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FOR MORE INFORMATION

Michael J. Morra
Soil & Land Resources Division
University of Idaho
mmorra@uidaho.edu

METAL(LOID) DIAGENESIS IN MINE-IMPACTED SEDIMENTS OF LAKE COEUR D'ALENE, IDAHO

G.R. Toevs¹, M.J. Morra¹, M.L. Polizzotto², D.G. Strawn¹, B.C. Bostick^{2,3}, and S. Fendorf²

¹Soil & Land Resources Division, University of Idaho; ²Department of Geological and Environmental Sciences, Stanford University; ³Department of Earth Sciences, Dartmouth College

Mining operations in northern Idaho have resulted in Pb, As, Hg, Cd, and Zn contamination of Lake Coeur d'Alene. Unfortunately, limited knowledge of sediment biogeochemistry precludes accurate modeling of metal(loid) flux to the water. We characterized the sediments to elucidate diagenetic processes potentially controlling contaminant release, showing that flood events bury ferric oxides present at the sediment-water interface, transitioning them to an anoxic zone where reductive dissolution occurs. Insufficient sulfur limits sulfidic mineral formation, but high carbonate concentrations promote siderite formation. Metal(loid) sorption and release is thus a dynamic process intimately tied to reactions involving iron minerals within the sediments.

Lake Coeur d'Alene (CDA) is a natural lake of glacial origin located in northern Idaho. As a result of mining activity within the region, mine tailings and mill slurries contaminated with Pb, As, Cd, Zn and other metal(loid)s have accumulated in the sediments of Lake CDA. Prior research to characterize sediment geochemistry has produced inconsistent and contradictory results. Our objective was to characterize Lake CDA sediments using spectroscopic techniques combined with *in situ* interstitial water data, thereby identifying the dominant solid-phase minerals and diagenetic processes controlling interstitial water metal(loid) concentrations. Ultimately, our results will facilitate the prediction of contaminant release from the sediments to the overlying water column.

Two sample sites, Harlow Point (HP) and Peaceful Point (PP), were located in the southern portion of Lake CDA in an area highly impacted by metal(loid)s. An uncontaminated control site, St.



Gordon Toevs

Joe (SJ), was also established. Interstitial water was collected *in situ* utilizing Plexiglas equilibrium, dialysis samplers (peepers) and cores collected in polycarbonate tubes.

Sulfur x-ray absorption near-edge structure (XANES) spectroscopy analyses were conducted at the National Synchrotron Light Source on beamline X19A. Iron XANES and extended x-ray absorption fine structure (EXAFS) spectroscopy analyses were conducted at the Stanford Synchrotron Radiation Laboratory on beamline 4-3.

Sediment sulfur was speciated in an attempt to identify specific components of the sediment solid phase that potentially participate in metal(loid) retention. XANES data clearly indicate that pyrite was the principle S mineral detected at the contaminated sites (**Figure 1**). Ester-bound sulfate decreased with depth at all sites (**Figure 1**). Increased pyrite percentages with depth are consistently accompanied by a corresponding decrease in organic ester sulfate species. Thus, diagenetic alteration of ester-bound sulfate is likely important in the generation of pyrite in these sediments. However, metal(loid) partitioning into and on sulfidic minerals in Lake CDA sediments must be re-evaluated given the high Fe to S ratios of the sediments.

The speciation of sedimentary iron, achieved with XAS spectra, offers additional evidence for the diagenesis of sedimentary Fe and S. Contaminated sites show an obvious trend in the speciation of solid-phase Fe that reflects changes in sediment redox potentials with depth, with both sites displaying a decrease in Fe(III) minerals below the

suboxic boundary and a concomitant increase in Fe(II)-containing solids (**Figure 2**).

Linear combination of Fe-EXAFS spectra indicated the majority of the Fe(II) increase was in the form of siderite. Thus, a cycle of Fe-diagenesis is established where Fe(III) minerals buried by depositional events undergo reductive dissolution in the suboxic and anoxic sediments, forming Fe(II) that precipitates as siderite or diffuses to the oxic zone and reprecipitates as an Fe(III) mineral.

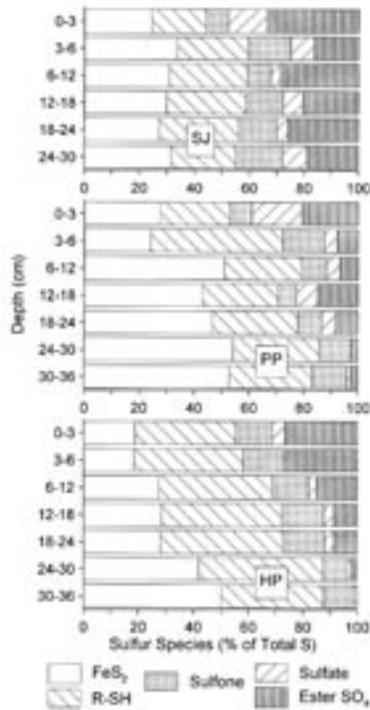


Figure 1. Comparison of S species as determined by S-XANES analyses of Lake Coeur d'Alene sediments at the contaminated sites (PP and HP) and the control site (SJ). Data shown for each depth are an average of two spectra from adjacent cores collected in May 2002 and have a fitting accuracy of $\pm 5\%$. Maximum total sulfur within all sediments was less than 0.5% by weight.

Ferric (hydr)oxides at the sediment-water interface restrict contaminant migration, but diagenetic reactions that occur during sediment burial and exposure to reducing conditions release metal(loid)s into the interstitial water. Metal(loid) cycling between the solid and aqueous phases in Lake CDA is thus a dynamic process intimately tied to diagenetic reactions involving Fe minerals within the sediments.

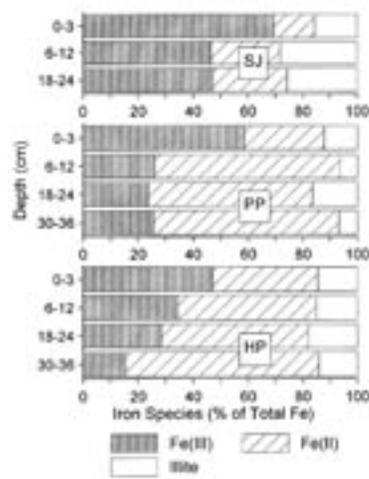


Figure 2. Iron XANES analyses of Lake Coeur d'Alene sediments as determined from linear combination fittings of Fe(II) and Fe(III) proxies and illite. Data are from cores collected in May 2002 at the control site (SJ) and two contaminated sites (PP and HP) and have a fitting accuracy of $\pm 5\%$. Iron comprised up to 10% of the sample by weight at the contaminated sites.