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Molecular properties of DOM: From peatland pore water to stream headwater

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Export of dissolved organic matter (DOM) from soils to aquatic systems is an important link in the global carbon cycle. The molecular properties of DOM control function and fate of DOM in the aquatic environment, but also allows for identifying DOM sources and mobilization processes. A range of different methods for DOM characterization exists, however, a systematic comparison of different approaches has rarely been conducted. This study compares the molecular composition of DOM from peatland pore water and the emanating headwater stream using a wide range of available techniques. The studied catchment is located in the Harz Mountains (northern Germany) and drains a bog and adjacent forest soils. DOM was characterized by spectrofluorometric indices, such as SUVA254nm, SR, HIX and FI, as well as by PARAFAC modelling of fluorescence spectra. In addition, molecular characterization of DOM in selected samples was conducted by Fourier transform-ion cyclotron resonance-mass spectroscopy (FT-ICR-MS) and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS).
Results showed major differences in pore water and stream water DOM molecular composition and properties. The aromaticity index SUVA254nm and FT-ICR-MS based aromaticity indices describe a congruent depth trend with highest aromaticity in pore water at about 40 cm depth. In general, pore water DOM was less aromatic and of smaller molecular size than DOM of stream samples. The spectrofluorometric index SR, as well as FT-ICR-MS indicated progressively smaller molecular size of DOM along the stream water course. Additionally, H/C, sugars and unsaturated aliphatic components proportionally decreased along the stream course, while aromatic and polyphenolic compounds increased. DOM thus seemed to be increasingly dominated by recalcitrant moieties, residually enriched in refractory compounds with increasing contribution from peaty riparian and mineral forest soils, compared to compounds within the bog area.
Both FT-ICR-MS and Py-GC-MS identified polyphenols as a major DOM fraction in stream water draining the peatland, but the relative contributions differed (22% and 39%, respectively). A high abundance of carbohydrates (25%) and monocyclic aromatic hydrocarbons (MAHs, 15%) was detected by Py-GC-MS. Smaller contributions of aliphatic compounds (0.6%) and PAHs (1.8%) were detected as well. Guaiacols, which are indicative of vascular plant-derived DOM (lignin), contributed about 3.5% to total DOM composition.
In summary, this study demonstrated the value of sophisticated analytical approaches on the one hand, enabling to disentangle different sources and different major functional moieties. On the other hand, there was a good correlation of several simple spectrofluorometric indices with results obtained by state-of-the-art analytical methods, suggesting that temporal or spatial patterns may be resolved combining such demanding analytical approaches with conventional techniques.