



## Electron Transfer Capacities and Reaction Kinetics of Peat Dissolved Organic Matter

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Humic substances are redox reactive compounds in the environment, involved in microbial processes, pollutant degradation, and metal mobility (Kappler and Haderlein, 2003; Lovley et al., 1996; Redman et al., 2002). Structural entities, such as quinones (Scott et al., 1998), take part in electron accepting and donating reactions. Methods proposed to quantify organic matter (OM) electron transfer capacities use diverse experimental procedures, making comparison humics from different environments difficult and limiting field application as well as the development of a conceptual understanding of OM redox processes. To address these research deficiencies we conducted dissolved OM reduction and oxidation experiments with reactants covering a wide range of redox potentials.

Experiments were conducted in batch design with two peatland derived dissolved organic matter samples. OM was incubated with reactants of different redox potential, including Fe(III) chelated by bipyridyl, cyanide, hydroxide and citrate as well as hydrogen sulphide and zerovalent zinc. Reaction kinetics and electron transfer capacities were determined from the reduced or oxidized reaction products (Fe(II),  $S_2O_3^{2-}$ ,  $Zn^{2+}$ ).

Both dissolved OM samples were able to donate electrons to complexed ferric iron with decreasing rate over time and reaction depended on pH, OM concentration and iron complex. Total Fe(II) production, and therefore electron donor capacity of OM, decreased in the order FeBipyridyl (pH 4.5) > FeBipyridyl (pH 6) > FeCyanide (pH 6) > FeCitrate (pH 6) > Fe(OH)<sub>3</sub> (pH 6). Electron acceptor capacity was higher for zinc than for sulphide. Model calculations (PhreeqC, Nernst equation) were performed

to determine the dominant reactant species under the given reaction conditions and its in situ redox potential. The results help to explain the observed reactivity pattern and show a clear trend: High negative and high positive in situ redox potentials lead to increased electron transfer to and from dissolved OM compared to low positive/negative potentials. This indicates, that humics consists of redox active groups with different properties and structural composition. OM might therefore, in analogy to its acid-base properties, be comprised of a “redox ladder” of groups with differing redox potential.

In summary, our experimental results show, that amounts and rates OM electron exchange are related to the redox potential of the reaction partner. These findings have implications for field studies dealing with redox active species.

#### References:

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