

Interactive comment on “Nitrification and Nitrite Isotope Fractionation as a Case Study in a major European River” by Juliane Jacob et al.

Anonymous Referee #3

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Overall, the data presented in the study are novel, particularly since there exist vanishingly very few measurements of nitrite isotopes, in tandem with ammonium and nitrate isotopes in any environment.

The interpretation of these results yields some constraints, but is otherwise wanting, for two overarching reasons: (1) The system is complex, and the data at hand are insufficient to resolve inherent dynamics and (2) interpretation of the isotope data is coarse, relying on over-simplifying assumptions.

(1) Evident when considering first of two main conclusions cited in the abstract

“We found that in the water column, ammonium and nitrite derived from internal recycling processes, whereas nitrate mainly leached from catchment area.”

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While this seems like a reasonable conclusion, I cannot decipher how the authors' data and their interpretation yield these conclusions.

For the sake of argument, could the ammonium and nitrite not be imported from the catchment, from internal cycling therein (in soil)? Which aspects of the isotope data enable partitioning of processes that happened in situ vs. the catchment? Does it even matter?

I think the general arguments/assumptions as to the origin and fate of ammonium, produced by recycling and consumed by nitrification are reasonable. Nevertheless, one could argue for some role of ammonium assimilation. Nevertheless, assuming negligible assimilation, could the authors not generate plausible scenarios of nitrite production/oxidation and associated isotope effects that could constrain the relative fluxes, given the measured isotope composition of ammonium and nitrite? I realize the range of solutions may be too broad, but perhaps some scenarios could be ruled out with such an exercise.

(2) The second conclusion stated in the abstract is facile and could be construed as misleading:

“Our data are a first approximation of the isotope effect of nitrite oxidation in natural environments and highlight that pure culture results cannot readily be extrapolated to natural microbial assemblages or water bodies.”

The isotope composition of nitrite in the environment is implicitly the result of multiple co-incident reactions, each of which is associated with an isotope effect. It's self-evident that a single Rayleigh fit to NO₂ consumption will not describe a single uni-directional reaction on said NO₂, which does not mean that culture results cannot be extrapolated to the environment. What an odd conclusion! I urge the authors to refine this conclusion so as to appear less incongruous.

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