



Can spectroscopic analysis improve our understanding of biogeochemical processes in agricultural streams?

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In agricultural catchments diffuse fluxes of nutrients, mainly nitrogen (N) and phosphorus (P) from arable land and livestock are responsible for pollution of receiving waters and their eutrophication. Organic matter (OM) can play an important role in mediating a range of biogeochemical processes controlling diffuse pollution in streams and at their interface with surrounding land in the riparian and hyporheic zones. Thus, a holistic and simultaneous monitoring of N, P and OM fractions can help to improve our understanding of biogeochemical functioning of agricultural streams.

In this study we build on intensive in situ monitoring of diffuse pollution in a small agricultural groundwater-fed stream in NW England carried out since 2009. The in situ monitoring unit captures high-frequency (15 minutes to hourly) responses of water quality parameters including total phosphorus, total reactive phosphorus and nitrate-nitrogen to changing flow conditions. For two consecutive hydrological years we have carried out additional spectroscopic water analyses to characterise organic matter components and their interactions with nutrient fractions. Automated and grab water samples have been analysed using ultraviolet-visible (UV-Vis) absorbance and excitation-emission (EEM) fluorescence spectroscopy. In addition, a tryptophan sensor was trialled to capture in situ fluorescence dynamics.

Our paper evaluates patterns in nutrient and OM responses to baseflow and storm flow conditions and provides an assessment of storage-related changes of automated samples and temperature and turbidity effects on in situ tryptophan measurements. The paper shows the value of spectroscopic measurements to understand biogeochemical and hydrological nutrient dynamics and quantifies analytical uncertainty associated with both laboratory-based and in situ spectroscopic measurements.