Subsurface reactivity dominates regional patterns of riverine nitrate concentration variability

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The mean surface water concentration and the concentration variance of nutrients are major water quality characteristics of catchments that directly relate to exported nutrient loads and ecosystems functioning. The mean concentration reflects nutrient input, discharge (Q) and retention within different compartments of the catchment. The concentration variability defines the export regime of a certain solute and can be characterized by the ratio of CVₐ and CVₕ and the slope b of the logC-logQ relationship. Recent explorative modelling studies argue that the export regime is shaped by spatial variance of the solute source in the catchment and by the subsurface reactivity (Musolff et al. 2017, Zhi et al. 2019). Here, we seek large scale evidence of this hypothesis by analyzing nitrate concentration and discharge (C-Q) time series in more than 1400 catchments across France and Germany. We found a consistent relationship between mean nitrate concentrations and the fraction of cultivated area within the catchments pointing to agriculture as the dominant nitrate source. The upper boundary of this relationship follows an exponential function with catchments showing mean nitrate concentrations around this envelope function being characterized by chemostatic export regimes with low concentration variance and slope b near zero. In contrast, catchments deviating from this relationship i.e. with lower than expected mean nitrate concentrations are characterized by higher concentration variance and steep, positive logC-logQ slopes. We argue, that subsurface retention is the major control of this behavior: i.e., effective denitrification decreases groundwater nitrate concentration. This was mainly observed in catchments with sedimentary aquifers and low topographic slopes. Here, old water components in the catchment storage that dominate discharge under low flow conditions are low in nitrate. Under high flow conditions, young water components high in nitrate concentrations are activated. Catchments without effective nitrate retention are characterized by a low concentration gradient between younger and older water components. The observed relationship between the fraction of cultivated areas, mean nitrate concentration and export regime was found to be surprisingly consistent across the wide range of hydroclimatic conditions, geology and topography. In consequence, steeply positive logC-logQ slopes can be used as indicators of effective subsurface reactivity. Future work will further elucidate the catchment characteristics that favor effective denitrification.

References
