

## ***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.***

**M. Voss et al.**

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Detailed response to the reviewer’s comments I would like to thank the reviewers for all the work they obviously put in the revision, and for the constructive and extremely helpful suggestions. We considered them all in the revision. Detailed explanations are given below. Unfortunately, we cannot refer to the page and line numbering of the version from the Biogeosciences web page, since we have to make the changes in the original word document. We feel that this may cause quite some confusion also for the reviewers and editors and want to apologize for this extra work. Furthermore, it took us much extra work.

Referee #1 Divided into major issues #1-7 and specific comments #1-71 Major issues

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/ general comments (gc) #1-7

1.the title was changed to “Source identification of nitrate by means of isotopic tracers in the Baltic Sea catchments”

2.The last sentences in the abstract were modified: “. The results of an isotope mixing model (IMM-1) agree reasonably well with same estimates for agricultural land derived from a Global Land Cover (GLC) data base with deviation from -16% to +26%. The comparison with an emission model (EM) reveals good agreements for intensively used catchments (-18 to +18% deviation). Rather unsatisfactory agreement was found for the IMM-1 and GLC calculations for pristine catchments (-36 to +50% deviation). Advantages and limitations of the tested model types are discussed.”

3.This point was also raised under #19 Material and Methods. We added the removal step of NH<sub>4</sub><sup>+</sup> and now write: “The acidic filtrate samples were brought to a pH of 10-11 with NaOH and MgO and briefly boiled to remove traces of ammonium from the sample.” Reference materials for the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  analysis and their isotope values were added to the text.

4.Here an important issue is raised since urea and ammonium are also converted to nitrate in soils. We therefore decided switch from isotope values for mineral fertilizers to isotope values measure in soil nitrate beneath field which received mineral fertilizers (Amberger and Schmidt 1987) and recalculated the fractions for the IMM-2 model. Furthermore we decided to make this calculation for the rivers with high nitrate inputs from fields only and not for Neva, Kemijoki and Kokemaenjoki. We added to the text: “We tried to verify the information from the EM and IMM-1 model by means of a second IMM run (IMM-2, end members in Tab.2). Since urea- and ammonia- fertilizers also contribute to the nitrate pool in the soils we decided to use the isotope values from soils fertilized with mineral fertilizers (Amberger and Schmidt, 1987) and not the NO<sub>3</sub><sup>-</sup> fertilizer values from the Haber-Bosch process. Since the differentiation between nitrates from mineral fertilizers and sewage/manure is only meaningful for the rivers

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with a high share of N from agricultural runoff (and sewage/manure input) we selected the rivers Vistula, Oder, Peene and Paimionjoki for this new calculation.” Table 2 was changed accordingly.

5. A test of how the variability of isotope sources affects the outcome of the model is desirable and depends on the availability of data. It is difficult to make such a test due to a lack of data.  $^{15}\text{N}$  and  $^{18}\text{O}$  values from soil nitrate samples are still rarely published. This is the reason why we took the 1987 (Amberger and Schmidt) data for the soil nitrate under fertilized fields. We tried with minima and maxima of published data sets. They gave useless results with high negative percentages for some sources. For these reasons we feel it is impossible to make an error estimate for this study. However, to address this issue appropriately we wrote in the discussion: “We are aware that it might be difficult to fully disentangle the contribution of various anthropogenic sources such as nitrate from sewage vs. nitrate from diffusive sources due to a lack of published  $^{15}\text{N}$  and  $^{18}\text{O}$  - $\text{NO}_3^-$  data as end members. Therefore, we discuss our results with caution when it comes to the relative share of point sources versus diffusive sources in the cultivated watersheds. However, this study aims additionally to show large scale isotopic patterns relevant to the Baltic Sea catchment and the adjacent major basins of the Baltic Sea.”

6. To correctly address the issue of high N-concentrations we added a paragraph to the first chapter of the discussion (“Seasonal variations in the isotopic composition of river nitrate”). It reads: “Our highest  $^{15}\text{N}$  - $\text{NO}_3^-$  and lowest  $^{18}\text{O}$  - $\text{NO}_3^-$  values were recorded in rivers with catchments dominated by fields and agricultural land. However, these catchments also have population densities  $>50$  inhabitants  $\text{km}^{-2}$  and may therefore be more affected by effluents from STPs than catchments of the other rivers studied. Both N-sources have high nitrate (and potentially high ammonium) concentrations and contribute to the in-stream DIN concentrations. They cannot clearly be differentiated by the applied stable isotope methods. Sewage/manure can thus come from agricultural practices and STP alike.” Additionally to this paragraph we

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refer to this fact later again in the discussion and the conclusion (e.g. sc #59, 66, 67).

7. Conclusions were already given in the last paragraph of the discussion: They read “IMMs are helpful tools for verifying land use estimates made with other approaches. Careful interpretation is necessary for catchments dominated by nitrate sources not well constrained. Large catchments with little anthropogenic influence like the Kemijoki and the Neva (excepting the city of St. Petersburg) in our study need to be addressed separately. Variations of end members in additional IMM runs, like the IMM-2 in this study, can be useful for differentiating the contributions from different fertilizer types in catchments with a high proportion of farmland. Additional isotope pairs may be useful to differentiate between runoff from farmland and sewage treatment plant effluents. In pristine areas EMs are not useful to apportion sources, unless they explicitly include pristine nitrogen.”

Specific comments (sc) Abstract (1-5)

1. now reads: “ $\delta^{15}N$ , in relation to the vegetation cover, land use, and fertilization of agricultural land of their catchments. 2. we added “nitrate” so it reads “riverine nitrate isotope signatures” 3. it reads now “Seasonal signals were found” 4. it reads now “data from the three major N sources” 5. it reads now “and rather unsatisfactory agreement for pristine catchments” 6. salinities are correctly given without any units. Units still often used are PSU (practical salinity unit) and permill weight, which can be confused with the delta notation.

7. Stålnacke is the correct Swedish way of writing.

8. Where does the nitrogen in the rivers come from - is the presented argument logic? We understand that sewage from treatment plants (STP) contribute to the riverine nitrate as well. The “Third Pollution load Compilation (PLC)” HELCOM report # 70 (1998) states that most nitrate (and N) enters the Baltic Sea via the rivers. The source apportionment concludes that between 80 and 90 % are of anthropogenic origin and come from monitored rivers. The diffuse load - typical for runoff from agricultural land - en-

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tering the Baltic Proper varies between countries between 35-91%. This can be taken as indirect evidence for land runoff from agricultural fields. Point sources - which are the STP effluents - contributed max. 46% to the anthropogenic load but were usually much lower. To clearly establish the relationship between fertilizer use in the catchment and river nitrogen load entering the Baltic Proper we cite now Nausch, G., Nehring, D., Aertebjerd, G., 1999. Anthropogenic nutrient load of the Baltic Sea, *Limnologica*, 29: 233-241. However, we also added the input by STP effluents to the text. (please see also sc#59,61)

9.As far as indicated in the PLC (see above) the paper production industries in Scandinavia are one major point source of nutrients. 10.“separate” was replaced by “partition” 11.“ratios” was replaced by “values” 12. $\delta^{15}\text{N}$  was added to the sentence. 13. $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  instead of just N and O 14.we wrote “no apparent fractionation” 15.at the Conference

#### Material and Methods (16-29)

16.upstream of the river mouth 17.Silva et al. (2000) 18.Reference materials and their isotope values were added to the text. IAEA standard substances N1 (0.4‰), N2 (-20.3), and N3 (4.7‰) were used for the  $\delta^{15}\text{N}$  measurements. For  $\delta^{18}\text{O}$  -  $\text{NO}_3^-$  measurements international reference materials were IAEA-N3 and IAEA-C-3 where we measured a  $\delta^{18}\text{O}$  value of 25.1‰ and 32.2‰, respectively.

19.Here we added the  $\text{NH}_4^+$  removal step and now write: “The acidic filtrates were brought to a pH of 10-11 with NaOH and MgO and briefly boiled to remove traces of ammonium from the sample.”

20. $n=70$  21.The calibration is done with the substances of known isotopic composition in the same way as the samples are prepared and measured. In case some thermal influence happens it acts on both the reference materials and the samples likewise. The calibration of the reference gases that are always measured along with each sample,

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thermal decomposition can be neglected because they do not pass the elemental analyser but are directly injected into the source of the mass spectrometer. This analytical performance is standard in all stable isotope labs.

22.To clarify the references we used, we write now: “Values are conventionally given in  $\delta$  deviation from the standards which were air N<sub>2</sub> for nitrogen (PON and NO<sub>3</sub>-) and V-PDB for CO<sub>2</sub> from POC combustion.” The V-SMOW is used for the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  - NO<sub>3</sub>- .

23.Sampling of CO<sub>2</sub> was done in some cases but unfortunately most of them lost during transport, therefore we omit this aspect here and deleted the line in table 1.

24.Here we would like to keep the term “emission” because it is the one usually used in this context. 25.We agree that more complete removal by denitrifiers should result in higher  $\delta^{15}\text{N}$  values, but this has not yet been published. Published values show data of sewage and other effluents and are usually significantly higher than the ones of mineral fertilizer produced from atmospheric N.

26.yes 27.The header now reads “isotope mixing models (IMM) and statistics.

28.We added to the text: “We tried to verify the information from the EM and IMM-1 model by means of a second IMM run (IMM-2, end members in Tab.2). Since urea- and ammonia- fertilizers also contribute to the nitrate pool in the soils we decided to use the isotope values from soils fertilized with mineral fertilizers (Amberger and Schmidt, 1987) and not the isotope values from NO<sub>3</sub>- manufactured by the Haber-Bosch process. Since the differentiation between nitrates from mineral fertilizers and sewage/manure is only meaningful for the rivers with a high share of N from agricultural runoff (and sewage/manure input) we selected the rivers Vistula, Oder, Peene and Paimionjoki for this new calculation.” Table 2 was changed accordingly. See also gc#4.

29.We explained EM when first used.

Results (30-47)

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30.catchment 31.The nitrogen deposition in the precipitation of the catchments 32.The nitrogen deposition in the precipitation of the catchments 33.We changed Ind. to individuals. 34.The word “to” was deleted and it now reads: “The nitrogen deposition in the precipitation of the catchments correlates well with the population density ( $n=11$ ,  $r^2=0.897$ ,  $p<0.001$ ); varying from 200 kg N km<sup>-2</sup> yr<sup>-1</sup> in the Kemijoki catchments with just 2 individuals km<sup>-2</sup> to almost 1700 kg N km<sup>-2</sup> yr<sup>-1</sup> in the Oder River catchments with mean population of 138 individuals km<sup>-2</sup> (Tab. 3).”

35.Please read now: “The Peene catchment has only 17% forests left, while the Swedish watersheds, the Finnish Kemjoki river catchment and part of the Neva catchments have largely kept its original vegetation and still have up to 86% forests (Tab. 3).”

36.We refer also to the Tab. 3 now. 37.The reviewer is correct and we changed the description accordingly. For the Kemijoki with its very low nitrate concentrations there was no co-variation with flow, but for the other rivers there is a significant exponential relationship. It reads now: “Nitrate concentrations co-vary with the flow for the rivers with high nutrient concentrations (Figs. 2-3), and for the Kemijoki, nitrate concentrations peak before the flow (Fig. 4).” The next sentence is still correct because nitrate concentrations are always highest in spring.

38.We formulated this more precisely to “and have highest deviations from the Redfield ratio in March through May”.

39.We omitted the Neva value here since it is not important and reduced the sentence to “and have highest deviations from the Redfield ratio in March through May (up to 189 in the Vistula River in January/February 2002).”

40.The sentence was reformulated and reads now: “while their corresponding isotope values have no obvious relationship to the PON.”

41.There is a whole new story in the seasonal data evaluation of the Vistula and Oder

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River data which is cannot be included in this manuscript. We found significant relationships e.g. between nitrite and  $\delta^{15}\text{N}$  of the  $\text{NH}_4^+$  in the winter months indicating nitrification activity. These will not be presented here and we decided to delete the respective sentence from the text (Within season, more significant relationships between concentration and isotopic signature can be seen.).

42.The description was better formulated and reads: “A comparison of all rivers reveals a similar variation in  $\delta^{15}\text{N}$ - $\text{NO}_3^-$ , with decreasing values from winter towards spring and some increase towards summer (Fig. 5A). Here the development in the Kemijoki lags the more southern rivers.”

43.For clarification we added: “The Vistula, while belonging into the same group of farmland dominated catchments (66%), had a less clear isotopic pattern than the Oder, Peene, and Paimionjoki and no  $\delta^{15}\text{N}$  - $\text{NO}_3^-$  peak in summer.”

44.with only a slight peak 45.Better specified “load weighted  $\delta^{15}\text{N}$  values of -0.1 and 2.4‰”

46.We are aware of the fact that atmospheric deposition is loaded with nitrogen from anthropogenic activities and presumably most of the N is from combustion or evaporation of  $\text{NH}_3$ . For the purpose of the differentiation between sources it is still desirable to make the differentiation between atmospheric deposition and soil runoff and STP effluents, respectively. Pristine soils are the ones not intensively used but affected by N-deposition (added to the text). We hope to be clear throughout the text, that the word “pristine” is used for slightly impacted soils. We state in the beginning of the discussion that “Pristine, here means soils/forests that are not intensively used but may be affected by N-deposition.” Furthermore we write “The forests in the Kokemaenjoki and Kemijoki catchments can be regarded as near-pristine, and receive little or no artificial fertilisation.” But the reviewer is right that in the southern catchments it is even more difficult to distinguish between pristine and near-pristine soils.

47.We changed the isotope values and recalculated the IMM-2 (see #28). Therefore

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this paragraph has changed as well. It now reads: “We then tested the EM results with an IMM calculation (IMM-2) using the end members mineral fertilizer, sewage/manure and atmospheric deposition (Fig. 8 B). The calculation was done for the catchments with > 50% N from agricultural runoff in IMM-1. The IMM-2 results confirmed the IMM-1 calculation in that all rivers with high nitrate concentrations also had high contributions from mineral fertilization and only 0 to 21% from sewage/manure. The percentages for sewage/manure from the IMM-2 are well correlated with the percentages of nitrate from agricultural land from IMM-1 but less with the GLC estimates (Tab. 3, Fig. 9 A). For nitrate from atmospheric deposition, IMM-1 and -2 give very similar contributions (Fig. 9 B), since  $^{15}\text{N}$  values of atmospheric deposition do not overlap with the chosen values for soil nitrate after mineral fertilization.”

#### Discussion (48-71)

48. Fractionation during nitrate uptake results in isotopically light phytoplankton and isotopically heavy remaining nitrate. We added “The fractionation effect is known from laboratory cultures and the marine environment (Montoya et al. 1999).”

49. We had some indication for denitrification in winter from detailed evaluation of river nitrate data, but this should not be discussed here. It would make the story too complicated. We deleted the statement from the text since it can hardly be convincingly presented. The sentence was changed to “Denitrification and nitrification in soils are effective around the year, especially nitrification after fertilization with ammonia and urea compounds.”

50. “may be caused by nitrification/denitrification” 51. “Identified different N-sources by means of the isotopes values in river nitrate.” 52. We added “...the soil-N signatures” 53. This may truly become a problem when there are closely located sources of both kinds. We added “as do sewage treatment plant effluents”. 54. done 55. “load weighted mean” was added. 56. The hint from the reviewer was used to back up our argument. We added: “This is supported by our finding of the spring flow peak which coincides

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with increased  $\delta^{18}\text{O}$ - $\text{NO}_3^-$  values (Fig. 4).”

57.done 58.done

59.To address the issue raised under gc#6 we added here: Values of  $\delta^{15}\text{N}$   $>10\text{‰}$  seem therefore to be typical for the contribution of manure/sewage from either animal husbandry or STPs (Aravena et al., 1993; Fogg et al., 1998; McClelland and Valiela, 1998).

60.done 61.Here we suggested 12-13 $\text{‰}$  to be typical values for agricultural soils. STP may also release nitrate with these values but it is more probable that plants with better treatments (fluidized beds) produce much higher  $\delta^{15}\text{N}$  values. As far as we know  $\delta^{18}\text{O}$ - $\text{NO}_3^-$  values from STP are also not yet published. Therefore, we left the sentence as it was.

62.correct, we changed it to “Mayer et al. 2001”.

63.Here we do not try to combine latitudinal increase of  $\delta^{18}\text{O}$  -  $\text{H}_2\text{O}$  with the nitrate isotope values we found. We try to give a consistent explanation for the values we find which is a combination of precipitation/snow melt and nitrification processes in soils to generate the lower  $\delta^{18}\text{O}$ - $\text{NO}_3^-$  values in the northern catchments. The reviewer is correct that the water in the north should be isotopically heavier, but we have no information on that and found our explanation appropriate and not too speculative.

64.It reads “Thus,  $\delta^{18}\text{O}$  values are heavily influenced by land use practices in the southern catchments”

65.done 66.“Nitrate from farmland and/or waste water effluents” was added.

67.“..nitrate from farmland and/or STP..” was added.

68.We replaced “pristine soils” with “soils hardly affected by human perturbations”

69.“nitrite” was missing. Now it is “Includes nitrite, which is at most a few percent”

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70. The determination of  $^{15}\text{N} - \text{NO}_3^-$  actually measures the sum of  $\text{NO}_3^-$  plus  $\text{NO}_2^-$ , since both compounds are converted to  $\text{NH}_4^+$  during the reduction process. To avoid confusion we stick to the usual naming with just  $\text{NO}_3^-$ . DIN/DIP is given in weight not in moles, therefore [tons] as unit were given, and are now replaced by weight. Digits in last column were deleted.

71. units were changed

Referee #2

Divided into and specific comments #1-13 and technical comments #1-23 Specific comments (sp) #1-13

Abstract, Methods, Results (1-10) 1. Changed to “their”

2. replaced by “those”

3. “is” written in sentence

4. done

5. The methods to concentrate the total dissolved nitrogen (DN) uses the capillary effect of the glass fibre filters. When the small volume it freeze dried, the DN is quantitatively collected on the filter surface. We added the following sentence “During freeze drying all liquid containing the dissolved N is trapped on the glass fibres.”

6. We moved the sentence “For the mixing model calculation we had to restrict ourselves to three sources because nitrate contains only two pairs of stable isotopes. Additional isotope pairs would have been necessary for a finer resolution” to the beginning of the Methods paragraph, where we explain the mixing models and deleted it in the later text.

7. We feel that the movement of parts of this chapter would fragment the information. Although it is correct that few sentences are very general and not our own results, they are closely related to the data presented in table 3. We therefore prefer to leave this

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paragraph as it is.

8.The reviewer is right. It is other way round and we corrected that. It now reads “A comparison of all rivers reveals a similar variation in  $\delta^{15}\text{N-NO}_3^-$ , with decreasing values from winter towards spring and an increasing trend towards summer (Fig. 5A).” Thus, the next remark is now correct in the text, where we say “A comparison of all rivers reveals a similar variation in  $\delta^{15}\text{N-NO}_3^-$ , with decreasing values from winter towards spring and an increasing trend towards summer (except for the Vistula, Fig. 5A).”

9.For clarification we added “Neva  $\delta^{15}\text{N-NO}_3^-$  data show no seasonal pattern (Fig. 5 A) which may be due to a “buffering effect” of the huge Lake Ladoga, located some 70 km upstream from the city of St. Petersburg (Kuuppo et al., in press). Lake Ladoga prolongs the residence of the water and receives precipitation modifying the original isotope patterns in the catchment.”

10.Although we received an expected result from the PC analysis we feel that the data set presented asks for this sort of statistical evaluation and should be kept. In case we delete this a number of readers may miss this piece of data evaluation and thus the confirmation of the expectation. Since it is just a short clearly limited paragraph we left it in the manuscript.

## Discussion

11.Three comments have been made: First, denitrification only in winter? This was addressed by rev#1 sc49 and changed in the text (see above). Second, nitrification should lead to lower  $\delta^{15}\text{N}$  values. Here we now write: “Denitrification and nitrification in soils are effective around the year, especially nitrification after fertilization with ammonia and urea compounds. The latter process would lower the  $\delta^{15}\text{N}$  in the  $\text{NO}_3^-$  generated, but usually uptake and denitrification raise the isotope values immediately so that isotope values rise with increasing depth in the soil (Nadelhoffer and Fry, 1994). Therefore, high  $\delta^{15}\text{N-NO}_3^-$  values in the rivers may result

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from nitrification/denitrification transformation.” Third, what is meant with biological production? For clarification we added here “and seem to further increase when biological production e.g. phytoplankton growth starts.”

12.To stress the drop in  $\delta^{15}\text{N}$ -NO<sub>3</sub>- we added: “Since the nitrate concentration and the  $\delta^{15}\text{N}$  increase almost simultaneously until April 2002 and then drop (Fig. 4) there must be a source of nitrate with low  $\delta^{15}\text{N}$  values and low nitrate concentrations in April 2002.”

13.The reviewer is correct that we cannot include all processes and fractionations in a simple mixing model, but that we assume only source of different isotopic signatures. This fact was added to the text. The other point is already addressed due to the comments from rev#1 gc#4, and sc#28. We adapted the calculation and chose other end members for mineral fertilizers to get more realistic results. Please read comments above. Furthermore we added to the discussion the following sentence “We thus distinguished three different major nitrate sources but cannot consider fractionation processes.”

Technical comments (sp) #1-23

1.We indeed mean “humid” 2.same comment as ref#1, sc#16 3.“during transport or in a refrigerator in the laboratory” 4.we added “L” 5.The” was added. 6.same comment as ref#1 sc#30 7.Done “The Peene catchment has  $\check{E}$ ” 8.We changed to “ $\mu\text{mol l}^{-1}$ ”. 9.“the” was added 10.done

11.Since the particles are affected as well, and the concentration and  $\delta^{15}\text{N}$  values included in the Figs. 2-4 we left the expression as it was.

12.done 13.done 14.done 15.For clarification we added: “The numbers are the numbers of samples analysed” to table 1. 16.done 17.we write “artificial”

18.Error bars would be nice to have. But in most cases only one sample per month was taken and weighted with the load. In the case of Vistula and Oder River bimonthly

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sampling was performed which is still too little to draw error bars.

19.This is correct, and we deleted the lines where necessary in Figs. 2-4. 20.see #19  
21.We left the paragraph and the Figure 6 in the manuscript. 22.Yes, we included that  
in legend 23.We did that as well.

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