Enzymatic oxidation of phenolic moieties in dissolved organic matter

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Dissolved organic matter (DOM) is ubiquitous in both terrestrial and aquatic systems. While chemical oxidation and photochemical transformation of DOM has been extensively studied, the enzymatic oxidation of DOM remains poorly characterized and understood on a mechanistic level. A better understanding of this process is warranted as it governs DOM stability in natural systems and, as such, plays a key role in the cycling of nutrients and carbon.

This contribution present the results of systematic investigations of the kinetics and extents of enzymatic oxidation of phenolic moieties in DOM. Enzymatic oxidations were carried out by three different laccases, which are copper-containing oxygen oxidoreductases that catalyze the transfer of electrons from phenolic moieties to dioxygen under formation of phenoxyl radicals and water. The tested DOM included well-characterized isolates from both terrestrial and aquatic systems as well as DOM samples directly collected from three ombrotrophic bogs in central Sweden. The oxidation was monitored by simultaneous quantification of oxygen consumption using optrode technology and the depletion of electron donating phenolic moieties in the DOM using mediated electrochemical analysis, a novel analytical approach.

Enzymatic oxidation of all tested DOM samples in the presence of O_2 was fast, extensive, and largely irreversible over the course of a few days. Fast and extensive oxidation implies that the catalytic sites of the tested laccases had access to a significant fraction of the phenolic moieties in the DOM. Irreversible oxidation is consistent with the formation of phenoxyl radicals that subsequently underwent coupling reactions to form higher molecular weight products that could not be re-reduced to the original phenolic structures. Coupled measurements of oxygen consumption and loss of phenolic moieties for selected DOM reveled 1:4 molar stoichiometric ratios, consistent with the transfer of four electrons from DOM to one oxygen to form two water molecules and hence demonstrating a closed electron balance in the studied systems.

The results of this work will be discussed in the context of organic matter turnover in natural systems with a focus on DOM preservation and transformation across anoxic-oxic interfaces in temporarily anoxic wetlands.