

***Interactive comment on* “Seasonal variations in nitrate isotope composition of three rivers draining into the North Sea” by A. Deek et al.**

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Received and published: 8 November 2010

We thank the anonymous reviewer for the review and the valuable comments. Our responses to the suggestions are as follows:

Assumption #1: Nitrate d15N delivered to rivers from the catchment is invariant inter-seasonally. The authors present no evidence that this is so. What if denitrification were occurring in soils? What would that do to the d15N and d18O of nitrate delivered to rivers?

The statement “Nitrate d15N delivered to rivers from the catchment is invariant inter-seasonally” is unclear to us, because we do not find such a thesis in the manuscript. We mention that nitrate sources interfere with the basic isotope signal of nitrate (p.6068,

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l.16–19), and also that other processes like partial denitrification and selective assimilation leads to an enrichment of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ (p. 6061, l. 29 – p. 6062, l. 4). However, we rephrased this paragraph to underline that soil denitrification may influence the isotope signal as well (. . .denitrification in soils causes the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ to increase as nitrate concentrations decrease e.g., denitrification of fertilizer nitrate with an original $\delta^{15}\text{N}$ value of around 0‰ can yield residual nitrate with high values between 15‰ and 30‰ similar to values expected from nitrate from manure or septic tank (Kendall and Doctor, 2005)).

Assumption #2: a) Assimilation of nitrate in rivers accounts for the seasonal decrease in nitrate concentrations What if: the lower nitrate concentrations were to reflect lower nitrate loading into rivers from the catchment. Given less precipitation or snow-melt in summer, it seems plausible that less nitrate would make it to rivers from the catchment. The authors hint at this but then state that the decrease in nitrate in summers reflects assimilation.

We agree that decrease of nitrate concentrations in summer may be caused by a combination of higher assimilation in summer and less nitrate loading from the catchment. We intended to discuss the interrelation between nitrate loading and discharge yield in the section “Influence of river discharge” and state that “low nitrate concentrations in summer months increase towards winter accompanied by higher discharges fed by precipitation events by that season” (p. 6067, l.5-7). We rephrased some expressions on p. 6067 and p. 6068 and clarified that assimilation together with lower nitrate inputs from the catchments cause a decrease in riverine nitrate loading.

b) Moreover, the longer residence time of nitrate in soils in summer could make it more likely to be denitrified directly in soils, thereby delivering even less nitrate per rain event.

We added this point in the section “Nitrate from organic and synthetic fertilizers” noting that in summer, denitrification rates in soils may be even higher.

c) And: what if sediment denitrification in rivers caused some of the decrease in nitrate?

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We mention that sedimentary denitrification is likely to occur, but the isotopic effect is negligible (p. 6068, l.2–4)

d) And: Assimilation does not, in and of itself, cause a net loss of reactive N from rivers. In the riverine N mass balance, what happens to PN produced from nitrate? Does it disappear, does it get trapped upstream and remineralized there, is it recycle in the water column into ammonia, or is it remineralized right back to nitrate? In the latter case, denitrification in soils or in riverine sediment would need to be invoked to account for the loss of fixed N evidenced by the decrease in nitrate. In order for there to be a loss of nitrate only to assimilation, the nitrate-N assimilated needs to be in another pool, for which the authors do not account. The authors need to consider other more plausible scenarios to account for the decrease in river nitrate in summers.

It would be interesting to study the fate of nitrate and how the rN pool is recycled. This study was limited to the characterization of the isotope signal of riverine nitrate. Thus, questions regarding remineralisation, denitrification or nitrification rates remain unanswered. Still, other plausible scenarios have to be taken into account (i.e., nitrification of riverine ammonium) and as suggested by Ref#2, we added a supplemental table with measured ammonium concentrations demonstrating that other rN species than nitrate are of minor importance in the rivers under study. Thus, water column nitrification would not change the overall nitrate concentrations significantly.

Assumption #3: Nitrate assimilation in rivers accounts for 15N-enrichment of nitrate in summers relative to winter What if: denitrification in soils imparted 15N and 18O enrichment to nitrate that is delivered to rivers?

This point is a bit confusing because the Ref#1 referred Assumption #3 before as follows: “particulate d15N mirrors the d15N of nitrate in rivers” (C3171). However, the suggestion about denitrification in soils has been adapted (see also Assumption #2b).

Assumption #4: a) the d15N of reactive N in rivers reflects that of the source(s), directly (i.e. more elevated d15N of PN among rivers reflects more elevated d15N of N sources

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to the catchment), implying that the d15N is not modified while in the catchment relative to its initial source d15N. Catchment biological N transformations must hence be non-fractionating, although the opposite is clearly stated by the authors (p. 6061, lines 10 and 28).

We do not understand this comment, and we did not intend to state N transformations are not fractionating (of course this hypothesis would be erroneous). Although the Ref refers to page and line, we do not find a clear statement like this. In contrast, we discuss fractionation processes in detail on p. 6060-6061.

b) What if: the d15N of nitrate delivered to rivers were 15N-enriched in soils by denitrification, in proportion, in part, to the residence time of reactive N in soils before entering the river? Then scenarios could emerge where riverine d15N were particularly elevated in spite of a relatively lower source d15N, due to soil N dynamics. Seems plausible to me.

We are not sure if we understood this comment, but concerning soil denitrification we adapted this point (Assumption #2b+#3). On the other hand, we did not conduct a mechanistic study on N recycling in soils (i.e. residence time of ammonium or nitrate in soils, nitrification-, and denitrification rates), and these questions remain unanswered.

Assumption #5: a) the d18O of nitrate is determined by that of atmospheric oxygen (1/3) and that of water (2/3), as per Equation (2), which was prevalent in older literature. However, Equation (2) has been demonstrated as inaccurate. More recent studies involving careful investigation of mono-cultures have clearly illustrated that this is an oversimplification that is likely to yield erroneous prediction of the d18O of nitrate anticipated for nitrification (Casciotti 2002, Casciotti et al. 2008, Buchwald and Casciotti, 2009). While the value is not determined with absolute certainty, a number of studies narrow the range anticipated (Casciotti et al. 2002, Casciotti et al. 2007, Sigman et al. 2009, Pantoha 2009, Buchwald and Casciotti 2009).

We agree with the Ref. that Eq. 2 is an oversimplification. We intended to put our

findings into perspective, because the correspondence between the theoretical value according Eq. 2 and found $\delta^{18}\text{O}$ were somewhat surprising to us (p. 6063, l. 9-10). We are aware of recent findings and cited the published studies the Ref listed (p. 6063, l.17) even though at this time, the mechanism of oxygen fractionation during nitrification is still poorly understood. For better understanding we rephrased this paragraph stating that we found a correspondence with Eq. 2 (which should be mentioned) but assumptions underlying Eq. 2 were recently questioned.

b) What if: The authors determined the d^{18}O of nitrate anticipated for newly nitrified nitrate based on the d^{18}O of ambient water, and were then able to assess d^{18}O enrichment relative to newly nitrified nitrate.

This suggestion would require a pure culture study and/or incubation experiments.

Assumption #6: The d^{15}N of PN is determined by the d^{15}N of riverine nitrate. What if primary production relies largely on regenerated N in rivers, and thus reflects the d^{15}N of regenerated N primarily?

This point cannot be discussed on the basis of this data set.

Specific comments:

a) Abstract, line 20: “both are uncorrelated in time series due the lateral and temporal mixing of PN.” Not clear to me what this means or how that works.

We deleted this sentence, because the statement was too general and not funded.

b) Abstract, line 27: “human dominated land use” how is that measured. It’s the first we hear of it in the abstract. Learn later in the text that it’s in reference to another paper.

We replaced this expression by “urban and agricultural land use”.

c) Abstract, last sentence: The meaning is unclear. And what is nitrate consumption efficiency? What is it about humans that cause higher nitrate consumption efficiency?

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Within the abstract a short summary of the study is given whereas nitrate consumption efficiency and anthropogenic influence on nitrate degradation is discussed in more detail in the section “Biological processes in the rivers”. For better understanding, we rephrased the last sentence.

d) p. 6053 line 15: the Rhine and Elbe are considered large rivers, I surmise?

rephrased

e) p. 6053 line 27: What is the meaning of sources of nitrate within rivers have been overlooked? N₂-fixation?

We specified this sentence (sources: i.e., water column nitrification).

f) p. 6054, line 11: It seems to me that the d₁₅N of nitrate produced by nitrification is not a “range” per se, but rather determined by (1) the N isotope composition of ambient ammonia (2) the isotope effect and (3) the extent to which ammonium is nitrified to nitrate.

We agree, this sentence has to be corrected. It is not correct to mix up sources of N that have isotopic fingerprints with N transformation processes.

g) p. 6054, line 27: shed light on assimilation of what? Nitrate, ammonium, reactive N?

corrected: nitrate assimilation

h) p. 6055: paragraph 1: What did the previous study contribute and how does this one differ, or how can it improve findings, other than being a longer time series?

It is a longer timer series and confirms results from a year-study, thus the representativeness is given. Furthermore, the measurement of $\delta^{18}\text{O-H}_2\text{O}$ in combination with $\delta^{18}\text{O-NO}_3^-$ values is a valuable hind to nitrification even though the Eq. 2 may be partially revised. Additionally, first data of $\delta^{15}\text{N-PN}$ in these rivers are presented.

i) p. 6055, line13: loads of what? To what? Would “N loading” be a more appropriate

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term here?

corrected

j) p. 6055, line 23: the pore size of a GF/F is $0.7 \mu\text{m}$

corrected

k) p. 6056: How can the $\delta^{18}\text{O}$ of nitrate be compared to that of H_2O knowing that the correction is off?

We agree that $\delta^{18}\text{O}\text{-H}_2\text{O}$ and $\delta^{18}\text{O}\text{-NO}_3^-$ values are not directly comparable due to the revised correction. Thus, we may adapt the $\delta^{18}\text{O}\text{-NO}_3^-$ values to the assigned 25.6‰ or add an offset of 3‰ (25.6 minus 22.7‰. Adding an offset of 3‰ would result in mean $\delta^{18}\text{O}\text{-NO}_3^-$ value in winter (Tab. 1) between 3.4‰ and 5.2‰ for the rivers under study. Still, compared to potential sources such as atmospheric deposition and synthetic fertilizers, the $\delta^{18}\text{O}\text{-NO}_3^-$ values are relatively low and bear an imprint of ambient $\delta^{18}\text{O}\text{-H}_2\text{O}$ that is used during nitrification. We corrected/rephrased the paragraph “Nitrate from nitrification”.

l) p. 6058, line 7: “load” and “N discharge” are used interchangeably to mean N loading and or water discharge – should stick to single term for single process. And units should be specific (kt per year, rather than kt between this and that time).

corrected

m) p.6059, line 3: too vague a description of $\delta^{18}\text{O}$ nitrate

corrected (... $\delta^{18}\text{O}\text{-NO}_3^-$ values in the Rhine River are not significantly different in summer comparing to $\delta^{18}\text{O}\text{-NO}_3^-$ values in winter (Student’s t-test; $p>0.1$), $\delta^{18}\text{O}\text{-NO}_3^-$ values in the rivers Ems and Weser are significantly different in summer comparing to $\delta^{18}\text{O}\text{-NO}_3^-$ values in winter (Student’s t-test; $p<0.05$)...)

n) p. 6060, line 19: the $\delta^{18}\text{O}$ of which direct sources? And what are these values?

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corrected: ...such as atmospheric deposition (55–75% and synthetic fertilizers (18–22%.

Interactive comment on Biogeosciences Discuss., 7, 6051, 2010.

BGD

7, C3682–C3689, 2010

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