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

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We investigated aging effects on As retention mechanisms in historically lead-arsenate contaminated urban soils using synchrotron-based micro-focused (μ) XRD, μ -XRF, and μ - and bulk-XAS analyses. Whereas As is predominantly present as As(V) adsorbed onto amorphous iron oxyhydroxides with a residue of schultenite ($PbHASO_4$) at an oxic site, there is no trace of schultenite from a semi-reduced site. Instead, adsorbed As(V) phases on amorphous iron oxyhydroxide, amorphous orpiment, and As(V)-Ca co-precipitates were identified. This study shows that aging effects can significantly alter the original chemical constituent in soils, resulting in multi and site-specific As solid-state speciation.

Arsenic (As) solid-state speciation is one of the most important factors controlling dissolved As concentrations at As-contaminated sites. In this case study, we utilized a combination of *in situ* bulk- and μ -XAS, *in situ* μ -XRF, and μ -XRD to investigate As solid-state speciation in aged As-contaminated urban soils in the northeastern United States. The origin of As in the soils (predominantly lead arsenate) is the disposal of former commodity, specialty, and agricultural chemicals. There are two distinct sites with average redox potential values of approximately 33 and 275 mV in the top 4 meters. Subsurface samples at 2-4 m depths from a semi-reduced site A and an oxic site B (thereafter sample A and B), where total As was most concentrated (80 and 284 ppm, respectively), were chosen for detailed spectroscopic investigation.

In situ μ -SAXS analyses indicated that elevated As counts (regions 1, 2, 4, and 6 in **Figures 1a and 1b**) are similarly distributed with Ba, Ca, and Fe in sample A and with Fe in sample B (XRF maps of the metals are not shown). Regions 2, 3, and 5 (**Figures 1a and 1b**), where the As concentrations are

not elevated, do not seem to be co-distributed with elements such as Cu, Ni, Zn, Mn, and Ca. The μ XANES analyses show 1) a predominant As(V) oxidation state at regions 1, 2, 4 and 5; and 2) regions 3 and 6 contain As(III)-S and As(III), respectively (**Figure**



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2a). Selected diffractograms of the μ -XRD measurements on sample B (**Figure 2b**) show the presence of calcite, rutile, and quartz in all 26 diffractograms, and schultenite ($PbHASO_4$) in about half of the diffractograms.

In the bulk EXAFS analyses, results from μ -XRF, -XRD and -XANES analyses were considered, and

coordination numbers of species at low R were correlated with the expected proportions of the species at high R (e.g., an As-Ca shell with an As-As shell). **Figures 2c and 2d** shows the least-square fits of samples A and B. The CN ($\pm 30\%$) and R ($\pm 0.03\text{\AA}$) of the first and second shells (As-O: 4.3 and 1.7 \AA , As-S: 3 and 2.27 \AA , As-Fe: 2 and 3.3 \AA , As-Ca: 2 and 4.06 \AA , As-Pb: 2 and 3.9 \AA and As-As: 1.5 and 4.09 \AA) in each sample correspond to surface species that consist of approximately 25% amorphous orpiment (As_2S_3), 28% adsorbed As(V) on iron oxyhydroxide, 46% of Ca-As(V) coprecipitates and/or substitution of arsenate into gypsum in sample A, and approximately 71% As(V) adsorbed species on iron oxyhydroxide with approximately 29% residual schultenite.

In this study, multi-scale spectroscopic techniques (μ -XANES, -XRF, and -XRD and bulk-XAS) were effectively combined to elucidate 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). 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. The variability in spatial and temporal scale may be important in assessing the environmental risk

and in developing in-situ remediation technologies.

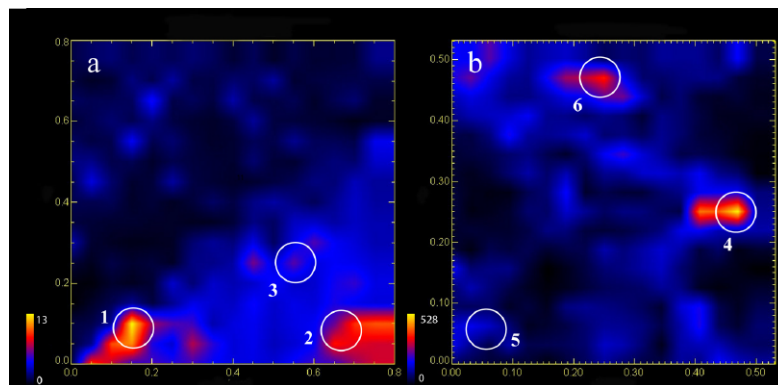


Figure 1. In situ As $k\alpha$ and $k\beta$ μ -X-ray fluorescence maps of sample A and B, respectively. Scale of maps in x- and y-axis is in mm. Fluorescence counts of each element are indicated by color contour bars on the left side of each map, and the intensity of each color is proportional to the amount of the corresponding element. Regions 1, 2, 3, 4, 5, and 6 indicate the area where μ -XANES spectra were taken.

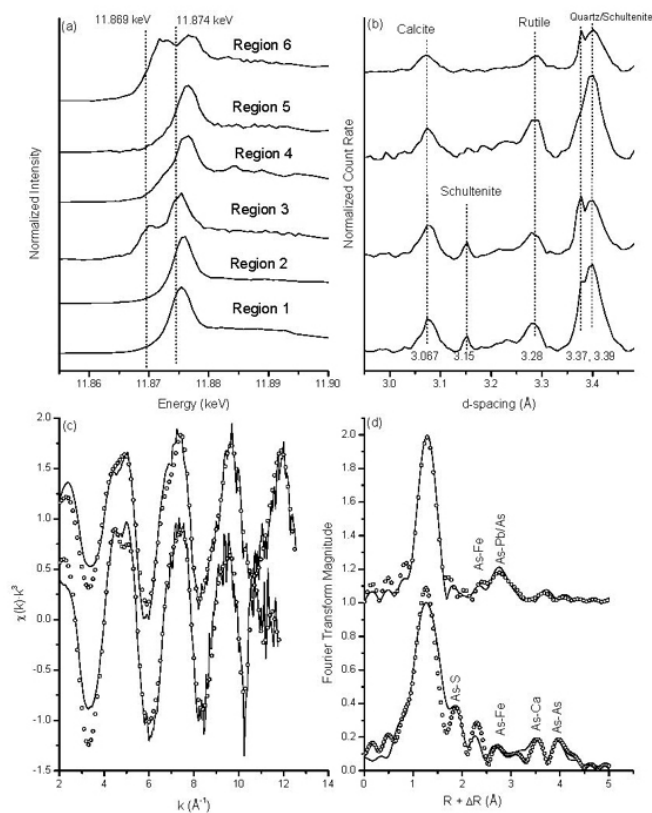


Figure 2. (a) Microfocused XANES spectra at regions 1-6 of selected areas of the As fluorescence maps shown in Figure 1. (b) Microfocused SXRD patterns ($\lambda=0.7598 \text{ \AA}$) of As concentrated areas of sample B. Selected diffractograms show $2.8 \text{ \AA} < d\text{-spacing} < 3.6 \text{ \AA}$. (c) Non-linear least-square fits to normalized k^3 -weighted EXAFS spectra of the reference compounds and samples A and B. Raw data and fits are shown by solid lines and open circles, respectively. (d) Non-linear least-square 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.