

The influence of rain events on spatial and temporal changes of DOM composition in a peat-dominated headwater stream in Scotland

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Peat-dominated catchments are particularly vulnerable and have the potential to release large quantities of organic carbon, providing a positive feedback to atmospheric greenhouse gas emission. Superimposed on annual and seasonal cycles, rain events have the potential to mobilise large amounts of organic carbon and nutrients from vegetation and soils of the surrounding landscape that can dominate the overall carbon flux. Importantly, the composition and reactivity of dissolved organic matter (DOM) has a large variability and they can greatly modify the fate and as it is moving along headwater river systems.

We investigated the compositional changes of DOM in a headwater stream of rain events during an exceptionally dry period and compared these with rain events during a generally wetter cooler period from 2017 to 2018. A novel size exclusion chromatography technique allowed elucidation of five different DOM pools including Humics to Biopolymers, Building Blocks, lower molecular weight (LMW) Acids, and LMW Neutrals, without isolating or modifying the original sample.

Our results show that high temporally resolved sampling of our headwater rivers is required to capture notable changes in DOM composition during rain events from humic dominated to LMW organic substances. We also found that rain events mobilise predominantly humic based substances (\sim 80% of the total DOM pool) in summer and winter. Conversely, during longer dry periods the amount of LMW DOM increased by up to 60%, becoming the more dominant pool of organic matter in the river. Importantly, this LMW DOM consists of 'neutral' compounds that are not amenable to UV-Vis absorbance of fluorescence measurements and are therefore "invisible" (iDOM) to typically utilised DOM quantification and characterisation methods. This implies that riverine carbon fluxes are under quantified from peatland environments, especially as these LMW compounds are not observed downstream (\sim 2km) indicating a highly labile DOM component is remineralised within the water column.