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High frequency DOM dynamics in urban rivers revealed by in-situ fluorometry.

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To-date Dissolved Organic Matter (DOM) dynamics have been quantified poorly in urban rivers despite substantial water quality problems. Research has been hindered by the low temporal resolution of observations and over-reliance on manual sampling which often fail to capture precipitation events and diurnal dynamics. High frequency data are essential to quantify DOM fluxes/loads and understand DOM furnishing and transport processes. While recent advances in optical sensor technology are yielding new high resolution DOM information, there is a lack of consensus regarding the monitoring resolution required for urban systems, with no studies routinely monitoring at <15 min time steps.

High-frequency monitoring (5 min resolution; 4 week duration) was conducted on a headwater urban stream in Birmingham, UK to determine the optimum temporal resolution to characterize DOM event dynamics. A through-flow GGNU-30 monitored wavelengths corresponding to tryptophan-like fluorescence (TLF; Peak T1) (Ex 285 nm/ Em 345 nm) and humic-like fluorescence (HLF; Peak C) (Ex 365 nm/Em 490 nm).

Five minute temporal resolution reveals distinct peaks in TLF and HLF indicating separate DOM pathways are apparent during storms. Initial pulses in TLF and HLF appear to relate to scouring of streambed biofilms, whilst secondary TLF and HLF peaks may relate to terrestrial OM inputs from the wider catchment. High temporal variation occurs during storm events in TLF and HLF intensity: TLF intensity is highest during the rising limb of the hydrograph and can rapidly decline thereafter, indicating the importance of fast flow-path and close proximity sources. HLF also peaks on the rising limb, but exhibits little decline as flow recedes, with a hysteresis effect apparent. Furthermore, the ratio of TLF:HLF, which aids in identifying inputs from Combined Sewage Overflow suggests smaller events (< 3mm precipitation) tend to be more Peak C dominated, whereas large events (> 3mm precipitation) tend to be more Peak T dominated, indicating that sewage discharges are more prominent during larger events.

Our work highlights the need for future studies to utilise shorter temporal scales than previously used to monitor urban DOM dynamics. The application of higher frequency monitoring enables the identification of finer-scale patterns and subsequently aids in deciphering the sources and pathways controlling urban DOM dynamics.