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Eco-hydrological controls on the seasonal variations of NO_3 and DOC concentrations in headwater catchments at the regional scale

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Studies of spatial and temporal variation of Nitrate (NO_3) and Dissolved Organic Carbon (DOC) concentrations in rivers can inform on the control of their exports by hydrological processes, soil biogeochemical processes and catchment characteristics (geomorphology, land use, etc…). However, such studies are often conducted on large river basins, in which in-stream processes obscure soil-to-stream processes and landscape effects. This study has two objectives: 1) characterize NO_3 and DOC concentration dynamics on small headwater streams, and particularly their dyssynchrony, 2) identify their controlling factors.
We used time series of public dataset on water quality together with spatial information on climate, soil, geology, hydrology, agricultural land, domestic pressures and landscape features from 185 independent headwater catchments located in Brittany, Western France. Rivers and streams have been monitored for NO_3 and DOC concentrations between 2007 and 2017, with at least eight samples per year. Catchments sizes vary from 1 to 200 km^2 (median of 38 km^2). We used Generalized Additive Models to describe seasonal variations of NO_3 and DOC concentrations and flow rates and extract amplitude and phase metrics. Potential controlling factors were identified using a correlation analysis between seasonal metrics and hydrological and land use variables.
Respectively for NO_3 and DOC, 85% and 71% catchments present a significant seasonal cycle and amplitudes are 3.3 ± 2.1 mgN/L and 3.1 ± 1.7 mgC/L. Four groups of catchments were identified based on seasonal metrics. In group A, 66 catchments depict an anti-correlation between NO_3 and DOC seasonal pattern. NO_3 maximum occurs in winter synchronously with DOC minimum and discharge maximum, while NO_3 minima and DOC maximum occur in autumn. In group B (12 catchments), NO_3 maximum occurs in summer synchronously with DOC minimum and the lowest summer flows. Group C (64 catchments) shows an intermediate pattern with two annual maxima for NO_3 (and two minima for DOC) occurring in winter and summer, but sometime with a lag time for the pattern of NO_3. Group D (26 catchments) is composed of catchments without significant seasonal variation for NO_3 and DOC concentrations. The spatial variability of seasonality was mainly explained by differences in hydrological reactivity and to a minor extend by differences in geological substrate characteristics. In catchments with lowest groundwater contribution and highest hydrological reactivity, NO_3 and DOC seasonal fluctuations are high and correspond mainly to group A. In catchments with highest groundwater contributions, NO_3 seasonal fluctuations are small and those of DOC strong (mainly associated with group B). These results indicated that water transit time through the catchment as a result of mixing between groundwater and sub-surface runoff is a key element explaining opposite seasonal patterns of NO_3 and DOC.