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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.

Anonymous Referee #2

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GENERAL COMMENT: This paper presents some interesting results about nitrogen distribution and speciation and the isotopic composition of various N pools. Particularly, the study of the 15N in the NH4+DON pool is quite innovative and deserves attention. Introduction, material and methods and result sections are in general clear and well written (but see minor comments) but unfortunately, the discussion suffers from many shortcomings and clearly needs to be re-evaluated. In general discussion stays superficial, hypotheses are not tested in depth or, worse, not supported by observations or by convincing references. Interpretation never considers the variations of water flow, as controlling factor for observed concentrations variations. The authors calculate and present loads but do not use them in their discussion. Another difficulty is the fact that NH4 and DON profiles are grouped as a single N pool without any justification. I believe the authors have at least concentration measurements for both N

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species they should present and use to support their arguments.

SPECIFIC COMMENTS 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 d15N-PN 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.

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)

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? Re-suspension from sediments for PN?

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 (see for example the paper of CHESTERIKOFF, GARBAN, BILLEN & POULIN (1992) Inorganic nitrogen dynamics in the River Seine downstream from Paris (France). Biogeochemistry 17: 147 - 164).

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As the isotopic composition of this nitrate pool can be different from the one that is present in the summer base flow, part of the observed seasonal variability could come from the simple mixing of these 2 end members ("base" flow + "diffuse" flow) – and you should be aware that this mixing can also perfectly explain the linear relationship you have between the 15N and 18O isotopes of nitrate and the slope of 0.8 (= range of 18O/range of 15N). See example of 2 end-member mixing curves applied to your data in Figure 1. Careful discussion taking into account all possible causes of variability should thus be considered.

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?

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. . .)

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?

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

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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?

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")

P7557 L26-27: "Furthermore, such nutrient limitation induces an uptake of DON. . ." and all discussion of the following paragraph: Uptake potential of phytoplankton for low nuts conditions is not relevant in explaining an increase of DON+NH4 and 15N in summer. . .

P7758 L15: "..while the DON released due to nutrient limitation should cause a decrease in d15DON+NH4 . . . " Not necessarily if your PN pool is 15N enriched compared to you DON pool, which is the case. Is there any info about fractionation during this DON release by phytoplankton? My guess is that fractionation should be low as the release occurs quickly after or during production – so you could imagine the production of "heavy" DON by phytoplankton.

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?

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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?

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

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

P7547 L14: "...d15N−NO3 of nitrate... Âż 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...

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?

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

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"

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

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

p7553 L18 and 21: "In the next section ... seasonality and correlations between the measured parameters. " and "Furthermore we wanted investigate the correlations of

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the different N pools. . .". In these 2 phrases you repeat similar things (correlations) – better group these 2 in 1 sentence

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

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

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

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

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

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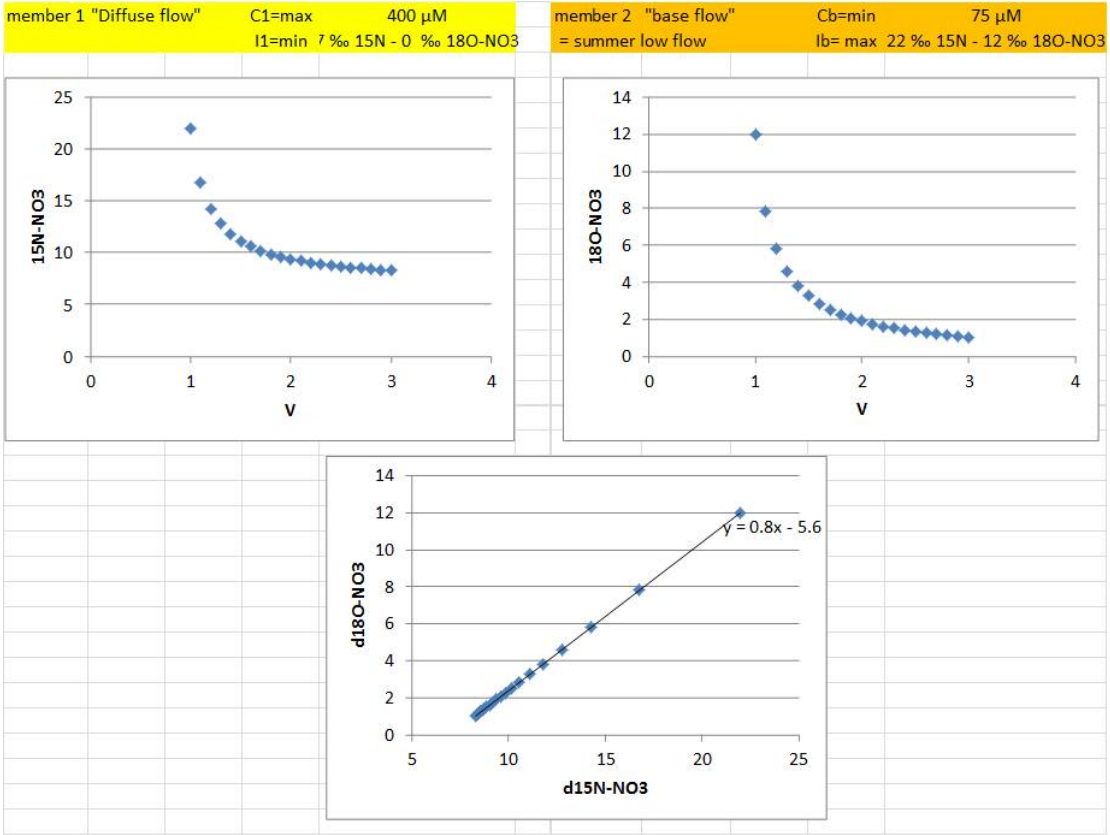

Fig. 1. Conceptual Two end-members mixing curves (constant base flow + variable diffusive flow) for 15NO3 and 18NO3

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