

Metal Speciation in Soil, Sediment, and Water Systems via Synchrotron Radiation Research

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The speciation or chemical form of metals governs their fate, toxicity, mobility, and bioavailability in contaminated soils, sediments and water. To assess these chemical properties and to accurately gauge their impact on human health and the environment we need to characterize metals at the atomic level. To attain in situ atomic level information on the speciation of metals we utilize high-energy synchrotron X-rays to probe chemical structure. At the Advanced Photon Source (APS) of Argonne National Laboratory (Argonne, IL) (Fig. 1), we incorporate X-ray absorption (XAS), X-ray fluorescence (XRF), and microtomography spectroscopies to analyze environmental samples to determine the true, in situ speciation of metal contaminants. Currently, several Divisions within NRMRL are assisting in the development of EnviroCAT, a dedicated synchrotron radiation facility at the APS for research on environmental science problems on a wide range of issues concerning worldwide human welfare, spanning problems in both pure and applied science and engineering. This innovative research tool is expanding our ability to directly identify the role of metal speciation on many dynamic processes that influence risk. Several research projects made possible by the application of synchrotron techniques are highlighted below.

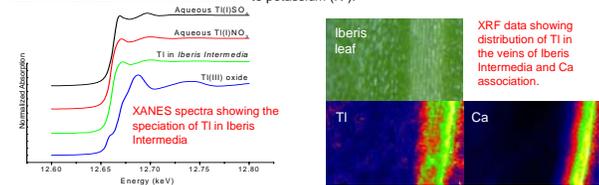


Figure 1. Advanced Photon Source, Argonne National Laboratory, Argonne, IL.

Phytoremediation of Thallium



Thallium (Tl) is an extremely toxic element. Australian and British scientists discovered that a common landscape plant, *Iberis Intermedia* (candytuft), was capable of phytoextracting up to 2% of its mass in Tl; however they were unable to determine the in-situ speciation of Tl. We examined live plants in the X-ray beam to determine the speciation (XAS) and distribution (XRF) of Tl in *Iberis Intermedia*. We observed Tl distribution within the vascular network of the plant as aqueous Tl(I) with similar chemistry and metabolic properties to potassium (K⁺).



Fate of Arsenic During GW-SW Interactions at a Superfund Site

At this Superfund site, arsenic from a contaminated ground water plume is entering a small lake where it is being scavenged by Fe-bearing precipitates in oxic waters at the shore. Our objective is to assess the attenuation capacity and stability of the arsenic contaminated sediments in the lake.

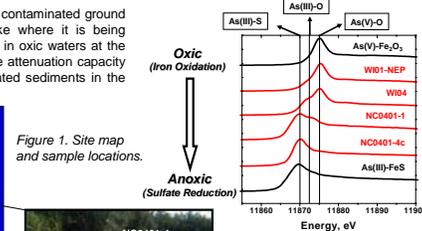
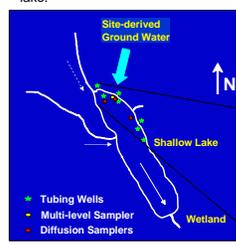


Figure 1. Site map and sample locations.

Figure 2. Arsenic XANES data as a function of lake sediment redox condition. Arsenic speciation (III or V) is found to be dependent on sediment redox conditions.

Chromium Speciation in Permeable Reactive Barriers (PBRs) used for Groundwater Restoration

Zero-valent iron PBRs are used to reduce toxic Cr(VI) to Cr(III) by reaction with iron. The speciation and mechanism of Cr transformation in the barriers however was unknown. To answer this question XANES was applied to confirm the reduction of Cr(VI) to Cr(III) and study the mechanism of its transformation. (Figure 1).

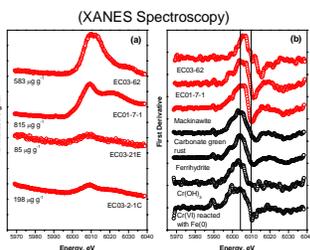
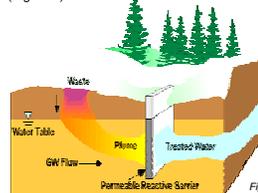


Figure 1. XANES of Cr(VI) after reacting with zero-valent iron in the PBR and secondary minerals identified in the reactive barrier due to corrosive processes.

Figure 2. Schematic of a PBR treating groundwater plume

Microprobe and μ -EXAFS of Zinc Contaminated Sediment

Zinc contaminated sediment at the Indian Head Naval Warfare Center, Indian Head, Maryland

Synchrotron microprobe techniques can map the elemental composition of environmental materials at the micrometer scale (Figures 1 and 2). This allows for both the physical relationship between elements to be determined and the location of trace elemental species to be identified, some of which may be very harmful and not observed in bulk analyses. This information is used to determine the best remediation strategies.

Figure 3. μ -EXAFS of zinc at points A and B (Figure 2) and reference minerals. Point A is identified as smithsonite, point B is closest to Zn(OH)₂, likely a surface precipitate.

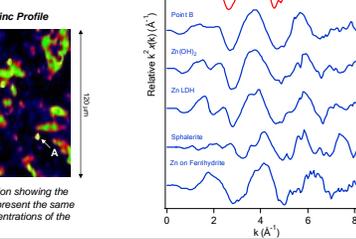
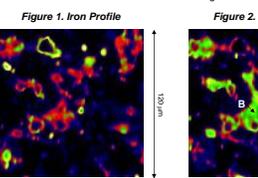


Figure 1 & 2. Microprobe of Indian Head sediment thin section showing the physical relationship between iron and zinc. The profiles represent the same 120 x 120 μ m area with brighter colors indicating high concentrations of the respective element, iron or zinc.

Figure 3. μ -EXAFS of zinc at points A and B (Figure 2) and reference minerals. Point A is identified as smithsonite, point B is closest to Zn(OH)₂, likely a surface precipitate.

Arsenic in Ironite[®]

What is the mineralogical form of arsenic in Ironite[®]?



Ironite[®] is a common fertilizer made from mine tailings available at any lawn and garden store. The presence of heavy metals in Ironite[®] has resulted in its banning in Canada and lawsuits in the United States due to the potential release of heavy metals, most notably arsenic and lead, from the fertilizer.

Bioavailable arsenic released from Ironite[®] is dependent on its mineralogical form. Previous work identified the arsenics bearing phase as arsenopyrite, however, a closer look with EXAFS has identified the arsenic phase within Ironite[®] as scorodite. Scorodite is more soluble than arsenopyrite, in fact, the dissolved arsenic released from scorodite can exceed the US drinking water standard.

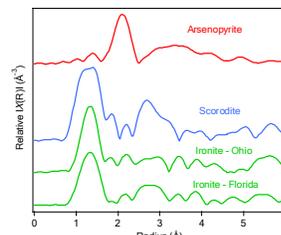


Figure 1. Radial distribution function showing the distance between arsenic and its coordinating oxygen atoms in the studied minerals. Standard reference minerals were compared to two separate packages of Ironite[®], one from Florida and one from Ohio.

Lead Release from Pipe Scales in Washington DC



As a result of changing water disinfectants lead pipes in DC, previously protected by layers of corrosion, were made soluble due to changing Eh-pH conditions (Figure 1). XANES was used to study the mechanism of lead release by determining lead speciation (Figure 2).

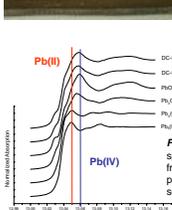
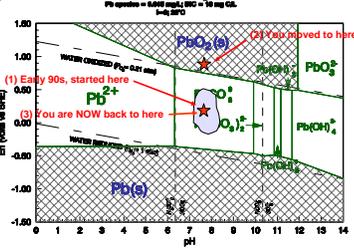


Figure 2. XANES spectra of lead deposits from Washington DC pipes. Pb(IV) is more soluble.

Figure 3. EMF-pH Diagram for Pb-H₂O-CO₂ System



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