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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 #1

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General comments:

This manuscript summarizes a very comprehensive data set on the chemical and isotopic composition of nitrate in several rivers draining into the Baltic Sea. The goal of the study was to determine the sources of nitrate in riverine systems based on stable isotope data supported by isotope mixing and emissions models. In my view, this paper deserves publication mainly for two reasons:
a) it addresses an issue of significant international concern, namely the cause of increasing riverine nitrate fluxes to oceans and inland seas, and

b) it contains one of the most comprehensive data sets on the isotopic composition of

riverine nitrate published so far.

The chosen analytical techniques are rather innovative and the presentation of the data is for the most part adequate (see specific comments for some exceptions). However, not all conclusions presented in this paper seem to be fully supported by the presented data. There are some open questions regarding the isotopic composition of some of the chosen end-members (see point 4 below). In addition, the impact of nitrate from waste water treatment plants in the catchments with high population densities appears to be hardly discussed and potentially confused with nitrate from agricultural land (see point 6 below). Other major issues to consider are:

1. The title refers to “River Biogeochemistry” but most of the data and the discussion focus on riverine nitrate and its sources. Also the abstract does not contain any biogeochemical data other than nitrate concentrations and isotope ratios, and the objective stated at the end of section 1 (introduction) only mentions nitrate sources. Hence it appears appropriate to remove “River Biogeochemistry” from the title.

2. In the abstract, the authors state that they isotopically assessed contributions from 3 sources and report good agreement with other methods. However they do not report any data for approximate contributions from the 3 sources. It would be very desirable for the reader if such results were reported in the abstract of a revised version of this manuscript.

3. In the method section, additional information is required on how the authors dealt with NH_4^+ during nitrogen isotope analysis of nitrate. Also the authors should list the international reference materials and their assigned $\delta^{15}N$ and $\delta^{18}O$ values used for calibrating or normalizing the reported isotope values. This is particularly important for $\delta^{18}O$ values of nitrate, where the reported values in the literature assigned to IAEA-NO3 vary from +23.0 to +25.6 per mil.

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4. For the Isotope Mixing Model 2 (IMM-2) the authors assigned a δ^{18}O value of +23 per mil for mineral fertilizers. This may be correct for nitrate-containing mineral fertilizers, but there are a vast number of synthetic fertilizers based on ammonium and urea. Nitrification of ammonium and urea from these fertilizers will yield nitrate with δ^{18}O values much lower than +23 per mil. The authors should comment on how this affects the outcome of their calculations. It may also be useful to report what percentage of the mineral fertilizers used in the respective countries was indeed of the nitrate-containing variety.

5. The authors state correctly that "it is important to evaluate how the variability of the source signals affects the reliability of the calculated source attribution" (page 486, lines 25-26). However, there are no calculations shown on what would happen if different δ^{15}N or δ^{18}O values were chosen for certain end-members. Such an exercise may be useful in order to test the robustness of the chosen approach.

6. A lot of the discussion in section 4.2 (page 489-490) refers to the use of fertilizers and the percentage of agricultural land and their influence on the isotopic composition of riverine nitrate. Hardly discussed is the population density and its impact on waste water effluents that are often directly piped into the rivers (see Mayer et al., 2002). It seems notable that the three catchments with population densities $>$50 inhabitants km^{-2} (Vi, Od, Pe) happened to have the highest δ^{15}N and lowest δ^{18}O values of riverine nitrate. This seems to suggest that there is a factor other than agricultural activity at work that deserves some more detailed consideration in a revised version of this manuscript. Since the catchments with high population densities are typically also those with high percentages of farmland, the waste water effluent influence may be easily confused with agricultural impact. In my view, this is one of the major flaws of this paper.

7. In the objectives, the authors state that they will report on the practical limitations

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of their chosen approach. It would be desirable to end the manuscript with a concise paragraph clearly stating what the authors view as the main limitations for applying the proposed scientific tool for identifying riverine nitrate sources.

From a technical viewpoint, the manuscript is well organized and for the most part written in good English. The literature list is adequate and up-to-date. I have made numerous minor suggestions under “specific comments” that may be helpful in improving the next version of this manuscript.

In my view, this study deserves publication in Biogeosciences Discussions after moderate to major revisions. I recommend that the authors carefully address the general issues listed above and the specific comments summarized below, before re-submission of an improved version of this paper. Thereafter, I assume that this contribution will be of considerable interest to the readership of Biogeosciences Discussions.

Specific comments

Page Line Comment

Abstract

475 4 Statement misleading: the authors did not only compare to vegetation cover but also to land use etc.

475 6 indicate that you mean isotope signatures for nitrate

475 10 replace “could be” with “were”

475 11 you may want to say “major N sources”

475 14 replace “rather bad ones” with “unsatisfactory agreement” or something along those lines.

Introduction

476 6 I am not familiar with the unit-less salinity scale used here. Are the given numbers

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per mil, %, PSU, or something else? Please clarify.

476 18 Should read: Stalnacke et al. according to the reference section.

476 22 This argument is not entirely logic: It does not follow automatically from the fact that the rivers drain densely populated agricultural areas that agriculture is a major source of riverine nitrate (could be mainly waste water N). Please provide additional evidence to back-up this statement.

476 23 Which industries are releasing sewage?

477 5 “separate” is a rather unfortunate choice of words. What about “partition”?

477 7 Little technical flaw: the text mentions “isotope ratios” but the authors show in brackets δvalues.

477 8-9 Comment also on the resulting δ^{15}N values (not only δ^{18}O)

477 10 . . . for δ^{15}N and δ^{18}O . . .

477 13 You may want to say: no “apparent” fractionation.

477 22 . . . presented “at” the Conference . . .

Material and Methods

478 7 “Upstream” of what?

478 17 Should read: Silva et al. (2000)

479 7 What international reference materials were used (IAEA NO-3, others)? Also state the δ^{18}O value you assigned to the international reference materials used.

479 8-10 It appears to me that any NH_4^+ present in the water samples would cause a problem with the reported method for δ^{15}N analysis on nitrate. The authors should comment on how they dealt with NH_4^+ contained in the water samples.

479 13 Give number of analyses in brackets (n = ??).

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479 16-18 Usually, calibration is performed using standards and reference materials that undergo thermal decomposition in the elemental analyzer followed

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by isotope ratio mass spectrometry, making the isotope values of the reference gases irrelevant.

479 20 The statement that V-PDB was used as a standard for CO_2 is confusing, since the authors have previously described that CO_2 was used for determining $\delta^{18}O$ values with respect to V-SMOW. You may want to say that carbon isotope measurements are reported with respect to V-PDB.

480 3 Table 1 suggests that $\delta^{13}C$ values of dissolved inorganic carbon (DIC) were measured, but no method is reported (nor are data).

480 14 I am not sure whether “emissions” is the right term here? “Inputs” may be preferable.

480 20-21 I would expect that increasing treatment efficiency would result in increasing $\delta^{15}N$ values in the remaining nitrate. If so, is that not in conflict with the statement on line 15 that sewage has a characteristic $\delta^{15}N$ value?

481 13 program (with one m only)

481 19 Explain what IMM stands for at first use of this abbreviation.

481 20 For IMM-2 there is a nitrate source “mineral fertilizer”. Apparently, this refers only to nitrate-containing synthetic fertilizers with $\delta^{18}O$ values around +23 per mil (Table 2). Comment on how the application of ammonium- and urea-containing mineral fertilizers may affect these mixing model calaculations.

482 8 Explain what EM stands for at first use of this abbreviation.

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Results

482 24 . . . catchment (singular) . . .

483 2-4 The authors report N deposition rates, not “nitrogen contents” as stated in the text.

483 3 replace “rainfall” with “precipitation” which covers both rain and snowfall.

483 5 What is Ind.? Individuals? Why is it capitalized?

483 6 Sentence incomplete!

483 8-10 Peene catchment (singular); in the following replace “river” with catchment or watershed, since rivers have no forests.

483 14 Would it not be better to cite Table 3 that contains all catchments rather than Figs. 2-4?

483 19-23 I have some trouble seeing this “co-variation” in Figs. 2-4. In fact high nitrate concentrations appear to occur during base flow in January and February (not during high flow at snowmelt).

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483 24 Statement not correct for Figs. 3 & 4 where the highest values occur in March & April, not the early summer months.

483 25 The previous sentence claims that the highest ratios are found in the summer months. Now the extremes are in the winter. This seems contradictory.

484 1 Clarify what you mean with “less significant tendency”?

484 2-3 Within which season? Can you provide statistical data to support this statement?

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484 4-6 Again, I have some trouble with the first statement, which seems to be swiftly contradicted in the next sentence.

484 15 What to you mean with “less clear isotopic pattern? Less variability?

484 16 Reword: “with only slight peak”

484 19 Are the values reported here mean values?

485 17 Do the authors imply that atmospheric deposition is not in part an anthropogenic nitrate source? Also, do the authors mean non-agricultural soils with their term “pristine soils”? Many forest soils in the southern catchment may fall into this category but they are certainly not “pristine”.

486 3-17 As mentioned before, this calculation may be flawed since the δ^{18}O value of +23 per mil chosen for nitrate-containing fertilizers is not representative for other e.g. ammonium-containing mineral fertilizers.

Discussion

487 3 Do the authors mean “in-stream” consumption of nitrate? If so, would this preferentially remove the light isotope ^{14}N? What would be the effect on the δ^{15}N value of the remaining riverine nitrate? Any references to support this statement?

487 9 What is the basis for the statement that denitrification may only be important in autumn and winter?

487 11-12 Sentence incomplete: . . . may be caused by . . . .?

487 13 Reword: “by their isotopes”

487 15 Which “signatures”?

487 18 Note that waste water treatment plant effluents are also directly released into rivers.

487 20 Change “signal” to “values”

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488 4 Is the value reported here (-0.1 per mil) a mean value?

488 14-17 As currently described, the chosen explanation seems rather arbitrary. However, it may be possible to use flow data to either support or reject the provided explanations. If snowmelt is the cause for low nitrate concentrations and high δ^{18}O values of nitrate then this pattern should

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coincide with peak flow at snowmelt. If in-stream primary production is the cause, then this effect should occur weeks or months after peak snowmelt.

488 20-21 Refer to Figure 7 to support this statement.

489 10-11 It would be clearer to say: ... to increasing δ^{15}N values in the remaining NH_4^+. Next sentence, use δ rather than Delta.

489 15-17 This statement refers to soil water only, but nitrate from waste water treatment plants directly released into the rivers may also be responsible for elevated δ^{15}N values.

489 22 Replace “data” with “values”.

489 28 Wouldn’t these values also be typical for nitrate from waste water treatment plant effluents?

490 1 Should this be Mayer et al. 2001?

490 1-3 I do not understand this conclusion. If nitrification is a dominant process generating nitrate, would one not expect lower δ^{18}O values of nitrate in the northern catchments, since the δ^{18}O values of precipitation or soil water are more negative in the north than in the south?

490 8-9 δ^{18}O values are not generated by land use practices! Re-word this sentence.

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490 13 Add space between fertilization and gives.

491 5 Rather than farmland, these high δ^{15}N values could also be caused by waste water effluents, not only farmland.

491 14-15 Again I question whether indeed all the nitrate is from farmland, rather than from sewage effluents in these highly populated catchments?

491 20 Poor choice of words: “Pristine nitrogen”.

Table 1 Footnote not understandable.

Table 3 Was δ^{15}N really determined for NO_2^-? Unit for DIN/DON appears wrong. Reduce number of significant digits in last column (atm. deposition).

Figure 9 y-axes do not show percentages (otherwise scale would go to 100%).

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