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Biogeochemical processing of nutrients in groundwater-fed stream during baseflow conditions - the value of fluorescence spectroscopy and automated high-frequency nutrient monitoring

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Recent research in groundwater-dominated streams indicates that organic matter plays an important role in nutrient transformations at the surface-groundwater interface known as the hyporheic zone. Mixing of water and nutrient fluxes in the hyporheic zone controls in-stream nutrients availability, dynamics and export to downstream reaches. In particular, benthic sediments can form adsorptive sinks for organic matter and reactive nutrients (nitrogen and phosphorus) that sustain a variety of hyporheic processes e.g. denitrification, microbial uptake. Thus, hyporheic metabolism can have an important effect on both quantity (concentration) and quality (labile vs. refractory character) of organic matter. Here high-frequency nutrient monitoring combined with spectroscopic analysis was used to provide insights into biogeochemical processing of a small, agricultural stream in the NE England subject to diffuse nutrient pollution. Biogeochemical data were collected hourly for a week at baseflow conditions when in-stream-hyporheic nutrient dynamics have the greatest impact on stream health. In-stream nutrients (total phosphorus, reactive phosphorus, nitrate nitrogen) and water quality parameters (turbidity, specific conductivity, pH, temperature, dissolved oxygen, redox potential) were measured in situ hourly by an automated bank-side laboratory. Concurrent hourly autosamples were retrieved daily and analysed for nutrients and fine sediments including spectroscopic analyses of dissolved organic matter - excitation-emission matrix (EEM) fluorescence spectroscopy and ultraviolet-visible (UV-Vis) absorbance spectroscopy. Our results show that organic matter can potentially be utilised as a natural, environmental tracer of the biogeochemical processes occurring at the surface-groundwater interface in streams. High-frequency spectroscopic characterisation of in-stream organic matter can provide useful quantitative and qualitative information on fluxes of reactive nutrients in streams with extensive hyporheic zone.