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Biogeosciences Discussions

Interactive comment on "Deposition of nitrogen and phosphorus on the Baltic Sea: seasonal patterns and nitrogen isotope composition" *by* C. Rolff et al.

C. Rolff et al.

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Reviewer 1 This manuscript reports the results of a "2 year programme sampling rainfall at four sites in the western Baltic for nitrogen and phosphorus deposition and nitrogen isotopic composition. The study appears to have been thoroughly done, with appropriate care taken to control for potential contamination of rain samples collected over relatively long time periods. The work is well reported and the discussion of the results is generally clear and concise. In my opinion the manuscript is suitable for publication in Biogeosciences, although there are a few minor points which I think might need some clarification.

Since the abstract must stand alone, I would suggest including some definition of "Baltic

Proper" there to help readers who might be unfamiliar with this term.

We now write: "Atmospheric deposition of nitrogen and phosphorus on the central Baltic Sea (Baltic Proper) was estimated."

In section 2.2 I would suggest including a citation for the persulphate digestion method for total nitrogen and phosphorus analysis.

We added the citation for the methods description. Koroleff, F. 1983. Determination of nutrients, p. 125-139 phosphorus, 162-173 nitrogen. In K. Grasshoff, M. Erhardt, and K. Kremling. [eds.], Methods of seawater analysis. Verlag Chemie.

At the top of page 3020: "... because of draught.". I think this should be "... because of drought."

Corrected

Also on page 3020: "Monthly precipitation (Fig. 2) ranged from zero at SH in August 2002... ", but this particular data point does not appear to be plotted in Fig. 2.

We changed the figure slightly so that the line for SH ends at the zero. It was dry at both station GS and SH in Aug 2002. In the first version we did not add the data for SH because it was totally dry so there was no sample while GS had 1.9mm.

Bottom of page 3020: "Pollman et al. (2002) found replicate precision.... The same limit was adopted... " I am not quite sure whether this means that Rolff et al. have excluded all data $>$ 80ug L-1, or that they excluded data with low replicate precision (and, if so, how was this assessed?).

We have excluded samples with concentrations above 80 micrograms per litre exactly like Pollman et al suggested. To make that clearer we reworded the sentence to: "The same criterion was adopted in this study, which excluded 3 analyses out of 56."

On page 3022-3 the regression of d15N on percentage of DIN as ammonium is used to derive end-member isotopic signatures for nitrate and ammonium. I am not sure that

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the authors have done enough at this point in the manuscript to alert the reader that these "end-members" are likely to show some variability in their isotopic signatures. Later in the manuscript (page 3030) this extrapolation is stated to give the "long-term average isotopic composition of nitrate and ammonium", and I think this is probably correct and a better statement of the results of the extrapolation. Perhaps some citations to other works (either for nitrate and ammonium nitrogen isotopic composition in rainfall or aerosol) can be added to clarify this.

As suggested we wrote on page 3019: "End member calculations of nitrate and ammonium in the deposition based on the stable isotope ratios should be considered with some caution since the estimates can only be approximations of long term averages." On page 3022 we added for clarification: "Therefore, our isotope based end-member calculations cannot consider the isotopic variability of the sources (see discussion, 4.3)."

I am not entirely convinced by the authors suggestion that the winter nitrate peak at the northern sites is caused by NOx emissions from shipping. NOx emissions are almost certainly the source, but why should the source be shipping? If there is some evidence that shipping, and not other sources (such as higher terrestrial combustion emissions during the winter, or seasonal changes in atmospheric transport pathways), is the dominant source then this evidence should be presented. Otherwise this looks rather speculative.

We added a citation of a report from the Helsinki Commission on the Maritime Activities (please see http://www.helcom.fi/stc/files/Krakow2007/Maritime_activities_MM2007.pdf) which shows a map with the major routes of ships traffic, which pass the island of Gotland. Furthermore, the report pointed out how important ships emissions are for the NOx deposition and we therefore feel that we can otherwise leave our carefully phrased sentence unchanged.

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In Table 1 most of the Average data for nitrogen species appears to have been shifted one column to the right. This was corrected.

Reviewer 2 In INTRODUCTION: The introduction consists of 3 distinct parts with the aim of the study spread over the second and 3d part. The 3 parts are each very clear and well written, but parts 2 and 3 could be better integrated too each other in order to better link the 2 main objectives (isotopes of N deposition and N2 fixation control by P deposition). Merging parts 2 and 3 with in final a clear phrase exposing the aim of the paper would contribute to better linking the 2 subjects considered in the paper.

We agree with this observation, and tried to change the introduction however, only slightly because of two reasons; first of all there is very little material on P-deposition. Secondly, there is only a weak link between atmospheric N and P deposition the latter only affecting nitrogen-fixing species in summer. We have tried to make a more elegant bridge between the two paragraphs. We deleted - "nitrogen fixing Cyanobacteria in the Baltic Proper" - from the header. This may distract the reader from our main topic which is the atmospheric P deposition. Furthermore we begin the paragraph with the sentence: "The most interesting aspect of atmospheric P-deposition is their effect on the summer blooms of filamentous nitrogen-fixing cyanobacteria of the genera Nodularia and Aphanizomenon which are a considerable internal source of nitrogen for the Baltic Sea." To structure the introduction this way makes the difference in the deposition of both elements very clear since N is a serious nutrient source for the open oceans while P is not.

In SAMPLING: The water in the collectors is replaced once a month. This probably does not affect the total N content (neither its isotopic signature) in the sample but may change the N speciation, especially during warmer periods. It would be good to mention this. The authors mention an eventual underestimation of the organic N content later in the discussion but do not comment on the eventual effects on NH4/NO3 ratio.

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We point out that a certain risk exists as to the NH4+/NO3- ratios. On page 3018 we added: "Any effects on the concentrations of NH4+ and NO3- and the NH4+ to NO3- ratio during collection and storage should be small." Furthermore, these samplers are in use in the national monitoring program in Sweden and carefully chosen and tested. They are kept dark to prevent any changes related to phototrophic processes. Sweden uses both N-compounds from their samplers for reports.

A second and more technical remark also concerns the functioning of the collector in winter when precipitation comes as snow. Snow settles in the funnel and when it melts the water is collected in the bottle, unless there are very large snowfalls so that there is a pile on top. To our recollection there was not much snow at all during the period the samplers were out, particularly not in these open coastal sites. There were no changes made in the text.

In RESULTS: In Table1- there is an error in the AVERAGE line of the table: the values for the NO3, organic N and total N loads are shifted 1 cell right. This was fixed.

In DISCUSSION part 4.2 NUTRIENT LOADS: As the authors analyze collected rainwater and calculate deposition rates by multiplying concentrations with precipitation data, their results and conclusion should normally only concern wet deposition of N and P. However, their deposition rate estimates for N do quite agree with total deposition rates (including dry deposition) in the Baltic from literature. This seems quite surprising to me but is not discussed by the authors, and needs some clarification. Does this mean that dry deposition is not (or less) important in this region?

We cannot separate dry from wet deposition. We collected total deposition with an open funnel as described in the methods section. From that sample we measured nitrate, ammonia, and organic N separately again, not separating dry and wet deposition. The data presented therefore comprise total N-load and 3 specific components. This may be the reason why the overall concentrations did not deviate in any particular way from the ones previously reported and we write in the discussion (chapter 4.1):

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"The concentrations of ammonium and nitrate agreed well with those generally found in the Swedish national monitoring (Kindbom et al. 2001)." Since organic nitrogen is such a little share of the total (<10% of total N) we did not discuss that in detail, but rather write: "Organic nitrogen was generally below 10 % and showed no obvious dependence on load, precipitation or season. Since the nitrogen concentrations found in this study agree well with the literature on nitrogen in precipitation for the region (e.g. Bartnicki et al. 2004), the discussion will be focussed on the isotopic signatures rather then on nitrogen concentrations and loads." To address the reviewers point we checked out the differences between dry and wet deposition from a very detailed study in the Skagerrak (Spokes et al 2006 a position not far away from our sites) and found that wet deposition clearly dominates total deposition. The authors point out that during phases of overall low deposition the dry deposition of ammonia may be important. However, we cannot separate the sources of those compounds in our study. Instead we clarified that point in the methods section and amended the discussion. On page 3017 we are saying: "Atmospheric deposition (rainwater and dry deposition) was collected." And in the discussion page 3025 we added: "Applying the calculated average annual load of total N-deposition in this study."

In CONCLUSION: Again as for the introduction, the P story is not integrated to the N story. For this reason, the P story seems not to belong to the general outline of the paper.

We fully agree with this point but see only little potential to change our text. We wanted to present both elements (which is often not done in papers dealing with atmospheric deposition). There is very little data on P deposition to compare our data with as we could do it for N. The only integrating part is the reasoning on P deposition on nitrogen fixation through cyanobacterial blooms. We tried to make a better link in the Conclusions through the cyanobacteria blooms. There we write: "In large-scale isotope-based nitrogen budgets, atmospherically deposited nitrogen could therefore be interpreted as nitrogen fixed by cyanobacteria, potentially leading to overestimates of nitrogen fixa-

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tion. While the atmospheric phosphorus load is not likely to be the major source of phosphorus for summer cyanobacterial blooms in the open Baltic Proper, P deposition in precipitation could potentially prolong an existing bloom."

END

Interactive comment on Biogeosciences Discuss., 5, 3013, 2008.