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## ***Interactive comment on “Nitrate source identification using its isotopic ratios in combination with a Bayesian isotope mixing model in the Baltic Sea” by F. Korth et al.***

### **Anonymous Referee #1**

Received and published: 7 May 2014

The authors apply a Bayesian mixing model to determine the relative contribution of various nitrate sources to 4 regions of the Baltic Sea. The assessment is based on dual nitrate isotopes and relies on the fact that different nitrate sources carry distinct isotopic signatures. Based on model estimates, the authors conclude that the southern regions of the Baltic Sea are mainly influenced by river inputs, whereas the influence of nitrate from pristine soils is highest in northern basins. The contribution of atmospheric deposition is always low and negligible in the southern part of the study area.

The manuscript and dataset is interesting, and the use of the SIAR mixing model is a promising approach. Nevertheless, the manuscript in my opinion will still need some revision. The main part of the study, the use of the mixing model (albeit a valuable way

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of addressing the different input sources) is where I see the most serious issues:

(1) In general, I doubt the source assessment for d18O in nitrate from N2 fixation. Naturally, this fixed nitrogen will primarily not contain any O. The authors try to solve this by using a fractionation factor computed by Buchwald and Casciotti (p. 5874, lines 15–19), but this is problematic. Buchwald and Casciotti actually state that the 18O value of freshly produced nitrate should be

$$\delta^{18}\text{O}_{\text{NO}_3} = \frac{2}{3} \delta^{18}\text{O}_{\text{source}} + \frac{1}{3} (\delta^{18}\text{O}_{\text{H}_2\text{O}} - \epsilon)$$

It is true that they, based on their measurements of d18ONO2 and the fractionation factor  $18\epsilon$  during nitrite oxidation (12.8‰, get to a range of d18O for freshly produced NO3 that is 0.7 to 8.3‰ below that of seawater. However, they also note that this is \*considerably\* lower than measured values of NO3 in the open ocean, and reckon that the largest uncertainty stems from the isotope signature of nitrite. This isotope signature is not known, mentioned, or measured in this study. How plausible is it then to use this theoretical value as a source signature? I am not aware of any study that actually found such low nitrate isotope signatures in any system that is influenced by nitrification. A good example are actually pristine (or agricultural, for that matter) soils/catchments. The authors themselves assume that pristine soils have an isotope signature of ~2‰ – but this actually is a nitrification signal. Hence, I don't think it is valid to use the theoretically assumed value of (seawater minus X) as a source signature for freshly produced nitrate.

Is it possible to estimate the contribution of N2 fixation based on nitrogen isotope data alone - especially as N2 fixation was excluded in areas with possible input of atmospheric deposition, the other source of depleted N? That would make this specific part of the model much more trustworthy, even if uncertainties rise. While I do not specifically question the relevance of N2 fixation, I do doubt the general applicability of the model if these source signatures are used.

(2) In line with this, I can imagine that it is nearly impossible to separate influences

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by atmospheric deposition and nitrogen fixation. I believe the authors were aware of this problem, as they excluded N<sub>2</sub> fixation from the northern parts of the study area – but how much would it have altered the results if all 4 potential sources had been considered?

(3) the source assessment is an integral part of the model and the study. In Table 1, source signatures are listed, but clear references are missing (this study? previous studies?) This might all be in the text, but it is well-hidden. This is especially important as the referencing scheme for  $\delta^{18}\text{O}$  changed when a new value was assigned to IAEA-N3 – older data can have an offset of  $\sim 3\%$ .

(4) The importance of atmospheric deposition should be discussed. Mayer et al (2002), cited in this study, find only a slight elevation of  $\delta^{18}\text{O}$  values even at 40% contribution of atmospheric deposition. Is this due to recycling? That may also apply to the Northern rivers, where atmospheric deposition seems to be the most important N source- but after assimilation into plant biomass, and upon remineralization/nitrification, the  $\delta^{18}\text{O}$  signal will of course be lost. These effects should be mentioned.

Specific comments:

- I find it quite awkward that the authors chose to merge the results and discussions section. I find this very unpleasant to read, as it is not always easy to disentangle their own work and previous studies or assumptions based on those. If this is in accordance with the BGD style, I would highly recommend splitting this up into separate sections.

Introduction, p. 5870, line 25: "N-fluxes have doubled" – please specify. Which fluxes? p. 5872, lines 8-15: might be a stylistic issue, but to me, the Baltic Sea is anything but a typical temperate ocean.

- I suppose it has been ensured that sampling (February) was before the onset of the spring bloom (Feb/March, p. 5872, line 11). Still, this should be mentioned in the Material and methods section.

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p. 5873, line 10: What was the sampling interval, i.e., how long were samples left in the samplers before filtration? Model results: I noticed that mean values for individual source contributions are not the mean of minimum and maximum values. This is probably due to the distribution of model results?

#### Results/Discussion

- p. 5878, lines  $\frac{1}{2}$ : “concentrations in winter were almost identical” – This is impossible to see in figure 2. The color coding encompasses values from 0-250  $\mu\text{M}$ . This figure could be split, and low-concentration ranges could be expanded in the color scale.

- p.5878/5879, lines 27-4: This does not sound like a novelty, but like a mere reporting issue to me.

-p. 5879, line 27: Referring to 3.9‰ here is not quite correct, as far as I know, Knapp et al refer to DON, not nitrate. This number is not needed, it is quite clear that N from N<sub>2</sub> fixation is relatively light.

- p. 5880, line 3: where do these -9.8 +/- 3.8‰ come from? I can't follow that calculation.

-p. 5888, lines 21-23: I would be interested to know if this result can be attributed to the (questionable) 18O source assignment for N<sub>2</sub>-fixation.

- p. 5882, lines 2-19: Can you please include some numbers on pool sizes etc. to put these calculations into perspective? same later in this section, when referring to the kalix river.

-The last section, 3.3, the comparison of water column versus sediment isotope values, is entirely isolated from the rest of the manuscript. Can you define a specific objective to incorporate these results in your study? Else, they might as well be omitted. Also, I don't quite get what you're trying to say in line 10/11. I can imagine that during a spring bloom, there is lots of uptake, and afterwards, sinking particles, and complete consumption, too, but this is a strange way to put it.

Does a comparison of  $7.9 \pm 1.8\%$  to  $7.3 \pm 2.1\%$  really suggest significant differences? Did you test this?

Conclusions – Highlighting the importance of atmospheric deposition, right at the end of a study that basically showed that this source is not relevant, seems a bit strange. To catchments, maybe, but to the Baltic?

technical corrections:

p. 5871, line 8: change influences to influence

p. 5883, line 25 – change remain to remains

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