Investigating Nitrate heterogeneity in a basement aquifer: A NO$_3$ isotopes, CFCs-SF6, microbiological activity, geophysics and hydrogeology approaches in the critical zone

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Nitrate contamination of groundwater remains one of the major water quality concern despite all the efforts undertaken over the last decades to protect water resources. This study focuses on a small catchment in Brittany (France) facing nitrate pollution with concentration > 50 mg.L$^{-1}$, representative of many catchments where measures, supposedly effective, have been applied to reduce the loss of N towards groundwater with limited effects. Within this small aquifer (0.6 km$^2$), nitrate concentrations are very heterogeneous.

We have applied an interdisciplinary study, coupling complementary and robust approaches in order to explore and better constrain the nitrate fate and processes. A geological approach was conducted to accurately identify the lithologies, tectonic structures and weathering layers, together with a geophysical survey based on Electrical Resistivity Tomography (ERT) method. These approaches have highlighted the very complex geological structures with numerous compartments delimited by faults, as well as highly variable thickness of the weathered layer, pointing out the heterogeneity of the hydrosystem with some compartments appearing to be disconnected from the general present day underground flow. This was further confirmed by geochemical analysis and apparent groundwater residence time assessment based on CFCs-SF6 and noble gas analyses, revealing locally old and nitrate-free groundwater, and a very old water, with a recharge temperature colder than the current average temperature of the area, reflecting water originating from the last period of glaciation (-19 to -17 ky). The nitrate isotopic approach has clearly evidenced denitrification processes in a few piezometers, that was generally supported by the microbiology and molecular biology approach highlighting the presence of functional genes involved in denitrification as well as the capacity of the groundwater microbial community to denitrify when in favourable $in situ$ conditions.

This study demonstrated the benefits of the multi-disciplinary approach to better understand the nitrate fate and processes at a small catchment scale in a basement aquifer and to explain the temporal and spatial variability of groundwater quality. This type of combined approaches, appear to be paramount to properly assess effectiveness of implemented programs of measures by taking into account the timeframe between measures and impact on groundwater quality.