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Dissolved organic matter dynamics during storm events: combining in-situ and laboratory optical measurements to improve understanding

Kieran Khamis (1,2), Chris Bradley (1), David Hannah (1), and Rob Stevens (2)

(1) School of Geography, Earth and Environmental Science, University of Birmingham, Birmingham, B15 2TT, UK., (2) RS Hydro Ltd, Leask House, Hanbury Road, Stoke Prior, Worcestershire, B60 4JZ, UK

Despite the crucial role of dissolved organic matter (DOM) in catchment biogeochemistry; DOM fluxes from watersheds still remains poorly characterized. Recently, the mobilization and transport of DOM during storm events has received increased attention; with significant changes in DOM quality and quantity reported for forested and agricultural catchments. However, for urban systems, our understanding of the extent to which storms drive changes in DOM concentration and composition remains limited, particularly with regards to intra/inter-seasonal variability. In this study, we address this research gap by characterizing a number of storm events on a small urban stream (Bournbrook, Birmingham, U.K) during the winter and summer of 2014. An in-situ submersible fluorometer (Cyclops 7, Turner Inc.) was integrated with a traditional water quality sonde (Manta 2, Eureka) to obtain a continuous record of tryptophan-like fluorescence (TLF: BOD surrogate), turbidity, electrical conductivity (EC), water temperature (Tw) and stage. River water samples were collected using an automatic pump sampler at $\leq$ 1hr intervals and returned to the lab for a suite of analyses (total carbon quantification, absorbance and excitation emission spectrofluorometry).

The flow regime was typical of an urban/suburban catchment with river stage extremely responsive to rainfall with lag times of <3 hrs. Both winter and summer storm events exhibited first flush responses with peak turbidity either on the rising limb or at peak discharge for all events (max. turbidity = 400NTU). Field and lab data highlighted systematic overestimation of in-situ TLF during base flow and high flow. Robust correction factors were developed and significantly improved the relationship between field and filtered lab measurements ($R2 > 0.8$).

The highest TLF values (in-situ and lab) were recorded during summer events, with corresponding winter events consistently displaying lower TLF concentrations. Antecedent hydro-meteorological conditions exerted a strong control on DOM quantity with both dissolved organic carbon concentrations and TLF lowest after periods of prolonged precipitation. Lab-derived optical properties and PARAFAC analysis indicated significant changes in DOM composition during and between events highlighting the complex hydrological nature of the catchment. Together, laboratory and in-situ data provided insights into the timing and magnitude of changes in DOM quantity and quality during storm events and highlighted the potential utility of real time monitoring of TLF fluorescence for a range of environmental applications.