Biogeosciences Discuss.,
doi:10.5194/bg-2015-627-RC1, 2016

Biogeosciences Discussions

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 #1

Received and published: 15 February 2016

1 General comments

This paper by Tsunogai et al. builds on previous research by Ohte et al. (2010) at Lake Biwa. The authors have quantified the relative contribution of atmospheric nitrate to stream nitrate using oxygen triple isotope measurements, their seasonal variability and interannual variability. In conjunction with Lake isotope measurements, the data are used to present a nitrate budget for Lake Biwa as a whole.

The study is comprehensive in its spatial coverage and includes data from 32 streams.

Temporal resolution (4 sampling periods over 1-year interval) is somewhat limited, but in light of the residence time of nitrate in the Lake (5.5 years), it is sufficient.

Compared to the work of Ohte et al. (2010), the main advance of the present study is the inclusion of oxygen triple isotope measurements. Other aspects (e.g. the correlation between nitrogen isotope ratios and population density) have been noted before.

The paper is generally well-written and complete, with a few exceptions, notably the Conclusions section disregard large fractions of the discussion (e.g. on seasonal and interannual variations as well as the Lake Biwa nitrate budget). The presentation quality (except for the figures) is mostly good, but there are a number of grammatical errors. Language copy-editing will be required.

Before the paper could be accepted for publication in Biogeosciences, several major areas need to be improved as detailed below.

In line with the Biogeosciences data policy (http://www.biogeosciences.net/about/data_policy.html) , all data (water fluxes, nitrate and nitrite concentrations, isotope values, etc.) should be publicly available, preferably by deposition in a data repository, or alternatively as electronic supplementary information. Please add a section on "Data availability".

The figures are somewhat antediluvian in their appearance due to the lack of colours. While the stated aim to make them compatible with black and white printer is commendable, most readers will either view them on a colour display or printed in colour. The figures should be redrawn in colour. The current use of different shapes to distinguish time series can be retained, for the benefit of the small number of readers without access to colour displays and printers, and for those with impaired colour vision.

The figures in the supplementary information are discussed at crucial points and called out in the text. Fragmentation of the text into different documents is undesirable. They should be merged with the main text. The supplementary information should be used

instead to present the full dataset in a table (water fluxes, nitrate and nitrite concentrations, isotope values, etc.), unless the authors can give a URL or DOI at a repository, at which they have lodged the data.

The treatment of systematic uncertainties and propagation of measurement uncertainties to derived properties is insufficient and/or has been insufficiently well presented. In particular, variations in the isotopic composition of the atmospheric nitrate end member (delta17O, delta15N and delta18O) should be better documented and listed in a table. The resultant uncertainties in the calculation of the atmospheric nitrate fraction and the delta15N and delta18O values of the remineralised nitrate should be included in the text and figures of the paper.

A major systematic uncertainty arises from the current disregard of nitrate sinks and associated isotopic fractionation (section 3.5). Specifically, the delta15N and delta18O values of so-called "remineralised nitrate" may have undergone large modifications due to nitrate assimilation or denitrification. These processes have been currently ignored. While their effect on delta17O is most likely negligible, they cannot be discounted for delta15N and delta18O. In other words, assimilation and denitrification could have enriched "remineralised nitrate" in both 15N and 18O isotopes. The possibility of this should be explored further, perhaps in the first instance using delta15N and delta18O scatter plots of the "remineralised nitrate" component. If there is a noticeable potential influence, this should be quantified as good as possible. The authors may also want to consider renaming the "remineralised nitrate" component as "residual nitrate" or another less prejudiced term.

2 Specific comments

The term "17O anomalies" has been criticised for its subjectivity and biased nuances. A more neutral term, which has been adopted by many authors, is "17O excess" (similar

to deuterium excess and thermodynamic "excess" properties; a negative "17O excess" reflects a deficit). Alternatively, "delta17O values" would also be acceptable.

The term "mixing ratios" is ambiguous and should be replaced by "mole fractions" or "mass fractions".

Averages and uncertainties should be enclosed in round brackets so that the unit applies to both, e.g. p. 2/3 "(2.3$\pm$1.1) μmol L-1", in line with standard practice in natural sciences.

In line with international conventions, chemical phase information should be added in round brackets after the chemical formula, i.e. NO3-(atm) and NO3-(re), not as subscript index. Alternatively, text abbreviations should be used, e.g. AN for atmospheric nitrate and RN for remineralised / residual nitrate.

Title: The words "accurate and precise" should be dropped from the title. The claimed "accuracy" would require an absolute measurement method and/or validation by an independent laboratory, neither fo which have been performed. "Precision" is not a meaningful metrological term. In any case, the quantification method has known significant systematic uncertainties, e.g. the isotopic composition of atmospheric nitrate deposition, temporal undersampling, etc., so neither the qualifications "accurate" nor "precise" apply.

Abstract: A sentence should be inserted at the beginning of the abstract that explains the motivation for the present study. The current first sentence of the abstract is too long and should be split into two.

Abstract p. 2, lines 14 to 18 should be moved up to before "We conclude ..." in line 4.

Introduction: The discussion misses fertiliser inputs and groundwater recharge as nitrate sources - see also p. 12.

4/9: Use of beta = 0.5247 is unusual. Most other research groups use 0.528, based on the meteoric water relationship (e.g. Savarino, Hastings, Michalski). The references

given by the authors either do not express a preference (Miller 2002) or also use a coefficient of nearly 0.528 (Kaiser et al. 2007).

4/12: This statement only applies to mass-dependent fractionation processes following a slope of 0.5247. It also does not apply to mixing applications because mixing follows linear, not power-law relationships. As in the present case, the authors are primarily using delta17O as a mixing tracer, a linear definition of delta17O would be preferable. At the least, the potential systematic error due to fractionating processes following other mass-dependent relationships (e.g. beta = 0.5) and the effect of linear mixing on the non-linear delta17O definition used here should be quantified and carried forward to the subsequent discussion.

Sections 2.1 and 2.2 should be merged. Sections 2.1.2 and the last paragraph of sections 2.2 are highly repetitive.

The use of Japanese "financial years" should be abandoned in favour of the use of calendar years as mandated by the manuscript submission guidelines for Biogeosciences. All dates should be revised accordingly, as well as the calculation of annual averages.

7/7-14: This discussion is confusing. At the least, it needs to be made clear that there is no 5th sample and that the authors have instead used the data from the previous year (March 2013) to calculate changes over the so-called "winter period", i.e. the difference between October 2013 and March 2013. Rather than using "sampling" numbers, the calculation scheme could perhaps be better presented in a table.

7/28-8/2: The H2O isotope measurements referenced here have not been presented in the manuscript. Please include the results as a figure or table and include the data in the supplementary information.

8/3-11: There are too many references given here. Please give just the one that documents the method used here.

The azide method is known to require larger isotope exchange corrections for oxygen

isotope ratios. How large was the required exchange correction applied to the raw measurements?

8/12-17: It is not appropriate to use ion chromatography as a reference method to determine the efficacy of N2O conversion. Ion chromatography can also be affected by measurement biases. Nitrate standards should be used instead to check the azide method is working properly. Please explain how many samples have been excluded based on the ion chromatographically determined concentrations.

8/24: What "error" do these values represent? Are they the standard deviations of 3 replicate measurements?

8/28: Please replace "approximation" by "definition". The definition of delta17O can be made in any arbitrary fashion; there is no approximation in a definition. However, of course, the interpretation of the resultant delta17O values may change, depending on the definition.

9/4: A 5 % contribution of nitrite leads to a significant bias in the delta18O value and cannot be neglected. The bias could be as large as -1.3 ‰ because the isotopic fractionation associated with conversion of nitrite to N2O is about 27 ‰ lower than for conversion of nitrate to N2O (e.g. Casciotti et al. 2007). All measurements need to be corrected for this bias, or re-analysed after NO2- removal (e.g. following the sulfamic acid protocol of Granger Sigman 2009).

9/11-13: It is unclear how the monthly stream flow measurements are used together with the less frequent nitrate concentration and isotope measurements. Do you ignore the flow measurements from the months when no sampling has occurred? Do you interpolate the concentrations to match each flow measurement with a corresponding nitrate concentration or isotope delta value? It seems that you ignore major parts of the flow (based on the counting index of 4). How much stream flow is "missed" due to this temporal undersampling?

10/13: Please replace "isotopic compositions" with "excess" - see above. "Composition" is not an extensive quantity.

11/13-16: What are uncertainties / variability in the atmospheric end member values? Which values and which uncertainty did you actually use when you calculated the delta values of residual nitrate (see also p. 12, l. 26-31)? Which error do you estimate the systematic neglect of dry deposition has caused?

14/4: What do you mean by "almost correlated"? Please give a quantitative measure of what "almost correlated" constitutes.

15/28-31: The last sentence does not make sense at the end of a paragraph. It should appear at the beginning of a new paragraph. You should then explain how you verified that the "remineralised" portion was actually responsible for the positive correlation with delta15N and population density.

16/14: It is unclear why a uniform Catm (atmospheric nitrate contribution to the total nitrate concentration) is indicative for low denitrification. This could be offset of atmospheric inputs of equal magnitude. A more sensitive approach would be to look for a correlation (or absence thereof) between delta15N and delta18O of "remineralised" nitrate.

17/23: delta15N measurements should be used to verify this hypothesis, especially in combination with delta18O (scatter plots).

22/17: Which value was used for alpha?

23/15: Which value was used for gamma?

23/25: Please speculate on the fate of nitrogen. Are they lost due to gaseous emissions (denitrification, anammox?) Sedimentary deposition? Eutrophication (secular nitrate concentration increases)?

24/29-25/2: This is not a conclusion, this is the premise/rationale of the present paper.

These lines should be deleted.

25/19-25/25: This is not a conclusion, this is the premise/rational of the present paper. These lines should be deleted.

The section Conclusions is incomplete. Seasonal and interannual changes in stream nitrate concentrations and isotopic composition are missing. Also, the substantive section on the lake nitrogen budget is not reflected by a corresponding conclusion. I would expect a statement on the apparent nitrogen sink and possible identification including any relevant past or future work.

3 Technical corrections

The internationally recommended symbol "a" should be used to abbreviated "year", not "yr" and "y", which have both been used in the present paper.

1/25: The word "However" does not apply - there is nothing contradictory in this sentence.

2/1: Please insert "stream" between "average" and "nitrate".

2/3: Please delete "in the streams".

10/1: Please delete "each".

12/5: Please cross-reference the location of Rishiri island in Fig. 1.

12/16: What "recession period"?

14/12: "strongly" should be deleted.

17/8: Please replace "river" with "stream".

22/1: A different symbol than alpha should be chosen because alpha is usually used

to denote isotopic fractionation factors.

Figure 7b: The numbers should be explained (stream numbers?).

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