

Abstracts

Section 1: Interaction of organic compounds with NOM Role of Lipids in the Binding of Contaminants to Humins

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The humin fraction of humic substances is the predominant organic material in most sediments; humin organic-carbon typically represents substantially more than 50% of the total organic-carbon present. A significant fraction (typically >50%) of most anthropogenic hydrophobic organic compounds (e.g., polynuclear aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs)) introduced into the sediment environment bind rapidly, and in many cases, irreversibly, to it. Yet very little is known about the actual nature of organic contaminants bound, or the nature of their interaction with humin.

In this study ^{14}C -, ^{13}C -, and ^{19}F -labeled PAHs (naphthalene, phenanthrene and benzo[a]pyrene) and PCBs (4,4-dichlorobiphenyl and 2,2',5,5'-tetrachlorobiphenyl) are incubated with harbor sediments in separate microcosm experiments. This paper presents results which demonstrate that at least 2 binding domains can be observed via solid-state ^{19}F NMR. Sorption experiments show that removal of lipids from the sediment samples increases the nonlinearity of the sorption isotherms.

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Pyrene Sorption by Natural Organic Matter

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A sorption study of pyrene to a series of natural organic matter (OM), which represents a wide range of chemical composition (e.g. high aliphaticity vs. high aromaticity), was performed together with ¹³C-NMR analysis. In this study we have tested the hypothesis that aliphatic moieties of OM derived from soils or sediments contribute significantly to the binding of polycyclic aromatic hydrocarbons (PAHs) in aqueous media. Cuticle and humin samples exhibited the highest distribution coefficients (K_{oc}). Both samples were rich in aliphatic structures and had very low aromaticity (0 and 2.3%, respectively). A positive correlation ($r^2=0.85$) was observed between the total sorbed pyrene and the OM aliphaticity as calculated from the ¹³C-NMR spectra. An opposite trend was observed for the OM aromaticity. Previous studies have concluded that the aromatic content of OM determines the binding of nonionic compounds and that the polarity of OM reduces the binding coefficient of the aromatic OM moieties. This study demonstrates that aliphatic OM compounds significantly sorb pyrene in aqueous solution. Thus, the aliphatic OM moieties can contribute significantly to the sorption of aromatic nonionic pollutants in complex OM matrices.

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LFERs for Polyhalogenated Alkane Transformation by Electron Transfer Mediators in Model Aqueous Systems

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Linear Free Energy Relationships (LFERs) based on Marcus theory were generated for transformation of C₁- and C₂-polyhalogenated alkanes (PHAs or R—X, where X = H, F, Cl, Br) in model aqueous systems containing bulk reductants and the electron transfer mediators iron porphyrin or juglone (5-hydroxy-1, 4-naphthoquinone). The model systems are representative of common natural environments where iron species and natural organic matter serve as electron shuttles from bulk reductants to pollutants such as PHAs. *Ab initio* and semi-empirical computational theories were tested for their ability to generate rapid, accurate, and precise estimates of the R—X bond dissociation energy, the largest energetic term in the Marcus equation. The LFERs that had the highest correlation coefficients for the two model systems were:

$$\log(k_{\text{FeP}}) = -0.0777 (\pm 0.0105) D_{(\text{R-X})} - 0.00804 (\pm 0.00961) G^\circ + 21.7 (\pm 2.82)$$
$$r^2 = 0.953; n=16$$

$$\log(k_{\text{Jug}}) = -0.103 (\pm 0.0308) D_{(\text{R-X})} - 0.00958 (\pm 0.00513) \text{LUMO} + 22.7 (\pm 9.72)$$
$$r^2 = 0.963; n=12$$

$D_{(\text{R-X})}$ is the bond dissociation energy of the R—X bond that dissociates the transition state, G° is the standard free energy of one-electron reduction, LUMO is the lowest unoccupied molecular orbital of the PHA, and the numbers in parentheses are 95 % confidence limits of the regression coefficient estimates. All coefficients in these equations were significant at 90 % C.L. These results support earlier hypotheses based on PHA kinetic results, reaction intermediates, and products in the model systems that the initial, rate-limiting step in the reaction in both model systems is a dissociative one-electron transfer. In the iron porphyrin system the reaction is outer-sphere, whereas in the juglone system the reaction is inner-sphere and X-philic. The study supports earlier studies that showed, for electron transfer reactions involving homolytic bond dissociation, the overall reorganization energy term in the Marcus equation is composed primarily of the bond dissociation energy. Correlation of rate constants measured in related aqueous systems with $D_{(\text{R-X})}$ and G° suggests one-electron transfer limits the rate of disappearance in those systems.

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Interactions of Minerals-Organic Matter-Living Organisms and the Fate of Allelochemicals in Soil

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Allelochemicals are chemicals exuded by plants to protect themselves from adverse environmental conditions and from surrounding plants and microbes. They are, by nature, biologically reactive, and they interact actively with both the mineral and organic components of the soil. These interactions are important processes in soil and can provide further understanding of the dynamics of the active phase of the immobilization processes in soil organic matter transformations. The specific identity of most allelochemicals has not yet been deciphered with certainty. They are commonly associated with the phenolics, terpenoids, alkaloids, and other types of secondary metabolites found in the plant roots or surrounding rhizosphere. In comparison with primary metabolites, these secondary metabolites have not been studied extensively.

The rhizosphere is probably the most reactive region for mineral, organic matter, and living organisms interactions. The allelochemicals exuded into this environment is too reactive to remain intact and stable for any extended period of time. Because of this reactivity, they are also likely candidates as an important contributor to the active phase of the soil organic matter transformation processes. These chemicals are often too transient and elusive to be studied and characterized by traditional methods of extraction and analysis. However, many chemicals suspected to have allelopathic properties have similar features as many synthetic pesticides and xenobiotics. Thus, these xenobiotics can serve as useful model compounds for characterization of the fate of allelochemicals in the soil environment, and methodologies developed for characterizing the fate of xenobiotics have been applied to study allelochemicals. While these cross-over in methodology adaptation have been useful, there is also need to appreciate the differences between the allelochemicals and the xenobiotics in regard to their interactions with the mineral and organic components of soil, especially in the presence of living organisms.

This paper provides a comparison of the processes affecting the fate and transport of allelochemicals and xenobiotics in the soil environment and attempts to point out methodological considerations needed to obtain valid data. Examples will be given to illustrate the reactivity of these chemicals in the presence of minerals, organic matter, and living organisms. The usefulness as well as pitfalls of radioisotope tracing methods will be examined. It is suggested that study of allelochemicals can be fruitful not only in understanding plant ecological interactions, but also in providing an approach for characterizing the process of soil organic matter transformations.

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Application of a General Energy Model for Limited Systems to Adsorption

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Adsorption of a solute or gas on a surface has been described by Freundlich, Langmuir, Brunauer-Emmett-Teller, Frenkel-Halsey-Hill and Harkins-Jura models. Many of these models have been developed to describe adsorption on a relatively rigid and stable surface. Flexible surfaces such as macromolecules like humic substances may expose additional adsorption sites with increasing concentration of adsorbate. Such adsorption isotherms appear as 'stair step' curves when plotted as a function of concentration. By combining the Arrhenius and Mitscherlich models, a general energy model for limited systems (GEMLS) is described that may be applied to adsorption studies of flexible surfaces. With this model, adsorption is viewed as an exchange reaction between a weakly adsorbed substance and the adsorbate of interest. In GEMLS, the coefficient of adsorption is a measure of the energy exchanged. The critical concentration represents that portion of the surface already occupied by the same substance or one having a similar exchange energy. The function coefficient represents the total adsorption capacity. By combining GEMLS functions, estimates of the change in surface area due to flexible rearrangement are obtained.

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Identifying Anthropogenic Markers in Natural Organic Matter Using Pyrolysis-GC/MS

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Water scarcity has become a worldwide problem due to rapid population growth and booming industrial and commercial development. This poses an increasing need for water reuse. In the Western United States, most cities obtain their drinking water from a supply that is an ensemble of wastewater effluents from other cities.

Given the large number of compounds potentially present in wastewater, our general inability to analyze for all but a small percentage of them, and the lack of toxicity information for many of the chemicals, the organic matrix present in wastewater effluents pose one of the most serious challenges to public health officials. In addition, secondary biological treatment leaves a mix of organic compounds that are very susceptible to chlorine substitution. Therefore the chlorination of wastewater may lead to the formation of disinfectant by-products (DBPs) which are considered to display some cancer risk. Current drinking water standards are not intended to ensure the safety of reclaimed water associated with wastewater derived organic matter. Since we cannot quantify or have not identified specific wastewater compounds of concern, there is a need for a method that can identify the dissolved organic mixture associated with treated wastewaters and that can track its fate in surface water systems. Pyrolysis-GC/MS has been used in this way to monitor the quality of wastewater impacted surface waters that are used as drinking water sources. In addition, this method has also been employed to follow the transformation or persistence of wastewater organic signature in a constructed wetlands used to enhance the quality of a surface drinking water source.

In pyrolysis-GC/MS, four liters of each water sample were filtered through 0.45 μm glass fiber filters and concentrated down to about 3 milliliters. Microsamples of the concentrates were loaded into quartz tubes to a final amount of approximately 1 mg of carbon per tube. Once dried, samples were thermally degraded (pyrolyzed) in an inert environment (chromatographic grade helium) under controlled condition and rapid temperature ramp. Under these conditions, the scission and rearrangement of certain bonds and linkages occurred in a reproducible and predictable manner, while other types of bonds were resistant to cleavage, *i.e.* aromatic. The volatile products were then swept onto the polar GC column to be separated. The GC retention indices and MS spectra were used to identify fragments to produce a characteristic fragmentation pattern or fingerprint of the parent material making up the sample.

We will present two examples describing the use of pyrolysis-GC/MS to characterize the impact of treated wastewater discharge on the organic quality of surface waters used as drinking water sources. In the first example, we characterized the quality of a river system used by a number of cities as drinking water source and various discharges to the system over the course of various seasons. The results showed that the downstream river quality was not equivalent to the upstream quality. We have identified the major attributes of the samples as a function of season and source. In addition, we have characterized the persistent features of the wastewater impact to the river and illustrated how it dominates downstream quality in all seasons. In the second example, pyrolysis-GC/MS was used to monitor the organic matrix of a river that is dominated by highly treated, nitrified tertiary effluent as it flowed through a constructed wetlands. Pyrolysis-GC/MS data showed that the chemical fingerprint of this river was typical of surface waters heavily influenced by wastewater discharge, whereas most samples of the wetlands effluent displayed a distinct biological signature. The constructed wetlands, then successfully transformed the anthropogenic signature.

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Section 2: Characterization of NOM components

A New Understanding of Humic Substances Using Modern NMR and Pyrolysis G.C. Mass Spectrometry

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The advent of modern analytical methodologies, namely nuclear magnetic resonance, pyrolytic methods coupled to gas chromatography and mass spectrometry, and thermochemolytic methods have provided a wealth of new structural information that has allowed for a more advanced understanding of the chemical structure and reactivity of humic substances in soil. For example, solid-state ^{13}C NMR has demonstrated the presence of significant aliphatic components in many humic substances and the relative contribution of these varies widely among humic substances from differing environmental settings. Also, pyrolytic methods have reinforced this view and provided additional molecular-level details of structure. The advent of thermochemolysis or *in situ* methylation of pyrolysis products has partially overcome the quantitative drawbacks of pyrolysis and provided complementary information that can be used in conjunction with conventional pyrolysis to obtain a more comprehensive evaluation of structural entities.

In this presentation, the combined techniques of NMR, pyrolysis, and thermochemolysis are used to compare the structures of various soil and sedimentary humic substances. These are then compared with current understanding to show how the combined approach has been useful in depicting more realistic structures and how much more we've learned about humic substances in recent years. Knowledge regarding the geochemical transformations of plant biopolymers is integrated into the model development.

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Capillary Electrophoresis: A New Tool for the Characterization of Natural Organic Matter

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Natural Organic Matter (NOM) is an important component in the chemistry of natural waters; however, despite many years of work on humic substances we still have only a very limited understanding of their structure and reactivity. Development of innovative and effective methods for characterizing NOM is needed. Capillary electrophoresis (CE) is a relatively new analytical technique that separates chemical species based on differences in electrophoretic mobility, which is affected by both molecular size and charge. Because NOM is composed primarily of anionic macromolecules, CE appears to be an ideal separation method for use in NOM characterization. Potential advantages of CE for NOM characterization include little or no sample pretreatment requirements, relatively short analysis times (10 to 30 minutes), small sample size, and ease of CE system operation and maintenance.

The main goals of this research are to develop methods for characterizing NOM from aqueous sources using capillary electrophoresis (CE) and to use these methods to evaluate the impact of NOM composition on important environmental reactions. Specific objects include:

- 1) develop a method or methods for characterizing NOM by testing various modes of CE operation using model macromolecules and standard NOM samples;
- 2) use the CE methods to evaluate the composition of a variety of NOM sources representing a broad spectrum of NOM composition; and
- 3) develop correlation linking NOM composition to reactivity with chlorine and the corresponding production of disinfection by-products

Capillary zone electrophoresis (CZE) results were obtained for model macromolecules, standard humic substances, and five different aquatic NOM samples. The measured electrophoretic mobility of a standard fulvic acid sample was greater in magnitude than a standard humic acid sample at pH 8.3. These results are consistent with what is known about the structures of humic and fulvic acids in that humic acids tend to have higher molecular weights and a lower proportion of carboxylic acid groups than fulvic acids. In addition, the NOM from two "brown water" lakes had similar electrophoretic mobilities. The aforementioned samples were also analyzed using capillary gel electrophoresis (CGE), which separates compounds on the basis of differences in molecular size. As expected, the molecular weight of the humic acid sample determined by CGE was greater than that for the fulvic acid sample. The two "brown water" lake NOM samples had higher molecular weights than the other NOM samples, which suggests that they have higher humic content.

Trihalomethane formation potential (THMFP) results were obtained for the aforementioned samples and the corresponding hydrophobic fractions of each sample. The results show that the hydrophobic fraction is the main contributor to THMFP and that the humic acid sample had much higher THMFP than the fulvic acid sample. The two "brown water" lake samples had similar THMFP. The THMFP results agreed with the qualitative structural information obtained from the CGE and CZE analyses. Finally, the THMFP was also observed to correlate with specific UV absorbance (UV absorbance at 254 nm normalized by total organic carbon concentration).

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The Application of Multi-Dimensional NMR to the Study of Soil Humic Substances

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Humic substances are the most abundant organic macromolecules in soils and comprehension of their chemical structure is essential to understanding their role in terrestrial ecosystems. The one-dimensional nuclear magnetic resonance (NMR) spectroscopy techniques now widely used to study humic substances have provided important insight into humic structures, but the complexity of these macromolecules gives rise to resonance signals that are broad and have spectral overlap. This has prevented the definitive functional group assignments necessary for structural determination. Hence, interest has focused on more powerful two-dimensional NMR experiments, such as the homonuclear **T**otal **C**orrelation **S**pectroscop**Y** (TOCSY) and **H**eteronuclear **M**ultiple **Q**uantum **C**oherence (HMQC), which were employed in the study of a soil humic acid standard. The purpose of this paper is to outline the potential of the techniques to the study of soil humic structures. The 2-D spectra produced were extremely encouraging with multitudes of crosspeaks produced from both TOCSY and HMQC experiments. The identification of fatty ester/acid chains and amino acid couplings are given as examples. Results obtained with these NMR experiments indicate substantial improvements in functional group assignment capabilities and the potential for marked progress in the determination of the chemical structure of soil humic substances.

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Session 3: NOM in Natural Systems

Predicting DOC Generation from Wetlands

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It is desirable to be able to predict DOC concentrations and characteristics in natural waters in order to predict metal speciation and toxicity, transport of organic pollutants, and energy budgets for ecosystems. Existing predictions are based on the total area of wetlands within catchments. This approach towards prediction ignores the differences among wetland types. The study discussed here entailed sampling of 180 sites from 15 wetland types in the Upper Peninsula of Michigan for DOC concentrations and chemical characteristics. Fluorescence and absorption properties of the DOC also were examined. Multi-variate statistics revealed no relationships between wetland classification and DOC concentration, although a coarser (i.e., less detailed) classification of wetland can predict DOC concentration ranges. The DOC characteristics varied systematically among wetland types. Concentrations of DOC were correlated with polyvalent cation content. Wetlands appear to function analogously to mineral soils; DOC is retained when polyvalent cations are present to induce flocculation and binding to soils. The sorption process selectively retains some fractions of DOC.

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Effects of Fulvic Acids on Lead Uptake and Transport by Sunflowers

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Sunflower (*Helianthus annuus*) seedlings were exposed to lead concentrations of 30, 60, and 120 ppm in hydroponic solutions with and without fulvic acids, to determine uptake and transport of lead. After 3 days exposure, plants were harvested, divided into root and shoot portions, and analysed for lead.

In the absence of fulvic acids, Pb concentrations were highest in whole plants exposed to higher lead levels, but uptake was not proportional to exposure concentration. Root concentrations were 10 fold higher than shoot concentrations, but did not vary significantly among Pb exposure levels, indicating an uptake/storage limitation. Shoot concentrations were directly proportional ($R^2=0.98$) to exposure levels, with 10 - 27% of the absorbed lead translocated to the shoots.

In the presence of fulvic acids, plants absorbed similar concentrations of Pb, regardless of the Pb exposure levels. At low exposure levels, fulvic treated plants absorbed similar concentrations as control plants. At higher Pb exposure levels, control plants absorbed significantly more lead than fulvic treated plants. No significant differences were observed in root Pb concentrations of fulvic treated plants compared to controls. However, the translocation of lead from roots to shoots was significantly greater in fulvic treated plants, especially at lower Pb exposure levels, where up to 40% of the absorbed Pb was found in the shoots.

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Tracer Carbon Dynamics After a Shift to Continuous Corn

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Long-term field experiments with measured ¹³C abundance give among the best analysis and prediction of soil management impacts on soil organic carbon (SOC). SOC and ¹³C abundance ($\delta^{13}\text{C}$) were sensitive to tillage, corn stover, and N management during 13 years of continuous corn (*Zea mays* L.) after a long history of low input pasture and hayland to a C₄ corn crop after a C₃ crop history. Tillage systems were: no-till (NT), chisel (CH), and moldboard (MB) without secondary tillage. Corn stover was either returned or removed. The N rates were 0 and 200 kg N ha⁻¹ (high rate). There were 12 combinations of these treatments. Soil samples for SOC and $\delta^{13}\text{C}$ in the 0 to 15-cm and 15 to 30-cm depths were taken each spring after planting. SOC accumulation in the 0 to 30-cm layer was sensitive to all three inputs, but NT accumulated while the annual tillage systems, especially MB, reduced SOC. $\delta^{13}\text{C}$ increased linearly with time but at a different rate depending on tillage system, stover return, and N rate. Corn-derived SOC was not sensitive to N rate, increased from 5 to 15% with stover return in NT, and averaged 10% in the annual tillage systems. Except in the NT, the efficiency was much lower when stover was returned to an expression of greater root resistance to decomposition. Half life for decomposition of the relic SOC was especially sensitive to how the N fertilizer and current corn residue were separated in the tillage system.

A sensitivity analyses with the simulation model NCSWAP calibrated on the naturally occurring ¹³C tracer characterized the contribution of below ground corn photosynthate into SOC. Simulation of the N and C transformations in the layered soil was performed by NCSOIL embedded in NCSWAP, which was calibrated using above ground biomass, root biomass distribution in the soil, SOC, and $\delta^{13}\text{C}$ over the 13-yr period of corn production in the CH tillage. Six units of photosynthate-C translocated as exudates were required per unit translocated into the root. Efficiency of corn derived SOC was based upon only 32% of the net primary production translocated to the root biomass.

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Session 4: Metal Interactions with NOM

X-Ray Mass Spectroscopy Studies of Metal Ion Binding in Various Soil Organic Fractions

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Atmospheric deposition of anthropogenic mercury Hg has resulted in a rise in Hg concentrations in surface waters of forest and wetland ecosystems at northern latitudes, and fish frequently accumulate Hg at levels above health recommendations. The predominant form of Hg under most environmental conditions is Hg²⁺, but methyl Hg (metHg) is very important because Hg²⁺ can be transformed into metHg, a very toxic form of Hg which strongly bioaccumulates. The bonding of Hg²⁺ and metHg in soil and aquatic organic matter is very important in controlling the transport and biological reactivity of Hg. In studies using a competitive Br⁻ complexation method and x-ray spectroscopy, we found that Hg²⁺ is bonded very strongly to soil organic matter (SOM) at RSH sites. Using data for reduced S concentrations, determined by x-ray absorption near-edge spectroscopy (XANES), we determined model dependent surface complexation formation constants, at native Hg concentrations. The constants for SOM were consistent with solution complexation constants for mercaptoacetic acid. Hg extended x-ray absorption fine structure (EXAFS) spectral data yielded bond distance values that are consistent with the participation of both O and reduced S in the bonding of Hg²⁺.

The bonding of Hg²⁺ to NOM was studied in a peat soil obtained from the edge of a fen in the Marcell Experimental forest in Northern Minnesota. Mercuric nitrate was added at Hg to reduced S mole ratios in the range of 0.5:1 to 10:1. EXAFS was used to determine the changes in bonding with the increase in the quantity of Hg²⁺. At a Hg: reduced S ratio of 0.25 the EXAFS radial structure function shows a 2-coordinate environment involving one reduced S atom and one O atom. At this loading the two peaks were well resolved and interatomic distances corresponded to the bond lengths for Hg-O and Hg-S bonds. At a ratio of 0.81:1 both the S and O peak were broadened but the relative magnitudes of the two peaks was unchanged. At a ratio of 8:5:1 the O peak was very predominant and the S peak was hardly visible. At this ratio there is only enough reduced sulfur to bond with less than 12% of the added Hg and the quantity of Hg in the SOM is more than 10,000 greater than for *in situ* soil organic matter. When Hg²⁺ is added greatly in excess of the reduced S the bonding of the additional Hg²⁺ is to O sites. This accounts for the low binding constants found in laboratory studies by previous workers who used high Hg²⁺ additions.

We have some EXAFS spectral data for metHg in a thiol resin and in humic acids. The humic acid data suggest that at low pH metHg is bonded predominantly to reduced S, but at higher pH values binding to N sites may be very significant.

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The Role of Natural Organic Matter in the Complexation of Ionic Copper in an Oxisol

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Natural organic matter, NOM, is known to have a substantial influence on trace metal binding to individual soil minerals and to many soils. However, our research involving suspended and bed sediments in streams contaminated with acid mine drainage suggests a minimal role for NOM in metal sorption to such sediments. We hypothesized a similar lack of influence for NOM in other systems characterized by abundant presence of Al and Fe oxyhydroxides, in particular, oxisoils. Accordingly, copper complexation was measured in a Typic Acrustox soil from an area near Brasilia on Brazil's central plateau. At the study location, samples from the top six meters of a soil profile were obtained. The samples were subsequently characterized for mineralogy, elemental composition, NOM content, pH, and cation exchange capacity. In the laboratory, the hypothesis was verified after examination of sorption edges and isotherms for copper complexation to samples from three selected horizons and various operationally defined fractions of the sample from the soil surface horizon.

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Plant Growth Promoting Activity of Humic Substances

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Studies on the effects of humic substances (HS) on plant growth, under conditions of adequate mineral nutrition, consistently show stimulative effects on plant biomass. Enhancement of root growth was usually more apparent than stimulation of shoot growth. Both increase in root length and development of secondary roots have been observed for HS in nutrient solutions. Typical response curves showed enhanced growth with increasing HS concentration, followed by a decrease in growth at high concentrations. Shoots generally showed similar trends in growth response to HS. Some researchers attributed the stimulative effects of HS to higher uptake of nutrients. Others, however, suggested that hormone activity of HS promotes plant growth. A small fraction of lower molecular weight components of HS can be taken up by plants. These components are considered to increase cell membrane permeability and to exhibit hormone-like activity.

In soils, addition of composts was found to stimulate growth beyond that provided by mineral nutrients, presumably because of the effects of HS. The hypothesis that HS originating from various sources contain plant growth hormones was tested recently. The results will be discussed, in light of supporting literature data, that plant growth enhancement results from increased nutrient availability, due to their chelation by HS. The application of HS to golf courses and sports turf is widespread, due to an increasing demand for high quality turfgrass, high cash returns and environmental concerns advocating reduced fertilizer use. Present research focuses on the activity of laboratory-grade and commercially prepared HS on root and shoot growth of creeping bentgrass (*Agrostis palustris*, Huds., cv. Providence) and ryegrass (*Lolium perenne* L., cv. Omega), in growth chamber microsystem experiments.

A novel screening system for HS effects on corn (*Zea mays* L.) and soybean (*Glycine max* L.) plants grown in nutrient solution will also be described. Our results indicate that the system is responsive to nutrient and HS dynamics. Specific HS samples gave significant increases in grass root and shoot growth over fertilizer controls. Larger scale greenhouse experiments in simulated golf green mixes of sand or sand/peat showed some HS products to be effective turfgrass growth promoters. The feasibility and impact of HS utilization in agriculture and horticulture will be discussed.

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On the Ubiquity of Humic Substances in Aquatic Processes.

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Humic substances affect numerous chemical and biological processes and play a myriad of roles in aquatic ecosystems. This paper illustrates the diversity of these effects and roles by using examples from the author's past research, which are linked to a variety of ongoing studies. For example, humic substances affect basic lake typology, including trophic states of lakes. Evidence for this includes greatly different chlorophyll-phosphorus relationships in colored versus uncolored lakes. Humic material is a potential interference in monitoring lake clarity and chlorophyll levels by satellite imagery, and ongoing studies to circumvent this problem will be discussed. Humic substances also play important roles in the organic and inorganic photochemistry of aquatic systems, serving as both photosensitizing and scavenging agents. The role of humic material in the photochemistry of iron, hydroxyl radicals and mercury will be described. Humic substances are well known as important complexing agents for heavy metals in both soils and aquatic systems, but scientists long have had difficulty quantifying this process because of analytical difficulties and the inherent heterogeneity of humic material, which leads to the fact that complexation cannot be characterized in terms of a single binding constant. Some approaches to circumvent these problems will be described briefly. Finally, humic materials affect many biological processes in aquatic systems, including the bioavailability of metals. This will be illustrated by examining the effects of humic material on bioaccumulation of mercury and methylmercury by zooplankton.

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Poster Abstracts

Effects of Sunlight on the Bioavailability of Limnetic and Marine Dissolved Organic Matter

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Filtered lake and seawater samples collected from different depths in Lake Superior and the Gulf of Mexico were exposed to sunlight. Subsequently, these samples were inoculated (1:10) with unfiltered surface water, and bacterial growth rates were measured by ³H-leucine incorporation into bacterial protein in the dark. Exposure of dissolved organic matter (DOM) collected from surface layers to sunlight caused a net reduction in the bioavailability (bacterial growth ~40% of dark control). Exposure of DOM collected from below the euphotic zone to sunlight resulted in a net enhancement in the bioavailability (bacterial growth ~150% of dark control). The net effect of photochemical alterations of both limnetic and marine DOM on bioavailability appeared to depend on its origin and composition. Photochemically driven processes are involved in the production of labile as well as refractory organic matter and thus play a critical role in the cycling of the carbon reservoir within lakes and the ocean.

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Influence of Organic Matter on the Sorption of Hydrophobic Organic Compounds by Soil Micro-Aggregates

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The sorption of naphthalene (NAP) and phenanthrene (PHE) to two bulk soils and to clay, and coarse silt-, and fine silt-size micro-aggregates separated from each soil was evaluated using sorption isotherms. The influence of organic carbon content (OC) and nitrogen specific surface area (SSA) of the sorbents on the sorption of NAP and PHE was inferred from modified Freundlich coefficients (K_f') and Freundlich exponents (n) obtained from the sorption isotherms. The K_f' values for both NAP and PHE strongly correlate with OC but not with SSA. The K_f' values were higher for the fine silt fraction of each soil due the higher OC. The deviation from isotherm linearity (indicated by n) was greater for PHE ($n = 0.5$ to 0.7) than for NAP ($n = 0.7$ to 0.9). Desorption hysteresis of both NAP and PHE was insignificant for all the sorbents. Despite deviations from isotherm linearity, sorption of NAP and PHE at aqueous equilibrium concentrations ranging from low to high is strongly correlated to OC.

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Humic Stimulation of Hydroponic Tomatoes

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This preliminary experiment tested the hypotheses that: 1) humic substances will stimulate the growth and yield of tomatoes grown under hydroponic conditions; 2) different humic fractions and concentrations will have different effects; and 3) foliar application will affect tomatoes differently compared to root application. Humic fractions were extracted from reed-sedge peat at pHs of 3.5, 8.0 and 12.0. Extracts containing humic concentrations of 50, 100 and 200 ppm were added to some vermiculite bags containing the hydroponic solutions. Tomato plants in other bags (treatments) received the three humic fractions/ concentrations via foliar sprays. Humic treatments of tomatoes were initiated at the seedling stage, when plants were placed in the hydroponic bags, and continued through harvest of tomatoes. Chlorophyll contents of tomato leaves, stem diameter and tomato yields were monitored throughout the experiment; root lengths were measured at the end of the experiment.

The treatment of tomato plants by either foliar or root application of humic substances produced significant increases in stem diameter and tomato yields, and variable effects on chlorophyll content of leaves. Root application of humic substances produced significantly greater root lengths, and the greatest increases in tomato yields. Root treatment with pH 3.5 extract produced the greatest tomato yields, followed by foliar treatment with pH 3.5 extracts.

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Sulfur in Biosolids Fulvic Acid: Characterization by XANES Spectroscopy and Wet-Chemical Analyses

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Sulfur-containing ligands in biosolids fulvic acid (BFA) may play an important role in determining the fate and transport of metals in soil. To understand the chemistry of S in BFA, we used wet-chemical analyses and x-ray absorption near-edge structure (XANES) spectroscopy to estimate the major classes of S (C-bonded and ester S) and oxidation states of S in BFA, respectively. The BFA was fractionated into total hydrophilic (Hi), hydrophobic acid (Hb), and hydrophobic neutral (Hn) fractions using XAD-8 resin. The wet-chemical analyses show that ester S is a dominant class of S in the Hi fraction, whereas C-bonded S was dominant in the Hb fraction. The XANES results suggest that oxidized forms of S are dominant in the Hi fraction, whereas reduced forms of S are dominant in the Hb fraction. Neither wet-chemical nor XANES indicated a trend in S classes or oxidation states in the Hn fraction. Our results clearly show that BFA fractions separated by XAD-8 resin contain distinct classes and oxidation states of S, which could influence their role of BFA in metal complexation.

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Fluorescein Diacetate Hydrolysis of Native and Cropped Soils of the Brazilian Cerrado

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The biological component of soil is key to many soil processes and overall soil quality. Soil enzyme assays can be used as soil quality indicators since they are closely related to other soil quality parameters and processes and can indicate change much sooner than other parameters such as organic carbon. We measured fluorescein diacetate (FDA) hydrolysis on native and cropped soils from the Brazilian Cerrado. No-till cropping systems maintained higher enzyme activity in the topsoil compared to conventional tillage systems. In soils from the native Cerrado, soils within the same treatment varied considerably indicating variability in the soil biology between similar sites. Fluorescein diacetate hydrolysis is a sensitive indicator of general soil enzyme activity and may be useful in tracking soil quality changes due to management or disturbance.

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Investigation of Copper Sorption Domains of Natural Soil Organic Matter

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Natural soil and sediment organic matter is considered an important sorption domain for heavy metal contaminants in environmental systems. Copper, in particular, is thought to preferentially associate with humic-type natural organic matter through complexation, chelation, or sorption to carboxylic organic functional groups. This research investigated copper sorption to two humic-type soils and two peat samples. Superheated (250C) liquid water was used as an extraction medium to selectively remove humic functional groups from soil and peat organic matter. This technique has been shown to eliminate carboxylic acid functionalities from soil and peat matrices, as evidenced by solid state ^{13}C - NMR and FTIR. Copper isotherms measured at pH 5.5 for a humic soil were identical to the isotherms for the same soil after superheated water extraction. Thus, elimination of carboxylic acid functional groups did not effect copper sorption to the soil, indicating that carboxyl organic functional groups were not significant binding sites for copper ions. Furthermore, the four humic-type geosorbents were contaminated with copper and then subsequently extracted with superheated water. In this case, superheated water extraction removed less than 2% of the bound copper from any of the four contaminated sorbents, even though this technique completely extracted the carboxylic functional groups. Superheated saltwater with 0.05 molar calcium chloride, on the other hand, extracted between 60 and 100 percent of the sorbed copper, suggesting that copper ions are preferentially bound to cation exchange sites.

Further work is underway to characterize copper binding sites on the humic soils and peat samples, but research to this point has at least revealed that copper does not significantly associate with carboxylic acid functional groups of natural organic matter.

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Natural Abundance Isotope Identification of Carbon in Earthworm Casts

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The role of earthworms in cycling carbon from plant residues into soil organic matter and CO₂, has been known for eons. Soil organic matter is affected by ingestion and translocation and by the mixing and enhanced microbial respiration which occurs within the earthworm gut. Cast from three common earthworm species *Aporrectodes tuberculata*, *Lumbriscus rubellus* and *Lumbriscus terrestris*, which range from a small surface dweller and feeder to a large surface-feeder and deep-dweller, were collected periodically and frozen immediately for later analysis of total and isotope carbon. Individuals of each species were incubated in three soils ranging in carbon content between 1.5 to 3.0 percent. The earthworms were fed either corn or soybean residues for several weeks. Results indicate that the fecal deposition carbon content can be doubled and the increase is related to the relative consumption of soil and residues and that the increased carbon in the worm casts is entirely due to fresh residue.

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Strong Interactions Between Aqueous Humics and Synthetic Surfactants not Observed.

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The literature on humic substances has many mentions of certain surfactant-like characteristics of humic acid. Since synthetic surfactants are sometimes used for polluted soil clean-ups, possible interactions between humic substances and synthetic surfactants were investigated. Humic acid, (Savannah River, Aldrich Chemical Co.), and fulvic acid, extracted from peat using a standard method, were used. Fluorescence and viscosity were used to monitor the critical micelle concentration (CMC) of aqueous solutions of synthetic anionic and cationic surfactants in the presence of various amounts of humic and fulvic substances. The results indicate that the presence of humics or fulvics does not greatly change the CMC's of the surfactants tested.

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Reactions of S(II) and NOM in Water: A Study Employing the Natural Naphthoquinone, Juglone

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Under sulfate-reducing conditions, humic substances can react with reduced inorganic sulfur forms through addition reactions. The addition, under ambient conditions, of hydrogen sulfide onto α,β -unsaturated carbonyl compounds that are found in humics has been demonstrated in earlier studies in the laboratory. We studied the addition of hydrogen sulfide onto 1,4-hydroxynaphthoquinone, or juglone, a quinone found in plants that facilitates electron transport and photosynthesis. In parallel experiments, we examined the reactivity of juglone with respect to transformations of polyhalogenated alkanes, which are often found at contamination sites.

Electrochemically-reduced juglone was unreactive with respect to reductive dehalogenation of hexachloroethane. However, aqueous solutions containing juglone and hydrogen sulfide were reactive in reductive dehalogenation of the polyhalogenated alkanes including hexachloroethane. The increased reactivity in the latter system appears to be caused by a mercaptojuglone hydroquinone addition product, which is expected to have a lower reduction potential and higher nucleophilicity than juglone hydroquinone. Products of the addition reaction were separated and characterized using ^1H and ^{13}C nuclear magnetic resonance spectroscopy, by X-ray photoelectron spectroscopy, and by derivatization followed by high performance liquid chromatography-fluorescence detection. The structure of the observed product and the influence of pH on the yield of the addition reaction will be presented. The results suggest that either a 1,4-Michael addition or a radical addition reaction mechanism most likely occur. This study demonstrates the need to study biogeochemistry in disturbed environments in order to understand the transformation of organic xenobiotic compounds in such environments.

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