



Nitrate and Water Isotopes as Tools to Resolve Nitrate Travel Times in a Mixed Land Use Catchment

Christina Radtke¹, Stefanie Lutz², Christin Mueller¹, Jarno Rouhiainen¹, Ralf Merz¹, Xiaoqiang Yang³, Rohini Kumar⁴, Paolo Benettin⁵, and Kay Knoeller¹

¹Helmholtz-Centre for Environmental Research, Catchment Hydrology, Germany

²Utrecht University, Copernicus Institute of Sustainable Development, the Netherlands

³Helmholtz-Centre for Environmental Research, Aquatic Ecosystem Analysis and Management, Germany

⁴Helmholtz-Centre for Environmental Research, Computational Hydrosystems, Germany

⁵Laboratory of Ecohydrology ENAC/IIE/ECHO, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland

For the sake of food production, nutrients like nitrogen (N) are applied on agricultural land to supply crops. However, due to common agricultural practice, the amount of N provided very often significantly exceeds the uptake potential of the plants resulting in a N surplus that accumulates in the soil. Organic soil nitrogen is slowly transformed to nitrate, which is then mobilized by water and moves through the subsurface, with the risk of contaminating receiving water bodies. High nitrate loads cause poor chemical states for 27% of all groundwater bodies in Germany and foster eutrophication in lakes and rivers and by this a loss of biodiversity. The main problem are legacy issues of nitrate pollution, because there is a time lag between N input and nitrate mobilization and transport. Research on nitrate travel times is highly relevant for a reliable prediction of the capability of catchments to store, buffer and release nitrate. However, it is not clear how long nitrate is stored and transported in catchment's storage. For this study, a 11 km² headwater catchment with mixed land use within the Northern lowlands of the Harz mountains in Germany was investigated from spring 2017 until the end of 2020. A monitoring program was set up, starting with biweekly samples for the first two years and daily samples for the remainder, with sub-daily samples during precipitation events. Samples were taken from stream water and when available from precipitation water. Nitrate concentrations as well as isotopic signatures of water ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) and nitrate ($\delta^{18}\text{O}$ and $\delta^{15}\text{N}$) were analysed. To investigate nitrate travel times, the numerical model tran-SAS (Benettin and Bertuzzo, 2018) was set up und modified for this catchment. Here, a time-variant power law function was used as rank StorAge Selection (SAS) function to select the composition of fluxes considering their age. Nitrate with a distinct $\delta^{18}\text{O}$ from water, formed during microbial activities in the upper soil zone is transported with leaching water into the subsurface storage where denitrification with the corresponding isotope fractionation occurs. The combination of stable isotopes of water and biogeochemical equations to describe the forming of nitrate isotopes and the fractionation of nitrate isotopes during denitrification, which depends on transit times is a novel tool to investigate nitrate age and nitrate transport. Together with the usage of a SAS-based transit time model to simulate nitrate transport and denitrification in the subsurface, tran-SAS is transformed into a simplified reactive transport model (RTM).

A decoupling between nitrate age and water age as well as between nitrate travel times and water travel times is expected. Especially during precipitation events catchment's processes and travel times are changing due to altering hydrological conditions. The model allows to investigate the age of water and nitrate during different hydrological conditions. This will become more and more important considering more frequent hydrological extremes (droughts and floods) and associated N mobilization in agricultural catchments.