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Redox properties of dissolved organic matter along redox gradients in two peatland-dominated forested catchments

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Dissolved organic matter (DOM) contributes significantly to the carbon cycle and influence the mobility of metals and contaminants. Water logged, riparian wetlands have been identified as an important source of DOM in catchments. As DOM export from wetlands often involves transitions in redox conditions, for a more mechanistic understanding of sources, mobilization processes and fate of DOM under different redox conditions additional analytical approaches are needed.

In this study we combined established methods for DOM characterization, such as fluorescence spectroscopy and $\delta^{13}C_{DOC}$, with mediated electrochemical reduction and oxidation of DOM for the determination the electron accepting and donating capacity (EAC/EDC). With this approach, we intended to test if the redox state of DOM can be used to identify and characterize its sources in catchments. To this end, we collected samples in two catchments - one dominated by fens and forest, the other by an ombrotrophic bog - from different hydrological compartments and from different source materials.

EAC strongly decreased from oxic groundwater (6.4 ± 2.1 $mmol_{e-}$ gC $^{-1}$) to anoxic peat pore water (0.6 ± 0.5 $mmol_{e-}$ gC $^{-1}$). Contrarily, for EDC, there was no clear pattern to separate water compartments with different redox states. EDC seemed thus to depend mainly on the DOM source materials. Results of fluorescence spectroscopy and $\delta^{13}C_{DOC}$confirmed that changes in EDC were presumably due to changes in DOC quality rather than redox state. Moreover, comparing peat pore water and DOM in an adjacent erosion rill, EDC increased from 0.7 $mmol_{e-}$ gC $^{-1}$ in the anoxic pore water to 1.7 ± 0.2 $mmol_{e-}$ gC $^{-1}$ along the flow path in the oxic stream. This further suggested a different mobility of different DOM fractions, with higher EDC in more mobile DOM.

This study indicates that combining electrochemical and spectroscopic methods for characterization of DOM quality and redox state can improve our understanding of source and fate of DOM in peatland-dominated forested catchments.