



Electron transfer reactions of dissolved organic matter

Markus Bauer (1), Donald Macalady (2), Stefan Peiffer (1) and Christian Blodau (1)

(1) Dept. of Hydrology, University of Bayreuth, Germany, (2) Dept. of
Chemistry/Geochemistry, Colorado School of Mines, Colorado, USA

(markus.bauer1@uni-bayreuth.de / Fax: +49/0921/552366 / Phone : +49/0921/552170)

Dissolved organic matter (DOM) has been shown to take part in oxidation/reduction reactions with a variety of natural compounds and anthropogenic organic chemicals. Hydroquinone-like moieties were confirmed to be ubiquitous in DOM molecules (Scott, D.T., et al., 1998), and are seen as the primary redox reactive functional groups (Dunnivant, et al., 1992). But still we are lacking a conceptual understanding of DOM redox processes. Organic molecules seem to react with many oxidizing or reducing agent, but reactive amounts can vary by an order of magnitude or more and reaction rates were found to differ strongly. Abiotic reductive properties of DOM towards certain substrates (e.g. As(V), Redman, et al., 2002) were reported even after the DOM had been exposed to atmospheric oxygen for long periods of time. We report progress in a series of experiments, designed to elucidate the nature of, and variations in, the redox properties of DOM samples. Individually, each of these experimental designs can be criticized for certain experimental flaws, but collectively they seem to provide a consistent pattern for abiotic organic matter redox reactions.

Sample of untreated DOM (either whole waters or reconstituted standard humic acids) that had been exposed to fully oxygenated waters for a variety of periods of time were investigated to determine their ability to be further oxidized by chelated Fe(III) species or reduced by highly reductive compound (H_2S , H_2 , electrons, Zn).

All DOM samples were able to donate electrons to complexed iron. The extent of the reduction reactions was shown for a given NOM sample to be dependant on the redox potentials of the reactant used (and the pH) in a thermodynamically consistent manner. Consequently the highest electron donor capacity (EDC) of DOM was observed when iron was chelated with ferrozine (high redox potential). The e^- -transfer of DOM to iron complexes decreased in the order ferrozine ($1,52 \text{ mmol } e^-/\text{g C}$) > cyanide ($0,56$

mmol e⁻/g C) > citrate (0,12 mmol e⁻/g C) > hydroxide (0,03 mmol e⁻/g C). Similar kinetics were observed for the various iron species (as a function of pH and DOM concentration) and were also found to decline with decreasing redox potential of the chelate. Samples of DOM acted as electron acceptors upon exposure to the above reducing agents and exhibited concomitantly higher Fe-reducing capacities after such treatment (Kappler, A., et al., 2003). Direct determination of DOM electron uptake (measuring sulfide or Zn oxidation) revealed much higher values for the Zn/Zn²⁺ reaction (6,1 mmol e⁻/g C; Eh (W) = -0,81 V) compared to the sulfide/thiosulfate couple (0,55 mmol e⁻/g C; Eh (W) = -0,14 V).

In summary, we have shown that DOM exhibits the predictable and ubiquitous ability to reduce Fe(III) added in various chelated forms and oxidize, even after exposure to dioxygen for periods immediately prior to the experiments. Altogether our experimental results indicate a relation between the observed amounts and rates of electron transfer with the redox potential of the reaction partner. The extent of this redox reactivity varies for DOM samples from different origins and can have implications for field studies dealing with redox active species.