Organosulfur speciation and dynamics in forest floor leaf litter and dissolved organic matter

M.B. HAY[1]*, A.C. LERI[2] AND S.C.B. MYNENI[3]

[1]U. S. Geological Survey, Menlo Park, CA 94025, USA (*correspondence: mbhay@usgs.gov)
[2]Division of the Sciences, Marymount Manhattan College, New York, NY 10021 (aleri@mmm.edu)
[3]Department of Geosciences, Princeton University, Princeton, NJ 08544, USA (smyneni@princeton.edu)

In many forest soils, the majority of the sulfur pool comprises S groups bound within natural organic molecules originating from decaying plant, animal, and microbial residues. This organosulfur plays an active role in soil S cycling, mineral weathering, and contaminant mobility, serving as a source of S for plants and microbes and as a soft-metal chelator. The chemistry of this organosulfur is highly dependent on speciation, as some forms are more bioavailable than others, and metal chelation is dominated by thiol groups.

In this study, we investigated the speciation and dynamics of organosulfur in decaying oak and maple forest leaf litter and litter-derived dissolved organic matter (DOM) using S K-edge X-ray absorption spectroscopy. Field stations were installed for controlled leaf degradation and collection of rain water leachate to study S speciation in leaves and DOM as a function of time. The study includes sample preparation methods and optimized spectral deconvolution procedures for the determination of absolute S species abundances from the X-ray spectra while minimizing self-absorption effects.

Leaf spectra collected as a function of decay time indicate a preferential loss of reduced sulfur, resulting in relative enrichment of oxidized S, particularly sulfonate. Total S estimates are consistent with a direct conversion of reduced to oxidized forms, rather than a differential loss of both forms. This conversion starts while the leaves are still senescing on the tree in autumn, continuing for several months after leaf fall. Spectra were also collected on leaves in different mulch layers to study leaf decay over multiple seasons. Reduced vs. oxidized S trends were found to differ in oak- and maple-dominated forest mulch layers. In the maple leaf litter, reduced S increased in proportion in lower (older) layers, suggesting a microbial growth component that outweighed oxidative organosulfur degradation. DOM collected from freshly-fallen leaves exhibited higher concentrations of sulfoxide, highlighting the importance of intermediate S species in organosulfur cycling. Collectively, these results yield new insights into the evolution of organosulfur forms during litter decomposition and soil organic matter formation.

Speciation of Lead and Zinc in weathered arid mine tailings

SARAH HAYES AND JON CHOROVER

Department of Soil, Water and Environmental Science, University of Arizona, Tucson, AZ (shayes@email.arizona.edu)

Understanding the biogeochemical weathering of mine tailings in an arid environment is essential to predicting the long-term feasibility of phytostabilization intended to minimize wind and water driven transport of metal-laden particles into surrounding ecosystems. The Klondyke Site in Arizona processed Pb and Zn sulfide ore in the 1950's and retains 1.5% and 0.5% by mass, respectively, of these contaminant metals in tailings piles that are devoid of vegetation. Lead and zinc x-ray absorption spectroscopy (XAS), sulfur near edge x-ray absorption of fine structure (NEXAFS) and bulk x-ray diffraction (XRD) indicate that surficial tailings have undergone nearly complete oxidation and the secondary minerology is dominated by sulfate phases including jarosite, plumbojarosite, anglesite, a mixed zinc sulfate, and gypsum. Geochemical calculations indicate that, after only 24 h of reaction with tailings, pore water solutions are at or above equilibrium saturation with respect to several sulfate and (oxyhydr)oxide phases that may control Pb and Zn speciation,.

Micro-focused x-ray fluorescence (XRF) and XAS demonstrate the association of Pb and Zn with manganese and iron oxides, such as hetaerolite, that have precipitated on the surfaces of silicate particles. Although these phases do not represent a significant fraction of the Pb and Zn in the tailings, this indicates that the tailings weathered from sulfide ore to sulfate phases that are now weathering to oxide phases that show strong metal sorption.