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TECHNICAL PROGRAM ABSTRACTS

Iron L-edge XANES studies of smectite clays

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Abstract This study investigates iron reduction in smectite clays using iron L-edge XANES, which previous studies show is very sensitive to spin state, crystal field strength and symmetry. Our results demonstrate iron reduction changes the intensity but not the position of two peaks dominating x-ray absorption at the L_3-edge. The intensity ratio of these two peaks is linearly correlated with the iron oxidation state in the clay, permitting us quantify the Fe(II)/Fe(III) ratio using Fe L_3-edge XANES spectroscopy.

Our data confirm that D_{3d} symmetry and spin state determines the L-edge XANES line-shape of Fe in smectites. Line-shape analysis of both L_2 and L_3 edges and the branching ratio establish octahedral Fe in smectites is high-spin. We also conclude the TEY intensity ratio $I_{708.7\ eV}/I_{706.9eV}$ of background corrected L_3-edge spectra can be used to calculate the ferrous iron content and provide the basis for quantitative image analysis of the ferrous iron distribution in clay minerals using soft x-ray chemical microscopy.

Challenges for Determining Hg^{2+} Complexation Constants in NOM

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At environmentally realistic Hg/C ratios, Hg^{2+} in NOM is very strongly bonded to thiol S groups, making it very difficult to determine complexation constants. Over the last 5 years several groups have published constants that vary over many orders of magnitude. Comparison of constants is difficult because different investigators use different experimental methods and different models for calculation of the complexation constants. However, it is possible to make model independent comparisons by comparing linear partition coefficients, K_{oc}, for Hg^{2+} adsorption. This comparison works because the S concentration in NOM generally does not vary greatly. The major problem that confronts researchers is that little or no free soluble Hg^{2+} is in equilibrium with NOM at loadings approaching levels found in natural system. Most researchers have used soluble ligands that bind strongly to Hg^{2+} in order to increase total soluble Hg^{2+} to concentrations greater than supported by dissolved NOM. We used penicillamine and others have used bromide, diethyldithiocarbamate, glutathione and EDTA. However one group used iterative calculations to estimate constant for both the dissolved and solid phases in peat suspensions without addition of a ligand. The results yield Koc values that at near neutral pH range from 10^{22} to 10^{35}. The competitive complexation methods generally yield higher constants than if no ligand is used. Several characteristics of mercury chemistry could account for the discrepancies. Ligand exchange with Hg^{2+} is slow and given that in NOM suspensions there is little or no free Hg^{2+} the exchange must be bimolecular. Added Hg^{2+} should be allowed to equilibrate with NOM before addition of the competing ligand, and then reaction times with added ligand must be sufficient. Although 2-coordinte complexes with Hg^{2+} are common, 3 and 4 coordinate complexes have been observed. Thus, the formation of three coordinate Hg^{2+} complexes with thiol in NOM, and mixed ligand complexes involving the both the added ligand and NOM, should considered. We have evidence that mixed ligand complexes may occur when Br^- is used as a competing ligand. Also, the pH dependency of our penicillamine data is consistent with the formation trithiol complexes in NOM.

EXAFS ANALYSIS OF PHOSPHORUS ADSORBED ON IRON OXIDES

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The adsorption affinity of soil minerals for phosphate depends on the molecular coordination of the surface species. Previous research using Fourier-transform infrared (FTIR) spectroscopy techniques suggested that phosphate sorption on iron oxides may be either monodentate or bidentate. Our objective was to more definitively determine the coordination mechanisms of phosphate adsorbed on iron oxides. Moist samples of ferrihydrite and goethite containing between 25 and 1200 mmol/kg of adsorbed phosphate at pH 6 were analyzed using extended x-ray absorption fine structure (EXAFS) spectroscopy. Analyses were completed at Beamline X-15B at the National Synchrotron Light Source at Brookhaven National Laboratory. Phosphorus K-EXAFS spectra indicate second-shell Fe(III) in the coordination environment, confirming inner-sphere surface complexation as has been proposed from FTIR and P K-XANES analyses. Interatomic P-Fe distances determined from the spectra will be used to determine whether bidentate or monodentate surface complexes are dominant at various adsorbed phosphate concentrations.

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Metabolic Profiling of Fungi Using Synchrotron-Based Chemical Microscopy

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ABSTRACT: Metabolic profiling is the analysis of all cellular metabolites, providing a powerful tool for gaining insight into functional biology. The goal of this presentation is to make a case for the use of synchrotrons for metabolic profiling of fungi. Metabolic profiling allows several hundred fungal metabolites (generally of low molecular weight) to be assayed in a single analysis, increasing significantly the amount of information available for hypothesis testing. The approach is to develop and use state-of-the-art synchrotron-based x-ray microscopy to detect, analyse, identify and quantify several hundred fungal compounds in a single analysis. The approach will also require development of the relevant databases and statistical/computational systems to facilitate data interpretation on such a scale. The techniques will complement proteomics and molecular genetics research. Synchrotron-based x-ray microscopy will provide tools for acquisition of metabolic profiling data and computational approaches for analysis and modeling that are based on the data. Potential practical applications of metabolic profiling include efficacy testing for wood preservatives, pesticide toxicity to invasive species and surrogate organisms, and modeling biochemical mechanisms of lignocellulose degradation.

Localization and Probable Mechanism of Arsenic Retention in the Rice Paddy Soils of Bangladesh

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The extensive use of As-contaminated water from the Ganges-Meghna-Brahmaputra groundwater aquifer for irrigation (especially for dry season rice production) has introduced significant risks of increased As in soil and the food chain and loss of land and agricultural sustainability. The objective of the current study was to determine the concentration, localization and predominant mode of As bonding in rice-paddy soils representing the major rice-producing regions of Bangladesh.

The current studies were conducted at beamline X26A, NSLS, utilizing synchrotron x-ray microprobe and micro-XANES procedures. Samples were observed as particle mounts of particle-size separates, thin sections of particle size separates, and thin sections from “undisturbed” soil columns. The synchrotron-based procedures were augmented by selective extraction procedures for soil Fe and soil As, As adsorption isotherms, powder XRD, TEM, and SEM/EDAX.

The rice-producing soils of Bangladesh exhibit very high spatial variability in soil arsenic concentration, texture and mineralogy at all spatial scales, because of differences in sediment source and deposition pattern, variable weathering and soil management, and localized influences of biological and transport processes. Soils contain quartz, feldspars, di- and tri-octahedral micas (especially Fe-rich micas), chlorite, smectite, free Fe oxides, calcite (in soils deposited in the Ganges floodplain), and sulfides (in some soils). Concentration of inorganic S is generally low in the rice paddy soils of Bangladesh. As is found in the clay, silt and sand particle-size separates. Microprobe analysis and selective dissolution has indicated that As is largely associated with free Fe oxides (especially the poorly crystalline Fe oxides), Fe-oxide plaques at rice-root surfaces, and weathered mica schist fragments. Retention of As by quartz and feldspar particles was negligible and by discrete mica and chlorite particles was very low. Several sand-size mica grains were scanned across the ab plane of the crystal. There was no evidence of preferential adsorption at the mineral edges, indicating that As bonding to phyllosilicate edge sites was negligible compared to As bonding to the Fe-oxide surfaces.

Discrete As-rich sulfide phases were not detected, though it is possible that these phases were destroyed during the sample preparation procedures. Though the possibility of retention of As by sulfide bonding cannot be excluded, it is unlikely to play a dominant role in As retention and bioavailability due to the relatively low concentrations of inorganic S and the oxidized zones at the surfaces of rice roots that persist under flooded-rice culture.

The rock fragments contained bands of high Fe concentration resulting from spheroidal weathering. Microprobe analysis indicated As in the schist fragments was associated predominantly with these Fe-rich weathering rinds. The enrichment of the As in the rock fragments could be the result of a diffusion gradient, from the more highly reduced bulk pore water to the less reduced intraparticle pore water, and the resulting adsorption of As on the Fe-oxide bands.

The adsorption of arsenic by minerals in the rice-paddy soils of Bangladesh soils is likely strongly impacted by changing redox conditions and localized redox gradients in soils under flooded-rice cultivation. Weathered rock fragments and the Fe-oxides coating on plant roots have two characteristics in common when compared with the bulk soil: (i) high Fe concentration and (ii) a micro-environment in which localized reduction and dissolution of Fe oxides might lag behind that of the bulk soil under reduced conditions. Each of these environments inhibits reduction and dissolution of Fe oxide. Oxygen from plant roots produces a localized oxidizing redox zone that favors precipitation of Fe oxide. The micro-porosity of the aggregated rock fragment provides a diffusion barrier to both soil microbes and the reduced soil solution, which would inhibit dissolution of existing Fe oxides. Hence, an Fe-oxide surface is maintained which is likely favorable for adsorption of dissolved As. In both environments, the

Fe oxides act as electron acceptors for oxidation of dissolved Fe^{2+} and a surface for continued crystal growth. The loss of Fe^{2+} from solution by precipitation as Fe^{3+}-oxide and loss of As by adsorption would produce a self-perpetuating diffusion gradient, which would result in increased concentrations of precipitated Fe oxide and adsorbed As. Each of these processes would also impact the potential loss of dissolved arsenic by leaching, under reduced conditions.

CHEMICAL AND MINERALOGICAL FORMS OF Pb, As, Cr, AND Cd IN A CONTAMINATED SOIL

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Metal contamination of soils is a widespread problem at many current and former industrial and military sites. Lead, As, Cr, and Cd are of particular concern because of their potential toxicity. *In situ* immobilization is one strategy for reducing bioavailability. Mineralogy is a key factor in the bioavailability of the contaminant metals. We sampled a Histosol in a peat bog that receives runoff and seepage water from the site of a former lead smelter. The water table is at or slightly above the surface for most of the year and the site is covered with common reed (*Phragmites australis*) and cattail (*Typha* sp.). There is an intense redox gradient with depth that probably varies as the water table fluctuates. Along with major elements such as Fe and S, the soil contains 1,700 mg kg^{-1} Pb, 2,200 mg kg^{-1} As, 930 mg kg^{-1} Cr, 210 mg kg^{-1} Cd. We used a binocular microscope to select aggregates ~100 to 200 μm in diameter that had distinctive morphologies and appeared to be inorganic. We used the synchrotron x-ray microprobe on beamline X26A at the National Synchrotron Light Source at Brookhaven National Laboratory to obtain micro x-ray diffraction and x-ray fluorescence patterns of each aggregate. Preliminary results indicate that Pb is associated with akaganeite in the surface 0-10 cm. Gypsum ($CaSO_4 \cdot 2H_2O$) is abundant, particularly for samples collected during drier periods, and goethite (FeOOH) is a common precipitate around roots. Several sulfide minerals have been identified in reduced horizons. They include realgar (AsS), greigite ($Fe^{2+}Fe^{3+}{}_2S_4$), galena (PbS), and possibly sphalerite ($(Zn,Fe^{2+})S$). Most of these minerals occur as almost pure phases in the submillimeter aggregates and appear to be secondary phases that have precipitated from solution. The close physical association of minerals that are stable under different redox conditions makes this soil a challenging material for *in situ* remediation.

Microtomographic Quantification of Intraaggregate Pore Geometries
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X-ray computed microtomography (CMT) imaging of soil aggregates is a non-destructive approach for accurately quantifying intra-aggregate pore responses to environmental conditions controlling their formation and function. CMT is being used to compare internal pore geometries with permeability, ion flux, carbon sequestration and many additional soil water flow properties which control the biological, chemical and physical properties within soil aggregates. Analysis of 3D porosity, pore size distribution histograms and pore connectivities within soil aggregates from agroecosystem soils are used to compare intraaggregate hydraulic conductivity measurement at multiple water potentials. Repeated imaging of the same aggregate following various drying and wetting treatments have been produced by the Advanced Photon Source. Intra-aggregate morphological changes, identified by newly constructed algorithms combined with the *3DMA-Rock software package for automated analysis of rock pore structure in 3-D CMT images*. http://www.ams.sunysb.edu/~lindquis/3dma/3dma_rock/3dma_rock.html These results demonstrate highly useful applications of CMT information applied to the organizational structures of aggregates, their pore geometries and their functional contributions to soil hydrology, convective-dispersive fluxes and carbon sequestration.

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Molecular-Scale Determination of Phosphorus and Metal Speciation in Natural Materials

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ABSTRACT

We have investigated aspects of Objectives 2 and 4 of Project NC1022. Specifically, we have used traditional macroscopic (e.g., sequential extraction) and molecular scale (synchrotron-based micro-XRF and micro-XAFS spectroscopy and microtomography) to investigate the speciation of phosphorus (P) in poultry litter (PL) and nickel (Ni) in smelter contaminated soils and hyperaccumulator plants (*Alyssum murale*) grown in the contaminated soils.

Alum ($Al_2(SO_4)_3$ has been added to decrease soluble P in PL (Moore and Miller, 1994). While alum amended litter (Al-lit) releases significantly less P to runoff and leachate, the P retention mechanism is not fully understood. Hunger et al. (Hunger et al., 2004) and Peak et al.(Peak et al., 2002) have provided direct observations of P speciation in these systems, using nuclear magnetic resonance (NMR) and x-ray absorption near edge structure (XANES) spectroscopies. Both studies showed the importance of aluminium surfaces as P sinks in alum amended PL. In combination with macroscopic techniques, these molecular-scale approaches can provide in-depth P speciation and distribution information about these heterogeneous samples. Sequential extractions have been routinely used to describe the distribution of P in mineral soils. These tools indirectly suggest how, and to what, P is bound. However, there is no direct evidence that these P associations are the ones exploited during the extractions. Soil P fractionation procedures have been applied to PL which likely contains a much larger proportion of organic components than soils. Therefore, organic P compounds and P bound to carbon based materials need to be considered. The first objective of this study was to understand how alum treatment of PL alters the distribution of P. Secondly, we aimed to elucidate the chemical nature of the P removed with each extraction step, through the use of a direct, molecular-scale technique. In doing so, information on the use of alum as a best management practice will be provided. Also, a better understanding of widely used extraction techniques will be gained. Sequential extractions were performed on several alum-amended and unamended PL samples. The method from Dou et al. (2000), a modification of the Hedley, was used. Following each step of the extraction, one replicate was freeze dried and stored for XANES analysis at beamline X-19A of the National Synchrotron Light Source at Brookhaven National Laboratory (Upton, NY, USA). Multiple scans were collected, in fluorescence mode, from 50 eV below to 50 eV above the P K-edge. Data reduction was conducted with WinXAS 3.0 and principal component analysis completed using software designed by Matthew Marcus (beamline 10.3.2. of the Advanced Light Source, Berkeley, CA). The extract analysis shows that HCl removes the largest proportion of total extractable P in all samples (from 40-60%). The Al-lit samples showed larger NaOH-extractable P compared to the control samples, which indicated that this fraction is metal bound. In addition, the unamended samples had elevated water-extractable P. Aluminum was mainly extracted in the NaOH extraction and Ca was removed during the HCl extraction, as expected. However, the proportion of Fe in the HCl extracts was much higher than in the NaOH extracts (75% verses 12-15%). Therefore, the acid extraction may be removing P bound to Fe surfaces more effectively than NaOH. Fitting our standards to three principle components in a target transformation, we found that aluminium complexes and organic P compounds best fit our Al lit extraction samples. For the control samples, spectra of calcium and sodium salts were among the best fits. While further data analysis is needed to differentiate between individual extractions, we do see that there is an overall difference in P speciation between the two treatments.

We also investigated the speciation of Ni in smelter contaminated soils that had been previously remediated with lime, and the effect of the speciation on plant metal availability and the mechanism of plant metal translocation and storage. Using a combination of macroscopic and microscopic techniques including SEM, micro-XAFS, and micro-XRF, it was found that the primary phases present in the soil were NiO and $Ni(OH)_2$ with minor solid phase Ni associations, possibly indicating the formation of mixed metal surface precipitates or neo-formed phyllosilicates. With the increasing use of metal accumulating plants for remediation, it is important then to assess what impact surface metal precipitates and other soil Ni species have on the accumulation, translocation and partitioning of the metal within plants. To ascertain this information, a combination of micro-XRF, micro-XAFS and micro-tomography was employed to study selected portions of the plant, *Alyssum murale*, a know nickel hyperaccumulator, that had been grown in limed and unlimed mineral soils collected from an area adjacent to the smelter. Tomographic results indicate a concentration of Ni on the periphery of the leaf with micro-XRF confirming this result as well as indicating an association of Ni with Mn at the base of the trichome. Micro-XAFS spectra were recorded from selected regions throughout freshly harvested plants with preliminary results identifying Ni-citrate and Ni-histidine complexes. Understanding how soil metal speciation affects plant metal availability and the mechanisms of metal accumulation will help in making decisions about remediating a site enriched with heavy metals and predicting long-term metal stability.

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Use of Synchrotron Radiation for characterizing transient flow processes in soils

David DiCarlo, Mike Walter and Tammo Steenhuis.

One of the main difficulties in validating models for transport of liquids and dissolved substances in the soil is the difficulty of observing and measuring the processes in the soil itself. Although there are a number of methods that can characterize steady state fluid flow, only synchrotron radiation is fast enough to measure transient flow processes in soils.

In this talk we will present examples of the research that we have performed over the last 10 years with the Cornell Synchrotron Radiation. This include preferential finger flow in sand, three phase flow of oil, water and air; instantaneous determination of hydraulic properties; swelling soils and colloid transport in soil.

Synchrotron Radiation as a Tool for Investigating Soil Chemistry

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X-ray absorption spectroscopy is perhaps one of the most powerful tools available for elucidating soil chemical reactions. In this presentation I will discuss how I have used synchrotron radiation to investigate speciation of metals and metalloids in soils throughout my educational and professional career. The capabilities of both XAFS spectroscopy and microscopic exploration using focused X-rays have increased over the years, as has my knowledge of how to prepare samples and analyze data. Despite my gaining years of experience and advancements that have made this tool easier to use, I am still finding ways to push the limits of what can be learned from this technique. I will provide a chronologic look into my research over the past 11 years, from my first XAFS experiments on Pb sorbed to aluminum oxide minerals to my most recent research using polarized XAFS to analyze Cu sorption on clay minerals. I will also show how I have used microscopically focused X-rays to analyze Se and As speciation in soils. By reviewing the use of this tool from a new graduate student perspective to that of a lead project investigator, I hope to provide insight into the potential and limitations for using synchrotron radiation in soil chemistry research and teaching programs.

Lead sorption on Phosphate Pre-sorbed Kaolinite

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ABSTRACT

The presence of the heavy metal lead (Pb) in soils is of major concern because of its highly toxic effects. The toxicity of Pb in the environmental is controlled by its bio-availability. Thus, remediation of Pb contaminated soils involves treatments that are designed to reduce Pb solubility. One remediation strategy involves adding phosphate to soil with the expectation that the Pb will react with phosphate to form the highly insoluble, and thereby biologically unavailable, lead phosphate known as pyromorphite. However, the application of phosphate as a heavy metal remediation technology in soils requires a detailed understanding of the nature of the products that form on soil mineral surfaces and how these products evolve as soil pH increases. The type of product that forms when divalent Pb ions absorb to the surface of aluminosilicate clay minerals depends on the compounds present in solution or adsorbed on the mineral surface. Prior research indicates that divalent Pb ions tend to form surface precipitates on mineral surfaces and, furthermore, phosphate, carbonate, and other common anions react with divalent Pb ions at the mineral surface. Our studies on the effect of phosphate ions on the pH-dependent adsorption of divalent Pb ions on kaolinite (an aluminosilicate clay mineral) surface strongly suggest that a reaction occurs between Pb and phosphate ions at the mineral surface which does not take place when phosphate is absent. Adsorption data shows that lead-to-phosphorus ratio at the mineral surface changes as the pH decreases, clearly indicating changes in the nature of the product formed at the mineral surface. In fact, in the presence of phosphate the Pb_{total}: P molar ratio exceeds the Pb:P molar ratio (close to 5/3) in pyromophite. In addition, the Pb:P molar ratios calculated from experimental results indicate the chemical status of Pb is changing dramatically in the pH range 4-7. Peer review of our adsorption experiments raises the question of whether a lead phosphate precipitate forms at the kaolinite surface, explaining the pH dependent-lead ion adsorption behavior. What cannot be explained by adsorption results alone is whether this change in lead:phosphorus ratio is due to the intrinsic changes in the chemical makeup of the product or whether these changes can be explained by the evolution of phosphate products independent of the principle Pb surface precipitate. This distinction is important because the solubility of a continuously changing product will be much different than if a single Pb surface precipitates forms at the surface. Resolving this question, however, requires the detailed characterization of the chemical environment surrounding divalent lead ions on the kaolinite surface.