

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 Fe⁰ 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.

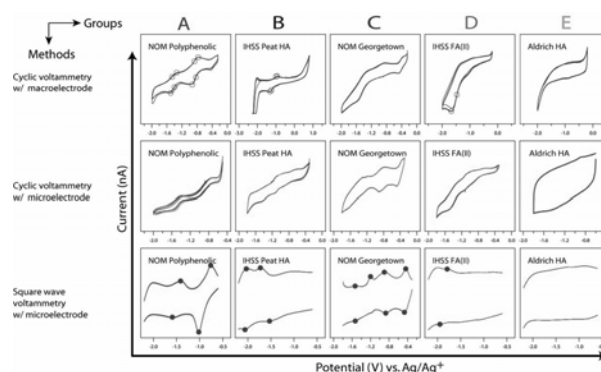


Figure 1. Representative cyclic voltammograms obtained using 3 amperometric methods on 5 samples of NOM.

References

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