

## Solubility controls that determine dissolved organic matter composition of surface- and ground-waters

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Various studies of organic precursors, diagenesis, and removal by water treatment of dissolved and colloidal organic matter in diverse surface- and ground-waters found dissolved organic matter (DOM) to be derived from amino sugar, condensed tannin, lignin, and terpenoid precursors. Terpenoid-derived DOM is not removed by sorption on sesquioxide coatings during infiltration of surface water into groundwater, and is not removed by water-treatment flocculation with ferric and aluminum salts (Leenheer et al., 2003). "Black waters", such as the Suwannee River, contains DOM derived from condensed tannins (Leenheer and Rostad, 2004) which is almost completely removed by water-treatment flocculation with ferric and aluminum salts (Croue et al., 2000). Recent studies of fulvic acids isolated from wheat straw (Wershaw et al., 2003) and from the Neversink Reservoir water supply of New York City found methoxy-lignin structures that did not bind to iron and aluminium sesquioxides. Therefore, both fulvic acid ligand structures and mineral coatings containing iron and aluminum sesquioxides act as solubility controls on DOM concentrations and composition in natural water.

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## A new understanding of reactivity and composition of humic substances using modern NMR and electrospray ionization mass spectrometry

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The advent of modern analytical methodologies, namely nuclear magnetic resonance (NMR) and electrospray ionization coupled to ultrahigh resolution mass spectrometry (MS) have provided a wealth of new structural information that has allowed for a more advanced understanding of the chemical structure and reactivity of natural organic matter (NOM) from a variety of environments. 1- and 2-D solution NMR techniques have demonstrated the presence of some new types of components from humic substances in different environments. Polyhydroxylated alicyclic structures are clearly noted as having proteinaceous origins and carboxylated condensed aromatic structures are probably derived from soot and charcoal (black carbon). Electrospray ionization MS has opened the door to obtaining detailed elemental compositions for nearly all ionizable components of NOM. With ultrahigh mass accuracy we can assign unique elemental formulas to the vast number of peaks observed. We can clearly differentiate black carbon components, from lipid-like substances, and from other biochemical components that contribute to NOM. We find that a significant amount of black carbon comprises NOM.

## Sulfide ligands in natural organic matter (NOM)

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Group B metals, such as Hg, Cu, Ag, Pb and Cd bind strongly to reduced inorganic and organic S(II-) ligands [1]. Most trace metal speciation studies until recently have been at elevated (micro-molar) metal concentrations and have blurred the effect of M-S binding for natural occurrences (pico- to nano-molar). S(II-) ligands in oxic waters are shown to exist at the 10-100s nM concentrations [2], and these ligands suppress the toxicity of Group B metals significantly [3].

We have developed a procedure for the determination of metal bound sulfides by use of Cr(II) and a purge/trap method [2]. The resulting chromium reducible sulfide (CRS) does not detect those thiolates found in nature. CRS has been shown to be equivalent to strong total ligand,  $L_T$ , that has been determined by competitive ligand titration scheme using Ag as the probe metal [4], for waste water plant effluent.

S(II-) ligands are associated with organic matter. There is a linear correlation of CRS (nM) with organic C (mg C/L) (OC). The slope of CRS-OC is 14.9nM CRS/mg C ( $r^2=0.75$ ), reflecting about 0.02 % S ligand in NOM. The scatter of the slope is quite large, however, suggesting direct measure of CRS is needed for accurate and specific results. The CRS is postulated to reflect an M-S coordination ( $M = \text{Cu(I)?}$ ) in NOM.

We used Ag as a metal titrant in a competitive ligand setup to determine the conditional binding constant,  $\text{Log } K'$ , for Ag and strong ligand.  $\text{Log } K'$  values decreased linearly with fraction of  $L_T$  filled from 12 to 8.8 for rivers, but were nearly constant for waste water treatment effluent ( $\text{log } K' = 11.3$ ).

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## Stochastic synthesis of DOM: Predicting Cu(II) complexation from precursor structures

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Equilibrium models of metal complexation by dissolved organic matter (DOM) typically are calibrated using experimental measurements from metal-DOM solutions. These models can represent the binding data quite well, but the model parameters are not easily interpreted on a molecular level. In addition, DOM from different sources with significantly different binding properties must be calibrated separately.

A stochastic, agent-based model of DOM synthesis from precursor molecules has been devised which treats DOM as a complex mixture of interacting molecules, each with a (potentially) unique structure. A quantitative structure-activity relationship (QSAR) using the same data model predicts the  $\text{log } K_{\text{Cu}}$  of well-defined ligands with  $r^2$  of 0.89 for a calibration data set which ranges over 14 orders of magnitude. This QSAR is used to predict  $\text{log } K_{\text{Cu}}$  of the molecules in simulated DOM samples, and these values are then used to predict Cu(II) complexation. Simulations beginning with small organic precursors (tannins, terpenes and flavonoids) produce N-poor DOM with Cu(II)-binding behavior similar to Suwannee River fulvic acid. Simulations beginning with biopolymers (protein, lignin) produce N-rich DOM with stronger Cu-binding behavior similar to that observed in the field. In the former simulation, but not the latter,  $\text{log } K_{\text{Cu}}$  correlates with molecular weight.

This agent-based model calibrated on known ligands currently fits experimental data less well than empirical models calibrated on NOM-metal equilibrium data, but has the advantages that 1) specific binding sites have structural properties which can be interpreted on a molecular level and 2) different ecosystems and DOM treatments produce distinct Cu-binding behaviors without separate calibration.

## Modelling metal-gill interactions and metal toxicity to fish: The influence of natural organic matter source

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Natural organic matter (NOM) binds metals, decreasing the amount of metal binding to fish gills and therefore decreasing metal toxicity to fish. Work from my laboratory has shown that optically darker, more allochthonous NOM binds metals like Cu, Pb, and Al better than does optically lighter, autochthonous-like NOM, as judged by metal binding to gills of rainbow trout (*Oncorhynchus mykiss*) and by metal toxicity to trout. In these experiments, NOM was isolated by reverse osmosis from diverse sources and added at up to 10 mg C/L. A good index of NOM source is the Specific Absorbance Coefficient (e.g., SAC<sub>340</sub>). Excitation-Emission matrix spectroscopy is also a good method to characterize NOM. In contrast to the results with Cu, Pb, and Al, NOM source appears to have minimal influence on the degree of inorganic Hg, Ag, and Cd binding to fish gills. The pattern appears to be that metals which bind more strongly to fish gills (higher metal-gill log *K* values) than to NOM (lower metal-NOM log *K* values) are not influenced as much by NOM source. These results have important implications for developing Biotic Ligand Models, which integrate water chemistry and organism physiology to better predict metal interactions with aquatic organisms.

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## Metal-organic matter interaction: Ligands as a functional group in oceanic DOM

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There is little understanding of ecological roles of oceanic dissolved organic matter (DOM) except one of food chain of marine bacteria. Chemical speciation studies revealed that trace metals (Cu, Fe, Zn and others) dissolved in seawater form complexes with binding sites (ligands) in DOM. However, we have no information about why most of the dissolved trace metals are associated with dissolved organic ligands (DOLs). In order to have better understanding of ecological roles of metal complexes in seawater, it is necessary to know chemical forms of DOLs in seawater. According to present knowledge of the DOLs being bound with metals in seawater, two classes of the DOLs coexist in seawater, which are classified as type-I (DTPA) and type II (EDTA) ligands.

We carried out speciation of the DOLs using estimated conditional stability constants of metal complexes with the DOLs in seawater. The results reveal that major part of the DOLs in seawater exist as complexed form, in which major species of the EDTA type ligand are Ca and Mg complexes. Therefore, only several percents of total ligand concentrations in sea water are present as non metal-binding forms. This finding suggests that free ligand concentrations in seawater, which are linearly related to the total ligand concentrations, show no drastic change due to variations of the ligand and trace metal concentrations because of constancy of Ca and Mg concentrations in seawater. To be controlled the free ligand concentrations in seawater means that free trace metal concentrations in seawater are controlled at optimal levels in growth of marine organisms.

## Organo-colloidal control on trace element distribution in shallow groundwaters: Fingerprinting by ultracentrifugal cells

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Dissolved Organic Matter (DOM) is ubiquitous in aquatic environments and plays a key role in the geochemistry of major and trace elements - acting as a major carrier and transport phase - through complexation, adsorption, dissolution ... reactions. It both does interact with mineral phases modifying the exchange rates with solutions and constrain part of pollutant mobilities such as that of trace metals or hydrophobic organic compounds. Not only does association with DOM influences the mobility of metals through the soil/water system, it also affects their bioavailability and toxicity.

In DOM-rich soil waters, Rare Earth Element (REE) and other trace element concentrations seem to be controlled by seasonal dynamics, involving both temperature whose onset at spring leads to higher organic matter decomposition rates by microbial mass, and redox changes resulting in REE and other trace element release in water when soil mineral phases occur to dissolve. In order to study DOM-metal interactions and the role of the colloidal pool in such groundwaters, small new ultracentrifugal filter units have been tested in a range of molecular weight cut-off - 30 kDalton, 10 kDalton and 5kDalton - to distinguish between organically colloidal complexed metals and 'free' metals. These 'free' metals consisting of hydrated metal cations and soluble inorganic metal complexes are considered to represent the bioavailable metal fraction. The Dissolved Organic Carbon (DOC) concentrations were determined in the different fractions as well as the trace metal concentrations by ICP-MS.

While Na, Rb, Mg or Ca appear to behave as 'free' ions, aqueous REE concentrations are directly correlated to DOC concentrations as well as that of Th and U, suggesting that the organic colloidal pool dominates the carrying of filter-passing REE, Th and U. The REE concentrations are lowered upon successive filtrations at decreasing pore size when REE patterns remain unchanged. Since the retention, transport and fate of trace metals mediated by organic matter has to be better constrained to understand the functional role played by DOM at the soil-water interface regards to trace metal dynamics, further studies dedicated to space- and time-linked variations of the joined colloidal pool and trace element distribution, are at present undertaken in waters recovered from different DOC-rich waterlogged environments.

## Understanding the redox properties of Georgetown NOM

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It is well known that NOM can act as a reducing agent (reductant). More recently, there has been growing interest in the role that NOM plays as an electron shuttle (mediator) in biogeochemical cycles and contaminant fate. For example, recent data from our lab indicate that the addition of some types of NOM (or fractions of NOM) increase abiotic redox reactions between Fe<sup>0</sup> and RDX. Such effects imply that NOM must have redox-active moieties with relatively low formal reduction potentials.

To characterize these reduction potentials, we developed an electrochemical protocol that allowed us to determine the electrochemical properties of NOM, fractions of NOM, and NOM model compounds. Here, we report on our most current electrochemical characterization of Georgetown NOM and its fractions. The results show one or more well-defined peaks—presumably indicative of a dominant redox active moiety—with quantifiable reduction potentials and currents.

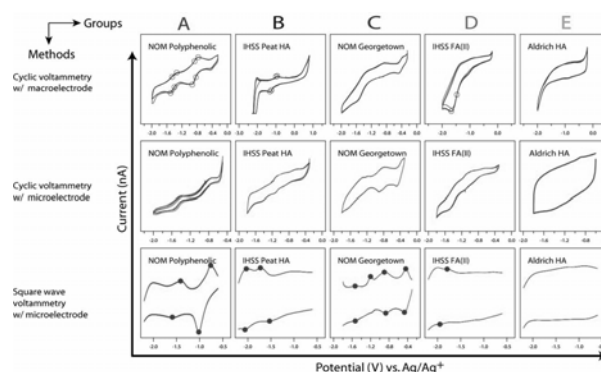


Figure 1. Representative cyclic voltammograms obtained using 3 amperometric methods on 5 samples of NOM.

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## Metal distribution with different molecular size fractions of dissolved organic matter in stream waters by HPSEC and ICPMS

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The distributions of metals Fe, V, Ce, Th, U, Mo, Cu, Ni, Co, Cr, Zn, Pb and Cd with different molecular size (MS) fractions of dissolved organic matter (DOM) in stream waters from south-central Ontario, Canada were investigated using high-performance size-exclusion chromatography (HPSEC, YMC-Pack Diol-300) coupled with on-line photodiode array detector and high-resolution inductively coupled plasma mass spectrometry (ICPMS, Finnigan MAT ELEMENT2). The MS distribution of metals in DOM fractions was evaluated and compared for reverse osmosis (RO) concentrated DOM samples and XAD-isolated humic substances (HS).

The results show the following decrease order of the average molecular weight in RO-concentrated samples: Cu>Ni>(Co, Zn, Cr)>Pb>Cd for the DOM-bound complexes of transitional metals, which is consistent with Irving-Williams series, and (Fe, V, Ce)>Th>U>Mo for the DOM-bound complexes of the other metals, indicating that the metal distribution among the different MS fractions was mainly related to its binding strength. Metals with high strength were more distributed in the larger MS fractions, and metals with low strength were more distributed in the smaller MS fractions of DOM. The MS distribution of metals in HS was different from that in RO-concentrated samples. The mechanisms for these observations were proposed. This study may have significant implications in the understanding of metal-DOM complexation in aquatic environments.

## Metal binding to NOM determined using component resolution and multiresponse modelling

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Natural organic matter (NOM) has fluorescent components, which can be characterized using excitation versus emission fluorescence scans. Through the application of numerical mixture resolution techniques it is possible to resolve a minimum number of fluorescent components necessary to describe the total fluorescence surface. Types of NOM can be "fingerprinted" in this manner. Fluorescence surfaces for samples of a wide range of NOM isolates were subjected to the SIMPLISMA component resolution technique (Windig and Guilment, 1991). Results show that four major components can be identified, two amino acid like components (tryptophan and tyrosine) and two longer wavelength "fulvic" and "humic" components. Samples where the NOM is algal in origin (e.g., Lake Erie sample) show strong tyrosine-like components, whereas sewage effluent show strong tryptophan-like components. Representative samples of allochthonous organic matter show mainly fulvic and humic-like fluorescence. Samples of mixed origin, such as Lake Ontario organic matter, have contributions from all major components. The fulvic and humic-like components can be further resolved into sub-components and possible molecular analogs for NOM-building blocks proposed (Smith and Kramer, 2000). Once fluorescent components are identified using mixture resolution techniques fluorescence changes for each component can be measured during metal titration (Smith and Kramer, 2000). This resultant multiresponse data can be fit to a chemical equilibrium binding model for metal with multiple sites in NOM. Results for Suwannee River fulvic acid show a mixture of five diprotic/bidentate sites for proton/metal binding with binding constants consistent with salicylic acid – like binding (Smith et al., 1999). Sewage derived organic matter tends to be higher in the amino acid-like components which show relatively large (logK 5) binding sites for silver.

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## Fluorescence characterization of dissolved organic matter in a city river of southwestern China

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Dissolved organic matter (DOM) in Nanming River and its streams, Southwest China was investigated using fluorescence emission spectra, synchronous fluorescence spectra and three-dimensional excitation emission matrix fluorescence (3DEEM) spectroscopy. There was a wide but featureless peak at  $\text{Em} = 430 - 440 \text{ nm}$  in the emission spectra, 3 - 4 components can be distinguished from the synchronous fluorescence spectra with a maximum peak at 280 nm. With 3DEEM technique, we can differentiate three major fluorophores in the DOM samples, which were responsible for two humic-like and one protein-like fluorescence (Coble, 1996; Baker, 2001; Wu and Tanoue, 2001). Strong protein-like fluorescence occurred in most of the samples. Significant relationships were observed between the fulvic-like and protein-like fluorescence, and between individual fluorescence intensity, DOC,  $\text{PO}_4^{3-}$ , COD and ammonium concentrations in the river. It is suggested that fluorescence technique is a powerful tool to indicate the pollution situation of city river waters. Most importantly, our results show that municipal wastewater can be the source not only of protein-like fluorescence substances, but also of the humic-like fluorescence substances in aquatic environments.

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## Mechanisms of organic matter and rare earth element release in soils: Experimental evidence

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We investigated the roles played by microbial activity, redox potential variations and pH changes on Organic Matter (OM) and Rare Earth Elements (REE) release in hydromorphic soils. Three types of experiments were conducted: (i) a soil suspension was incubated under anaerobic condition, without pH control (i.e. the pH was let to evolve in response to occurring biogeochemical reactions); this represents the "natural" reference case in which all tested parameters (pH, microbial activity, redox potential) can vary and control OM and REE exchanges between soil minerals and soil solution; (ii) a sterilized soil suspension was incubated under anaerobic conditions at pH 3 with hydroxylamine as chemical reducer; (iii) finally, three soil suspensions were incubated under aerobic conditions at pH 3, 5 and 7. Results demonstrate that large amounts of OM and REE are released from hydromorphic soils when soil Fe and Mn oxyhydroxides are reductively dissolved.

The role of micro-organisms appears to be secondary, the latter playing only a catalyst role. Incubations carried out with hydroxylamine at pH3 or in aerobic conditions at variable pH values demonstrate that the main mechanism controlling OM and REE release is OM desorption in response to pH increase.

REE patterns were very helpful in reaching this conclusion since OM adsorbed at the surface of soil minerals was found to have very specific and easily recognizable Z-shape REE pattern. This typical Z-shape signature was not found in experiment designed to promote reductive dissolution of soil Fe and Mn oxyhydroxides (flat REE patterns). This difference could be due to the release of REE co-precipitated within the soil oxyhydroxides solid or to the release of OM with different REE complexing capacities. Finally, experiments carried out under aerobic conditions at pH 3 yielded a third type of REE pattern (light REE enriched pattern). As a whole, these results demonstrate that REE may be used as a probe to monitor the activation of particular soil components during soil reduction and soil pH variations.

## **Organic speciation of rare earth elements in natural waters: Comparing speciation models and ultrafiltration experiments**

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Two speciation models (WHAM 6 and Visual Minteq) were compared together and with results of ultrafiltration experiments to assess the ability of models to accurately predict the speciation of rare earth elements (REE) in organic-rich water. Both river and groundwater samples were used ( $5.9 < \text{pH} < 7.4$ ;  $1 < \text{Dissolved Organic Carbon} < 30 \text{ mg.L}^{-1}$ ;  $0.2 < \Sigma\text{REE} < 10 \text{ ppb}$ ). Ultrafiltration of these samples was performed with a new method using small centrifugal filter devices of decreasing pore size ( $0.22 \mu\text{m}$ ,  $30\,000 \text{ Da}$ ,  $10\,000 \text{ Da}$  and  $5\,000 \text{ Da}$ ) to separate the organically bound REE from the inorganic REE species. REE and Dissolved Organic Content (DOC) were analyzed in each fraction. DOC-rich waters ( $> 4\text{-}5 \text{ mg.L}^{-1}$ ) have a higher proportion of organically bound REE (75 to 95%) than waters with lower DOC contents (50%). REE-complexing organic molecules have higher molecular weights in groundwater samples (10-30 kDa) than in river waters (5-10 kDa). The two tested models yield comparable results, although some differences are pointed out for the light-REE (i.e. WHAM 6 yields a 71% organic speciation for La while the proportion of organically bound La is 82% when Visual Minteq is used). Model predictions are in good agreement with ultrafiltration results, especially as regards heavy REE. This study shows that speciation models can be confidently used to assess the speciation of REE in circumneutral pH organic-rich waters.