



Nitrite: the key to understanding nitrogen cycling in ammonium-rich systems?

Naomi Wells (1), Kay Knöller (1), Vivien Hakoun (2), and Serge Brouyère (2)

(1) Helmholtz Centre for Environmental Research - UFZ, Catchment Hydrology, Halle (Saale), Germany (naomi.wells@ufz.de), (2) Université de Liège, Département ArGENCo, Hydrogéologie et Géologie de l'Environnement, Bât.B52/3 – Sart-Tilman, B-4000 LIEGE, Belgium

Mounting evidence for the importance of biological nitrogen (N) transformation pathways that do not use or produce nitrate (NO_3^-) (e.g., anaerobic ammonium oxidation, co-denitrification, and nitrifier-denitrification) necessitates the development of new approaches for determining a system's N balance. Efforts to parameterize groundwater N cycling are typically based on measurements of only the dominant ions (ammonium (NH_4^+) and NO_3^-), while isotope-based approaches rely on NO_3^- isotopes ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$). Looking beyond these two species, highly reactive nitrite (NO_2^-) is unlikely to account for an appreciable proportion of the inorganic N pool (and thus generally assumed to be insignificant). However, its role as a reactive intermediate makes it a potentially useful indicator of all microbial N transformations.

The isotopic composition of NO_2^- ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) therefore could be useful for identifying the N removal hotspots that would be missed by measuring only NO_3^- isotopes (i.e. those not driven by denitrification). We explored this possibility by measuring the variations in NO_2^- concentrations and isotopic composition from across NH_4^+ plumes in two aquifers, one in eastern Germany (L: 40 wells, sampled thrice) and one in western Belgium (C: 56 wells, sampled once). Nitrite concentrations were tightly coupled with NH_4^+ concentrations in both locations, which had maximum values of 100 mg NH_4^+ -N and 0.3 mg NO_2^- -N in L and 900 mg NH_4^+ -N and 1 mg NO_2^- -N in C. The importance of NO_2^- reduction processes was determined by comparing $\delta^{18}\text{O}$ - NO_2^- data to the calculated range possible for in-situ nitrification (ammonia oxidation and/or NO_2^- oxidation) based on the measured $\delta^{18}\text{O}$ - H_2O range. Discontinuities between NO_3^- reduction zones and NO_2^- reduction zones were then used to identify where N removal was driven by non-denitrification processes. Overall NO_2^- isotopic values spanned a range of values two- to three-times greater than that of either NO_3^- or NH_4^+ . For instance, $\delta^{15}\text{N}$ - NO_2^- ranged from -30‰ to +80‰ in L and from -20‰ to +40‰ in C). While denitrification at the plume fringe was the dominant N removal pathway in both systems, this NO_2^- data from within the plumes reveals an unexpectedly dynamic N cycling that necessitates a re-evaluation of our understanding of how biology handles N within NH_4^+ contaminated groundwater.