

# WORLD CONGRESS OF SOIL SCIENCE

Philadelphia, Pennsylvania, July 9-15, 2006

## Symposium 2.0A Synchrotron Spectromicroscopy of Particulate Matter Affecting Air, Water & Soil Quality

### Oral Session

Tuesday, 11 July 2006: 3:30 PM–5:15 PM

Abstract 50-1

RESOLVING BIOGEOCHEMICAL PROCESSES CONTROLLING METAL ION FATE AND TRANSPORT WITHIN SOILS.

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Soils are inherently complex systems, exhibiting extremely heterogeneity in their physical, chemical, and biological states. As a consequence, resolving processes controlling the fate and transport of ions/chemical is a challenging task. In order to meet this challenge and gain a comprehension of processes governing elemental cycling, we need to conduct multidisciplinary studies that capture chemical states derived from biogeochemical conditions resulting within specific physical environments of soils. Advances in spectroscopic and microscopic techniques now afford an unparalleled opportunity to obtain information not only on specific elements but on the microbial communities at a sub-micron scale. Thus, we are now able to obtain information at the scales of heterogeneity residing within soils. Of course, this opportunity is not easily realized and comes with the challenge of gaining information that is statistically relevant to field-scale processes. Here we illustrate the utility of (micro)spectroscopic and microscopic techniques in deciphering conditions and phases controlling, or stimulating, the migration of three elements that, independently, represent severe threats to environmental quality: arsenic, chromium, and uranium. The present case in Asia exemplifies the devastating impact these toxins can have on human health. At present, in Bangladesh alone more than 57 million people are being subjected to arsenic concentrations exceeding drinking water standards of 10  $\mu\text{g/L}$  set by the World Health Organization with catastrophic results. Nearly 2 million people have developed severe arsenicosis, 125,000 skin cancer, and up to 7,000 cases of internal cancer are attributable to arsenic exposure from drinking water. Thus, it is critical that we have a detailed understanding of the biogeochemical processes impacting their dissolved concentrations, and availability for biological uptake in general, along with their propensity to migrate within surface and subsurface waters. X-ray microspectroscopy has provided essential data on the solid-phases controlling dissolved arsenic levels, and, in fact, provided key information on redox fluctuations that serve to provide a continual source of arsenic to the aqueous phase. Similar to arsenic, the migration of chromium and uranium within soils is largely governed by redox reactions. In contrast to arsenic, however, chromium and uranium are typically more mobile under aerobic than anaerobic conditions. Within structured media such as soils, redox conditions are not uniform and rather vary depending on the proximity to advective flow paths. Thus, chromium and uranium oxidation state can vary appreciably at the sub-aggregate scale. We provide evidence from microspectroscopic examination that uranium reduction resides at the junction of advective and diffusive domains while chromium reduction transpires throughout the soil matrix.

## Abstract 50-2

### CHANGES IN ZINC SPECIATION DURING SOIL FORMATION FROM JURASSIC LIMESTONE: A SYNCHROTRON $\mu$ -XRF AND $\mu$ -XAFS STUDY.

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Zinc is an essential micronutrient for plants and animals, but can also become a potentially toxic metal contaminant in soils at high concentrations. The bioavailability of Zn to soil organisms and plants cannot be predicted based on total concentrations, because it strongly depends on the chemical speciation of Zn in the soil. Recent studies have demonstrated that Zn sorbed to clay minerals at neutral or slightly alkaline pH is slowly incorporated into newly formed mineral structures, such as layered double hydroxides (Zn-LDH) or phyllosilicates containing Zn in octahedral coordination. However, little information is presently available about long-term speciation changes of Zn in soils under field conditions. In this study, we investigated the speciation of Zn in three oolitic Jurassic limestones of the Swiss Jura mountain range and in the soils developed from these rocks in order to obtain new information about the long-term fate of Zn in soils. The rock and soil samples were analyzed by X-ray fluorescence analysis (XRF) for total elemental composition. The speciation of Zn was characterized using a combination of synchrotron micro-X-ray fluorescence ( $\mu$ -XRF) and micro-X-ray absorption fine structure ( $\mu$ -XAFS) spectroscopy (Beamline 10.3.2, Advanced Light Source, Berkeley). XAFS spectra were analyzed by linear combination fitting based on an extensive set of reference spectra of known Zn species. In addition, total Zn in the soil samples was fractionated using a classical six-step sequential extraction method. The rocks contained between 43 and 207 mg/kg total Zn. In the soils, total Zn concentrations ranged from 237 to 864 mg/kg, clearly exceeding the Swiss guideline value of 150 mg/kg. These Zn concentrations are considered to be lithogenic rather than a result of environmental pollution. During soil formation from limestone, trace metals including Zn are enriched due to preferential dissolution and leaching of calcium carbonate and residual enrichment of less mobile elements. XAFS spectroscopic results indicated that Zn in two of the three limestones (Gurnigel and Schleifenberg) is present mainly as Zn-substituted goethite. A small fraction of total Zn in both rocks was present as sphalerite (ZnS). These results were supported by extraction of powdered rock samples with 1M NH<sub>4</sub>-acetate solution (pH 6), which suggested that most of the Zn was bound in non-carbonaceous components not extractable with NH<sub>4</sub>-acetate. In contrast, XAFS results and extraction with NH<sub>4</sub>-acetate showed that nearly all Zn in the third limestone (Dornach) was present as Zn substituting for Ca in the calcite structure. The Gurnigel and Schleifenberg soils contained considerable amounts of Zn-bearing goethite, probably stemming from the parent rock, and smaller amounts of newly-formed Zn species, most likely Zn-containing phyllosilicates with Zn bound in octahedral sheets. These results suggest that Zn in goethite was very stable during pedogenesis. Sphalerite was detected in the soils only in minute quantities. For both soils, the results of sequential extractions confirmed that Zn was associated mainly with iron oxides and a residual mineral fraction, which included sphalerite and phyllosilicates. In contrast, XAFS analysis of the Dornach soil suggested that Zn is primarily bound in octahedral sheets of phyllosilicates. This was supported by the sequential extraction results, exhibiting the largest fraction of Zn in the residual fraction. In conclusion, our results demonstrate that Zn-substituted goethite occurring in limestones is very stable during pedogenesis, while Zn bound in carbonates is released and subsequently incorporated into newly formed minerals. Sphalerite also dissolves during pedogenesis, but was still detected in very

small quantities in the soils. The long-term speciation of Zn in soils developed from limestones therefore depends on the Zn speciation in the parent rocks.

Abstract 50-3

#### X-RAY ABSORPTION SPECTROSCOPY INVESTIGATION OF COPPER ADSORPTION MECHANISMS ON CLAY MINERALS.

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Clay minerals are ubiquitous in the environment and play critical roles in the fate and transport of metals. Cation exchange is a dominant reaction mechanism for metals on clay. However, in recent years evidence for surface precipitation and adsorption on variable charge edge sites has been confirmed by molecular spectroscopy, suggesting that sorption phenomena on clay minerals is varied and complex. The goal of the research presented here is to investigate reaction mechanisms occurring on clay mineral surfaces as a function of mineral and solution properties. Reaction mechanisms were investigated by conducting macroscopic sorption experiments and probing the reaction products using molecular-scale techniques, such as near-edge (XANES) and extended-fine structure (EXAFS) X-ray absorption spectroscopy (XAS). Because clay minerals preferentially align themselves with respect to their crystallographic axis, and synchrotron X-rays are polarized, the potential to preferentially probe the surface complexes using polarized XAS (P-XAS) exists. P-XAS allows for added insight into metal speciation on the clay mineral surfaces. In this research XAS and P-XAS was used to investigate copper sorption on vermiculite and montmorillonite as a function of pH, ionic strength, and loading level. At high ionic strength and pH 6 sorption occurred primarily on clay mineral edges. Polarized EXAFS and XANES indicated that Cu sorbed on Llano vermiculite was aligned with its equatorial ligands in the ab plane of the clay particle. The polarized XANES results were interpreted using molecular orbital theory, which confirmed the molecular environment and orientation of the sorbed Cu. In contrast to the Llano vermiculite, sorption of Cu on Wyoming montmorillonite indicated that binuclear-Cu clusters were sorbed on the clay surface. In none of the Cu-equilibrated clay minerals were vast multinuclear complexes observed, such as have been observed for sorption of Ni, Zn, and Co in systems in which the metals are unsaturated with respect to oxide and hydroxide phases. It is well known that the atomic characteristics of Cu are distinct from the other first row transition metals in that its molecular coordination favors an axially distorted environment, known as Jahn-Teller distortion. Interpretation of the XAS data confirm this atomic property, and offers an explanation for the unique behavior of Cu compared to Ni, Zn, and Co. Thus by using advanced spectroscopic methods we have gained atomic and molecular level insight into Cu speciation on clay mineral surfaces. By understanding reaction mechanisms occurring on the clay surfaces better models can be developed that will lead to improved understanding of metal fate in the environment.

## Poster Session

Saturday, 15 July 2006: 8:00 AM-11:00 AM

Abstract 134-1

MANGANESE OXIDE IN MINE SLUDGE: A REDOX BARRIER AGAINST ARSENIC MOBILIZATION?.

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In Canada, an estimated land area of 335 hectares is made waste annually for the disposal of neutralization sludge, a by-product of the mining activity. Neutralization sludge is produced following a lime treatment of acidic mining effluents to neutralize the acidity and precipitate the soluble metals. The sludge matrix consists of calcite, gypsum and a large hydrated Fe amorphous phase (ferrihydrite-like) with which several species of potentially-toxic metal contaminants are associated. The long-term environmental impacts of the sludge on surrounding areas is uncertain because the long-term stability of the metals in the sludge is not known. Knowledge of metal speciation would help in assessing the long-term stability of the sludge contaminants and provide a better understanding of how changes in chemical conditions and disposal scenarios may affect changes in sludge chemistry, thereby influencing metal mobility and toxicity. For example, reducing conditions that could potentially develop in a sludge stored under a water cover could favor the reduction and solubilization of Fe(III) to Fe(II), and lead to the mobilization of any contaminant associated with the Fe-phase. In the case of arsenic, the reduction of As(V) to As(III) would further result in the conversion of this contaminant into a more toxic and mobile form than the oxidized As(V) species. An incubation study was initiated to determine the impact of reducing conditions on the dissolution of arsenic in an As-rich neutralization sludge stored under a water cover. The total As concentration in the sludge was 250 mg kg<sup>-1</sup>. In the laboratory, the sludge was subjected to water cover treatments in air-tight, plexiglass columns. Three different gas treatments were imposed on the water cover to induce different reduction levels in the sludge (100%N<sub>2</sub>, 100%N<sub>2</sub>+glucose, 95%N<sub>2</sub>:5%H<sub>2</sub>). These treatments were compared with a control of oxidized sludge that was saturated with water but with no water cover. The pH, Eh and dissolved metal concentrations were monitored by collecting subsamples of overlying and porewaters at designed intervals (1, 4, 8, 16, 59, 63, 66, 70, 80, 93, 136, 191 and 216 days). After 9 months of reduction, the changes in As and Mn oxidation states in the sludge were characterized using X-ray absorption near-edge structure (XANES) spectroscopy. Electron micro-probe analysis (EPMA) was used to characterize the spatial elemental distribution of As, Fe and Mn in the control and treated sludge samples. The characterization of the sludge was then refined using spatially resolved X-ray fluorescence (XRF) and  $\mu$ -XANES spectroscopy. In all treatments and throughout the reduction experiment, the dissolved arsenic concentration remained < 5  $\mu$ g L<sup>-1</sup>. Dissolved Mn concentration in the N<sub>2</sub>+glucose treatment increased significantly compared to other treatments, indicating reduction activity in this treatment. In agreement with the solution chemistry, Mn and As K-XANES bulk analyses showed that Mn was the redox-active element in the system, while As was very stable. No change in As oxidation state was detected in the reduced samples, and As(V) was still the dominant species in all water-covered sludges at the end of the 9-month reduction. In contrast, the Mn(IV) characterizing the original and control sludge was partly reduced into Mn(II) in the sludge under water. The effect was most pronounced in the N<sub>2</sub>+glucose treatment. Results from EPMA suggested that As would be mainly associated with Fe in four different phases (decreasing order of abundance): low-

density particles (sludge), high-density particles (iron oxide), some rare grains of pyrite and arseno-pyrite. Mn occurred mainly as Mn-oxide localized micro-spheres, and no As appeared associated with these spheres. The number of Mn micro-spheres decreased after reduction. In the reduced samples, preliminary analysis with spatially resolved XRF and  $\mu$ -XANES indicated that Mn(II) was preferentially associated with high As concentration. The overall results suggested that Mn acted as a redox barrier to protect As from reduction in the system.

Abstract 134-2

SOIL ORGANIC C SPECIATION AND TRANSFORMATIONS FOLLOWING LONG-TERM ANTHROPOGENIC PERTURBATIONS IN TROPICAL ECOSYSTEMS: EVIDENCE FROM  $^{13}\text{C}$  NMR AND SYNCHROTRON-BASED C (1s) NEXAFS AND FTIR-ATR SPECTROSCOPY.

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Soil organic matter (SOM) is a physically and chemically heterogeneous conglomerate ranging in size and complexity from simple monomers to mixtures of complex macromolecular humic substances or biopolymers aggregated together in the form of cellular debris that differ in stability. The amount, chemical composition and polyelectrolytic characteristics of these biomolecules vary along a continuum of decomposition and humification. Such variations create significant analytical problems to characterize SOM and thus made studies investigating the effects of anthropogenic perturbations on the reactivity, fate and chemical speciation of soil organic C (SOC) as well as the mechanisms and processes that determine the potentials of soils to sequester C in tropical and subtropical ecosystems very challenging. In the present investigation, we used synchrotron-based C (1s) near-edge X-ray absorption fine structure (NEXAFS) and Fourier transform infrared-attenuated total reflectance (Sr-FTIR-ATR) spectroscopy to identify and finger print the structural composition of SOC macromolecules and to evaluate the long-term impact (up to 100 years) of anthropogenic land-use and land-cover changes on chemical speciation of SOC in humic substances extracted from soils collected from tropical forest (Ethiopia and Kenya) and subtropical grassland (South Africa) agro-ecosystems. The results from NEXAFS and Sr-FTIR-ATR spectroscopy were evaluated against the results obtained from  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy, which is a more established SOC characterization technique. Carbon K-edge NEXAFS spectra showed that carboxylic-C and O-alkyl-C functional groups were the dominant forms of SOC, followed by moderate amounts of aromatic-C and phenolic-C groups. The aliphatic-C forms contributed only to a small portion of the total SOM associated with the humic substances extracted from the soils under investigation. NEXAFS spectroscopy, for the most part exhibited good selectivity, where specific energy regions tended to correspond to C in discrete organic functional groups. However, regions of slight overlap between the bands associated especially with  $1s\text{-}3p\rightarrow\sigma^*$  transition of aliphatic-C and  $1s\rightarrow\pi^*$  transition of carboxylic-C may not be excluded. Sr-FTIR-ATR spectroscopy, clearly demonstrated the long-term effects of anthropogenic land-use and land-cover changes on chemical speciation and structural stability of the different SOC functional forms present in the humic substances. Easily degradable SOM constituents such as polysaccharide-C and some labile components of aliphatic-C moieties were more prominent in

the humic substance extracted from the native forest and grassland soils, while aromatic-C and some recalcitrant forms of aliphatic-C dominated the SOM associate with the humic substances extracted from the continuously cultivated fields. Despite the wide range of origin and chemical heterogeneity of the humic substance, the results from the deconvolution procedure used for the semi-quantitative analysis of the C (1s) NEXAFS spectra, compared very well with the results from <sup>13</sup>C NMR spectroscopy.

Abstract 134-3

SORPTION OF ARSENATE ON LITHIUM/ALUMINUM LAYERED DOUBLE HYDROXIDE INTERCALATED BY CHLORIDE: MACROSCOPIC AND SPECTROSCOPIC STUDIES.

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Arsenic is a commonly occurring toxic metal in natural ecosystems and a known carcinogen in humans. Sorption, however, is one of the most important chemical processes to control the distribution of arsenic in the environment. Phyllosilicates, metal (hydr)oxides, and humic substances adsorb heavy metals by forming of inner- or outer-sphere sorption complexes, creating important sinks for these metals in ecosystem. Lithium/aluminum layered double hydroxide intercalated by chloride, as the sorbent for arsenate in this research, was formed by treatment with lithium chloride intercalated into the host structure of Al(OH)<sub>3</sub>. Li/Al LDH-Cl has not been well studied until 1977 and it is the first time that Li/Al LDH-Cl was used in environmental remediation for removing toxic anions. In this research, sorption of arsenate on Li/Al LDH-Cl was studied through sorption kinetics, isotherms, envelopes and mechanisms of arsenate sorbed on Li/Al LDH-Cl by extended X-ray absorption fine structure (EXAFS). The kinetics of arsenate sorption at pH 5.0 was studied at 278, 288, 298 and 308 K. Arsenate sorption on Li/Al LDH-Cl can be divided into the fast and slow reactions described by the second-order rate equation. This biphasic arsenate sorption behavior was partially attributable to: (i) micropore sorption sites on the Li/Al LDH-Cl surfaces, and (ii) Li exposed on planar surfaces and Al exposed on edges of double hydroxyl layers. The rate coefficient of the fast reaction of arsenate sorption was 9 to 14 times higher than that of the slow reaction. The pre-exponential factor value, which is a measure of collision frequency of arsenate with the reactive sites, was more than double in the fast reaction compared with the slow reaction. The activation energy of arsenate sorption on Li/Al LDH-Cl obtained from the Arrhenius equation was less than 42 kJ mol<sup>-1</sup>, indicating that the rate-limiting step of arsenate sorption was predominantly a diffusion process. Extended X-ray absorption fine structure (EXAFS) analysis of arsenate sorbed on Li/Al LDH-Cl shows that As(V)-Li and As(V)-Al interatomic distances were  $2.62 \pm 0.02$  and  $3.08 \pm 0.02$  Å and the coordination number of As(V)-Li and As(V)-Al were 1.6 and 2.3 atoms, respectively, indicating that the inner-sphere bidentate mononuclear and bidentate binuclear bonding were the predominant mechanism of arsenate sorption on the planar surfaces and edges of Li/Al LDH-Cl. In addition, the sorption behavior of arsenate on Li/Al LDH-Cl and on gibbsite (Al(OH)<sub>3</sub>) was studied to define how the intercalated lithium chloride participated in the sorption of arsenate through sorption isotherms, envelopes and EXFAS analysis. Arsenate sorption maximum on Li/Al LDH-Cl was approximately six times higher than that on gibbsite. At pH 4.0 to 9.0, all of arsenate sorption amounts on Li/Al LDH-Cl were more than that on gibbsite. Sorption envelopes of arsenate on Li/Al LDH-Cl showed a significantly pH-sensitive tendency at pH 4.0 – 7.0, but it was inconspicuous at pH 7.0 to 9.0. From EXAFS analysis, arsenate, sorbed

on Li/Al LDH, reacted not only with Al in the edges of Al(OH)<sub>3</sub> layers, but also with Li located in the vacant octahedral sites within Al(OH)<sub>3</sub> layers below pH 7.0, however, the As(V)-Al complex cannot be observed at pH 9.0. In addition, the reducing intensity of As(V)-Al peaks with increasing pH represented that fewer As(V)-Al complex existed at higher pH. By considering the results of sorption envelopes and EXAFS analysis, the superior sorption capability of Li/Al LDH-Cl to that of gibbsite could be attributed to the Li cations of Li/Al LDH-Cl which made the surface of Al(OH)<sub>3</sub> have high affinity to arsenate and served as the permanent sorption sites. Keywords: Arsenate sorption, Li/Al LDH-Cl, Extended X-ray absorption fine structure (EXAFS)

## Theater (Poster) Session

Thursday, 13 July 2006: 10:15 AM-12:15 PM

Abstract 63-1

FOLLOWING THE SPECIATION OF LEAD DURING HEAT-TREATMENT OF INCINERATED MUNICIPAL SOLID WASTE.

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Ashes from incinerated municipal solid waste (fly ash) contain high levels of heavy metals such as Pb, Cd and Cu. Deposition of these toxic fly ashes is therefore not without risks. An alternative to deposition is to heat-treat the fly ashes to produce secondary raw materials suited for reprocessing (heavy metal concentrates and detoxified ashes). The potential of the thermal treatment was studied by monitoring the evaporation rate of lead from a certified fly ash (BCR176) during heating between 300 and 950°C under oxidizing as well as reducing conditions. Samples at different phases of the heat treatment process were quenched for subsequent investigation with micro-focused X-ray absorption spectroscopy (XAS) to determine the solid state speciation of lead. Micro-spectromicroscopic data of the quenched heat treated samples were collected at the new MicroXAS beamline at the Swiss Light Source (Villigen, Switzerland). Evaporation data (under oxidizing and reducing conditions) coupled with unique spectromicroscopic observations from the state-of-the-art MicroXAS facility will be discussed. The micro-spectroscopic observations helped to explain the evaporation curves and showed that thermal treatment of municipal waste is a valuable alternative to the deposition of municipal solid waste.

Abstract 63-2

FORMATION OF Fe(III) CLUSTERS IN NATURAL ORGANIC MATTER.

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Iron oxides are considered one of the more important sorbents for oxyanions such as phosphate and arsenate in soils. However, published research indicates that oxyanions also bind as ternary complexes to Fe(III) ions associated with natural organic matter (NOM). In some cases, maximum sorption capacities of Fe-laden NOM approaches a 1:1 molar ratio of bound phosphate to NOM-bound Fe(III). Formation of such ternary complexes could be an important mechanism of oxyanion sorption, particularly in organic soils and organic-rich mineral soil horizons. We hypothesize that the oxyanion sorption capacity of Fe(III)-laden NOM would depend in part on whether the Fe(III) is bound as individual ions dispersed throughout the organic matrix, or as hydroxy-Fe(III) clusters or a precipitate associated with the organic matrix. Our research objective was to determine how Fe(III) concentration and pH affect clustering or precipitation of Fe(III) associated with NOM.

Aqueous Fe(III) was reacted under acidic conditions (pH <2.5) with Pahokee peat from the International Humic Substances Society. The peat had been hydrated and acid washed to



diminish residual Fe(III) and Al(III). Concentrations of added Fe(III) ranged from 0 to 10800 mmol Fe/kg peat (Fe/C molar ratios of 0 to ~0.25) in a 0.1 M KCl background electrolyte. The pH of the samples was slowly increased to pH 5.5, 6.0, or 7.0 with 0.1 M KOH solution. After equilibrating for 42 h at the target pH and at 25 °C, the solid-phase peat was separated by centrifugation. The moist peat samples were analyzed using transmission-mode Fe K-EXAFS spectroscopy at Beamline X-18B at the National Synchrotron Light Source, Brookhaven National Laboratory in Upton, New York. EXAFS data showed two trends that were evident in the radial structure functions (RSFs): (1) With increasing added Fe(III) concentration, the amplitude of an EXAFS peak near 1.6 Å (not corrected for phase shift) corresponding to first-shell Fe-O coordination decreased toward the amplitude found for ferrihydrite (and hematite). (2) Two overlapping peaks developed between 2.5 and 3.5 Å (not corrected for phase shift) in RSFs for samples containing 900 mmol Fe(III)/kg; the amplitude of these peaks increased with increasing Fe(III) concentration until they essentially matched corresponding peaks for ferrihydrite at >1800 mmol Fe(III)/kg peat. EXAFS data for control samples of aqueous Fe(III) brought to pH 5.5 or 7.0 in the absence of NOM exhibited similar peaks between 2.5 and 3.5 Å. These peaks result from the presence of Fe atoms in the higher coordination environment of x-ray absorber Fe atoms, and indicate hydroxy-Fe clustering or precipitation of a poorly-ordered ferrihydrite-like phase in the Fe/NOM mixtures. The Fe(III) concentration at which the transition to a cluster (or poorly-ordered precipitate) occurred was largely independent of pH between 5.5 and 7.0. In essence, the EXAFS results indicated a transition between separated Fe(III) ions bound to NOM and either hydroxy-Fe(III) clusters or a poorly-ordered solid forming in the presence of the NOM. One would anticipate that the oxyanion sorption capacity of Fe-laden NOM would vary, depending on the form of Fe(III).

Abstract 63-3

#### MICROSCALE SYNCHROTRON-FTIR MAPPING OF CARBON “HOT SPOTS” ON MINERAL SURFACES IN SOIL.

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Microscale interactions between mineral and chemically stable organic matter are not well resolved owing to the disruptive nature of existing soil analyses techniques. The use of bright light (> 100<sub>0</sub>) over thermal infrared sources, coupled to microscopy, now provide analytical capabilities for the in situ examination of microstructures in soil aggregates. We have used synchrotron FT-IR (Fourier Transform-Infrared) spectromicroscopy to study microscale spatial variability in the C and clay mineral complex of soil microaggregates from a tropical soil. Our objective was to elucidate C stabilization on mineral surfaces in the microstructure of the organomineral assemblage. Mapping the chemical profile of organic matter and clay mineral on ~1 μm thin sections, was achieved by illuminating the microaggregate surface regions with a 49 μm<sup>2</sup> aperture IR beam using Swarchzchild objectives, mounted on a Spectra Tech Continuum IR microscope that was connected to a Nicolet Magna 860 Spectrometer (NSLS, Brookhaven, NY, USA, Beamline U10B). Spectra were collected in transmission mode using Atμs software. Surface area C and mineral composition maps were extracted from the integrated spectral intensity signal, at a spatial diffraction limit of ~5 μm. Bond assignments to C and OH functional group chemistry were inferred from known vibrational fingerprints in the mid infrared region (650-4000 cm<sup>-1</sup>). Stretching vibrations of bound and non-bound OH showed that kaolinite (3696

cm-1, 3648 cm-1, 3620 cm-1) and gibbsite (3520 cm-1, 3440 cm-1) were the predominant secondary minerals forming interactions with microaggregate organic matter. Ratio intensity maps and spectra of mineral location and C functional group chemistry show evidence of a clay mineral to hydroxyl (OH) dependent mechanism for binding oxidized C to hydroxylated surfaces. Oxidized polysaccharide C forms (950-1120 cm-1) were unevenly distributed throughout the microaggregate structure. Chemigram profiles pointed to a patchy, non-ordered location of aliphatic and aromatic C forms exhibiting strong absorbance in ~2900 cm-1 and 1650 cm-1 (amide I) to 1540 cm-1 (amide II) band regions. These C forms had spectral signatures characteristic of microbial but not particulate light fraction organic matter and they appear not bound to mineral surfaces probably due to the absence of hydroxyl (OH) termini. Our data show that clay mineral binding of organic matter is primarily restricted by interactions between hydroxyl termini of oxidized C and hydroxylated/dehydroxylated mineral surfaces.

Abstract 63-4

#### IDENTIFYING THE IRON PHASES IN BIOSOLIDS-AMENDED SOILS VIA MÖSSBAUER SPECTROSCOPY THAT CONTROL CADMIUM SORPTION.

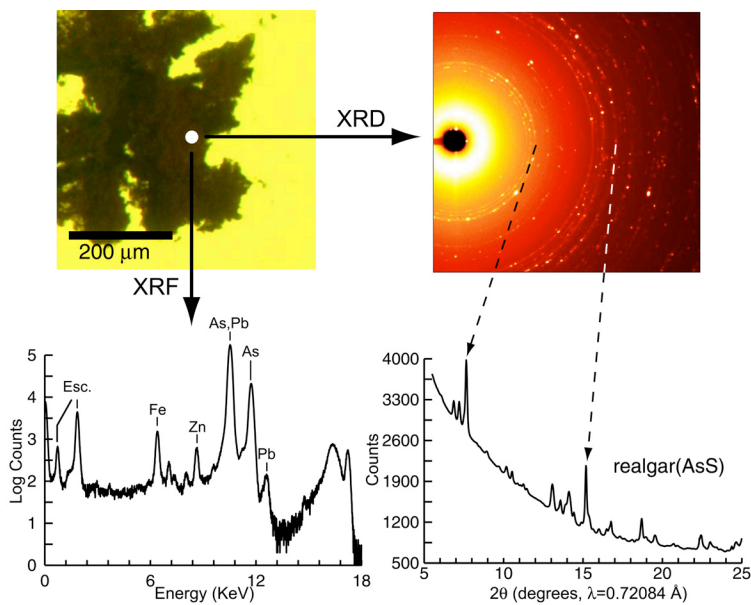
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Continuous debate regarding inorganic and organic phases in biosolids as prominent sorbents of metals has yielded limited definitive data. We have demonstrated with X-ray absorption and X-ray fluorescence spectroscopies that metals in biosolids have a significant association with Fe phases within biosolids and biosolids-amended soils; however, identification of these Fe phases has not been fully characterized and has been limited to a few samples. Additionally, the detection of Fe crystals in biosolids by X-ray diffraction is nearly impossible. The purpose of this presentation is to demonstrate the utility of Mössbauer spectroscopy in identifying the dominant inorganic/organic Fe phases in biosolids-amended soils. In this work, we present investigations into the role of inorganic (Fe) and organic phases in biosolids-amended soils on cadmium sorption. We employed a purely physical density separation to remove organic carbon, and thus diminish its role in cadmium sorption. Preliminary results from batch sorption work showed that cadmium sorption was reduced with decreasing organic carbon content of biosolids-amended soils, yet cadmium sorption was also controlled by total Fe content. Preliminary Mössbauer results show that Fe in biosolids-amended soils is predominantly found as yet-to-be identified ferric ( $\text{Fe}^{3+}$ ) oxides, with only a minor fraction of biosolids Fe associated with humic/organic domains. The results suggest that cadmium sorption and stability in soil is predominantly based on the interaction of the heavy metal with the inorganic ferric-oxide phases, which probably accumulate as precipitates when the soil dries. The lack of organic-Fe complexes suggests a reduced potential for mobilizing biosolids cadmium through humic/organic chelation.

## Abstract 63-5

### SPECIATION AND GEOCHEMICAL CYCLING OF Pb, AS, CR, AND CD IN A CONTAMINATED HISTOSOL: SYNCHROTRON MICRO X-RAY DIFFRACTION AND X-RAY FLUORESCENCE SPECTROSCOPY.

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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 toxicity and potentially harmful effects on the environment. In situ immobilization is a desirable strategy for reducing metal bioavailability through precipitation or adsorption by adding chemical amendments to contaminated soils. Speciation is the key factor in controlling mobility and bioavailability of metals in soils, and knowledge of the mineralogy and geochemistry of contaminant metals is critical for the development of effective remediation strategies. 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 soil 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. Distinct layers were observed from the surface to a depth of 65 cm. We collected soil samples from different depths during both wet and dry seasons. Along with major elements such as Fe and S, the soil contains 1,700 mg kg<sup>-1</sup> Pb, 2,200 mg kg<sup>-1</sup> As, 930 mg kg<sup>-1</sup> Cr, 210 mg kg<sup>-1</sup> Cd. We used a binocular microscope to select aggregates ~100 to 200 mm in diameter from different depths 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 patterns and micro x-ray fluorescence patterns of each aggregate. Results show a clear pattern of metal speciation changes with depth. The oxidized yellow surface layer was dominant by goethite ( $\alpha$ -FeOOH) and a poorly crystalline phase that is probably schwertmannite. Pb and As were highly associated with these Fe oxyhydroxides probably by formation of inner-sphere surface complexes. Gypsum

(CaSO<sub>4</sub>·2H<sub>2</sub>O) is abundant in this layer as well, particularly for samples collected during dry periods. Fe(II)-containing minerals, such as magnetite (Fe<sub>3</sub>O<sub>4</sub>), siderite (FeCO<sub>3</sub>), and possibly wustite (FeO) were identified in subsurface layers. These phases may have a strong influence on the fate and transport of chromate due to their highly reactive surfaces and reduction potential. A number of sulfide minerals have been identified in the most reduced horizons at depths >30 cm. They include realgar (AsS; figure below), greigite (Fe<sub>3</sub>S<sub>4</sub>), galena (PbS), sphalerite (Zn, Fe<sup>2+</sup>)S, alacranite (As<sub>4</sub>S<sub>4</sub>), pyrrhotite (Fe<sub>1-x</sub>S), and others. Most of these minerals occur as almost pure phases in the submillimeter aggregates and appear to be secondary phases that have precipitated from solution. Mineralogical and chemical heterogeneity and the presence of phases stable under different redox conditions make this a challenging soil for in situ remediation.

Abstract 63-6

#### METAL SPECIATION, BIOAVAILABILITY AND REMEDIATION AT SUPERFUND SEDIMENT SITES.

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Remediation strategies at Superfund sites are dependent upon the prevailing speciation of metals and their impact on the environment. These sites typically have limited human contact, but the impact of metal contamination can influence biological function within the ecosystem. This presentation will outline our efforts at three contaminated sediments sites which include in-situ and monitored natural attenuation remediation strategies. The objectives of the research are to link the speciation of metals to biological availability and demonstrate effective remediation.

In-situ amendments of phosphate and biosolids have demonstrated a change in Pb and Zn speciation leading to significant decreases in phytotoxicity and bioavailability. At the Indian Head Naval Surface Warfare Center (IHNSWC) (MD), Zn-contaminated sediments are observed adjacent to a historical Zn recovery furnace leading to phytotoxicity and biologically available Zn in the sediment pore water. Surface erosion transport of Zn slag to the sediment results in Zn oxide and Zn hydroxide-like species at very high concentrations. In-situ amendments of apatite and biosolids have eliminated Zn phytotoxicity and significantly increased survivability of lower food chain organisms. Down gradient of a pre-WWI shooting range, Pb-contaminated sediments at the Quantico Marine Base (VA) have been treated with apatite in an attempt to form pyromorphite. While the range site has been removed, the persistence of Pb in the sediments remains. Galena is the primary form of Pb under saturated conditions; however, seasonal water levels may cause oxidation of galena to less stable forms such as cerussite. Conversion of sediment-Pb to pyromorphite would yield a stable species for both saturated and oxic environments.

Monitored natural attenuation of sediment bound As from groundwater discharged landfill leachate in contact with As-bearing bedrock shows an amazing capacity of ferrous iron to form Fe-oxides capable of sequestering labile As at the Ft. Devens Superfund Site (MA). A monitoring well network is in place to examine the groundwater flow situation and explain the distribution of As. Sediment cores have been collected and analyzed to determine As speciation and retention capacity.

Synchrotron studies, coupled with Mössbauer spectroscopy and other laboratory methods, provide overwhelming details to aid in remediation approaches at metal-contaminated sites.

Abstract 63-7

#### THE INFLUENCE OF SURFACE PRECIPITATION ON NICKEL SOLUBILITY, BIOAVAILABILITY AND FATE IN CONTAMINATED SOILS.

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Sorption reactions at mineral/surface interfaces play a dominant role in determining trace metal mobility, toxicity, and bioavailability in soils. The formation of surface precipitate phases may result in permanent sequestration of trace metals into relatively bio-unavailable phases, thereby significantly reducing their impact on the surrounding environment. Understanding the true impact of metal soil contamination on the surrounding environment requires a better knowledge of the processes controlling surface precipitate formation and dissolution than is currently available, and the development of models for metal behavior that incorporate this knowledge. Recent advances in techniques, such as x-ray absorption spectroscopy (XAS), that allow us to obtain molecular scale information on metal speciation in soil samples with minimal disturbance of the surrounding matrix, coupled with observations of precipitate formation kinetics and thermodynamic stability, allow us to gain a more accurate picture of the factors influencing metal precipitation under natural conditions. In this work, we have used a suite of macroscopic and molecular scale techniques to investigate the speciation of Ni in several soils under a range of soil conditions and time scales. The results have been coupled with desorption and bioavailability studies to determine the effect of precipitate formation on the fate of Ni in contaminated soils.

Kinetic studies of Ni sorption onto three soils with different particle sizes, clay mineralogy and soil organic matter content were conducted at several pH values between 6 and 7.5 for times ranging from days up to one year. Measurements of Ni loss from solution were coupled with quick x-ray absorption spectroscopy studies to resolve the onset of precipitate formation during the first 24-72 hours after Ni addition. Ni speciation in the soils at 24 hours, 30 days, 6 months and 12 months was determined using both bulk and  $\mu$ -XAS to determine the extent of precipitate formation compared to Ni sorption and the identity of the precipitate formed in each case. Desorption studies were conducted after 1, 6 and 12 months to assess the impact of soil aging on the stability of the initially formed precipitates and the overall solubility of the surface bound Ni. These experimental results were then compared to models developed from previously determined thermodynamic solubility constants for a variety of model Ni precipitate phases.

Nickel speciation results from this series of experiments show that precipitate formation is dependent on a number of factors. Generally speaking, no precipitates were found in any of the soils below pH 6.5, a result consistent with predictions from equilibrium modeling. In kinetic experiments at pH 7, formation of mixed nickel-aluminum hydroxide surface precipitates occurred within 12-24 hours of Ni addition to the soil, but the final Ni speciation was highly dependent on the clay mineralogy of the specific soils. The availability of substrate cations, particularly aluminum, strongly influenced the type of Ni precipitate formed, with Ni-Al hydroxides dominating in the two kaolinite-containing soils and Ni phyllosilicate phases forming in the third, montmorillonite-dominated soil. The mixed Ni-Al hydroxide phases were preferred

over more thermodynamically favorable phyllosilicate phases due to rapid formation kinetics that act to bind up available Ni soon after Ni addition to the system. Increased presence of soil organic matter had a strong influence on Ni speciation within the first 72 hours, resulting in less surface precipitate formation, but the effect decreased at longer times.

The formation of surface precipitates had a significant effect on Ni desorption and bioavailability. The bioavailable Ni fraction, as measured by a Ni sensitive bacterial biosensor strain of *R. metallidurans*, decreased from 70-90% of total Ni in the sorption dominated systems (pH 6) to approximately 25% in soils containing either Ni-Al hydroxide or Ni phyllosilicate phases. Nickel desorption in 0.1 mM HNO<sub>3</sub> (pH 4) also decreased substantially when surface precipitates were present. Aging the soils for up to one year in contact with the Ni solution had no effect on Ni desorption percentages, suggesting that the initial precipitates formed are relatively stable over the long term. Overall, these results show that the formation of surface precipitate phases will have a substantial effect on Ni mobility and bioavailability in contaminated soils, and should be incorporated into models and predictions of both short and long term metal behavior in natural systems.

Abstract 63-8

#### CHARACTERIZATION OF SULPHUR SPECIES IN OXIC AND ANOXIC FOREST SOILS WITH SYNCHROTRON-BASED X-RAY SPECTROMICROSCOPY.

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Current routine methods of chemical analysis for sulphur (S) speciation in soil are highly unsatisfactory, in face of the enormous ecological relevance of S in soils. Wet chemical methods can only distinguish total soil S into operationally-defined fractions rather than destined S species. X-ray spectromicroscopy at the K-absorption edge reflects the chemical bonding state and particularly the electronic oxidation of elements and can be used to study individual species of S. Synchrotron-based X-ray absorption near edge fine structure spectroscopy (XANES) at the K-absorption edge (2465 eV to 2495 eV) of sulfur (S) was used for the speciation of different S forms in oxic and anoxic topsoil horizons. We analyzed forest soils with total S contents ranging from 840 to 6520 mg S kg<sup>-1</sup>. The analyses were conducted directly on freeze-dried and ground soil samples. To investigate the effect of aeration during the soil sampling and sample pre-treatment on the S speciation sub sample of each soil were proceed either with or without strict maintenance of anoxic conditions. The measurements were carried out at the Advanced Photon Source (Argonne National Laboratory, USA) with an intermediate energy scanning X-ray microscope (SXM). The incident X-ray energy was decremented in steps of 0.25 eV, using a 10 s dwell time per energy step, resulting in an acquisition time for a complete spectrum of 20 minutes. Each spectrum was recorded from two different locations within the sample to improve the statistical significance of the data. Our study was conducted on four different soil types, Cambisol, Planosol, Histosol C and Histosol D, in the Lehstenbach catchment in the Fichtelgebirge (Germany). The soils differ in the degree of groundwater influence. With increasing soils depth and concomitantly increasing groundwater influence, the allotment of reduced S-species (inorganic and organic sulphides) to the total sulphur of the respective horizon increase from 53% to 68%; simultaneously the portion of oxidised S-species (sulphite, sulphone, sulphonate and sulphate) decies from 41% to 23% Without maintenance of anoxic conditions during soil

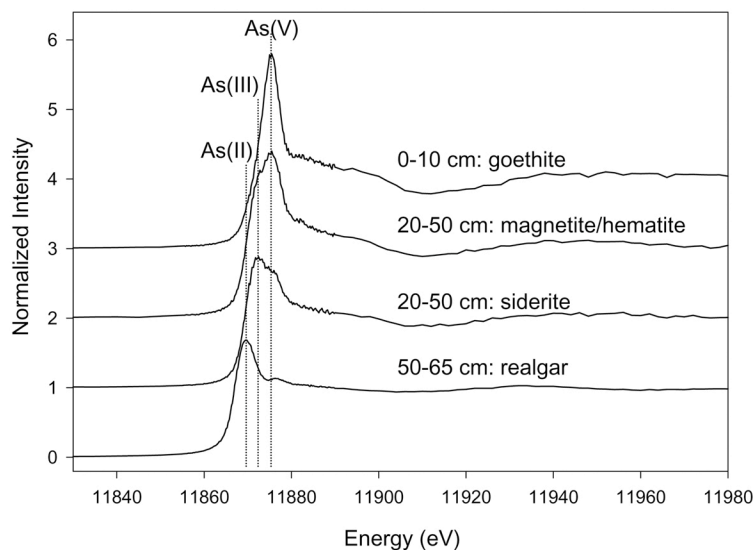
sampling, sample storage, and sample pretreatment considerable changes of the portions of reduced, intermediate and oxic S-species in the sample can be observed. These changes are more pronounced in soils with high groundwater influence than in soil with moderate groundwater influence. Synchrotron-based X-ray spectromicroscopy (S K edge XANES) allows a quick, direct quantification of different sulphur species in oxic and anoxic soils. In the studied soils, an increasing groundwater influence is correlated with an increased contribution of reduced S species to the total soil sulphur pool. For an accurate S speciation in anoxic soils, anoxic conditions have to be maintained during the entire procedure of soil sampling, sample storage, and sample pretreatment to avoid artificial changes of S speciation, particularly in anoxic soils.

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Abstract 63-10

SPECIATION AND GEOCHEMICAL CYCLING OF Pb, AS, CR, AND CD IN A CONTAMINATED HISTOSOL: X-RAY ABSORPTION NEAR-EDGE STRUCTURE (XANES) SPECTROSCOPY.

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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 toxicity and potentially harmful effects on the environment. In situ immobilization is a desirable strategy for reducing metal bioavailability through precipitation or adsorption by adding chemical amendments to contaminated soils. Most current investigations of soil heavy metal contamination emphasize the importance of speciation of metals rather than just the total amounts present. Speciation is the key factor in controlling mobility and bioavailability of metals in soils, and information on the mineralogy and geochemistry of contaminant metals can provide important information for risk assessment and remediation strategies. Nondestructive techniques, such as x-ray absorption near edge structure (XANES) spectroscopy, synchrotron micro x-ray fluorescence (SXRF) spectroscopy, and micro x-ray diffraction ( $\mu$ -XRD) are useful to investigate metal speciation. 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 soil 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 during the year. Distinctly different layers were observed from the surface to a depth of 65 cm. We collected soil samples from different depths during both wet and dry seasons. Along with major elements such as Fe and S, the soil contains 1,700 mg kg<sup>-1</sup> Pb, 2,200 mg kg<sup>-1</sup> As, 930 mg kg<sup>-1</sup> Cr, 210 mg kg<sup>-1</sup> Cd. We used a binocular microscope to select aggregates ~100 to 200 mm 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 patterns and micro x-ray fluorescence patterns of each aggregate. Arsenic K-XANES spectra were then obtained for aggregates with high levels of arsenic. Arsenic occurs mainly as inorganic +3 and +5 oxidation states in soils, with As(III) generally being more mobile and more toxic than As(V). XANES spectra show distinct differences in As oxidation state with depth (see figure below). Soil particles from the surface layer contained predominately goethite and schwertmannite and contained only As(V), probably as stable inner-sphere surface complexes between the arsenate anion and the Fe oxyhydroxide surface. The particles from subsurface layers that contained mainly magnetite contained predominately As(V) with some As(III). Particles that contained mainly siderite contained predominately As(III) with some As(V). Particles from the most reduced layer contained As(II), which is consistent with the presence of realgar as shown by  $\mu$ -XRD. From the XANES results we postulate that arsenic mobility is low in the oxidized surface layer and in the deepest, most reduced subsurface layer. Arsenic is controlled by the adsorption to iron oxyhydroxides in the oxidized zone at the soil surface, and by metal sulfides in the most reduced zone. Substantial mobilization of arsenic may occur, however, under shifting redox conditions such as in the layers that contain magnetite and siderite and high contents of As(III).

Abstract 63-11

DIRECT OBSERVATION AND QUANTIFICATION OF COLLOID RETENTION IN UNSATURATED POROUS MEDIA.

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Colloid transport through the vadose zone is of growing concern in recent years. Non-water-soluble contaminants can enter an aquifer very quickly (colloidal facilitated transport) or colloids can be pathogens itself (for example *Cryptosporidium parvum*), thus yielding the risk of polluting drinking water. Little is known about the complex mechanisms of transport and retention of colloids at the pore scale in soils. Measurements of colloid and microbial transport have been limited to the evaluation of breakthrough curves from column experiments in which only an integrated signal of all retention processes in the column is obtained or to the visualization in micromodels with limited applicability to realistic conditions. The objective in this presentation is to observe and model colloid transport and retention on the pore scale. Flow experiments were run in a horizontal flow chamber using clean quartz sand as porous medium and synthetic fluorescent microspheres or bacteria (*Escherichia coli*, containing a green fluorescent protein) as colloids. The water phase was stained with Rhodamine B. In order to establish unsaturated conditions, porous plates were mounted at the inlet and outlet of the chamber. The chamber was mounted under a Laser Scanning Confocal Microscope (Leica TCS



SP2) which allows the acquisition of time series and 3D reconstruction of pore-scale images. Three spectral channels were used: a 488 nm (argon) line excites the colloid fluorescence, a 543 nm green (HeNe) line excites Rhodamine B fluorescence, and a transmitted light channel detects the reflectance of laser light at the grain surfaces. Thus, three 8 bit images were detected simultaneously for every time step. The system is also capable of obtaining image stacks in the z-direction, which allows the determination of the position of attached colloids relative to the interface between air, water menisci, and solid grains. The 3D z-stacks reveal that the colloids are attaching at the air/water meniscus/solid (AWmS) interface, where the water menisci diminish into a thin film covering the grains. Methods of digital image analysis are presented for quantification of the number and area of moving and retained colloids. After thresholding, binary images are obtained. Colloids that appear at the exact same position in two consecutive images are counted as attached. The results show that once the first colloid is attached at the AWmS interface, the attachment rate increases until the number of locations where the colloids can be attached near other colloids becomes limiting. The attachment continues until there is no space for the colloids to attach anymore. A theoretical model is presented that is capable of predicting the observed colloid attachment processes. Forces acting on the colloids are discussed.

Abstract 63-12

#### IRON L-EDGE AND K-EDGE X-RAY ABSORPTION STUDIES OF NONTRONITE REDUCTION.

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The reduction and re-oxidation of the iron-rich smectite mineral nontronite causes changes in short-range structure discernible by polarized extended x-ray absorption fine structure (EXAFS) spectroscopy. Reduction causes shifts that indicate internuclear distance changes and a broadening in the overall EXAFS spectrum caused by increased structural disorder. Re-oxidation in air restores the nontronite EXAFS spectrum but not to its original state. Non-reversible structural changes occur mainly during the first reduction cycle; peak width and intensity after a second redox cycle resemble values observed after the first reduction cycle. No differences appear in the polarized EXAFS spectra of nontronite samples reduced by *Shewanella oneidensis* when compared to samples reduced by sodium dithionite. We also evaluate the iron-migration hypothesis that predicts a significant redistribution of octahedral iron during nontronite reduction. Our polarized EXAFS data and analysis fails to support this hypothesis and proposes a different structural model for ferrous nontronite. Previous studies show iron L-edge XANES 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<sub>3</sub>-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<sub>3</sub>-edge XANES spectroscopy.

## Symposium 2.5A Soil Physicochemical-Biological Interfacial Interactions: Impacts on Transformations and Bioavailability of Metals and Metalloids

### Theater (Poster) Session

Tuesday, 11 July 2006: 3:30 PM–5:15 PM

Abstract 51-12

MINERALOGY AND ARSENIC BONDING IN ARSENIC CONTAMINATED RICE-PADDY SOILS OF BANGLADESH.

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The natural arsenic contamination of the Ganges-Meghna-Brahmanputra groundwater aquifer in Bangladesh and the extensive use of this water for irrigation of dry season rice are resulting in increased concentrations of arsenic in paddy soils. The arsenic in these soils was found to be associated with sand and silt particle-size fractions even though most of the arsenic was extractable by ammonium oxalate in the dark, a characteristic more often associated with small, poorly crystalline materials in clay fractions. The apparent incongruent nature of these observations led a detailed examination of the mineralogy and arsenic localization of several paddy soils. The alluvial paddy soils of Bangladesh contain high concentrations of Fe-rich di- and trioctahedral micas and trioctahedral chlorites in all size fractions. The trioctahedral micas and chlorites are highly susceptible to weathering in the alternating oxidizing and reducing environment present in rice paddies. It was shown that most of the arsenic is associated with a poorly crystalline Fe-oxide component formed from the Fe released during the weathering of trioctahedral micas and chlorites. Examination of particle-size fractions using X-ray diffraction and scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDS) showed that most of the trioctahedral micas and chlorites were partially weathered to vermiculite and smectite. Examination of the sand fraction using synchrotron X-ray microprobe analysis indicated that most Fe-oxide grains and mica aggregates contained adsorbed arsenate. Appreciable arsenic was not observed at the edges of most individual mica or vermiculite flakes. Especially high arsenate concentrations were associated with small micaceous rock fragments and Fe-oxide coatings on root surfaces. It is hypothesized that Fe oxides at the internal surfaces of weathering mica schist aggregates provide sites favorable for oxidation of dissolved Fe<sup>2+</sup> and continued accumulation of Fe oxide, even under reduced soil conditions. These reactions have important implications to retention, solubility, movement, and bioavailability of arsenic in the seasonally reduced paddy soils of Bangladesh.