DI) water. Lepidocrocite (γ-FeOOH) was prepared by continuous aeration of 60.0 mM FeCl₂ solution while maintaining a pH between 6.7–6.9 with dropwise addition of 1 M NaOH [21]. Gibbsite (γ-Al(OH)₃) was prepared by adding 4 M NaOH to 1 M AlCl₃ while stirring until the pH stabilized at 4.6. After heating (40 °C) for 2 h, the precipitate was transferred to cellulose tubing, dialyzed with DI water for 36 d followed by drying at 40 °C. Amorphous Al hydroxide (am-Al(OH)₃) was prepared by mixing 300 mL of 1.5 M AlCl₃ with 800 mL of 4.0 M NaOH and shaking for 15 min (final pH 4.3). The suspension was transferred to 250 mL centrifuge bottles, centrifuged (10,000 g) for 20 min, and the supernatant decanted. All synthetic solids and illite were air-dried and crushed with a mortar and pestle to pass a <500 μm sieve. Characterization of the soils and minerals was carried out by X-ray diffraction (XRD) of random powder mounts and were investigated in previous work [19, 20]. The am-Al(OH)₃ sample showed no peaks by XRD analysis and the identities of the Al hydroxides and Fe oxyhydroxides and was confirmed by XRD analysis (data not shown).

As(III) and As(V) Adsorption Procedure

Stock solutions of 13.33 mM As(III) and As(V) were made from NaAsO₂ (Sigma) and Na₂HAsO₄ · 7H₂O (Sigma) dissolved in DI water. Adsorption of As(III) and As(V) on soil and illite was accomplished by shaking suspensions containing 2.0 g soil or 500 mg clay in 20 mL of 1.00 mM As(III) or As(V) for 48 h. Adsorption of

As(III) and As(V) on metal oxides (goethite, lepidocrocite, gibbsite and am-Al(OH)₃) was performed by reacting 500 mg solid with 200 mL of 0.133 mM As(III) or As(V) for 48 h.

After the reaction time the tubes were centrifuged (10,000 g) for 20 min and the solids separated from solutions by filtering (0.2 μm). Dissolved As(III) and As(V) were analyzed by high performance liquid chromatography hydride generation spectrometry (HPLC-HGAAS) [22]. The As(III) and As(V) uptake was calculated from the difference between initial and final measured As concentrations in the reaction solutions. The solids were rinsed once with DI water to remove dissolved As(III) and As(V) and stored as wet pastes for XANES analysis which occurred within 7 d.

X-Ray Absorption Spectroscopy (XAS)

All solid samples were analyzed at the Stanford Synchrotron Radiation Laboratory (Stanford, CA, USA) on beamline 4–2. A Si(220) double crystal monochromator with a 1 mm upstream aperture was used and detuned 30% or more to reduce second order harmonics. The *K* edge of As was scanned in increments of 10 eV (between 11635–11845 eV), in 0.30 eV increments between 11855–11895 eV (X-ray absorption edge region), and 2 eV increments from 11985–12860 eV (post-edge and extended region). Samples were mounted on plexi-glass plates, sealed with Kapton tape, and oriented at 45 ° to the incident X-ray beam. X-ray fluorescence was collected with a 13-element Ge-detector (Canberra). A Ge filter with a thickness of 6 absorption lengths was used to reduce scattered radiation from elements with atomic numbers less than As. Soller slits were used to reduce the fluorescent radiation from the filter. In addition, aluminum foil was used to reduce the fluorescence from Fe relative to As. Each sample was scanned 8 times and averaged for data analysis. Edge energy calibration was performed with As metal foil and As salts (NaAsO₂ and Na₂HAsO₄ · 7H₂O) mixed (diluted) with solid boron nitride.

XANES Curve Fitting

XANES spectra were normalized by setting the average intensity below the *K* edge (11635–11800 eV) to zero, and the average intensity above the edge (12200–12860 eV) to one. Normalized spectra were analyzed using a linear combination of As-treated materials of known As content using Microsoft EXCELTM. Satisfactory fits were derived by minimizing the sum of squares of differences between the calculated and experimental data. To determine the confidence in the fit, a 95% confidence interval was used to investigate the range of fitted values (scale factors) which gave good fits. Our analysis found a range of ±10% for our samples. Quantitative XANES uses the known surface coverage or bulk As content of a material in combination with fitted parameters such as the scale factor to derive the actual partitioning of As between phases in a solid sample. In our samples, the As surface coverage is known from dissolved As measurements made in batch reaction experiments.

Results and Discussion

As(III) and As(V) Speciation by XANES

Figure 1 shows a typical XAS scan for As(V)-treated soil (Aiken clay loam). The data consist of the absorption pre-edge (region 1) where the X-ray energy (*hν*) is less than the binding energy (BE) of the 1s core

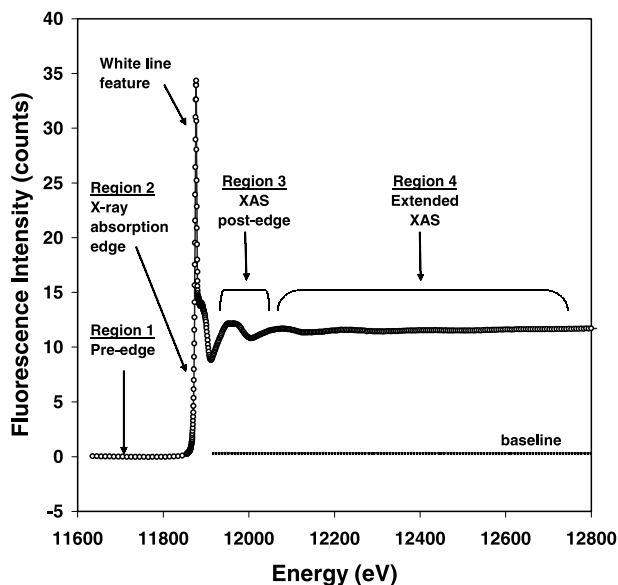


Fig. 1. Typical X-ray absorption K edge scan with spectral regions shown. Sample is As(V)-treated Aiken soil

electron ($h\nu < BE$), the X-ray absorption K edge where $h\nu = BE$ (region 2) for the As atom, the “white line” feature which results from a quantum transition of the core $1s$ electron to an unoccupied p orbital, the XAS post-edge (region 3) where $h\nu > BE$ and the effects of backscattered photoelectrons from neighboring atoms cause an oscillation in the XAS signal, and the extended XAS (region 4) where $h\nu \gg BE$. In this paper we use XANES spectroscopy (regions 2 and 3) to determine the speciation of As in solids.

The As K -edge XANES spectra of NaAsO_2 and Na_2HAsO_4 (Fig. 2) display the energy shift associated

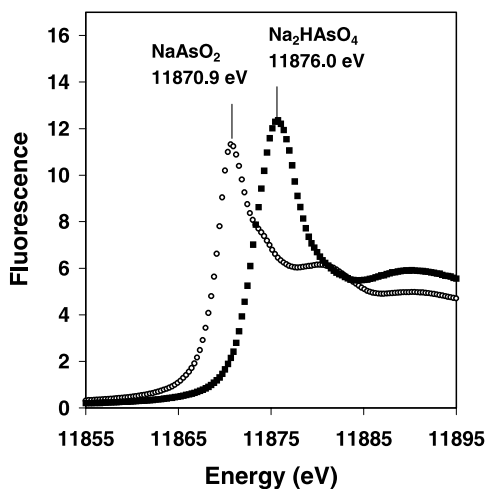


Fig. 2. X-ray absorption K edge for NaAsO_2 and Na_2HAsO_4 salts (Data are not normalized)

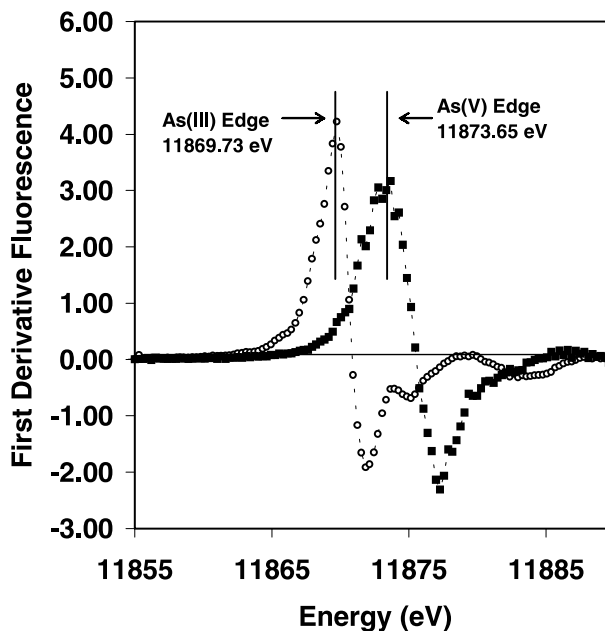


Fig. 3. First derivative diagrams of X-ray absorption edge for NaAsO_2 and Na_2HAsO_4 salts (Data are not normalized)

with As(III) and As(V) redox states. The white line peak energies of 11870.9 and 11876.0 eV for As(III) and As(V), respectively, reflect differences in binding energies of the $1s$ core electron in the two As redox states. The first derivative of the XANES data (Fig. 3) display the inflection point of the K edge and the As(III) and As(V) maxima at 11869.7 and 11873.6 eV. The As(III) and As(V) K -edge energies differ by ~ 2 eV per unit oxidation state change in As and are used for absolute energy comparisons and As(III)/(V) speciation in solids.

XANES Spectra of As(III)- and As(V)-Treated Metal Oxides and Illite

XANES spectra of As(III)- and As(V)-treated Fe(III) oxyhydroxides are shown in Fig. 4. The As(III) and As(V) K edge energies (vertical lines) derived from the NaAsO_2 and Na_2HAsO_4 spectra are shown for comparison. The spectra are consistent with previous results obtained by others [9, 11, 13, 23, 24]. It should be noted that absolute K edge energy and overall shape of the XANES spectrum is affected by both the formal oxidation state of As and by nearest neighbor atomic environment around the As atom in the sample. Further XANES spectrum perturbations are the result of differences in bonding environment

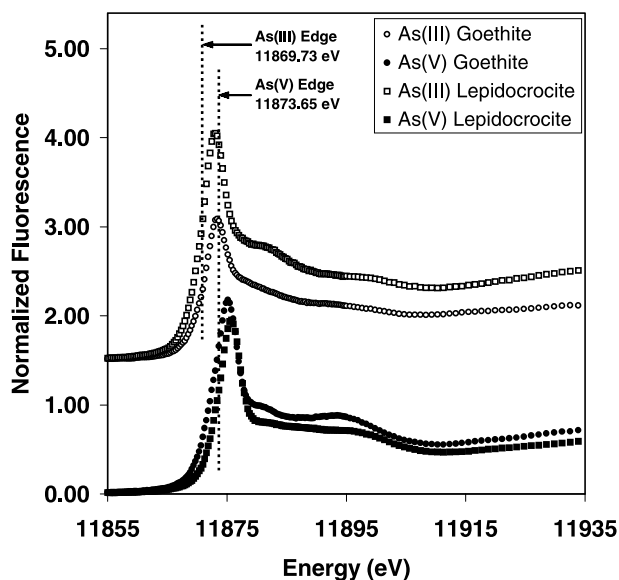


Fig. 4. XANES spectra for As(III)- and As(V)-treated goethite (α -FeOOH) and lepidocrocite (γ -FeOOH) model compounds. (Data are normalized to the post-edge region)

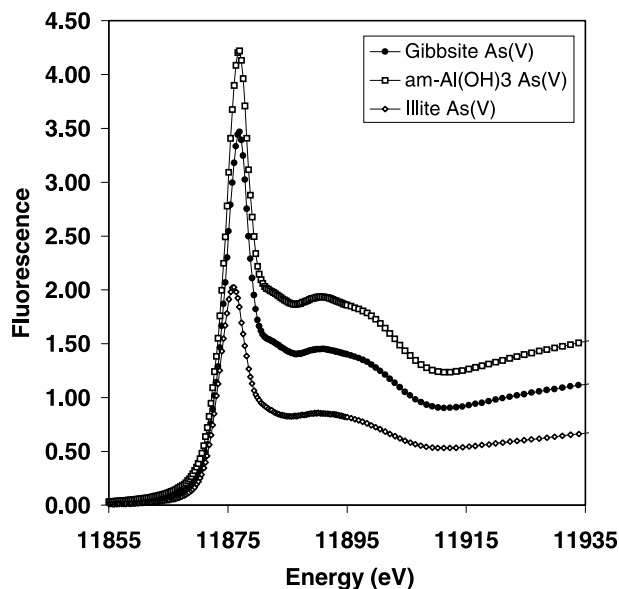


Fig. 5. XANES spectra for As(V)-treated gibbsite (γ -Al(OH)₃), amorphous-Al(OH)₃, and illite model compounds. (Data are not normalized)

between H_3AsO_3 and H_3AsO_4 molecules on different mineral surfaces. Noticeable features in Fig. 4 include the characteristic *K* edge energy difference between As(III) and As(V) and fine structure differences in the post-edge region (11876–11890 eV). Adsorption of As(III) and As(V) on the two Fe(III) oxyhydroxides did not result in As(III) oxidation or As(V) reduction and thus these samples were suitable As(III)/Fe(III) and As(V)/Fe(III) model compounds for XANES curve fitting.

Arsenic(V)-treated Al(OH)₃ samples were also analyzed by XANES (Fig. 5). The characteristic As(V) *K* edge at 11869.7 eV is observed. The magnitude of the pronounced white line feature is dependent on the concentration of As in the X-ray light path, which

in turn depends on the quantity of adsorbed As in the sample. The highest As(V) adsorption achieved in this study ($38.0 \text{ mmol kg}^{-1}$) was observed on am-Al(OH)₃ (Table 2). The As(III)-treated am-Al(OH)₃ sample, however, displayed an X-ray absorption spectrum with poor signal/noise ratio resulting from low As(III) uptake ($0.20 \text{ mmol kg}^{-1}$) (Table 2). Based on this result, a detection limit of 0.2 mmol kg^{-1} As was established for the XAS technique run under the conditions of this study. In addition, partial oxidation of As(III) to As(V) was observed on illite and therefore this sample was not included in the fitting analysis. The As(V)-treated illite was stable, however (Fig. 5), and was used for fitting the soil XANES spectra.

Table 2. As(III) and As(V) adsorption and surface coverage on soil and soil mineral materials

Sample	Surface area ($\text{m}^2 \text{ g}^{-1}$)	As(III) Adsorbed (mmol kg^{-1})	As(V) Adsorbed (mmol kg^{-1})	As(III) Surface coverage ($\mu\text{mol m}^{-2}$)	As(V) Surface coverage ($\mu\text{mol m}^{-2}$)
Aiken soil	44.8	1.39	2.77	0.031	0.062
Fallbrook soil	28.5	1.97	3.77	0.069	0.132
Wyo soil	78.2	6.53	5.47	0.084	0.070
Illite	24.2	2.72	14.1	0.112	0.584
am-Al(OH) ₃	42.9	0.20	38.0	0.005	0.886
Gibbsite	45	3.97	33.1	0.088	0.735
Goethite	43.7	36.8	30.7	0.842	0.702
Lepidocrocite	64.1	35.6	34.7	0.555	0.541

XANES Spectra of As(III)- and As(V)-Treated Soil

The XANES spectra of As(III)-treated soil show evidence for both partial or complete As(III) oxidation by the soil (Figs. 6–8). Experiments conducted to test the hypothesis that oxidation of As(III) is the result of exposure to high intensity X-rays in the beam line concluded that this was not the case. Therefore we suspect that either microbial oxidation of As(III) or

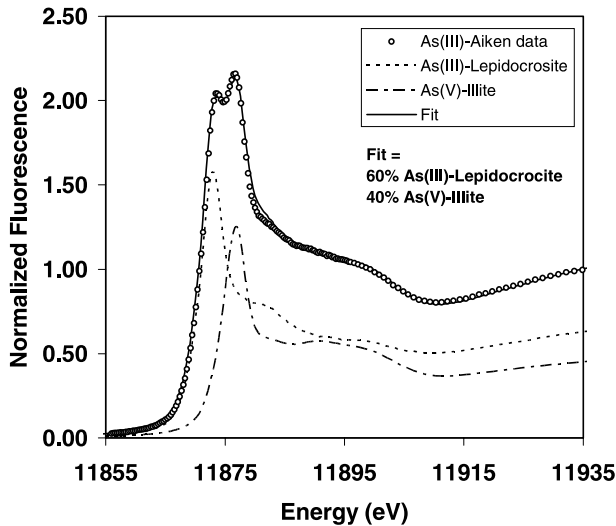


Fig. 6. Normalized XANES spectrum of As(III)-treated Aiken soil and linear combination fit of model compounds to the soil data (solid line)

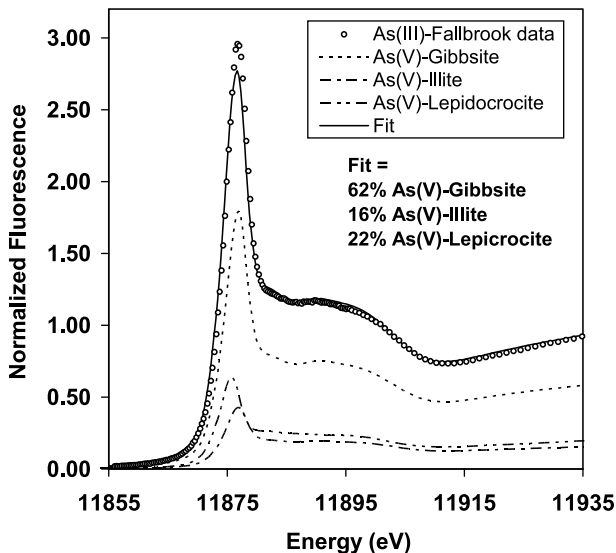


Fig. 7. Normalized XANES spectrum of As(III)-treated Fallbrook soil and linear combination fit of model compounds to the soil data (solid line)

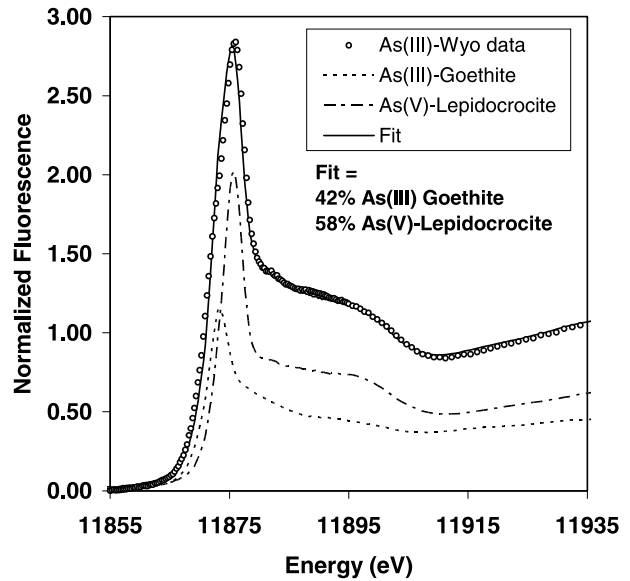


Fig. 8. Normalized XANES spectrum of As(III)-treated Wyo soil and linear combination fit of model compounds to the soil data (solid line)

contact with oxidative soil components such as manganese oxides are responsible. To our knowledge, synchrotron-based XAS is the only known technique capable of directly detecting As(III)/(V) mixtures resulting from oxidation of As(III) in the solid phase. The double white line feature in the As(III)-treated Aiken sample (Fig. 6) and the lower energy shoulder in the *K* edge of As(III)-treated Wyo soil (Fig. 8) are clear features of mixed As(III)/As(V) in the solids. In contrast, the XANES spectrum of the As(III)-treated Fallbrook soil sample (Fig. 7) contains only As(V) resulting from complete oxidation As(III) to As(V).

The XANES spectra of As(III)-treated soils were analyzed by fitting linear combinations of normalized data from Figs. 4, 5 to the soil XANES spectra in Figs. 6–8. The As(III)-treated Aiken sample was best described by a combination of 60% As(III)-lepidocrocite +40% As(V)-treated illite (Fig. 6). The As(V)-illite sample is representative of an As(V)-treated aluminosilicate clay mineral and some smoothing of the post-edge region is noticeable when compared with As(V)-treated $\text{Al}(\text{OH})_3$ samples (Fig. 5). The As(III)-treated Aiken spectrum was also well described by using As(III)-treated goethite, though a better numerical fit and comparison with features in the post-edge region was observed with As(III)-lepidocrocite. An excellent fit was achieved in both the *K* edge and post-edge regions of the spectrum and the doublet white line feature is well described.

The As(III)-treated Fallbrook sample XANES spectrum showed only As(V) and no contribution from As(III) (Fig. 7). Apart from the slight difference in the white line intensity at 11877 eV, the As(III)-Fallbrook XANES spectrum was well described by model spectra from As(V)-gibbsite (62%), As(V)-illite (16%), and As(V)-lepidocrocite (22%). The sum of squares of the residuals (SSR) for the fit in Fig. 7 is 3.98. A reasonable fit was also achieved with 72% As(V)-am-Al(OH)₃ and 28% As(V)-illite (SSR = 8.00). Due to the importance of Fe(III) oxyhydroxide in As(V) adsorption in soils, however, the lepidocrocite material was a more reasonable choice. Some difficulty was found in satisfactorily fitting the post-edge region with combinations of model spectra which would simultaneously give an accurate description of the height and position of the white line feature as well as the height of the post-edge region. It is expected that small differences in the normalization procedure may be responsible for this.

The As(III)-Wyo sample (Fig. 8) was another example of a mixed As(III)/(V) system and was best fit using a combination of 42% As(III)-goethite and 58% As(V)-lepidocrocite (SSR = 1.58). Interestingly, Wyo soil had the highest extractable Fe (~0.816% w:w, Table 1) and the XANES fit indicates the importance of the FeOOH polymorph mineral surface in As(III) and As(V) adsorption. Attempts to fit As(III)-Wyo data with Al hydroxides were not successful. The As(III)-treated Aiken sample, which contains a total As content of 1.39 mmol kg⁻¹ after As(III) treatment and is composed of 60% As(III)-lepidocrocite +40% As(V)-illite, would be ~0.84 mmol kg⁻¹ As(III)-lepidocrocite and ~0.55 mmol kg⁻¹ As(V)-illite. These estimates are reasonably accurate to within ±10% of the true values.

Iron(III) oxides, hydroxides, and oxyhydroxides are known to have a high affinity for As(III) and As(V) [27, 28] and total As uptake by soil is strongly dependent on total Fe [19, 20, 29, 30]. Therefore, it is expected that even small quantities of crystalline α - and γ -FeOOH polymorphs will preferentially adsorb As(III) and As(V) due to the extremely high adsorption capacity of these materials. Though good fits were achieved using model XANES spectra to describe the soil spectra, verification of the existence of the specific mineral phases used in this study was more problematic. Only the major primary and secondary mineral phases (aluminosilicate, mica, illite, and kaolinite) were evident in the XRD patterns for

the whole soils (data not shown) and evidence for the discreet α - and γ -FeOOH polymorphs could only be inferred by analysis of extractable Fe in the soils. The soils in this study contain between 2260 and 8160 mg kg⁻¹ (0.226–0.816% w:w) total extractable Fe (Table 1) and only a fraction of this is likely to be composed of the crystalline α - or γ -FeOOH polymorphs. Therefore it is expected that these levels are too low for identification by XRD in the whole soil. Oxalate buffer extracts amorphous Fe from soil [31] and the Aiken, Fallbrook, and Wyo soils yielded 309, 345, and 2660 mg kg⁻¹ of this Fe material, respectively (Table 1). These values are between 14–32% of total Fe (crystalline + amorphous) measured by citrate-dithionite extraction.

Previous investigations of α -FeOOH and γ -FeOOH have shown that both As(III) [11, 25] and As(V) [11, 23, 24] form inner-sphere, bidentate binuclear surface complexes on the FeOOH surface. The As(V) species also forms strong surface complexes with Al hydroxides [18] and this has been confirmed by EXAFS [26]. Studies on As(III) adsorption on Fe(III) oxyhydroxide materials have shown that As(III) is stable toward oxidation to As(V) on the α -FeOOH and γ -FeOOH surface [15, 25].

Studies of As speciation in mine tailings under natural weathering conditions indicate As occurs as As(V) linked by inner-sphere bidentate surface complexes in Fe oxyhydroxide and/or scorodite (FeAsO₄) and the As content is strongly correlated with total Fe in the solid [9, 13]. Adsorption reactions on mineral surfaces regulate As(III)/(V) redox transformation reactions by removing these species from solution [29–30, 32]. Thus, As(III) adsorbed on FeOOH in soil is expected to be stable and thus modeling with As(III)-treated α -FeOOH and γ -FeOOH is reasonable. However the stability of As(III) over long periods has not been confirmed and slow oxidation to adsorbed As(V) may occur.

The XANES results of As(V)-treated soils and the fitting analysis using As(V)-treated model compounds are shown in Fig. 9. Our analyses showed that As(V) was stable and normalized soil XANES spectra were well modeled using linear combinations of As(V)-treated illite, gibbsite, and lepidocrocite. The representations of As(V)-treated soil by linear combination fits are extremely precise and display consistently lower SSR values than the As(III)-treated soils (Fig. 9). Different combinations of model compound XANES spectra were investigated until the fit simul-

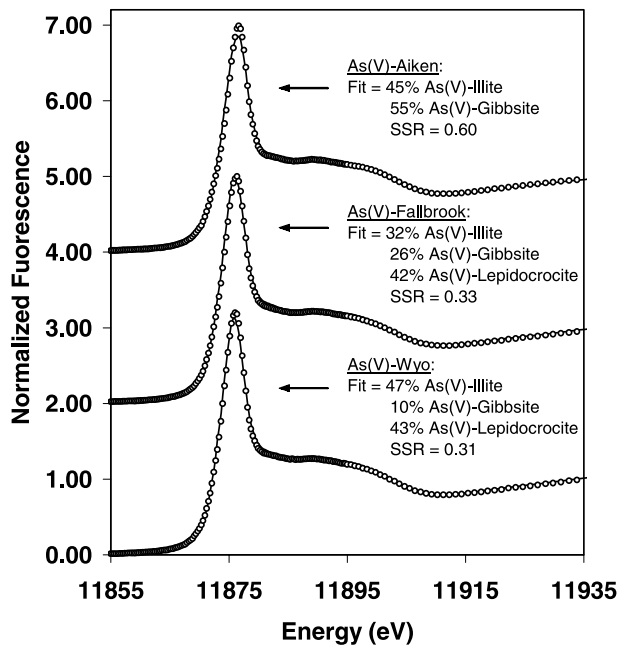


Fig. 9. Normalized XANES spectra of As(V)-treated Aiken, Fallbrook, and Wyo soils including linear combination fits of model compounds to the soil data (solid lines)

taneously gave good descriptions of the white line feature, the post-edge region, and a minimum SSR was achieved. The results are consistent with other studies where As(V) is strongly associated with Fe and Al metal hydroxide and clay mineral weathering products [9, 11, 12].

The results of this investigation show that As(III) will become either completely or partially oxidized to As(V) and mixtures of As(III)/(V) adsorbed on mineral surfaces will occur. The fitting of model XANES spectra to As(III)-treated soil XANES data suggest that As(III) is predominantly bound to Fe(III) oxyhydroxide minerals whereas As(V) is less selective, binding to Fe(III) oxyhydroxide, Al hydroxide, and aluminosilicate. Soil weathering products have been shown to be strong adsorbents of As(III) and As(V) and the application of XANES spectroscopy allows approximate proportions of these materials to be estimated.

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