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Electron transfer properties of peat organic matter: from electrochemical analysis to redox processes in peatlands

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Peat organic matter contains redox-active functional groups that can accept and/or donate electrons from and to biotic and abiotic reaction partners present in peatlands. Several studies have provided evidence that electron accepting quinone moieties in the peat organic matter may act as terminal electron acceptors for anaerobic microbial respiration. This respiration pathway may competitively suppress methanogenesis and thereby lead to excess carbon dioxide to methane formation in peatlands. Electron donating phenolic moieties in peat organic matter have long been considered to inhibit microbial and enzymatic activities in peatlands, thereby contributing to carbon stabilization and accumulation in these systems. Phenols are expected to be comparatively stable in anoxic parts of the peats as phenoloxidases, a class of enzymes capable of oxidatively degrading phenols, require molecular oxygen as co-substrate. Despite the general recognition of the importance of redox-active moieties in peat organic matter, the abundance, redox properties and reactivities of these moieties remain poorly studied and understood, in large part due to analytical challenges. This contribution will, in a first part, summarize recent advances in our research group on the analytical chemistry of redox-active moieties in peat organic matter. We will show how mediated electrochemical analysis can be used to quantify the capacities of electron accepting and donating moieties in both dissolved and particulate peat organic matter. We will link these capacities to the physicochemical properties of peat organic matter and provide evidence for quinones and phenols as major electron accepting and donating moieties, respectively. The second part of this contribution will highlight how these electroanalytical techniques can be utilized to advance a more fundamental understanding of electron transfer processes involving peat organic matter. These processes include the redox cycling (i.e. repeated reduction and re-oxidation) of peat organic matter under alternating anoxic-oxic conditions as well as the oxidation of phenolic moieties in peat organic matter by phenol oxidases in the presence of molecular oxygen. Overall, this contribution will attempt to link molecular-level insights into the redox properties of peat organic matter to larger scale redox processes that are important to carbon cycling in peatlands.