

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

## **Anonymous Referee #2**

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Review of “Nitrification and nitrite isotope fractionation as a case study in a major European River” by Jacob et al.

### Summary

The authors present a study that depicts the evolution of nitrogen cycling dynamics during a large flood of the Elba River in Germany during June 2013. Using a combination of both concentrations and isotopes of nitrate, nitrite, ammonium and particulate nitrogen, the authors aim to understand the nature of the biogeochemical processes responsible for these changes and what can be learned about the controls on them – in this case under flood conditions – but perhaps in rivers in general. In particular, the authors argue that light limitation by the elevated suspended load during the flood acts to limit photosynthetic uptake by phytoplankton in the river – offering a perspective on

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nitrogen cycling largely in the absence of assimilatory processes. Based on this and other assumptions, the authors conclude that nitrification is driving the majority of the observed patterns and then use the isotope data to make estimates of nitrogen isotope fractionation for nitrification.

General Comments Overall – this is an interesting dataset with relevance to understanding the nature and magnitude of nitrogen cycling processes in large rivers. To my knowledge these type of datasets are fairly novel (especially the nitrite isotope analyses) – and certainly reflect a complex array biological and hydrological processes. To the degree that a mechanistic understanding of the processes reflected in the concentrations and isotopic compositions can be refined, this study represents a novel step forward in the development of such isotopic tools. However, my primary concern is that rivers are inherently dynamic, non-steady-state systems – and that it may be difficult or impractical for the authors to isolate a single biogeochemical process within this physically complex and hydrologic system (confounded by factors such as dilution?, source-mixing?, hyporheic flow?). Studies of hydro-biogeochemical processes are notoriously complex – in particular over the course of a large episodic event – in which the proportions of primary flow paths, for example, (e.g., soil water, shallow groundwater, deep groundwater, hyporheic exchange, surface runoff, etc.) may also be changing over time. In fact, the authors acknowledge that the increase in the nitrate and SPM concentrations on the rising limb and crest of the flood reflect changes in sources of watershed inputs (e.g., P6 L10-14).

Since samples were collected at only one point on the river – the perspective for quantitatively evaluating N cycling processes within the river is somewhat limited. As presented, it is hard to discern to what degree hydrologic changes might account for the observed changes in isotopes and concentrations. Indeed this perspective embodies a classic sampling perspective for riverine/hydrologic studies: Eulerian (fixed point or volume) versus Lagrangian (fixed water parcel). The authors' study is intrinsically Eulerian observing a defined volume (control volume) occupying a fixed point (or box) in

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space. However, since many (most?) of the features being observed by the authors' measurements may indeed be related to changes in the hydrologic and geochemical inputs to this volume – it becomes virtually impossible to assign the biogeochemical changes observed to processes occurring within the box (as the authors have attempted to do). Rather, the authors' questions (how much nitrification occurs and/or plays a role in the isotopes, for example) would be better addressed by a Lagrangian approach in which a parcel of water is tracked down river over – such that changes in the inputs to the system can be more or less neglected and the changes in the nitrogen content and isotopic composition can be directly related to 'in-river' processes.

Clearly, one cannot expect the authors to repeat the study of this extreme flood event. Can any other conservative tracers of flow ( $\delta^{18}\text{O}$  water, bromide, chloride, major ions, etc.) be measured to help constrain water (and N) sources during the flood hydrograph? I wonder whether a simple box model could be constructed, in which, one might solve for varying rates of nitrogen cycling processes required in order to fit the observed data – and something then be learned about the operation of varying processes under such flow conditions? If we can make the assumption (based on conservative tracers?) that the water and N sources are conservative (and constant?) and that all biogeochemical reactions happen in the river (including hyporheic exchange?) – and make estimates of them using conservative tracers - then perhaps variations of the observed compositions could be used to constrain rates of those biogeochemical processes.

Another thought is that the overall discussion might benefit from a re-focusing around the “fate of nitrite” and “nitrite-consumption processes” – rather than solely on nitrite oxidation (including nitrite assimilation, oxidation or denitrification). Ultimately the authors conclude that multiple processes are in play here. Thus, while the authors may not be able to nail down one specific process – perhaps they could make reasonably well-constrained estimates of the rates of multiple processes.

Additionally, I don't think a closed system Rayleigh model can be justified here. In

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general - use of the Rayleigh fractionation model implicitly assumes that only one, uni-directional process is occurring. In addition to nitrite oxidation, however, by the authors' own argument – the nitrite isotope data likely reflect at least one other processes (ammonia oxidation) – thereby invalidating the use of a Rayleigh model for estimating the isotope effect of a single process. While it is possible that the decrease in  $\text{NO}_2^-$  concentration is caused by a river-hosted biological (e.g., fractionating) process – leading to the observed increase in N isotopic composition, can it be demonstrated that the nitrite concentrations are not the product of low levels of  $\text{NO}_3^-$  reduction occurring in sediments/hyporheic exchange/groundwater? In fact, the nitrite concentrations vary in a smooth fashion (in contrast with the  $\text{NH}_4^+$  concentrations, for example) – which to me might suggest more of a hydrologic control on their dynamics.

After much confusion - I think that the Figure 2B legend is wrong.

The decrease in nitrate concentrations on the falling limb of the flood are explained by phytoplankton assimilation – why could this not also possibly explain the concomitant loss of nitrite and the positive isotope excursion?

#### Specific Comments

P1 L9: 'bulk isotope effect of nitrification' is not clear and should be defined.

P1 L11: 'divergent' is unclear

P1 L16: In concert with...

P1 L19: ...from the catchment area.

P1 L22: I'm not convinced that you can conclude the changes in isotopes are the result of nitrite oxidation only. You should state that this is the 'apparent' isotope effect of nitrite consumption (although this may also not be valid as calculated – e.g., violation of Rayleigh model assumptions).

P1 L30: ... has increased 20-fold...

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P2 L7: Or, the nitrate can be simply exported from the watershed.

P2: I think the imperative for understanding nitrification in riverine systems should be better justified – perhaps in terms of its frequent coupling to N loss processes (anammox and denitrification) and ecosystem services.

P2 L13: Not just nitrogen uptake – but any enzymatically catalyzed nitrogen transformation process.

P2 L14: This is somewhat of a colloquial expression – and should be restated to reflect that enzymatically catalyzed processes occurring slightly faster for lighter isotopes than heavy isotopes.

P2 L15: The Rayleigh model explicitly requires the assumption of a unidirectional process and no replenishment of the reactant pool. It's not clear that this can be assumed.

P2 L18: obstacle to what?

P2 L21: ...and the remaining nitrite...

P2 L26: what is meant here by the term 'healthy?'

P2 L37: Phytoplankton are light dependent...

P3 L8: ...the second largest river discharging...

P3 L25: Isotope analyses

P5 L4: Previous studies have found...

P5 L8: Either present data as singular or plural – not both. ... nitrate concentrations were... Nitrite concentrations were <1.2... and ammonium concentrations were below the detection limit...

P5 L28: Not sure I would say that the nitrite concentrations rose 'quickly' – they seem to evolve more gradually in fact.

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P5 L30: For reasons discussed above, I think it should be stressed here that this is an 'apparent' fractionation factor.

P6 L2: Remove "it is interesting, however" – opinions don't generally belong in a results section.

P6 L 20: Although as noted later – the relatively large nitrate pool is far more resistant to isotopic perturbations by biogeochemical processes.

P6 L25: While this may be true – the watershed flooding potentially may have also introduced a nitrate source having a slightly different isotopic composition.

P6 L29: As the phytoplankton are recovering – couldn't they be assimilating nitrite?

P6 L32: This  $\delta^{15}\text{N}$  vs  $\delta^{18}\text{O}$  slope is actually much lower than that observed by Granger and colleagues. Could this be indicative of nitrification?

P7 L3: Why can't phytoplankton be playing role in assimilation of nitrite and/or ammonium?

P7 L23: But phytoplankton activity was specifically invoked as explaining an increase in N and O isotopes of nitrate and contributing to a drawdown of  $\sim 100\mu\text{M}$  nitrate. Thus, it seems hard to discount phytoplankton activity for drawdown of  $\sim 1\mu\text{M}$  nitrite and  $\sim 3\mu\text{M}$   $\text{NH}_4^+$ .

P8 L10: ... suggesting conventional normal (as opposed to inverse) fractionation during...

P8 L29-30: The contribution of 25% sedimentary denitrification actually seems substantial – and therefore hard to rule out. Also – can the same conclusions of Deutsch et al., 2009 be drawn for the extreme flood conditions of this study? Couldn't flooding act to increase hyporheic exchange?

P8 L35: As conceptualized by the authors, since the  $\delta^{15}\text{N}$  of the  $\text{NH}_4^+$  is  $\sim +2\text{permil}$  to begin with ( $\sim 4\text{permil}$  lower than the SPM  $\delta^{15}\text{N}$ ) – the  $\delta^{15}\text{N}$  of the  $\text{NO}_2^-$  produced (in a

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closed system) would follow the accumulated product equation – and under conditions where  $\text{NH}_4^+$  was being completely oxidized to  $\text{NO}_2^-$  – the newly produced  $\text{NO}_2^-$  would have a  $\delta^{15}\text{N}$  of +2permil. In developing the argument about the contribution of heavy nitrite from ammonia oxidation, the authors should be careful to explain how this new nitrite composition will evolve in step with the degree of  $\text{NH}_4^+$  consumption. Initially the new nitrite will have a  $\delta^{15}\text{N}$  even lower than the existing nitrite, while as  $\text{NH}_4^+$  is consumed – the  $\delta^{15}\text{N}$  of the newly produced nitrite will approach the original  $\delta^{15}\text{N}$  of the  $\text{NH}_4^+$  ( $\sim +2\text{‰}$ ). This value of +2‰ is actually not the ‘isotopically enriched’ nitrite that seems to be invoked here by the authors. Later on P9 L18, the authors explain how the complete consumption of  $\text{NH}_4^+$  would quantitatively transfer the  $\delta^{15}\text{N}$  value of the  $\text{NH}_4^+$  pool into the nitrite pool – yet it is not clear whether the authors are using the evolving  $\text{NH}_4^+$  pool as a closed system – or simply invoking the instantaneous product equation at each step. Notably – these values and mass balance estimates will play importantly into their ‘back-of-the-envelope’ calculations.

P9 L21: I think the discussion could be clarified if these calculations were explained in more detail.

P9 L36: I don’t think there is any sort of cryptic ammonium cycle occurring here. More likely, it seems that the authors are just witnessing more ‘conventional’ N cycling processes (e.g., remineralization, nitrification, assimilation, etc.) from the perspective of nitrite isotopes for the first time in a river.

Figure 2b: Caption is wrong?

Figure 4b: this should be labeled as ‘apparent isotope effect for nitrite consumption’ (not nitrite oxidation). As articulated by the authors in the discussion, I don’t think you can tie these isotope changes to a single process.

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