



## Using in-situ monitoring and modeling to characterize isotope effects in nitrate cycling at an agricultural site

Juan Carlos Richard-Cerda<sup>1</sup>, Stephan Schulz<sup>1</sup>, and Kay Knöller<sup>1,2</sup>

<sup>1</sup>TU Darmstadt, Institute of Applied Geosciences, Hydrogeology Group, Darmstadt Germany (richard.cerda@geo.tu-darmstadt.de)

<sup>2</sup>Helmholtz Centre for Environmental Research UFZ, Department Catchment Hydrology, Halle, Germany

Stable isotopes of nitrate ( $\delta^{15}\text{N-NO}_3^-$  and  $\delta^{18}\text{O-NO}_3^-$ ) are powerful tools for tracing nitrogen sources and understanding transformation processes in soil-water systems. The isotopic composition of nitrogen and oxygen evolves due to isotope effects, which characterize processes such as nitrification and denitrification whilst offering insights into the environmental factors driving these reactions. Although isotope effects are often derived from laboratory experiments under controlled conditions, this study aims to derive them in situ within a dynamic natural system, where varying redox conditions, inflows, and substrate availability introduce complexities absent in controlled environments.

Combining high-resolution hydrochemical and stable isotopic monitoring of nitrate and water with numerical modeling and particle tracking using HYDRUS, we investigate the spatial variability of nitrogen transformations within an agricultural soil profile. Preliminary results indicate that nitrification, with nitrate concentrations exceeding  $200 \text{ mg}\cdot\text{l}^{-1}$ , is prominent in the upper soil layers and exhibits isotopic signatures ( $\delta^{15}\text{N} = 4.2\text{‰} \pm 0.9\text{‰}$ ) characteristic of soil nitrogen, likely derived from the immobilization of applied fertilizer. Denitrification, reducing concentrations to as low as  $0.2 \text{ mg}\cdot\text{l}^{-1}$ , occurs primarily within the capillary fringe, generating a linear  $\Delta\delta^{18}\text{O}:\Delta\delta^{15}\text{N}$  trajectory with a slope of 0.79 and a field based apparent isotopic enrichment factor for nitrogen of  $\epsilon = -4.8\text{‰}$ . Below this zone, regions dominated by nitrification on denitrification exhibit curved  $\Delta\delta^{18}\text{O}:\Delta\delta^{15}\text{N}$  trajectories, highlighting the incorporation of oxygen from ambient water during re-nitrification.