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Biogeosciences Discussions

Interactive comment on "Dissolved and particulate reactive nitrogen in the Elbe River/NW Europe: a 2-year N-isotope study" *by* T. Schlarbaum et al.

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First of all thank you very much to the referees for reading the manuscript and for their constructive and helpful comments.

Both referees are in agreement that we have an interesting set of data about the reactive nitrogen pool in the Elbe River, but both are of the opinion that our discussion to interpret the data is often too superficial and hypothetic. To take all the helpful comments into account, a complete revision of the discussion part will be necessary, but this will probably go beyond the scope of this interactive discussion. We will carefully consider the arguments of the referees when we get the opportunity for a revision of our manuscript.

In the following we will try to respond the single comments the referees pointed out.

Referee #2:

"Results P7552 - 3.4 Particulate nitrogen. When describing this profile you say there is no clear seasonal pattern of cPN, however, it seems to me that you have something quite evident with clear periods of high cPN and of low cPN. What is also clear is that cPN and d15NPN do not display the same seasonal variation pattern, they have a different periodicity (about 1 peak/year for cPN, 2 peaks/year for d15N-PN) - so periodicity of cPN close to the one of cNO3 and periodicity of d15NPN close to the one of c(NH4+DON) and 15N(NH4+DON). This should appear more clearly in the description and then your correlations (or the absence of correlations) become more clear. "

We agree and will describe the PN profile in more details.

"Discussion: Include the aspect of varying water discharge in your discussion. One way to look at your data is to plot all variables as a function of river discharge – this can be an interesting exercise to highlight the eventual importance of mixing processes and distinguish the importance of point and diffuse sources for each of your N pool (see my later comments too)"

We agree that we did not consider the discharge in a proper way and will do it in a revision of this manuscript. However, when we plotted discharge versus δ15N and concentration, no clear function could be observed.

"p7553 L21: ". . .since both DON and PN may be products of phytoplankton assimilation of the nitrate load; DON+NH4 may also originate from dissimilation of PN within the river. . .." This view about the origin of PN, DON and NH4 in the river is too simplistic. For example, assimilation of ammonium by phytoplankton ? External sources? Resuspension from sediments for PN?"

We agree that also other sources and sinks should be taken into account and we will do it in a revision, but our point of view is that our data should be a good hint for the

close relation of these two nitrogen species.

“4.1 Nitrate P7554 L4 and 5 : " The seasonal variability is essentially due to seasonal changes in biological activity,..” This is again, I believe, too simplistic and the variability of nitrate sources should also be considered. In rivers like the Elbe, high nitrate levels coinciding with high discharge situations show the importance of diffuse sources of NO3 rich waters percolating through fertilized soils”

We agree that also other nitrate sources may exist, but in our opinion, the seasonal variability is mainly due to seasonal changes in biological activity. However, we will argue this point in more details and take also other sources and sinks into account.

“P7554 L11: why “water column denitrification”, does it mean that denit occurring in the sediments have no effect on 15N-NO3 from the water column?”

To our knowledge fractionation in sedimentary denitrification can be neglected, since the rate limiting step is the non-discriminating process of nitrate diffusion with a low isotope effect near to zero as described by Deek et al. (Seasonal variations in nitrate isotope composition of three rivers draining into the North Sea, Biogeosciences Discuss., 7, 6051-6088, 2010, doi:10.5194/bgd-7-6051-2010), Sigman et al. (Distinguishing between water column and sedimentary denitrification in the Santa Barbara Basin using the stable isotopes of nitrate, Geochem. Geophys. Geosyst. 4(5), 1040, doi:10.1029/2002GC000384, 2003) and Brandes and Devol (A global marine fixed nitrogen isotopic budget: implications for Holocene nitrogen cycling, Global Biogeochem Cycles 16(4), 1120, doi: 10.1029/2001GB001856, 2002). We will add this to our manuscript.

“4.2 Particulate nitrogen P7555– See my previous comment for the 3.4 section. The interpretation is not satisfactory. For example P7555 L16-17: “After ammonium is exhausted, 15N-enriched DON and nitrate were assimilated, leading to increasing d15PN.” You cannot make this statement as you cannot prove it with your data – you should keep it hypothetic. Many other ways could explain that PN gets enriched in 15N:

when NH4 gets down (through assimilation but also nitrification, a process you do not consider, why?), its 15N increases (NH4 can become very heavy – especially if nitrification is active) so its assimilation results in an increased 15N-PN after a while. . .. Also, mineralization of PN can result in an increased 15N-PN. . .(as you explain for sedimentary PN). Later you notice the similar variation trends of 15PN and 15(NH4+DON) and say that PN is a source for DON which is the opposite of what you write before (PN is produced by DON assimilation. . .)”

We agree that the interpretation of our data is hypothetic and that this should be made clearer. We will rewrite this passage and we will point out the hypothetic part of our interpretation and will also take other possible explanations into account.

“4.3 DON+NH4 P7556 L4: “The combined DON+NH4 load of the Elbe River at the weir of Geesthacht apparently is fed by both external and internal sources.” What experimental result do you use to make this statement?”

We agree that this sentence is to general and we will restate it.

“Spring: Not relevant: Your whole discussion on NH4+DON uptake + reference is purely theoretical and hypothetical and is not supported by your data (decreasing 15N in this pool) as you say yourself. Your hypotheses is thus not relevant in explaining your observations. So what could explain a joint decrease in NH4+DON and their isotopic signal? In spring you also have a decrease of river discharge – so as for NO3, can this then not explain a decreasing importance of NH4+DON diffuse sources?”

We agree that we did not include the river discharge adequately in our examination, and we will revise the whole discussion part 4.3, taking the suggestions of the referees like river discharge or load calculations into account. We will figure out more clearly the parts we can demonstrate with our data and the parts we hypothesize.

“Summer P7557 L18-21: “In summer, elution of organic fertilisers in the form of slurry and liquid manure dispersed on farmland during the first main fertilisation period in

spring leads to an increase in DON concentration and d15DON (Heaton, 1996), in accord with our data." Can you go deeper into that argument: to reach the river, the organic fertilizers must be carried with a water flow so, can you estimate what load is necessary to increase the concentration and delta in your river water and see if that load is realistic in terms of volumes of water it represent, because your river water discharges are relatively stable in this period. Do you also have evidence (a reference) that organic fertilizers are used in the Elbe catchment close to you sampling stations and at what periods they are spread? (also for "winter")"

We have a personal comment of a member of the chamber of agriculture in Northern Germany who ensures us the use of organic fertilizers in the Elbe catchment.

Autumn P7559 L2-3: "We infer that sedimentation is also a major sink of DON as an explanation for decreasing DON+NH+4 concentration and d15DON+NH4 ." Why? What is the argument behind this?

As mentioned above for referee #1 we will go more into details for the DON sedimentation in a revision.

"Winter Contrary to summer, in winter you have peak discharge so here also, can you develop more your argumentation by estimating loads that can explain the observed increase in concentration?"

We will revise our argumentation and will take river discharge as a possible reason for the explanation of our data into account.

"P7545 L28-29: ". . .external rhythm on possible external DON and ammonium sources. . . " repetition, replace second external by allochtonous ?"

We will replace second external by allochthonous.

"P7546 L9-10: ". . .at stream kilometre 585. . . ". Is this the km from source or mouth ? or another reference point¿'

The stream kilometres are counted from the border between Germany and the Czech Republic.

"P7547 L14: ". . .d15N−NO3 of nitrate. . . ÂËŹz remove "of nitrate" "

We will remove "of nitrate".

"P7548 L10: "For the determination of d15TDN nitrate in oxidised samples and reagent blanks was converted to N2O using the denitrifier method... " something is missing in this phrase. . ."

We will rephrase this sentence.

"P7548 L15: ". . .and nitrate, because concentration of nitrite was consistently negligible. . ." But don't you analyse nitrate+nitrite with the AA3? Also, the denitrifier method converts NO2+NO3 to N2O, so normally you do not need to neglect the NO2?"

We measure nitrate+nitrite with the AA3 and also d15N of nitrate+nitrite. What we wanted to say is, that the concentration of nitrite is so low compared to nitrate, that nitrite has no measurable effect on our data.

"P7550 L4: ". . .calculate annual loads as:" replace by "calculate annual loads (L) as:" "

We will add (L) in the sentence.

"P7551 L12: ". . .A plot of d18O vs. d15N shows that the isotope values plot a slope of 0.81:1, which is close to a 1:1. . ." You can test this hypotheses (slope not significantly different from 1) by using a "bivariate least square regression" "

We will do it and add it to our manuscript.

"P7552 L2: ". . .The DON+NH4 contribution to TDN differs through the seasons,. . ." replace by ". . .differs through the seasons (not shown),. . ." "

We do not understand this comment since we presented the data in Table 2. But we

will try to accentuate this fact more clearly.

“p7553 L7: “. . .d15PN also showed lower values. . .”, remove the “also” because in the previous sentence about 15N-NO3, it is the opposite. The summer-winter variations of both 15PN and 15(NH4+DON) are similar, and they are opposite to 15NO3 variations”

We will rephrase this sentence.

“p7553 L18 and 21: “In the next section . . . seasonality and correlations between the measured parameters. " and “Furthermore we wanted investigate the correlations of the different N pools. . .”. In these 2 phrases you repeat similar things (correlations) – better group these 2 in 1 sentence“

We will rephrase this passage.

"P7554 L18: “18E:15E” instead of “18E:5E” P7554 L18: “15E and 18E” instead of “15E and 8E”

Sorry for this mistake, we will correct it.

“p7557 L21: "Heaton, 1996" in reference list = 1986”

We will correct this mistake.

“Table 3: are the annual loads in kt of N?”

Yes, the annual loads are in kt of N, we will add this to Table 3.

“Table 5: what are the dl for NH4, O-PO4 and NO2?”

The detection limit for NH4 is 2.8 μM, for O-PO4 0.3 μM and for NO2 0.7 μM.

“Fig 2; Very small and almost impossible to read the labels when printed”

We will rearrange this figure.

Interactive comment on Biogeosciences Discuss., 7, 7543, 2010.