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Using X-ray Absorption Spectroscopy to Unravel the Sequestration Mechanisms of Radionuclides and Metalloids in Natural Sediments

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Natural sediments are complex systems that contain minerals, bacteria, organic compounds, and dissolved complexants. The diverse binding sites in these components enable contaminant sequestration through adsorption, precipitation, and incorporation pathways. Predicting elemental transport in such environments is challenging and typically accomplished by using Reactive Transport Models that employ reactions with defined reactant and product species. The individual reactions are usually constrained under laboratory conditions; however, when multiple factors affect speciation as in natural sediments, it is possible that *in situ* speciation will diverge from model calculations. Disconnects between modeled and actual species imply significant uncertainties in predicted system behavior, so it is important to determine the molecular form of contaminants in the natural systems that are being modeled.

With its chemical specificity and ability to probe near-neighbor atomic coordination, X-ray absorption spectroscopy (XANES and EXAFS) provides an ideal tool for contaminant speciation in complex systems. We investigated the speciation of uranium, antimony, and zinc in sediments around facilities that produced them over several decades. The transformations of U were studied at Savannah River National Laboratory (USA), where production in the 1960s resulted in significant discharges in the nearby Tims Branch wetland. Cores were collected and analyzed intact for elemental distribution and U/Fe speciation. U was present in the top 5-10 cm of the sediment, with water-saturated areas showing reduced U(IV) that was adsorbed as individual atoms. In a separate study[1], the speciation of Sb near a refinery in South Korea was determined. Topsoil samples near the refinery and the nearby landfill had high Sb levels in the form of tripuhyite ($FeSbO_4$). The speciation of Zn in sediments was investigated along an ore transportation route to a refinery in South Korea[2]. Contamination from the sphalerite ore (ZnS) was transformed to O-coordinated Zn species along the route, and Zn was dispersed as franklinite, hydrozincite, and adsorbed species around the refinery. These results demonstrate the utility of EXAFS in providing the molecular-level information needed to predict contaminant transport in natural systems.

*[1] Park et al. Journal of Hazardous Materials, **2021**, 431, 123625.*

*[2] Kwon et al. Journal of Hazardous Materials, **2022**, 438, 129422.*