

**The Third Annual Symposium on
Natural Organic Matter in Soils and Water**

**North Central Region
March 8 and 9, 2002**



**Presented by the NOM Center at the University of
Minnesota**

**306 & 375 Borlaug Hall
1991 Upper Buford Circle
University of Minnesota
St. Paul, MN 55108**

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About the NC-NOM Symposium and the NOM Center at the University of Minnesota

A group of Universities from the north central region have organized to sponsor an annual regional symposium to bring together scientists from many disciplines that are involved in NOM research. This year the NOM Center at the University of Minnesota hosts the third NC-NOM Symposium.

The NOM Center at the University of Minnesota was established in 1999 to bring together scientists from many disciplines to collaborate on research and graduate education concerning NOM. This areas of focuse includes, but is not limited to:

- ◆ Structure of Humic Materials
- ◆ Interactions of NOM with Xenobiotic Organic Compounds
- ◆ Interactions of NOM with Metals and Clays
- ◆ The Role of NOM in Global Carbon Cycle
- ◆ The Role of NOM in Stimulating Plant Growth.
- ◆ The Role of NOM in Water Treatment

NC-NOM Symposium, 2002 Schedule

Friday, March 8

12:00 **Registration and poster set-up**, 375 Borlaug Hall

12:30 **Lunch**, 375 Borlaug Hall

1:30 **Welcome**

Session 1: Dissolved Organic Matter 306 Borlaug Hall

1:35 Keynote Speaker

Humic Substances and Electron Transport Reactions in Aquatic Ecosystems: The Role of Quinone Moieties.

Diane M. McKnight

Civil, Environmental and Architectural Engineering and a fellow of the Institute of Arctic and Alpine Research, University of Colorado, Boulder.

2:20 **Landscape Scale Patterns in Dissolved Organic Carbon, an Example from Northern Sweden**

Johan Temnerud¹ and Kevin Bishop²

¹Man-Technology-Environment Research Center, Örebro University, S-70182 Örebro, Sweden. ²Department of Environmental Assessment, Swedish University of Agricultural Science, Box 7050, S-750 07 Uppsala, Sweden

2:45 **Riparian Zone Controls on the Chemical Dynamics of DOC-Rich Runoff from a Boreal Hillslope**

Kevin Bishop¹, Stephan Köhler², Jakub Hruska³ and Hjalmar Laudon⁴

¹Department of Environmental Assessment, Swedish University of Agricultural Sciences, Box 7050, SE-750 07 Uppsala, Sweden; ²Géochimie : Transferts et Mécanismes CNRS (UMR 5563), University of Toulouse, 38 rue des trente-six ponts, F-31400 Toulouse, France; ³Czech Geological Survey, Klarov 3, CZ-118 21 Praha 1, Czech Republic; ⁴Ralph Parsons Lab. Civil and Environmental Engineering, MIT, Cambridge, MA, 02139, USA.

3:05 **Characterization of Dissolved Organic Matter in Soil Water and Streams of Olympic National Park, WA**

Rose M. Cory¹, S.A. Green², K.S. Pregitzer³

¹Civil & Environmental Engineering, Michigan Technological University, Houghton, MI, 49931, USA. ²Department of Chemistry, Michigan Technological University, Houghton, MI, 49931, USA. ³School of Forestry & Wood Products, Michigan Technological University, and USDA Forest Service North Central Experiment Station, Houghton, MI 49931, USA.

3:35 **Posters and Coffee, 375 Borlaug Hall**

Session 2. Spectral Studies of NOM
306 Borlaug Hall

- 4:05 Lead-off Speaker
Structural Studies of NOM by Solid State NMR
Klaus Schmidt-Rohr
Department of Chemistry, Iowa State University, Ames IA 50011
- 4:50 **Characterization of Natural Organic Matter Inputs and Persistent Components in Forest Soils**
Karl J. Dria and Patrick G. Hatcher
The Ohio State University, Department of Chemistry, 100 W. 18th Ave., Columbus, Ohio 43210
- 5:15 **Reduced S in NOM and the Chemistry of Hg in Soil and Water**
Abdul R. Khwaja¹, Chung-ming Lin², Paul Bloom², Patrick Brezonik³, Soh-Joung Yoon and William Bleam⁴
¹Water Resources Science Program, ²Department of Soil, Water and Climate, University of Minnesota, ³Department of Civil Engineering, University of Minnesota, ⁴Department of Soil Science, University of Wisconsin, Madison
- 5:40 **Posters with Wine and Cheese, 375 Borlaug Hall**
- 7:00 **Dinner at the St. Paul Student Center**

Saturday, March 9

- 8:30 **Continental Breakfast, 375 Borlaug Hall**

Session 3. Dynamics of NOM
306 Borlaug Hall

- 9:00 Lead-off Speaker
Freshwater NOM and Global Carbon Cycling
James B. Cotner
Department of Ecology, Evolution and Behavior, 100 Ecology, University of Minnesota, St Paul, MN 55108-6028

- 9:45 **The Effect of Biofilm and NOM on Removal of Cryptosporidium Oocysts by Granular Media Filtration**
Xiaojun Dai and Raymond M. Hozalski
Dept. of Civil Engineering, University of Minnesota, Minneapolis, MN 55455
- 10:10 **Investigating Organic Matter Decomposition in Grasslands Under Elevated Atmospheric CO₂**
Jennifer Y. King¹, Elise Pendall², and Arvin R. Mosier³
¹ Department of Soil, Water, and Climate and Department of Ecology, Evolution, and Behavior; University of Minnesota, St Paul, MN 55108-6028. ² Institute for Arctic and Alpine Research, University of Colorado, Boulder. ³ USDA-ARS Soil-Plant-Nutrient Research, Fort Collins, Colorado
- 10:15 **Posters and Coffee, 375 Borlaug Hall**
- 10:45 **Carbon and Nitrogen Dynamics in the Soil-Plant Continuum: Measured and Simulated.**
Hero T. Gollany¹, J.A.E. Molina¹, C.E. Clapp², D.R. Linden², R.R. Allmaras², M.F. Layese¹, R.H. Dowdy², and H.H. Cheng¹
¹ Department of Soil, Water, and Climate, University of Minnesota, St. Paul, MN 55108. ²USDA-ARS, Department of Soil, Water, and Climate, University of Minnesota, St. Paul, MN 55108
- 11:10 **Using GEMLS to Describe the Contribution of Organic Carbon to Soil Water Holding Capacity**
Alan E. Olness and David Archer
USDA-ARS-MWA, NCSCRL, 803 Iowa Ave., Morris, MN 56276
- 11:35 **The Relevance of Extracting Organic Matter Based on Binding to Polyvalent Cations**
Dan C. Olk
USDA, ARS, National Soil Tilth Laboratory, Ames, IA 50011.
- 12:10 **On the Formation of Bentonite-Humic and Bentonite-Fulvic Colloidal Systems**
Dragoljub D. Bilanovic and Steven A. Spigarelli
Center for Environmental, Earth and Space Studies, Bemidji State University, Bemidji, MN 56601
- 12:15- 12 30 **Wrap -up**

Posters

375 Borlaug Hall

- P1. Nitrogen-15 and Natural Abundance C-13 Changes Under Different Tillage, Residue and Fertilizer Management.**
M.F. Layese*¹, C. E. Clapp², R.R. Allmaras², J.A.E. Molina¹, D.R. Linden² and R.H. Dowdy²
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- P2. Degradation of Lignin Model Compounds by Singlet Oxygen**
A.M. McNally*, and Kristopher McNeill
Department, of Chemistry, University of Minnesota, Smith Hall, 207 Pleasant St. SE, Minneapolis, MN 55455
- P3. Thermodynamic Sorption Values of PAHs to SOM**
Scott D. Kohl* , and James A. Rice
Department of Chemistry and Biochemistry, South Dakota State, Box 2202, Brookings, SD 57007-0896
- P4. Investigations of Aromatics in Humic Acids by Solid-state NMR**
J.-D. Mao*¹, D.C. Olk², M.L. Thompson³, and K. Schmidt-Rohr¹
¹ *Department of Chemistry, Iowa State University, Ames, IA 50011.* ² *USDA, ARS, National Soil Tilth Laboratory, Ames, IA 50011.* ³ *Department of Agronomy, Iowa State University, Ames, IA 50011*
- P5. Characterization of ¹⁵N Labeled Humic Acids from a Nitrogen-tillage-residue Field Experiment**
R.S. Vial*¹, C.E. Clapp², M.H.B. Hayes³, G. Brunetti⁴, C.M. Hormann¹, J. Mao⁵, J.A.E. Molina¹, & C.M. Van Patten¹
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- P6. Nitrogen Transformations During a Long-term Incubation**
D.T. Lee*¹, C.E. Clapp, J.A.E. Molina, M.F. Layese, M.A. Miller, M.H.B. Hayes, A.J. Palazzo, and R.H. Dowdy
¹ *Department of Soil, Water, and Climate, University of Minnesota, St. Paul, MN 55108;* ² *USDA-ARS, St. Paul, MN 55108;* ³ *University of Limerick, Ireland;* ⁴ *US Army Corps of Engineers*

- P7. Comparison of CP-MAS ^{13}C NMR Spectra of Aquatic Humics Isolated using Hydrophilic (DEAE-Cellulose) and Hydrophobic (XAD-8) Adsorbents**
Abdul R. Khwaja*¹, Patrick Brezonik², Paul Bloom³, Bin Chen⁴ and Eric Munson⁵
¹Water Resources Science Program, ²Department of Civil Engineering, University of Minnesota, ³Department of Soil, Water and Climate, University of Minnesota, ⁴Chemistry Department, University of Minnesota, ⁵Department of Pharmaceutical Chemistry, University of Kansas
- P8. Quinone Mediated Reduction of Dinitroaniline Herbicides in Homogeneous Aqueous Solution**
Song Wang* and William A. Arnold
Department of Civil Engineering, University of Minnesota, Twin Cities

Oral Abstracts

Session 1: Dissolved NOM in Ecosystem

Humic Substances and Electron Transport Reactions in Aquatic Ecosystems: The Role of Quinone Moieties

Keynote Speaker: Diane M. McKnight

Civil, Environmental and Architectural Engineering and a fellow of the Institute of Arctic and Alpine Research, University of Colorado, Boulder, CO 80309.

Dissolved fulvic acids typically account for about half of the dissolved organic material (DOM) in freshwaters and 15-20% of DOM in marine waters. These fulvic acids influence a range of physical and biogeochemical processes, such as light absorption, metal binding and energy transfer in the ecosystem. The chemistry and spectral properties of fulvic acids can be related to the precursor organic material. Because lignin is a major precursor pool of biologically recalcitrant organic matter from higher plants, fulvic acids derived from terrestrial plants and soils have a greater aromaticity than fulvic acids derived from microbial material. In addition to a greater absorptivity in the visible and ultra-violet region, terrestrially-derived fulvic acids have distinct fluorescence spectra, which can be used to resolve differences in sources of DOM in natural waters in filtered water samples. This fluorescence method was applied in study of DOM transport in an alpine/subalpine catchment to show that during the summer the alpine lakes became "hotspots" of DOM production. We have also found that the fluorescence spectra of marine sediment fulvic acids change when the fulvic acids are used by microbes as electron acceptors in anoxic degradation of organic substrates. Further, in an Antarctic lake the changes in the fluorescence spectra are associated with the changes in Eh and metal concentrations through the oxycline. Fluorescence spectroscopy provides a tool for characterizing DOM biogeochemistry in both freshwater and marine ecosystems.

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Landscape Scale Patterns in Dissolved Organic Carbon, an Example from Northern Sweden

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In order to evaluate landscape scale patterns in dissolved organic carbon (DOC) in two boreal catchments (ca. 70 km²), 102 surface waters samples were collected at low discharge conditions in the county of Västerbotten, northern Sweden, during June 2000. This abstract will focus on the difference between headwaters and downstream.

Headwaters had lower pH's (mean 5.1, s.d. 4.7, n = 50), compared to downstream conditions (mean 5.9, s.d. 5.5, n = 52). No upstream/downstream difference in electrical conductivity was found, the values were generally low (mean 29 µS/cm, s.d. 41). There was a large variation in the DOC of the headwaters (2.5-38 mg/l). Headwaters had higher concentrations of dissolved organic carbon (mean DOC of 18.3 mg/l, s.d. 8.2) compared to downstream waters (mean 14.9 mg/l, s.d. 5.2). A simply downstream dilution could explain this pattern. Using volume weighted headwater DOC concentrations and assuming there are no in-stream processes that alter DOC concentration we were able to predict measured outlet concentrations of DOC. No systematically change of DOC character along the streams could be observed, measured as 254 nm and 436 nm per DOC and C/N-ratio, however a slight decrease in molecular weight could be detected between headwaters (mean 2697 Dalton, s.d. 107) and downstream (mean 2638 Da, s.d. 66).

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Riparian Zone Controls on the Chemical Dynamics of DOC-Rich Runoff from a Boreal Hillslope

Kevin Bishop¹, Stephan Köhler², Jakub Hruska³ and Hjalmar Laudon⁴

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The chemistry of stream water is often quite different from that of soil water and shallow groundwater in the extensive upslope areas of many catchments, particularly with regards to the amount and character of dissolved organic carbon. The riparian zone, which runoff traverses immediately before entering the stream channel, has often been invoked to explain the differences between upslope water and the stream, as well as the changes in runoff chemistry during episodes. This hypothesis was tested on a hillslope in boreal Sweden provides.

The variation of DOC during runoff events could be explained by the activation of more superficial lateral flow paths in the riparian soil profile 4 m from the stream when runoff

rates were high. Laterally flowing groundwater in the mineral soil 25 m from the stream had low DOC concentrations (2-6 mg/L). In the riparian soil profile, the groundwater level and flow paths varied less than 30 cm, but traversed a gradient in soil water DOC from under 6 mg/L to over 30 mg/L. That gradient corresponded to the change in runoff DOC during events (Fig. 2).

The riparian soil solution concentrations of some other constituents, most notably Aluminum, could not be explained by such simple mass balances between the stream and the riparian soil profile. (Indeed a simple mass balance would not have worked for DOC if one looks at the soil profiles 12 m and 25 m from the stream). While this study demonstrates the importance of the riparian zone for the DOC in runoff at this site, the study also illustrates the great difficulty of quantitatively observing the interaction of hydrology and hydrochemistry.

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Characterization of Dissolved Organic Matter in Soil Water and Streams of Olympic National Park, WA

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To understand the transformation of dissolved organic matter (DOM) as it moves through the soil and into streams, DOM concentration, stoichiometry and light absorbing properties were investigated in a soil water (shallow to deep) to stream continuum at forested study sites in Olympic National Park, WA. At 11 study sites in four major regions of the park, soil water was collected at depths of 15 and 40 cm in the soil. Stream water was collected from one stream in each of the four regions. Dissolved organic carbon (DOC) concentrations and absorbance at 300 nm were measured on each raw water sample. Isolation of DOM involved concentration by ultrafiltration followed by dialysis to remove inorganic ions and freeze-drying to remove water. Elemental analysis data for CHN and O were measured on each isolated DOM sample in order to investigate DOM composition as a function of molar ratios (N:C, H:C, O:C), average index of unsaturation, and average carbon oxidation state. At nearly every site, shallow soil water samples (15 cm) had lower molar ratios, higher specific absorbance, greater unsaturation

and higher DOC concentrations relative to the deep soil water samples (40 cm) from the same site. The specific absorbance of DOM (300 nm) decreased from shallow soil water to stream to deep soil water DOM. Overall, consistent depth differences in the chemical composition of soil water DOM were observed, despite the diversity of forested study sites across Olympic Park. However, it is unclear whether the transformations of DOM with depth extend in a continuous fashion to the streams.

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Session 2: Spectral Studies of NOM

Structural Studies of NOM by Solid-State NMR

Session Lead-off Speaker: Klaus Schmidt-Rohr

Department of Chemistry, Iowa State University, Ames IA 50011

Knowledge of the chemical structure of natural organic matter is critical for understanding their roles in the environment. Advanced solid-state nuclear magnetic resonance (NMR) techniques open new possibilities for identifying and quantifying the various functional groups in natural organic matter: Spectral editing of C-H groups yields clear NCH and OCH peaks; selection of nitrogen-bonded carbons reveals NCO, aliphatic NCH, and aromatic NCH groups, as well as other aromatic carbons bonded to nitrogen; acetal and ketal (O-C-O) carbons can be selected based on their small chemical-shift anisotropies; the aromaticity and the fractions of unprotonated and protonated aromatic carbons can be determined quantitatively; aromatic ethers can be distinguished from phenols based on OH-proton suppression in heteronuclear correlation experiments; and esters, amides, and carboxylates can be told apart. Common structural features in soil organic matter include: Aliphatic domains rich in polymethylene, with few branch-points; C(=O)-NH-CHR peptide groups; sugar rings; unprotonated O-alkyl and O-C-O groups; domains of partially oxidized charcoal; and aromatic ethers (but only few phenols) derived from lignin. These studies indicate that in spite of the complexity of natural organic substances, they are not “supermixtures” beyond human comprehension, and can be characterized in meaningful structural terms. There is good evidence that the compositional data can be of use for understanding aspects of contaminant sorption and of soil fertility.

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Characterization of Natural Organic Matter Inputs and Persistent Components in Forest Soils

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Many researchers believe aromatic precursors from trees and other forest plants, especially lignin, persist and accumulate in forested soils while aliphatic carbon structures are degraded. They conclude that carbon sequestration in northern temporal forests occurs in the form of lignin-type structures and is thought to be vital in the immobilization of nitrogen in forest systems. The common belief that lignin persists and increases with soil depth, is based on data produced using the standard wet chemical lignin analysis. However, work performed on samples from the Harvard Forest by solid-state carbon-13 NMR and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) do not support the conclusion that aromatic structures such as lignin persist in soil while aliphatic structures are degraded.

This observation that aliphatic rather than aromatic structures persist may have important implications for current forest nutrient cycling models. However, determination of the source, role and resident lifetime of these aliphatic components is even more important for these models and carbon sequestration calculations. Some sources of aliphatic structures are believed to be from leaves and fine roots. Therefore, we are currently in the process of trying to determine the portion of the leaves and roots that contain aliphatic components and follow these structures through the natural decay process in addition to evaluating other natural forest inputs. Samples are analyzed for chemical structural information by solid-state ¹³C NMR and molecular level detail by Py-GC-MS. Additionally, the wet chemical lignin analysis technique is being evaluated with various types of forest samples.

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Determination of Binding sites and conditional complexation Constants of Natural Organic Matter with Hg²⁺ and CH₃Hg⁺

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Mercury and methylmercury bind strongly with natural organic matter (NOM), and this phenomenon plays an important role in mercury cycling. In our research we have shown that in NOM from soils and fresh waters Hg^{2+} and CH_3Hg^+ bind to reduced sulfur (thiol, sulfide and disulfide), oxygen (carboxylic and phenolic), or nitrogen. At very low additions, sulfur sites are the predominant binding sites. We investigated S chemistry and Hg binding in soil samples and extracted humic acid from organic soil horizons collected along an upland, wetland transect from two wetlands, S2 and S3, in the Marcell Experimental Forest Area of northern Minnesota. Natural organic matter was also extracted from water samples collected from the two wetlands S2 and S3 and three lakes: Blandin, Spring and Scrapper, from the Marcell Experimental Forest. Soil humic acid (HA) was extracted using the standard NaOH method that was used by the International Humic Substances Society (IHSS) to prepare standard HA. The aquatic NOM samples were extracted using the diethyl aminoethyl cellulose (DEAE) and XAD-8 resin methods. We also used IHSS soil and aquatic humic samples.

We determined the fraction of reduced S using X-ray absorption near edge spectroscopy (XANES) and showed that with poorer drainage the fraction of reduced S in soils and soil HA increases. We determined the bonding environment for Hg and CH_3Hg^+ using x-ray absorption fine structure spectroscopy (XAFS) with Hg^{2+} and CH_3Hg^+ added at varying ratios of Hg to reduced S. At higher ratios both S and O (or N) participate in the binding while at molar ratios of less than about 0.4 only S is involved. The bonding of Hg^{2+} and CH_3Hg^+ with thiol groups is consistent with the high complexation constant, in the range of $10^{16.3}$ (at pH 3.8), that has been determined in organic soils and HA using, using both Br^- and I^- as competitive ligands.

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Saturday, March 9

Session 3: Dynamics of NOM

Freshwater NOM and Global Carbon Cycling

Session Lead-off Speaker: James B. Cotner

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Dissolved natural organic matter (NOM) is one of the largest pools of carbon on the Earth and constitutes a vital link in the global carbon cycle. Dissolved NOM in the ocean represents a quantity of carbon similar to that of CO₂ in the atmosphere and has a residence time of 4-6000 years. Rivers are the primary route whereby organic matter is exchanged between these two large reservoirs as dissolved organic carbon (DOC), but very little is known about the DOC that is transferred in rivers and how it is processed during its journey to the sea. I will discuss two important processes that alter the form, lability and composition of organic matter in freshwater basins, photo-chemical processes and microbial consumption and degradation. Photo-chemical oxidation is a significant process in the ocean but its significance is even greater in freshwater systems because they are shallow with much greater UV exposure. Furthermore, high nutrient levels and bacterial growth rates accentuate microbial processes in freshwater ecosystems. The relative importance of and interactions between these two processes will be discussed.

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The Effect of Biofilm and NOM on Removal of Cryptosporidium Oocysts by Granular Media Filtration

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Cryptosporidium parvum is a protozoan pathogen that can cause prolonged gastroenteritis in humans and possibly lead to the death of immunocompromised individuals. *C. parvum* enters water supplies as the hardy oocyst form by input of feces from infected animals or humans. Because chlorine is ineffective at inactivating *C. parvum* oocysts, properly designed and operated filters are essential for physically removing the oocysts from the water supply. The condition of the source water can influence the surface characteristics of the filter media and suspended particles, which, in turn, can influence the deposition of the particles during the filtration process. The purpose of this study was to evaluate the impact of natural organic matter (NOM) in the feed water and coating the filter media

with biofilm on oocyst removal. Bench-scale filtration experiments were performed with clean 0.55 mm diameter glass beads and biofilm coated glass beads in the presence and absence of NOM. The filters were operated at a loading rate of 5 m/h and 0.01 M CaCl₂ was added as "coagulant" in a direct filtration mode. The oocyst removal efficiency decreased from 51 +/- 6% for the clean bed to 23 +/- 3% with the biofilm coating. The removal efficiency in the presence of NOM was also reduced (14 +/- 1%). The oocyst removal for an experiment with a combination of biofilm coating and NOM (15 +/- 1%) was similar to that for the experiment with NOM coating alone. The zeta potential values (a measure of surface charge) for the oocysts pre-equilibrated with NOM were significantly more negative than the values obtained with "clean" oocysts. This suggests that NOM enhanced electrostatic repulsion between the oocysts and the negatively charged glass filter media. NOM also increased the hydrophobicity of the oocysts, as measured by hexadecane-water partitioning, but this was deemed to not have a significant impact on particle removal in these experiments. The results of these experiments suggest that source waters with high organic matter concentration have a greater potential for oocyst breakthrough either directly or indirectly (by contributing to biofilm formation) or both.

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Investigating Organic Matter Decomposition in Grasslands Under Elevated Atmospheric CO₂

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Elevated atmospheric CO₂ has important influences on plant productivity and plant tissue quality. Changes in these parameters are hypothesized to alter decomposition and element cycling with potential negative feedbacks on plant productivity. To determine the effect of growth under elevated CO₂ on decomposition rates of shortgrass steppe vegetation, laboratory incubations were conducted using soil amended with plant tissue grown under ambient (~375 ppmv) and elevated (~720 ppmv) atmospheric CO₂ conditions. The dominant species in this grassland are *Bouteloua gracilis*, a C₄ grass, and *Pascopyrum smithii*, a C₃ grass. Soil and plant litter were sealed in glass jars and incubated at 21°C for approximately 300 days. Samples of headspace gas were collected daily at the beginning of the incubation and less frequently towards the end of the incubation. The samples were analyzed for CO₂ concentration using an infrared gas analyzer and for ¹³C signature using a continuous flow isotope ratio mass spectrometer. The ¹³C values of respired CO₂ were initially heavier than the total soil organic matter, indicating respiration of highly labile

compounds. Through time the ^{13}C values became lighter than bulk soil organic matter values, which suggests degradation of lignin which can have a lighter ^{13}C signature overall. The technique of using ^{13}C measurements to trace organic matter cycling was particularly useful in this grassland system because of the mixture of C_3 and C_4 plants and the offset between ^{13}C of soil organic matter and new plant inputs. We found that root material produced under elevated CO_2 decomposed significantly faster than root material produced under ambient CO_2 . This result could have important implications for SOM cycling rates and ecosystem response under elevated CO_2 conditions.

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Carbon and Nitrogen Dynamics in the Soil-Plant Continuum: Measured and Simulated.

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Maintaining crop production and long-term environmental quality requires effective residue and fertilizer management. The objective was to verify the capability of the NCSWAP/NCISOIL model to simulate the dynamics of N and N^{15} in the soil-plant system. A long-term continuous corn (*Zea mays L.*) study was initiated in 1980, after a long history of low input pasture and hay, at Rosemount, MN. Conventional tillage (CT) plots with two levels of application rates (20 and 200 kg N/ha) and two types of residue management (residue removed, -R; and residue returned, +R) were used to calibrate the model. A sensitivity analysis was carried out for 30 years. The model accurately predicted N^{15} in the soil organic matter (SOM) at 0- to 15-cm depth for both fertilizer rates and residue managements. For the same amount of N^{15} added (8 kg N^{15} /ha), concentrations of N^{15} in the corn and SOM were higher for the 20 than 200 kg N/ha treatments. The predicted cumulative N lost during 12-years simulation indicates more NO_3 leaching to below 1m-depth for -R than +R plots, while higher denitrification rates were predicted for the +R than -R. These results are analyzed in terms of the simulated C and N dynamics.

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Using GEMLS to Describe the Contribution of Organic Carbon to Soil Water Holding Capacity

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A detailed descriptive model of the water holding characteristics of soil is needed to enhance the USDA-ARS N fertilizer decision aid and develop a systematic method for valuing organic C in soil. The General Energy Model for Limited Systems (GEMLS) was evaluated for this purpose by applying it to the US national soil inventory database (more than 100,000 entries). The database was segmented into narrow ranges of organic C content and silt content. The data from each subset were plotted as a function of soil clay content. Because of a matrix transition effect, two complementary GEMLS functions were used to describe the 33 kPa and 1500 kPa water content as a function of soil clay, silt, and organic C contents. This entailed 6 parameters (two function coefficients, two energy coefficients, and two critical clay contents) and required an initial manual fit of the models to the data subsets (about 100 ± 20 observations). Criteria for acceptance were uniform and homogenous distribution of the model residuals, absence of a detectable trend line in the residual distribution, zero error sum, and maximal R². The energy coefficient was a near linear function of silt content. After the initial manual fit, the data were subjected to analysis using SAS PROC MODEL and a variable energy coefficient. This work showed that the energy coefficient was also a complex function of organic C content. The two function coefficients appear to be constants and the two critical clay content values were linearly related to silt content. The R² values for C contents < 2 % often exceeded 0.9. The final product is a continuous function capable of predicting the water holding content of soil as a function of its physical separates.

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The Relevance of Extracting Organic Matter Based on Binding to Polyvalent Cations

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Soil polyvalent cations bind the calcium humate (CaHA) fraction of organic matter but not the mobile humic acid (MHA) fraction. These fractions are extracted with sodium hydroxide and have proven to be chemically distinct and relevant to nutrient cycling. In tropical lowland rice soils, the MHA was less humified than the CaHA in analyses by nuclear magnetic resonance spectroscopy for carbon, phosphorus and nitrogen (N), visible light absorption, elemental analyses, and other spectroscopic analyses. While

each fraction accounted for about 10% of total soil N, their roles in short-term N cycling were substantially greater. Seven days after pre-plant application of ^{15}N -labeled urea in one field, the MHA contained about 30% of all immobilized ^{15}N and the CaHA about 17%. By harvest, the MHA contained about 22% of all immobilized N and the CaHA about 10%, suggesting preferential mineralization of these fractions. In California cotton soils, the MHA was composed of more labile compounds than was the CaHA. Addition of the MHA to soil under controlled conditions increased potassium availability, as did field application of animal manure. Addition of the CaHA had no effect. The respective roles of the MHA and CaHA in nutrient cycling appear related to their chemical natures. Efforts are beginning to integrate their extraction with other organic matter fractionations.

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On the Formation of Bentonite-Humic and Bentonite-Fulvic Colloidal Systems

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Colloidal particles composed of clay(s) humic and/or fulvic acid(s) are frequently the major carriers of environmental pollutants like mercury (1) and atrazine (2). In fresh waters the amount of mercury associated with colloidal phase can be as high as 72% of total mercury (3). Humic and/or fulvic acids and clay colloids are also, either directly or indirectly, associated with almost all biological, chemical and physical phenomena in waters and soils. Our work (1) and lack of literature data on formation of fulvic-clay, humic-clay and fulvic-humic-clay particles directed us to the subject. Currently we are studying bentonite-humic and bentonite-fulvic particles. We will report on experiments conducted on concentration of humic and fulvic acids in range $\leq 10^{-5}$ M to 10^{-10} M while bentonite concentration range spans over two orders of magnitude. A laser counting technique is used in analysis of particle sizes in the systems studied

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Poster Abstracts

Nitrogen-15 and Natural Abundance C-13 Changes Under Different Tillage, Residue and Fertilizer Management.

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The objective of the study was to determine the changes in N and ¹⁵N as well as C and natural abundance ¹³C in soil samples taken from micro plots of enriched N superimposed on a tillage, residue and N fertilizer study. The experiment at Rosemount, MN was started in 1980 with 2 tillage treatments [till (T) or no-till (NT)]; 2 residue options [residue returned (r) or residue harvested (h)]; and 2 N rates [2 or 20 g N m⁻² as (NH₄)₂SO₄]. The 2 and 20 g N m⁻² rate corresponded to 4 and 40 atom% ¹⁵N, respectively. Corn was grown for 15 yr and subsequently cropped to soybean for 5 yr. Fertilizer N was not added for the soybean crop. Soil ¹⁵N increased to yearly additions of enriched N. Treatments with residue returned had higher ¹⁵N than residue harvested; NT had higher ¹⁵N than T. Among treatments, Th had the lowest ¹⁵N. Treatment effects on soil C and natural abundance ¹³C were most evident on the surface. Soil C was clearly affected by tillage, residue and N fertilization while ¹³C was affected only by tillage and residue treatments. Decrease in ¹³C due to soybean was evident only at the surface. Treatments with residue returned clearly were affected by crop change.

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Degradation of Lignin Model Compounds by Singlet Oxygen

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Lignin is one of the core components of terrestrially derived organic matter and understanding its degradation is important in determining lignin's role in the global carbon cycle. While it is known that lignin is degraded by photochemical means, the kinetics of lignin's photochemical degradation have not been investigated. Previous studies have shown that reactive oxygen species such as singlet oxygen play a critical role in the photodegradation of lignin, and the products of the degradation of lignin model compounds by singlet oxygen have been identified. In the present research, the kinetics of the degradation of lignin model compounds containing b-O-4 linkages is investigated. Laser flash photolysis is used to generate singlet oxygen in solutions of lignin model compound and singlet oxygen sensitizer (Rose Bengal) in EtOH or D₂O. The bimolecular rate constant for the degradation of the lignin model compound by singlet oxygen will be reported.

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Thermodynamic Sorption Values of PAHs to SOM

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Soil organic matter (SOM) is a critical control on the fate and transport of Xenobiotic nonpolar organic compounds such as polynuclear aromatic hydrocarbons (PAHs) or polychlorinated biphenyls in the environment. The magnitude of the initial interactions of these compounds with SOM is strongly influenced by their relative solubility in any aqueous phase present and their affinity for the SOM. Previous studies have shown that PAHs have a strong affinity for SOM in aqueous systems, however these interactions have not been carefully analyzed to determine the root causes of the observed affinities. This study looks more carefully at this sorption from the aqueous phase reporting thermodynamic values from sorption experiments with fluorene, phenanthrene, and pyrene at 10, 20, 30, and 40°C on three mineral soils. This analysis shows that as the size of the PAH increases: K_d increases (larger fraction found in SOM), DS is positive for all PAHs and increases in magnitude (increasing disorder), DH is negative for all PAHs and decreases in magnitude (decreasing heat of sorption), DG is negative for all PAHs and increases in magnitude (increasing affinity for SOM), and van't Hoff plots show decreasing linearity. The ramifications of these results will be discussed in the context of contaminant fate and transport. Humic Stimulation of Hydroponic Tomatoes

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Investigations of Aromatics in Humic Acids by Solid-state NMR

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Aromatics are important structural components of humic substances. In most humic acids, indications of two or three aromatic NMR ¹³C bands are observed but their assignments have remained unclear even with NMR techniques such as gated decoupling and short-CP selection of unprotonated and protonated sites. In this study, advanced solid-state NMR techniques were employed to characterize the nature of aromatics in humic substances. Lignin and charcoal appear to be the two main sources of aromatic residues. We quantify aromaticity by DP/MAS ¹³C NMR (Direct Polarization Magic Angle Spinning) combined with a ¹³C CSA (chemical shift anisotropy) filter, which makes it possible to separate out overlapping anomeric carbon signals. The fraction of unprotonated aromatic carbons has been quantified by DP/MAS with gated decoupling. It is found to be characteristically higher in charcoal-derived aromatics compared to lignin-derived residues. Aromatics bonded to nitrogen are detected using a new ¹H/¹⁴N/¹³C triple-resonance NMR technique. In a humic acid from tropical paddy soil, nitrogen is thus found to be incorporated into anilides [C₆H₅(NH)(C=O)-R]. Signals of N-containing heterocycles are also observed. ¹H-¹³C HETCOR experiments prove that aromatic C-O ethers predominate in lignin-derived aromatics, while phenolic groups are present in smaller concentrations. HETCOR NMR after OH suppression enables us to clearly identify lignin units in humic acids based on cross peaks between aromatic ether carbons and OCH₃ protons. Both lignin and charcoal are present in domains of > 1 nm diameter as shown by a ¹³C T₂ filter. Identifications of quinones and ketones in humic acids will also be reported.

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Characterization of ¹⁵N Labeled Humic Acids from a Nitrogen-tillage-residue Field Experiment

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Soil samples were taken from a Rosemount, MN long-term field experiment where 40 at-% ^{15}N was applied for 15 yr under N-tillage-residue management treatments. The plots were cropped to corn (*Zea mays* L.) for 15 yr, followed by 5 yr of soybean [*Glycine max* (L.) Merr.] with no N applied, and then 1 yr of corn before sampling. The samples represented combinations of till and no-till, with residue-removed or residue-retained, at 2 g N m⁻² as ammonium sulfate. Humic acids (HAs) were extracted using a modified IHSS method, and isolated by membrane-filtration, precipitated, dialyzed, and freeze-dried. Elemental analyses showed minor differences between HAs, with residue-retained samples having slightly higher C and N values. Differences were also noted between residue-removed and residue-retained treatments, for carbohydrates, amino acids and acidity components. FTIR, fluorescence, and CPMAS ^{13}C -NMR spectra provided valuable characterization and compositional information.

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Nitrogen Transformations During a Long-term Incubation

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Inorganic N was determined on a Waukegan silt loam soil during a 2-yr aerobic incubation experiment. ^{15}N labeled soil samples with N fertilization (2 g m⁻²) were taken from 2 different tillage treatments [till (T) or no-till (NT)], and 2 residue management techniques [returned (r) or harvested (h)]. Triplicate samples of 4 treatment combinations were incubated in polyethylene bags at 35° C under constant water conditions. Sub-samples were taken at periodic intervals for NO₃-N determination after extraction with KCl. Extracted samples were converted into NH₄-N by a Mason jar diffusion technique, for analyses of total N and ^{15}N . The initial NO₃-N concentration for Tr and NTr treatments were 70 to 30 mg L⁻¹ higher than the Th and NTh treatments (10 mg L⁻¹). At week 90, the values had risen to 425, 550, 150, and 180 mg L⁻¹ NO₃-N, respectively, with slight increases still occurring. The soil organic pools will be quantified from the kinetics of net mineralization with the simulation model NCSOIL.

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Comparison of CP-MAS ^{13}C NMR Spectra of Aquatic Humics Isolated using Hydrophilic (DEAE-Cellulose) and Hydrophobic (XAD-8) Adsorbents

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Humic substances are ubiquitous in freshwater aquatic environments. Aquatic humic substances can affect the fate and transport of organic and inorganic species through photochemical reactions, adsorption/partition, redox reactions and complexation. These physical and chemical interactions depend on the structural properties of the humic substances. Aquatic humic substances can be isolated/concentrated using a number of different methods e.g. adsorption, solvent extraction, reverse osmosis, freeze concentration etc. Among these methods adsorption chromatography is the most popular method.

We used two well-known adsorption chromatography techniques, which differed in their mode of extraction to isolate humic substances from three water samples collected from the Marcell Experimental Forest Area in northern Minnesota. These techniques were DEAE-Cellulose (a weak anion exchanger which preferentially adsorbs hydrophilic compounds) and XAD-8 resins (a non-polar resin which preferentially adsorbs hydrophobic compounds). We characterized the freeze-dried extracts with CP-MAS ^{13}C NMR spectroscopy on a 400 MHz Chemagnetics spectrometer and UV-VIS spectroscopy. Analysis of the NMR spectra reveals that there are differences in the amounts of ^{13}C functional groups in the extracts from the two techniques. This indicates that the two techniques preferentially isolate certain fractions as opposed to others.

We also isolated humic substances from five water samples collected from the Marcell Experimental Forest Area using the DEAE-Cellulose technique. We characterized these extracts for CP-MAS ^{13}C NMR, UV-VIS spectroscopy, elemental analysis and total acidity. Analysis of the characterization data indicates, that there can be significant spatial variations in the characteristics of the humic substances, collected from the same geographic locale.

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Quinone Mediated Reduction of Dinitroaniline Herbicides in Homogeneous Aqueous Solution

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The widespread use of dinitroaniline herbicides, such as trifluralin and pendimethalin, throughout the Midwestern United States has led to their detection as contaminants in groundwater, surface water, air, and precipitation. Reduction may play an important role in the fate of these compounds in groundwater. This study demonstrates hydroquinone moieties such as juglone within natural organic matter (NOM) are able to mediate the transformation of dinitroaniline herbicides in homogeneous aqueous solution containing hydrogen sulfide. The kinetic experiments were conducted anaerobically in batch reactors, from which pseudo-first-order rate constants, k_{obs} , were obtained and used to describe the initial degradation kinetics of the dinitroaniline herbicides. For the substituted dinitroaniline herbicides, the effect of substitution on the reaction rate could be described by a linear free energy relationship (LFER). By measuring the second-order rate constant, we have estimated the one-electron reduction potential of the four dinitroaniline herbicides. A similar LFER was developed when the reduction of dinitroaniline herbicides was investigated in suspensions containing goethite and ferrous iron. The results of this study suggest reaction rates of the dinitroaniline herbicides with a variety of chemical reductants can be predicted using one-electron reduction potentials.

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