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Interactive comment on "Accurate and precise quantification of atmospheric nitrate in streams draining land of various uses by using triple oxygen isotopes as tracers" *by* Urumu Tsunogai et al.

Anonymous Referee #2

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General comments

This paper presents interesting data on the quantification of unprocessed nitrate from atmospheric wet deposition in waters of 33 streams, discharging to Lake Biwa, Central Japan, by means of nitrogen (14/15N) and triple oxygen (16/17/18O) stable isotope analysis of nitrate. Stream waters were sampled four times in March, June, August and October 2013. Total nitrate inflow into the lake as well as nitrate stable isotope signatures were averaged over the year by interpolation between the four sampling dates. The main outcome was that unprocessed atmospheric nitrate made up about

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5% of the total nitrate transported into Lake Biwa by the 33 streams, that the lake removed a substantial portion of the nitrate before the water left the lake again, and that both quantity and anthropogenic source signature of nitrate increased in streams discharging areas with increasing population density.

While the topic is highly relevant and timely, and the data presented contain valuable information, the paper suffers severely from several weaknesses. Firstly, it is way too long, starting with the Abstract and ending with the Conclusions. The reader gets lost in the many detailed descriptions of results, while the description of methods is partly incomplete. For example, the method how the triple oxygen stable isotope analysis has been done is not described, even not briefly. Also statistical and data evaluation methods are not described. But most importantly, the conclusions with respect to the effect of different land uses on the fate of atmospheric nitrate (which was the main motivation of the study) were based on many assumptions and uncertain values, especially by excluding more than two sources of nitrate (from atmosphere and from nitrification only). Furthermore, there were no statistical data provided that proved an unambiguous relationship between land use in the different stream catchments and the signature of nitrate in the stream water. This weakens the key message of the paper on the effect of land use and population density on the fate of atmospheric nitrate, and needs to be rectified before the paper becomes acceptable for publication.

Please see below for specific comments.

Technical corrections can be found in the annotated pdf.

Specific comments

Abstract, Results and Discussion, and Conclusions should be shortened significantly, focusing on the main outcome of the paper. It would be good if Lake Biwa were mentioned in the Abstract.

The number of references should be reduced to about 50 (from almost 80). The number

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of figures should be reduced to about 6.

Title: I suggest deleting “Accurate and precise” from the title, as it suggests a very high accuracy and precision of the data presented in the paper, which is not the case (the fraction of unprocessed atmospheric nitrate in relation to total nitrate in the stream waters of about 5% had a relative error of 10%, and average δ15N and δ18O values were assigned with an absolute error of +/- 10‰ which is really large). Secondly, the reader might wonder why there is a differentiation between accurate and precise, which occurs also several times in the paper, but which is never explained, also not the way how to achieve both high accuracy and precision.

Data evaluation and regression methods as well as statistics are not described.

The English should be checked by a native speaker.

p. 2, l. 23-24: “important to primary production and thus eutrophication“: primary production does not in itself lead to eutrophication, but only a mismatch between primary production and heterotrophic consumption, usually induced by excess nutrient load. I suggest rewording to “important to primary production, and an excess of nitrate can lead to eutrophication downstream”.

p. 2, l. 28-29: I would separate assimilation by plants and microbes and denitrification by microbes in two separate processes, as they are of completely different nature.

p. 3, l. 4-10: Here you cite 25 (!) references for one statement, overshooting by far. Please reduce to the 5-6 most important papers.

p. 3, l. 10-12: As you use the bold statement “. . .can be quantified through a simple isotope mass balance approach”, you should give ranges reported in the literature for the two isotope ratios for the different sources to allow the reader to assess the feasibility of the simple isotope mass balance approach.

p. 3, l. 22-23: “the mixing ratios of unprocessed NO3−atm within total nitrate are minimum or uniform for whole or specific stream water samples”: Meaning of this sentence

is unclear. Please reword.

p. 4, l. 6: “By using the Δ17O signature…”: This term should be introduced and explained, not only by an equation, but also in words.

p. 4, l.12-13: “In addition, Δ17O is stable during the mass-dependent isotope fractionation processes within surface ecosystems.”: Yes, but only if there is no oxygen exchange with the surrounding water, otherwise the Δ17O information gets lost. That is the reason why only UNPROCESSED atmospheric nitrate can be traced, not the further processing of atmospheric nitrate itself.

p. 4, l. 14-15: “Therefore, although the atmospheric δ15N or δ18O signature can be overprinted by biogeochemical processes subsequent to deposition, Δ17O can be used as a robust tracer…”: Again, also Δ17O can be “overprinted” by oxygen exchange, not only δ15N or δ18O of nitrate.

p. 5, l. 14: “NO3−atm is stable”: I disagree. Nitrate from atmospheric deposition can and will be processed after deposition. Therefore, it cannot be considered as stable.

p. 5, l. 18-20: “Moreover, we exclude the contribution of NO3−atm in the determined δ15N and δ18O values to estimate the corrected δ15N and δ18O values for accurate evaluation of the source and behaviour of NO3−re.”: Totally unclear what that means. Please explain more clearly.

p. 5, l. 21-22: “influences of flow stagnation into the lake on nitrate”: What influence is meant here? On nitrate concentration? On isotope ratios? On total amount?

p. 6, l. 6-14: This paragraph should be moved to the end of the introduction as part of the motivation for the study.

p. 7, l. 7: “To calculate the annual influx/efflux of nitrate via each stream… we used the sampling number n”: Unclear how the annual influx/efflux of nitrate was calculated using the sampling number. Please provide a more detailed description of the calculation. How were peak flow events after strong precipitation events or after snow melt

(if there was) taken into account? Frequently, the solute composition of stream water is significantly altered during peak flow events, and the total annual discharge is often dominated by peak flow events.

p. 8, l. 4-6: The principle of the method should be briefly described, despite the references.

p. 8, l. 15: There is no mention of the method by which the 17O signatures of nitrate were determined. This need to be done here or above.

p. 8, l. 24: How do you define error here and elsewhere in the manuscript? Standard error of the mean? Standard deviation? Or else?

p. 9, l. 3-4: "showed $NO2-/NO3-$ ratios of less than 5%; thus, the results were used with no corrections.": How does that translate in the worst case to uncertainty of the nitrate isotope values?

p. 9, l. 8: "flow-weighted": There is no mention of flow measurements further up in the Materials and Methods section. This needs to be done, and the uncertainty of interpolating nitrate concentrations between four sampling dates only for a whole year needs to be addressed.

p. 9, l. 19: "For small streams with no data for the flow rate, we used a small and stable flow rate of 0.1 m3/s for fn.": For how many of the 33 streams was that the case?

p. 9, l. 21f.: The calculation of the δ15N and δ18O values of remineralized nitrate with a two end-member mixing model with atmospheric nitrate as second end member falls short of taking into account also other sources of nitrate, e.g. fertilizer or sewage water.

p. 10, l. 17: What is a "clear normal correlation"? Please specify.

p. 11, l. 6-7: "The present results imply seasonal and regional changes in the δ18O/Δ17O ratios of tropospheric ozone and in the OH radical.": Are there any references that back up this assumption?

p. 11, l. 8: “On the basis of both the temporal variation in the depositional flux of NO3−atm. . .”: No temporal/seasonal variation of the depositional nitrate flux has been described further up, and in Fig. 3c there is no clear seasonal pattern of the depositional nitrate flux visible, in contrast to the Δ17O values.

p. 11, l. 18-19: “additional corrections could be needed“: Were they required? And if yes, how exactly were these corrections done?

p. 11, l. 19-20 and 24: What do you mean with “NOx oxidation channel”? Pathway?

p. 12, l. 3: “correct for difference in arrival frequency “: What do you mean with “difference in arrival frequency? Please rephrase in an understandable way. And has it been corrected for in the present work?

p. 12, l. 9-12: This statement is too vague and weak. It needs to be backed up with literature, or it should be abandoned.

p. 12, l. 10: “by allowing an appropriate range of errors presented later”: This “range of errors should be specified here at its first mention.

p. 12, l. 14-18: The residence time of atmospheric nitrate could vary significantly between your different catchments with different land uses. How do you know whether the residence time was similar in all of your catchments to that of forested catchments reported elsewhere?

p. 12, l. 21: “we used the obtained Δ17Oavg”: At this stage it is not clear how the Δ17Oavg was obtained.

p. 12, l. 22-23: “. . .by allowing the error range of 3.0‰ considering the whole factor change of Δ17Oatm from Δ17Oavg.”: What does that mean? Please describe in an understandable way. Why exactly 3.0‰ and not 2‰ 1‰ or any other value?

p. 12, l. 28-30: “As a result, while using the δ15Navg and δ18Oavg values as δ15Natm and δ18Oatm, we assumed much larger error range on the values; i.e. $\pm$ 10‰ for both

δ15N and δ18O." Unclear, how this error was determined. Please describe in more detail.

p. 13, l. 10-12: "The spatially continuous variation in the values... imply that the values may represent land use changes in each catchment area.": The annual average values of δ15N and δ18O vary by 10‰ at the most. Given the uncertainty range of these values of +/- 10‰ (as stated on p. 12, l. 30), how do you want to discern any significant differences here, not to mention to derive any statements about land-use effects on the processing of atmospheric nitrate in the different catchments?

p. 14, l. 24: "determined recently": By whom? No reference provided.

p. 15, l. 2-4: "We concluded that the δ18O value of NO3$-$re produced through nitrification in the temperate watershed having δ18O(H2O) values of -7.8 ± 1.0‰ was -2.9 ± 1.2‰ and that we should use such a low δ18O value...": Did the soil and/or stream water have this δ18O(H2O) values of -7.8 ± 1.0‰ If yes, please make this clear in this sentence. If not, then the basis for this conclusion is not clear.

p. 15, l. 8: "Although the Δ17O values of nitrate were stable during the biogeochemical processing": Again, if nitrate is biogeochemically processed, then also the Δ17O gets lost.

p. 15, l. 13-16: "We concluded that the range of isotopic fractionations ... was generally small": The basis of this conclusion remains unclear. Please explain in more detail.

p. 15, l. 16-19: "This result also supports our assumption in section 3.1 such that the actual δ15N and δ18O values of NO3$-$atm in each stream water sample ... correlate with the δ15Navg and δ18Oavg estimated at Sado-seki monitoring station within an error of $\pm$10‰": This refers to the previous sentence, which does not report a result but a conclusion, the basis of which remained unclear. That is, the statement made in section 3.1 has been based on very weak grounds.

p. 15, l. 30-31: "...responsible for the positive correlation between the δ15N values of

total nitrate and population density.": Was this correlation significant? I could not find any statistical information.

p. 17, l. 1-3: "...the slight deviations in the reported δ15N and δ18O values from our results can be explained by the following factors...": Could also different sources of ammonium for nitrification could have played a role (soil, sewage water, fertilizer)?

p. 18, l. 17f.: It is unclear whether this snow signal of atmospheric nitrate could be captured by the sampling design of only four samplings per year.

p. 23, l. 3: "The estimated annual average Δ17O value of inflows, +1.3‰...": Unclear, where this value comes from. Please explain.

p. 23, l. 4: "...average mixing ratio of NO3−atm within total nitrate of 5.1 $\pm$ 0.5%...": This value shows only up here and in the abstract, but it is unclear how and when it was calculated.

p. 23, l. 6-7: "...the remainder of the nitrate was of remineralized origin (NO3−re) likely produced through nitrification within the catchments...": Again, what about direct input of nitrate via fertilizer and/or sewage water without remineralization?

p. 23, l. 25: "Lake Biwa also acts as a net sink for fixed N": The question is what happens with the processed nitrate? Very likely most of it is denitrified and lost to the atmosphere as N2O and/or N2. Thus, the statement that Lake Biwa acts as a net sink for fixed N is questionable.

Table 1: This table should also include the dominating land use in the respective catchment.

Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/bg-2015-627/bg-2015-627-RC2-supplement.pdf

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