

Event-scale concentration-discharge relationships across catchments

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The emergent relationship of riverine concentration of a given constituent and discharge (C-Q) measured at the catchment outlet can be used as a powerful tool to characterize dominant processes shaping water quality dynamics. C-Q relationships can both be applied to observations at inter-annual time-scales and at the scale of single discharge events when high sampling frequency (HF) data is available. With the development of robust in-situ probes, more and more HF data on nutrients and parameters such as electric conductivity allow analyzing a multitude of events within a given catchments and comparison of event responses between different catchments. Several methods exist that quantify event-scale C-Q relationships in terms of hysteresis characteristics and C-Q slope independent of each other. Here we propose a unified statistical modelling approach to characterize and quantify C-Q relationships at event-scale and apply that approach to HF water quality measurement in four neighboring catchments with contrasting land use and climatic conditions. We combine both, absolute Q and the first derivative of Q (dQ/dt) to predict C in a simple linear regression model: $\log C = a + b(\log Q) + c(dQ/dt)$. The derived model parameters allow us to characterize concentration level (a), C-Q slope (b) and hysteresis direction and size (c). In contrast to other techniques this model can also be applied to incomplete C-Q loops. We applied this model to in-situ measured nitrate concentrations, spectral absorption coefficient (SAC) at a wavelength of 254 nm representing dissolved organic carbon and electric conductivity (EC) from four neighboring catchments in central Germany. The catchments are characterized by a pronounced gradient in land use (forested to agriculture) and climatic conditions (wet to dry). We analyzed between 32 and 56 discharge events in each of the catchments separated from the measurements every 15 min for a period of two years. We found similarities in the event characteristics of the different constituents as well as distinct differences between the catchments. In general EC was characterized by dilution responses with weak hysteresis across all catchments. In contrast nitrate and SAC were mostly characterized by enrichment patterns with strong hysteresis in anti-clockwise but partly also in clockwise direction. We found that antecedent conditions such as averaged temperature and Q were powerful predictors for these intra-annual changes of model parameters. While responses in nitrate and SAC were positively coupled in the smaller and more forested catchments, C-Q responses were decoupled and partly even opposite in the agricultural catchments. We argue that the source zone of nitrate and dissolved organic carbon differ in the catchments. In the forested catchments, both nitrate and SAC stems for near stream riparian soils. In contrast, in the agricultural catchments nitrate mainly stems from shallow groundwater further upslope resulting in a delayed response with stronger hysteresis between C and Q. Further statistical analysis of the model parameter and catchment characteristics will reveal the interplay of source connectivity and availability of the constituents under differing event conditions.