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## Concentration-discharge slope as a robust tool for water quality management

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Recent technological breakthrough of optical sensors and analysers has enabled matching the water quality measurement interval to the time scales of stream flow changes and led to an improved understanding of spatially and temporally heterogeneous sources and delivery pathways for many solutes and particulates. This new ability to match the chemograph with the hydrograph has sparked renewed interest in the concentration-discharge (c-q) relationship and its value in characterising catchment storage, time lags and legacy effects for both weathering products and anthropogenic pollutants. The c-q relationship reflects the contribution of dominant sources and delivery pathways leading to solute/particulate dilution or concentration effects with varying flow and can be quantified as the slope of the c-q relationship on logarithmic axes.

In this paper we evaluate the stream c-q relationship for a number of routinely measured water quality parameters and intensively managed European catchments based on both high-frequency (sub-hourly) and long-term low-frequency (monthly) statutory data (the Water Framework and the Nitrates Directives). We analyse the data for total phosphorus, soluble reactive phosphorus, turbidity, nitrate nitrogen, dissolved organic carbon and specific conductivity from seventy 1st-3rd order agricultural catchments in Ireland, the UK, Norway and Sweden.

First, we use resampled high-frequency datasets obtained with optical sensors and analysers to analyse the uncertainty (Monte Carlo simulation) in water quality metrics derived from low-frequency sub-datasets (daily, weekly, forthrightly and monthly). We focus on the metrics routinely used for water quality management: standard deviation, mean and maximum concentration, 95th percentile and load estimation from instantaneous c and q. We show how the uncertainty in water quality metrics increases with reduced sampling frequency as a function of c-q slope for different determinands and catchments. We show how different sources and delivery pathways control c-q relationship for different solutes and particulates. Second, we evaluate the variation in c-q slopes derived from the long-term low-frequency time series for different determinands, catchments and sampling strategies (grab vs. flow-proportional sampling). Third, we show how the c-q slope derived from routinely measured data can be used as a robust stream water quality management tool to guide the selection of the optimal sampling strategies including location, interval and sampling conditions. This research highlights how improved understanding of solute and particulate dynamics obtained with optical sensors and analysers can be used by water regulators to reduce the uncertainty in the monitoring data and meet the statutory requirements.

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