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Linking major and trace element headwater stream concentrations to DOC release and hydrologic conditions in a bog and peaty riparian zone

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Peatlands and organic-rich riparian zones are known to export large amounts of dissolved organic carbon (DOC) to surface water. In organic-rich, acidic headwater streams main carriers for element export are dissolved organic matter (DOM) and organic-iron complexes. In this environment DOM might also act as major carrier for metals, which otherwise may have a low solubility. This study examines annual and short term event-based variations of major and trace elements in a headwater catchment. Patterns are used to trace hydrological pathways and element sources under different hydrologic preconditions. Furthermore, it elucidates the importance of DOC as carrier of different elements in a bog and a peaty riparian catchment.
The study was conducted in a small headwater stream draining an ombrotrophic peatland with an adjacent forested area with peaty riparian soils in the Harz Mountains (Germany). Discharge sampling was conducted weekly at two sites from snowmelt to begin of snowfall and in high resolution during selected discharge events in 2013 and 2014. Element concentrations were measured by means of ICP-MS and ICP-OES. A PCA was performed for each site and for annual and event datasets.
Results show that a large number of element concentrations strongly correlate with DOC concentrations at the bog site. Even elements like Ca and Mg, which are known to have a low affinity to DOC. Congruently, the first principal component integrates the DOC pattern (element loadings > 0.8: Ca, Fe, Mg, Mn, Zn, As, Sr, Cd, DOC) and explained about 35 % of total variance and even 50 % during rain events (loadings > 0.8: Al, Ca, Fe, Mg, Mn, Zn, Li, Co, As, Sr, Cd, Pb, DOC). The study cannot verify that all correlating elements bind to DOC. It is likely that also a common mobilization pattern in the upper peat layer by plant decomposition causes the same response to changes in hydrologic pathways. Additionally, a low mineral content and an enrichment of elements like Fe and Mn in the upper peat layers due to prevailing redox conditions might play a major role in a bog environment. At the peaty riparian zone only Ca, Fe, and Sr strongly correlated with DOC over the annual record. The PCA of the annual record display no clear DOC component here, but indicates that DOC is influenced by Component one (element loadings > 0.8: Ca, Mg, Zn, Co, Sr) and two (Al, V, La, Pb, U) suggesting different DOC sources in the peaty riparian zone. A large number of elements correlate with DOC during rain event sampling at the riparian zone. In contrast to the bog site the event-based riparian zone PCA distinguished a clear discharge related component with mineral, groundwater related elements (K, Rb, In, Cs, NO_3- and SO42-). Pattern of the mineral and DOC components prove that during base flow discharge is generated in a shallow groundwater layer and successively increases upward to the organic-rich upper soil layer with increasing discharge. Contrarily, bog element pattern confirm a dominating surface-near discharge, due to high hydraulic conductivities.