Redox properties of iron-ligand complexes in dissolved organic matter

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Background

Electron donating capacity (EDC) and accepting capacity (EAC) in dissolved organic matter (DOM) has long been attributed to quinone moieties that readily facilitate electron transfer in redox reactions. However, the complexation of iron by organic ligands, such as those present in DOM, can alter its redox potential. We propose here that naturally occurring complexed iron is an important component of the overall EDC and EAC of DOM. We also propose that complexed iron will change the overall redox potential of DOM, henceforth making it more reactive toward compounds susecptible to these reactions.

Discussion of Preliminary Results

DOM was isolated from a freshwater stream in New Jersey (MacDonald's Branch, Pinelands National Reserve, NJ, USA) with high background total iron concentrations (19 μM). Both EDC and EAC of this isolated DOM were acquired electrochemically using mediated electrochemical oxidation (MEO) and reduction (MER), respectively. Measurements were made with a glassy carbon electrode that doubles as a crucible to hold solutions and were initiated by spiking in an electron mediatior (ABTS for MEO, Diquat for MER) that faciliated electron transfer from the electrode to the sample. After spiking in electron mediators, a DOM stock solution was injected sequentially by increasing mass. Current response to mass injected reulted in peaks that could be integrated to calculate the moles e^- g^{-1} DOM (q). Following measurements, DOM was treated with a cation exchange resin (CEC) to remove complexed iron from within DOM. After treatment, electrochemical measurements (MEO,MER) were repeated. Initial results show a significant *decrease* in EAC following treatment with the resin, indicating loss of electron accepting components within DOM. Aliquots taken from DOM before and after CEC treatment were analyzed for total iron via ICP-MS, and show significant loss of iron (~40%). This suggests that the iron lost from the DOM is Fe^{3+}. DOM isolates and whole water samples will also be assayed with probe compounds before and after treatment with the CEC, to elucidate naturally occurring iron's role as a reductant in DOM.