Fundamental Aspects of Mn Oxide Reactions with Catechol.

C. J. Matocha, D. L. Sparks, University of Delaware

Oxidizable organic ligand interactions with soil Mn(III,IV) (hydr) oxides minerals are complex. Accordingly, an in situ electron paramagnetic resonance stopped-flow spectropokinetic technique was combined with batch techniques to measure the reductive dissolution kinetics of bismite (delta-MnO(2)), a common soil Mn mineral, by catechol (1,2-dihydroxybenzene). The reaction was rapid, independent of pH, and essentially complete within seconds under conditions of excess catechol at pH 4 to 6. The activation energy value of 58.7 kJ mol(-1) indicated that the reaction was surface chemical controlled. Rates of catechol disappearance from solution with simultaneous Mn(II) and ortho-quinone production were comparable. The efficiency and rapid reductive dissolution kinetics of bismite by catechol could have significant implications for C and Mn cycling in soils.

Christopher J. Matocha, 302 831-1595, cjmatocha@udel.edu

Characterization of pesticide desorption from soil using isotopic exchange technique.

r. celis@irnas-csic.es, w. c. koskinen, USDA-ARS

An isotopic exchange method was used to characterize the irreversibility of the sorption-desorption process of the insecticide imidacloprid and two of its metabolites, imidacloprid-urea and imidacloprid-quinadine, on a silt loamy clay and a loamy sand soil. The exchange between 12C-pesticide molecules and 14C-labeled pesticide molecules in 14C-pre-equilibrated suspensions was monitored and indicated that a fraction of the sorbed pesticide was resistant to desorption. A two-compartment model was applied to describe the experimental sorption data points as the sum of a reversible component and a non-desorbable, irreversible component, which was estimated from the isotopic exchange experiment. The isotopic exchange technique allowed for an accurate prediction of the sorption-desorption hysteresis during successive desorption cycles and appeared to be a suitable method to quantitatively characterize pesticide desorption from soil.

Rafael Celis, 34-95-4624711, rcelis@irnas.csic.es

Supercritical Fluid Extraction of Selected Pesticides from Soil.

B. L. Barber, University of Minnesota, W. C. Koskinen, USDA-ARS

The objective of this study was to determine the effect of supercritical fluid CO2 (SF-CO2) density and soil water content on supercritical fluid extraction (SFE) of selected pesticides from soil. 14C-labeled isopenthenos and triadimefon were extracted from two Minnesota soils, Webster clay loam and Wasekeon silt loam, at two soil water contents (3% and 12%) using two SF-CO2 densities (0.3 g/mL and 0.9 g/mL). Quantitative recoveries of both pesticides (>99%) were obtained under conditions of higher density and greater water content, while recoveries from drier soil using low density were poor (0.4 - 13%). At high density, water content had a greater effect on triadimefon extraction than for isopenthenos extraction, particularly for clay loam. These results show the importance of considering soil water content when developing and optimizing SFE methods for extraction of different classes of pesticides from soils with different physical and chemical properties.

Brian L. Barber, 612-625-2723, bbarber@soil.umn.edu

Supercritical Fluid Extraction (SFE) for Determining Linuron Sorption-Desorption in Field Moist Soils.


Experiments were performed using low density (i.e., 0.25 g/mL) supercritical carbon dioxide, to remove linuron from the soil water phase only, thus allowing calculation of sorption coefficients (Kd) at low water contents. Soil water content and temperature affected sorption. Kd values increased with water content, and decreased with temperature. Linuron sorption coefficients for silt clay, and sandy loam soils at 12% water content were 3.9, and 7.0 mL/g, respectively. Isotopic heat of sorption, were -41 and -35 KJ/mol, for the silt clay and sandy loam soils respectively. Comparable sorption coefficients were obtained for SFE and batch slurry methods. The Kf value for the sandy loam soil was 7.9 mL/g. This application of SFE to determine sorption coefficients should give a more accurate overall perspective of linuron fate in the field, than by sorption characterized by the batch method.

William C Koskinen, 612 625-4276, koskinen@soils.umn.edu

Sorption-Desorption of Phenolic Acids in Soils.


Phenolic acids are released into soils by plants as decomposition metabolites and, in some plants, as root exudates or leaf leachates. These chemicals are involved in several soil processes, including the formation of humus, nutrient availability, dissolution of minerals, and alelopathy. Their availability for these processes is controlled by sorption and degradation interactions. In order to understand allelopathic effects of phenolic acids, we need to understand their behavior in soil. The first step to a better understanding of soil behavior is to characterize the sorption-desorption interactions of these compounds in soil. In this paper, characterization of sorption-desorption of the phenolic acids p-coumaric acid, ferulic acid, vanillic acid, p-hydroxybenzoic acid, and veratric acid as a function of soil properties in relationship to the reactivities of these compounds with soil components will be examined.

Amy M. Cecchi, 612-625-4233, cecchi@soils.umn.edu

Organoclays as supports for controlled release formulations:

D. L. Carrizosa , w. c. koskinen, USDA-ARS, m. c. hermosin, j. correio, IRNAS-CSIC

Three smectites varying in surface properties were saturated with different alkanilamonium cations and dicamba sorption isotherms were determined. OCIs were effective sorbents for dicamba and sorption was the result of hydrophobic interactions between dicamba and organic cations. Sorption was greater for OCIs with high layer charge, basal spacing, organic carbon content, alkylammonium size, and organocarboxylation close to CEC. Desorption isotherms were irreversible, except for OCIs with cations with alkylammonium group, which exhibited hysteresis. pH studies indicated molecular dicamba was the main species sorbed. OCIs have potential as supports for controlled release formulations. OCIs also have potential to immobilizing agents for remediation of dicamba contaminated soils. When dicamba contaminated soil was mixed with large quartzenry alkanilamonium OCIs at different rates, aqueous CaCl2 extractability of dicamba decreased.

M. J. Carrizosa, 34-95-4624711, carrizosa@irnas.csc.es

Imidacloprid interactions with natural and organic exchanged clays.

I. Cox, w. c. koskinen, USDA-ARS, m. c. hermosin, j. correio, IRNAS-CSIC

Imidacloprid (NTN) sorption on octadecylammonium, C18, and docotadecylidimethyammonium, DOD, and Fe saturated montmorillonites, which have high (SA) and low (SW) layer charge, was determined. NTN- montmorillonite complexes were studied by X-ray diffraction and FT-IR techniques. NTN sorption decreased in order C18SbWy > C18Saz > FeSbW > DODSazWy >= DODSaz. Low layer charge and saturation by primary alkylammonium cation facilitated NTN sorption in the interlayer of the smectite, which is corroborated by an increase in basal spacing in X-ray diffraction and by the presence of shifted absorption bands in FT-IR spectra. Low layer charge facilitated the opening of the silicate layer and sorption between charged sites by hydrophobic interactions, whereas primary alkylammonium enabled the formation of polar bonds with NTN molecules. NTN sorption on FeSbW montmorillonite appears to be sorption by cation exchange as a result of high surface acidity of the clay.

Lucia Cox, 34-95-4624711, lexco@irnas.csic.es

Sulfate Sorption on Goethite in the Presence of Pb.

E. J. Elzinga, D. L. Sparks, University of Delaware

We studied the effect of lead (Pb) on sulfate (SO4)4 sorption at the goethite-water interface at pH 4.3, 5, and 6.0 using in situ ATR-FTIR spectroscopy. As base line information, SO44 sorption was studied in the absence of Pb over a range of SO44 concentrations. At all pH values, both inner-sphere and outer-sphere SO44 sorption complexes were observed. Inner-sphere SO44 complexes became more dominant with decreasing pH, and increasing SO44 concentrations. Adding Pb to the system resulted in an increase of the overall SO44 sorption and an increase in the contribution of outer-sphere SO44 complexes. This may be due to Pb competing with SO44 for inner-sphere sorption sites, and/or electrostatic effects due to inner-sphere Pb sorption. XAFS data for Pb sorbed on goethite showed that Pb forms inner-sphere complexes at the goethite surface. No differences were observed between Pb sorbed in the presence of SO44 and Pb sorbed in a system with a 500-fold excess of SO44.

E.J. Elzinga, 302 831-1595, elzinga@udel.edu

Determination of the Zero Point of Charge of Tropical Soil and other Constant Surface Potential Materials.

C. S. Appel, L. Q. Ma, E. Kenney, University of Florida

Highly weathered, variable charge soils (Oxisols, Ultisols, Andisols, and Alfisols) comprise roughly 58% of all tropical soils. Many times these soils possess a characteristic pH associated with the point at which the net surface charge is zero. An Oxisol and Ultisol from Puerto Rico as well as samples of