26.

DOUBLE RESONANCE SOLID-STATE ^{13}C-^{15}N NMR EXPERIMENTS FOR STUDYING THE HUMIFICATION OF TNT IN SOILS. ***Heike Knicker***, *Lehrstuhl für Bodenkunde, Technische Universität München, 85350 Freising-Weihenstephan Germany, knicker@pollux.weinenstephen.de*

TNT-contaminated soils from activities of munition and defense industries have become a subject of environmental concern. One bioremidiation strategy for such soils represents an anaerob/aerob treatment during which reduced TNT may be incorporated into the refractory soil organic matter pool. To test the efficiency of this strategy C-13-enriched plant material was incubated with N-15-TNT-spiked soils and the humification process was followed by solid-state N-15 NMR spectroscopy. A transformation of TNT-metabolites to heterocyclic compounds that cannot be released after extraction with methanol was observed. Solid-state C-13-N-15 double resonance NMR experiments were performed. First results demonstrate the high potential of solid-state double resonance NMR techniques for the examination of humification processes of natural and anthropogenic organic material in soils and sediments.

27.

CHARACTERIZATION AND FUNCTION OF HUMIC MACROMOLECULES EXTRACTED FROM DECOMPOSING ORGANIC MATTER. ***Yona Chen***, *Benny Chefetz, and Yitzhak Hadar. The Hebrew University of Jerusalem, P.O. Box 12, Rehovot, Israel*

During composting, many parameters must be monitored to ensure an optimal rate of decomposition. Although a number of these parameters stabilize at the cooling stage they do not provide means to determine the actual degree of decomposition (maturity) of the compost. An ultimate single parameter for compost maturity has not been identified to date. The fact that the organic matter keeps transforming even after most parameters measured in the solid phase achieve constant values, suggests that a close examination of the water soluble fraction in compost may provide attenuated information on compost maturity. We studied the properties and transformation of dissolved organic matter (DOM) extracted from municipal solid waste compost (MSW), at five stages of composting. The unfractionated DOM, the hydrophobic acids and neutrals (HoA and HoN, respectively) and the hydrophilic neutrals (HiN) fractions were studied using the solid-state 13C-NMR, FTIR, and DRIFT spectroscopy. This study provides improved indicators for compost maturity.

28.

^{2}H NMR CHARACTERIZATION OF NONCOVALENT INTERACTIONS BETWEEN MONOAROMATIC COMPOUNDS AND DISSOLVED HUMIC AND FULVIC ACIDS. ***Mark A. Nanny*** *and Jesus P. Maza. School of Civil Engineering and Environmental Science, University of Oklahoma, 202 West Boyd Street, Rm. 334, Norman, OK 73019, fax (405) 325-4217, nanny@ou.edu*

Deuterium NMR T_1 relaxation experiments were used to examine noncovalent interactions between monoaromatic compounds (pyridine-d_5, phenol-d_5, and benzene-d_6) and several humic and fulvic acids (Suwannee River HA, IHSS soil HA, IHSS peat HA, Suwannee River FA, Big Soda Lake FA, and Norman Landfill leachate FA). The type of noncovalent interaction was found to be dependent on the solution pH, polarity and hydrogen-bonding capacity of the monoaromatic compound, and the humic and fulvic acid structure. Noncovalent interactions identified were sorption to HA, hydrogen-bonding between the monoaromatic functional groups and the HA and FA polar functional groups, and enhanced solubilization of the monoaromatic compound. Most significant however, was that for several monoaromatic compound and HA or FA combinations, the type and extent of noncovalent interaction was extremely sensitive to pH over the environmentally-pertinent pH range of 6 to 8.

29.

2-D NMR SPECTROSCOPY OF HUMIC SUBSTANCES. ***N. Hertkorn***[1], *I. V. Perminova*[2], *Ph. Schmitt-Kopplin*[1], *A. Permin*[2], *D. Kovalevskii*[2], *and A. Kettrup*[1]. *(1) Institute of Ecological Chemistry, GSF-Research Center for Environment and Health, PO Box 1129, 85764 Neuherberg, Germany, fax +4989-3187-2705, hertkorn@gsf.de, (2) Department of Chemistry, Lomonosov State University of Moscow, Vorob'ovy Gory, 119899 Moscow, Russia*

NMR spectroscopy has for a long time been utilized for the structural analysis of humic substances. The second frequency domain available in 2D NMR spectroscopy provides information concerning spatial or bonding interactions between pairs of atoms. We will present two dimensional NMR spectra to demonstrate the great importance of this method, allowing a more precise characterization of terrestrial and aquatic humic substances. The applications of homonuclear 2D NMR spectroscopy range from the characterization of exchangeable protons to a description of extended spin systems, while heteronuclear 2D NMR spectra are very powerful tools for a detailed structural analysis of the carbon skeleton of humic substances.

30.

CHARACTERIZATION OF DISSOLVED ORGANIC MATTER FROM THE EMS-DOLLART ESTUARY AND THE NORTH SEA USING RAMP-CPMAS ^{13}C-NMR. ***J. D. H. van Heemst***, *K. J. Dria, and P. G. Hatcher.*
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Dissolved organic matter (DOM) from the Ems-Dollart estuary and the North Sea was analyzed using traditional low-field CPMAS ^{13}C-NMR spectroscopy and high-field ramp-CPMAS ^{13}C-NMR. The advantages of ramp-CPMAS ^{13}C-NMR is that this technique is many times more sensitive and therefore gives more detailed information than traditional CPMAS ^{13}C-NMR. This technique can therefore be applied to samples, which typically contain only low amounts of organic matter, such as DOM samples. Furthermore, major differences are observed in the quantification of the different carbon species present in the spectra obtained by traditional CPMAS ^{13}C-NMR and ramp-CPMAS ^{13}C-NMR. It has been demonstrated that ramp-CPMAS ^{13}C-NMR gives more reliable quantitative data than traditional CPMAS ^{13}C- NMR.

31.

CHARACTERIZATION OF HARVARD FOREST SOILS AND THEIR ASSOCIATED PLANT COMPONENTS BY NMR AND OTHER METHODS. ***K. J. Dria***, *D. B. Dail, J. D. Chorover, E. A. Davidson, and P. G. Hatcher.*
Department of Chemistry, Ohio State University, Columbus, OH 43210

Solid-state 13C NMR studies of samples collected from canopy-to-soil stratigraphic profiles of the Harvard Forest, containing leaf, fine root and organic and mineral soil samples from both hardwood and pine forests, were conducted to learn more about soil formation. Spectra from all samples contain predominantly signals associated with aliphatic and carbohydrate structures and low amounts of aromatic structures. The mineral soil samples exhibit minor amounts of aromatic peaks, suggesting little contribution of lignin structures to the organic matter. Lignin added to the soil by plant inputs may have been oxidized and/or leached out. Primary changes observed in the canopy-to-soil profile were a loss of carbohydrates and an increase in the paraffinic carbon region. Additional analyses of these samples are currently being obtained using pyrolysis GC/MS and tetramethylammonium hydroxide (TMAH) thermochemolysis GC/MS to determine the nature and origin of the various structural components.

32.

CARBONATE EFFECTS ON THE SURFACE COMPLEXATION OF CR(VI) AND PB(II) WITH GOETHITE. ***Mario Villalobos***[1], *John D. Ostergren*[2], *Maya A. Trotz*[3], *and James O. Leckie*[3]. *(1) Civil and Environmental Engineering, Stanford University, Terman B17, Stanford, CA 94305-4020, fax (650) 725-3162, marvilla@leland.stanford.edu, (2) Geological and Environmental Sciences, Stanford University, Green Earth Science, Stanford, CA 94305-2115, (3) Stanford University*

Carbonate/CO_2 is pervasive in the environment and affects adsorption of trace elements to colloidal surfaces. This has potential negative repercussions in increasing their mobility through aqueous environments. The normal effect is a decrease in adsorption, via competition and electrostatic effects, as occurs with anions such as Cr(VI), or via formation of aqueous carbonato complexes, as occurs with cations such as Pb(II). However, in the latter case, evidence was found that supports the formation of additional ternary Pb(II)-carbonate surface complexes, which at sufficiently high carbonate concentrations, increase total Pb(II) adsorption. A Triple Layer Surface Complexation Modeling approach was followed to describe the experimental adsorption behavior of Pb(II) and Cr(VI) onto goethite in the presence and absence of carbonate. Self-consistency was followed from the description of the goethite acid/base titration data and the binary adsorption systems.