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Biogeosciences Discussions

Interactive comment on "River biogeochemistry and source identification of nitrate by means of isotopic tracers in the Baltic Sea catchments" *by* M. Voss et al.

Anonymous Referee #3

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GENERAL COMMENTS In this paper several methods to determine the major sources of NO3- to Baltic Sea catchments are assessed. The authors utilize methods previously applied to other watersheds with the purpose of aiding in management of nitrogen driven eutrophication in the Baltic. First, the authors present NO3- isotope data (d15N, d18O) for several rivers, as well as other supporting data (PON, d15N-PON, DIN:PO4-, etc). Second, they apply two isotope mixing models (IMM) and an emission model (EM) to compare results of NO3- source attribution by each. This paper nicely presents the results of an interesting study. However, in a few instances there are gaps in the line of reasoning or direct contradictions in the text, which could be improved.

SPECIFIC COMMENTS

1- Corrections to language

The language needs careful editing. As a native English speaker, I realize I have an advantage. There are several instances where corrections are simply grammatical. In other instances, the use of incorrect language makes it difficult to follow the line of reasoning. I have made suggestions for some of the necessary corrections here and in the Technical Comments section.

Page 476, Line 8: with relatively pristine vegetation in THEIR catchments

Page 477, Line 3: catchments like THOSE of the Baltic Sea

Page 477, Line 24: the second largest diffuse nitrate source for the Baltic Sea and IS less well constrained

Page 478, Lines 21-24: since northern rivers drain near-pristine catchments, WHILE southern ones HAVE densely populated watersheds with much agriculture. The present study was presented AT the Conference on "Significant Processes, Observations and Transformation of Ocean Nitrogen" (SPOT-ON) as an example OF human influence on the catchment (delete 'S) scale.

2- Methods- filtering through GF/Fs

In the methods section, it is not clear to me why, for measurements from the Swedish rivers (Page 480, Lines 26-29), the authors filtered the water through a GF/F, then rotavapped and freeze-dried the filtrate onto a GF/F. It seems to me that anything that initially passed through the GF/F would pass through it again even after concentration down to 5 mls. Or, is the purpose just to lower the volume so it just wets the GFF without passing through it? Please clarify in the text.

3- Earlier mention of N sources to IMMs

Page 482, Methods section 2.4. Please include here the explanation of why only three

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sources can be included in the IMMs. The question immediately came to mind, and it wasn't until several pages later that this issue was addressed.

4- Site Description

Page 483-484. Much of this information (Longitude, area, nitrogen content in rain, etc) should go in the Methods Section since it is background information describing the sites.

5- Description of d15N-NO3- values

Page 484-485 It is not clear whether the d15N-NO3- is expected to be higher in winter or summer. Line 26 (p. 484) states that the d15N-NO3- values are usually higher in winter than in summer, based on Figures 2, 3, & 4. On the next page (p. 485), line 4 states that there are low (d15N-NO3-) values in winter which increase towards summer.

It may be true that d15N-NO3- is higher in winter in the Vistula (Fig. 2). However, for the Oder (Fig. 3), d15N-NO3- peaks in summer and for the Kemijoki (Fig. 4) the pattern is not clear. This discussion of d15N-NO3- values should be clarified.

6- Role of Lake Ladoga

Page 485, line 21. How would Lake Ladoga buffer the d15N-NO3- values in the Neva River? Please give a brief explanation in the text.

7- Principal components analysis (Section 3.3)

This section does not add much to the paper and could be cut. The information on identity between rivers is not addressed at other points in the paper and given the stated purpose of the study is of minimal interest. If this section of text is deleted, the associated figure (#6) should also be deleted.

8 - Controls on NO3-d15N values

Page 487-488. This paragraph discusses the processes responsible for both the loss

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of NO3- and the associated increases in the d15N of NO3-. Overall, the discussion is confusing, in large part because the processes that control NO3- concentration and stable isotopic ratios are complex. Several points need clarification. Why would denitrification only be important in only in autumn and winter? Wouldn't nitrification result in lower (than leftover NH4+) d15N values? What is meant by biological production (Line 22)? Primary production? Bacterial (denitrifier) activity?

There are some contradictions in this paragraph. The authors suggest that denitrification in soils is most active in autumn and winter and that this might explain the high d15N- NO3- values in the Vistula and the Oder. However, the plot for the Oder (Fig. 3) shows peaks in d15N-NO3- values in the summer and lower values in autumn and winter.

9- d15N-NO3- pattern in the Kemijoki

Page 489, Line 7 states that there must be a source of nitrate with low d15N values and low nitrate concentrations to explain why the d15N and concentration of NO3- increase, then drop in April 2002 in the Kemijoki. The text should be modified to make it more clear that the low d15N source must be introduced in April 2002 rather than during January, February, March when the d15N values are increasing.

10- Discussion of IMM and EM results

Page 492. On pages 487-488 and 490 the authors discuss the various processes that modify d15N values of different N sources. For example, we know that denitrification causes NO3- d15N values to increase. And, volatilization of fertilizer results in higher NH4+ d15N values. However, when the IMMs are applied, there is no way to include information about processing N sources. Thus, N coming from mineral fertilizers is given a d15N value close to atmospheric (0 L'). This could account for the poor performance of the models and would be an interesting point to bring up in the discussion.

TECHNICAL CORRECTIONS

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Page 476, Line 23: "humic climates". I am not sure what is meant by this. Perhaps "humid" climates?

Page 479, Line 7: "20 -30 km upstream" Need to clarify that this is upstream from where?

Page 479, Line 17: Resin columns were stored "cool". In a refrigerator? On ice? Please clarify.

Page 480, Line 7. Add units to the standard deviation measurement (0.38L').

Page 480, Line 16. THE calibration substance was... (add "the")

Page 483, Line 24: The catchments of the Baltic Sea STRETCH (not stretches)

Page 484, Line 8: The Peene catchments HAVE or THE PEENE CATCHMENT HAS... The verb needs to agree with the subject.

Page 484, Line 13: ... vary from 10 and 27 μMol in THE Kemijoki (add THE). Also, if these are concentrations, the units should be either μmol/ L or μM.

Page 485, Line 24: but THE Vistula (add THE)

Page 486, Line 2: Change wording to: A principal component analysis (PCA) explained 94.8% of the variance... (Unless this section is deleted, see comment above)

Page 487, Line 20. Delete "particulate matter" from the first sentence since the rest of the paragraph concerns nutrients.

Page 490, Line 16: also the velocity of the downward water flow DETERMINES the... (Change decides to determines)

Page 490, Line 24-25: Change wording to: a result ALSO FOUND IN other studies

Page 491, Line 18: Diffuse nitrogen sources INCLUDE atmospheric deposition...

Table 1. Note that the numbers in the table refer to number of samples (n).

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Table 3. “Catchments area” should be changed to “catchment area”

Table 3. Need to define abbreviations in the table legend. What is artif.? Artificial surfaces?

Figures: Is it possible to add error bars to any of the figures?

Fig. 4: It is better not to connect points when there are multiple monthly data points missing, since we do not know that the pattern was during that time. See the d15N-NO3-, d18O-NO3-, PON and d15N-PON during the summer months

Fig. 5: It is better not to connect points when there are multiple monthly data points missing as for the Kemijoki d15N-NO3- and Kemijoki and Neva d18O-NO3-.

Fig. 6: See comment on the principal component analysis in the Specific Comments section above.

Fig. 7: Define the abbreviations for the rivers.

Fig. 8: Need to indicate in the legend that Panel A is for IMM-1 and Panel B is for IMM-2.

Interactive comment on Biogeosciences Discuss., 3, 475, 2006.