

Role of Fe in the Breaking and Making of Natural Organic Molecules

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The abundance and composition of organic molecules in the environment play an important role in the solubility of metals in the natural waters. Comparably, the abundances and reactivity of metals associated with the dissolved organic molecules (DOM) determine the stability and the fate of organic carbon in soils and sediments. In the presence of strongly complexing cations, cation-DOM reactions leads to the production of particulate carbon in aquatic systems and mineral adsorbed organic matter in mineral-rich systems. However, the presence of redox sensitive metals, such as Fe, can promote the DOM breakdown and results in the production of new pool of oxidized DOM.

The role of Fe (Fe(II) and Fe(III)) on the stability, and neo-production of DOM is examined for model synthetic lignin and DOM from pineland (NJ, USA) stream water. Synthetic lignin is used as a model molecule to understand the DOM redox reactions in a greater detail. These studies are also conducted in the presence (photo-Fenton) and absence (Fenton) of sunlight, and with externally added oxidants (H₂O₂). The reaction products were characterized using FTIR, luminescence and XANES spectroscopies, and mass-spectrometry (FT-ICR ESI-MS).

The results suggest that Fe(II,III) promoted the breakdown and mineralization of both model lignin and stream DOM. The transformation products were similar in the presence of Fe(II) and Fe(III); however, the kinetics were faster for Fe(II). The synthetic lignin reactions with Fe (II,III) and in the presence of sunlight showed that ring opening and oxidation are the first steps in the lignin breakdown followed by decarboxylation. The decarboxylation reactions were common in the presence of sunlight. Lignin reactions with Fe in dark (Fenton) resulted in predominantly ring opening and oxidation rather than decarboxylation. The stream water DOM reactions with Fe, which is naturally associated with DOM at a few nano-micro molar concentration, showed similar reaction products. This suggests that redox reactions between Fe and lignin may be the key producer of O-rich DOM pool in natural waters.

These results highlight the abiotic transformation of plant biopolymers and DOM in the presence of redox-sensitive metals, and help explain the chemical variability of DOM in different aquatic systems.