SLAC Groundwater Quality SFA: Host Recalcitrance Protects Against Pb Mobilization in Floodplain Sediments During Seasonal Redox Cycles

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Project Abstract: Understanding the controls on sequestration and mobilization of heavy metals is essential for assessing the risk they pose to water quality. We examined the impacts of seasonal redox cycles on Pb speciation and potential mobility in sediments in the Slate River floodplain (near Crested Butte, CO), which is affected by several hard-rock mines. Through a combination of field measurements, X-ray absorption spectroscopic techniques, and sequential extractions, we find that, above the baseflow water table elevation, where sediments are unsaturated and oxidized, Pb within the solid phase occurs predominantly as surface complexes on goethite (Pb-Gt) and particulate organic matter (Pb-POM). Below the baseflow water table, where sediments are reduced, Pb occurs predominantly as galena (PbS) and Pb-POM and, to a lesser extent, Pb-Gt. In porewater from both unsaturated and saturated sediments, Pb concentrations do not exceed 5 ppb over a 5-month period, indicating that dissolved Pb is not mobilized in either zone (unless during undetected transient moments). As river discharge increases seasonally, sediments become saturated above the baseflow water table elevation, transitioning oxidized sediments into reducing conditions. We observe iron and sulfate reducing conditions develop as oxidized sediments become reduced, revealed by an increase in Fe(II)(aq) concentrations and the formation of sulfidic phases. With the return to baseflow conditions, sediments are re-oxidized. Throughout these redox cycles, Pb speciation changes minimally, and pore water Pb concentrations remain below 5 ppb, indicating that, in seasonally reduced sediments, partitioning of Pb to goethite and POM limits dissolved Pb concentrations and the formation of PbS. Further, the abundance of PbS in permanently saturated (and reduced) sediments indicates that prolonged (i.e., on the order of years, decades, or longer) reducing conditions are required for authigenic PbS formation and/or preservation of geogenic PbS. Together these findings reveal that partitioning to solid phases limits dissolved Pb mobilization, while long-term redox regimes, established by baseflow water table elevation, control Pb speciation. Finally, these findings illustrate that colloid-forming processes and sediment transport are the principal threats to water quality.