



## **Capturing temporal variation in phosphorus dynamics in groundwater dominated rivers using automated high-frequency sampling**

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High-frequency river water quality monitoring provides detailed hydrochemical information on the time scale of hydrologic response. Several studies (Kirchner et al., 2004; Johnes, 2007; Cassidy and Jordan, 2011) have shown previously that coarse sampling approaches fail to quantify nutrient and sediment loads and to capture the fine structure of water quality dynamics correctly.

A robust analysis of high-frequency nutrient and water quality time series can present a complex conceptual, analytical and computational problem. High-frequency nutrient monitoring provides new evidence of processes and patterns that could not be observed previously using standard coarse resolution sampling schemes. However, to fully utilise the wealth of information contained in high-frequency nutrient data, we need to address the following questions: how to detect complex coupling patterns and processes in high-resolution flow-nutrients data, how do these patterns and processes change throughout the period of observation, and how to distinguish noise signals from an evidence of real processes (Harris and Heathwaite, 2005).

Here, hourly measurements of total phosphorus (TP), soluble reactive phosphorus (SRP) and turbidity were carried out using bank side analysers to study the biogeochemical response of a 54 km<sup>2</sup> catchment of the River Leith, a tributary of the River Eden (Cumbria, UK). A remote automated mobile lab facilitates real-time high-frequency nutrient and water quality monitoring, with no time delay between collection and analysis of the reactive elements. The objectives of this study were two-fold: first to investigate the intrinsic complexity of the temporal relationship between phosphorus fractions (SRP, TP), turbidity and continuous hydrometric time series and secondly to investigate the possibilities of missing high-frequency phosphorus data infilling using continuous hydrometric time series.

Complex non-linear relationships between flow, TP and SRP, turbidity were observed which cannot be explained by existing simple flow-concentration approaches, e.g. load apportionment models (Bowes et al., 2008). High-frequency sampling was able to capture the temporal dynamics of hydrograph and chemograph at full range of flows. It revealed an existence of intermittent episodes of transport- and supply-limitation, complex hysteresis responses in phosphorus transfers, and importance of antecedent hydrometric conditions on the size and direction of hysteresis, providing evidence of temporally varying contributions of diffuse and within-channel mobilised phosphorus sources.

The remote lab was inevitably subjected to intermittent failures in sampling equipment due to freezing and fouling, analytical facilities, data storage and telemetry systems for remote data access, resulting in missing data in the nutrient time series. Nevertheless, having real-time nutrient data is invaluable as it excludes sample storage errors due to biochemical alterations to reactive forms of nutrients (Haygarth et al., 1995; Jarvie et al., 2002) and reduces the overall uncertainty of monitoring data. Attempts have been made to interpolate missing phosphorus data using hydrometric time series. However, complex interactions between hydrometric and in-stream nutrient responses produced a difficulty in infilling of missing phosphorus data and challenged our abilities to model high-frequency nutrient dynamics.

The understanding of this complex temporal patchiness in nutrient responses is therefore critical to predict the in-stream responses to catchment mitigation actions and to derive parsimonious water quality models.

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