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A classification scheme for concentration-discharge relationships based on long-term low-frequency water quality data

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Riverine nutrient concentrations represent the integrated response to hydrological and biogeochemical processes in the terrestrial phase of the catchment and in stream. Effective mitigation measures against nutrient pollution require in-depth knowledge of the spatio-temporal controls on water quality. The analysis of concentration-discharge (c-Q) relationships allows investigating solute sources and pathways. The hysteresis behaviour in c-Q relationships is often analysed based on high-frequency data (event-based or continuous time series in experimental catchments).

We developed a classification scheme to describe hysteresis patterns in c-Q dynamics also for low frequency observations of concentrations (given sufficiently long records). Nine classes of c-Q relationships are distinguished as a combination of export behaviour (dilution, neutral, enrichment) and rotational pattern of the hysteresis (clockwise, no rotation, anti-clockwise). To that end, power-law functions are used to describe the relationships between concentration and discharge. These relationships use distinct parameter values for rising and falling hydrograph limb and for low flows and high flows. The export behaviour is assessed based on the theoretical c-Q relationships by testing whether concentrations decrease, do not change or increase with discharge (Mann-Kendall test). The rotational pattern is determined by comparing concentrations at the rising and the falling limb of the hydrograph (Kruskal-Wallis test).

The classification scheme has been applied to daily stream-flow and monthly nutrient concentration data of 45 Scottish catchments (time period: 1987-2016, catchment area between 55 and 4587 km^2, covering in total around 50 % of mainland Scotland). For these catchments, similarity in terms of stream-flow variability and nutrient exports has furthermore been investigated by hierarchical cluster analysis of mean values and variability indices of runoff depth and nutrient concentrations.

The classification of c-Q relationships often relates to catchment characteristics. Dilution behaviour of total organic nitrogen, ammonia and nitrate often occurs in catchments with high annual precipitation and low proportions of arable land. Areas with high proportions of (sub-)urban land often show dilution behaviour of nitrate, total and soluble reactive phosphorous. Total and dissolved organic carbon mostly are characterized by enrichment behaviour especially in catchments with relatively low annual runoff. Total and soluble reactive phosphorous mostly show clock-wise rotation, which is most pronounced in catchments with relatively high (sub-)urban land and low wetland proportions. The clusters of stream-flow variability can be ascribed to climatic conditions and topography, whereas land cover is the main control for concentration variability clusters. Furthermore, we will explore the extent to which soil hydrological characteristics and soil organic horizons explain the c-Q relationships.

The classification scheme for c-Q relationships presented is transferable to other catchments and allows increasing the information content of low frequency data of concentrations as typical for regulatory monitoring data. Understanding the catchment-specific controls on water quality can inform efficient pollution mitigation measures against, monitoring strategies, as well as water quality modelling and regionalization approaches.