

## Identification of nitrate sources and discharge-dependent nitrate dynamics in a mesoscale catchment

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During the last decades, nitrate concentrations in surface and groundwater have increased due to land use change and accompanying application of fertilizer in agriculture as well as increased atmospheric deposition. To mitigate nutrient impacts on downstream aquatic ecosystems, it is important to quantify potential nitrate sources, instream nitrate processing and its controls in a river system. The objective of this project is to characterize and quantify (regional) scale dynamics and trends in water and nitrogen fluxes of the entire Holtemme river catchment in central Germany making use of isotopic fingerprinting methods.

Here we compare two key date sampling campaigns in 2014 and 2015, with spatially highly resolved measurements of discharge at 23 sampling locations including 11 major tributaries and 12 locations at the main river. Additionally, we have data from continuous runoff measurements at 10 locations operated by the local water authorities. Two waste water treatment plants contribute nitrogen to the Holtemme stream. This contribution impacts nitrate loads and nitrate isotopic signatures depending on the prevailing hydrological conditions.

Nitrogen isotopic signatures in the catchment are mainly controlled by different sources (nitrified soil nitrogen in the headwater and manure/ effluents from WWTPs in the lowlands) and increase with raising nitrate concentrations along the main river. Nitrate loads at the outlet of the catchment are extremely different between both sampling campaigns (2014:  $\text{NO}_3^- = 97 \text{ t a}^{-1}$ , 2015:  $\text{NO}_3^- = 5 \text{ t a}^{-1}$ ) which is associated with various runoff (2014:  $0.8 \text{ m}^3 \text{ s}^{-1}$ , 2015:  $0.2 \text{ m}^3 \text{ s}^{-1}$ ). In 2015, the inflow from WWTP's raises the  $\text{NO}_3^-$  loads and enriches  $\delta^{18}\text{O-NO}_3$  values. Generally, oxygen isotope signatures from nitrate are more variable and are controlled by biogeochemical processes in concert with the oxygen isotopic composition of the ambient water. Elevated  $\delta^{18}\text{O-NO}_3$  in 2015 are most likely due to higher temperatures and lower discharge resulting in a higher impact of evaporation on water isotopes and a higher/different level of biological activity (esp. in the WWTP). Enriched isotope values for nitrogen and oxygen are not indicative of a significant impact of bacterial denitrification, because they are accompanied by increased nitrate concentrations (1 to  $16 \text{ mg L}^{-1}$ ).

Based on the presented study, 50 % of the nitrate export from the Holtemme river catchment can be attributed to WWTP effluent. The remaining amount is related to agricultural land use. Consequently, nitrate load reduction in the river system cannot rely on internal processing but needs to be regulated by preventive measures especially by an improved wastewater treatment and land use management.