

Interactive comment on “Sources, fate and geochemical dynamics of nitrate in an oligotrophic lake” by U. Tsunogai et al.

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Dear Prof. Barth,

Thank you very much for your comments on our manuscript.

Although the problem of transparency in the lake was one of the important motivation to start our study on the nitrate dynamics in the lake, clarifying the cause was not the goal of this paper, as presented in title/introduction of the submitted manuscript. To discuss the possible causes, much more data and much more length must be needed. Furthermore, most of the authors (U.T. S.D. D.K. and F.N.) are not included in the on going NIES project to clarify the cause of the problem so that our paper is not suitable to discuss this. We would like to limit the topic of our paper to nitrate dynamics in the

C4132

lake.

We would like to reply to you by citing each of your comment/question.

> Abstract If the nitrate isotope compositions were only determined in June and August 2007 it seems difficult to make annual assumption such as mean residence times of 1.2 years. How could seasonality be accounted for?

Because the $\Delta^{17}\text{O}$ value of nitrate represented the long-term mean relative feeding ratio between atmospheric nitrate and remineralized nitrate to total nitrate in the lake prior to our first sampling on June 2007, we can estimate the annual feeding rate of remineralized nitrate and thus the residence time of nitrate by using the data of annual deposition rate of atmospheric nitrate, without actual observation on the lake water through a year. This is one of the most useful merit in the $\Delta^{17}\text{O}$ tracer of nitrate. The detail have been presented in section 3.6 in the submitted manuscript.

> P7230(P4)/L1 how can nitrate be remineralised to nitrate? Do you mean nitrite to nitrate?

What remineralized is “assimilated nitrate”, not nitrate. The “assimilated nitrate” means organic nitrogen. If this expression is misleading, we would like to revise.

> P7230/L8 can you name the international standards?

The international standards we used in this paper have been clarified in P7235/L20 (section 2.3) in the submitted manuscript. The delta-notation, however, is independent from the standards used, so that we did not clarify them here.

> P7230/Eqn 1: what does the X mean?

We are sorry for lacking the notations. The “X” means sample and “REF” means standard. We would like to remove both “X” and “REF” in the equation during revision.

> P7231(P5)/ L 16: Seasonal variations from when to when?

C4133

The average seasonal variation around the year of 2007. We would like to clarify this.

> P7231/L 25 Are you sure the autumn over turn occurs in December to January after the lake is already covered with ice and snow?

The ice coverage was always partial during December, January, and April. We would like to revise this.

> P7233(P7)/L12 Name the temperature of the refrigerator

The temperature was around 4 °C. We would like to add this in the revised manuscript.

> P8(P7234) /L5 can you describe the reaction leading to HN3 and subsequently to NO2?

The first reaction using Cd was from NO₃⁻ (nitrate) to NO₂⁻ (nitrite). The second reaction using HN₃ reagent was from NO₂⁻ (nitrite) to N₂O (nitrous oxide). We would like to clarify this in the revised manuscript.

> P7234(P8)/L 8 made basic to which pH exactly.

The pH more than 13. We would like to clarify this in the revised manuscript.

> P7234(P8)/L27 “Defined schedule”, what do you mean?

That was mistype of “definite schedule”. We would like to revise this.

In usual CF-IRMS technique, 100% machine-working reference gas is introduced to MS just before and/or after the sample (nitrate-derived N₂O, in this case) is introduced to MS. To avoid the reference N₂O overlies sample N₂O eluting from GC in a certain schedule, we introduced the reference N₂O under a definite schedule.

> P7235(P9)/L2&3 if you want for daily variations, it does not seem enough to run a control standard once per day

We used the words “daily variations” as the day-to-day variations (variations between a day and an another day), so that the calibration once per day is enough to calibrate

C4134

them. Because the sub-daily variation (variations in a single day) can be calibrated by the 100% machine-working reference N₂O, we trusted that combinations of these two calibrations are sufficient for whole calibrations using CF-IRMS. If the words “daily variations” were not appropriate to express the day-to-day variations, we would like to revise. Would you please suggest us more suitable words ?

> P7237(P11)/L 24 what is the end member value of NO₃(atm)?

The end member value of Delta17O of NO₃(atm) we used in this paper was +26.2 ‰ as presented in section 3.2 (P7241/L16) in the submitted manuscript. Because NO₃(atm) is the only source of nitrate having Delta17O more than zero, we did not clarify the end member value at this section.

> P7238(P12)/L5 it is surprising that during June there should have been no stratification of the lake and only two months later there was? How can you explain this? Do you have seasonal climatic and temperature data?

We did not say that there was no stratification in June. Because the spring overturn was always April/May in the lake (P7231/L26) and the surface temperature was already around 9 °C in June (Fig. 3), the lake water was under the stratification not only in August but also in June, at least for top 30 m. Thus, little primary production (little nitrate assimilation) after the spring overturn until June must be responsible for the homogeneous vertical distribution of nitrate in June. The temperature during each observation was presented in Fig.3.

The seasonal climatic data on a nearby city of the lake can be obtained from web site of the Meteorological Agency of Japan. No seasonal data is available for lake water temperature in 2007. In either would be the case, however, we don't think more detailed discussions on the physics of lake water are needed to clarify the nitrate dynamics in the lake.

> P7238/L8 point out that this enrichment happened in surface waters

C4135

We pointed out the enrichment of both ^{15}N and ^{18}O in the whole water column, including the surface waters, in the submitted manuscript. Was it insufficient ?

> P7239(P13)/L24 can you show either by calculation or by reference that the molecular diffusion of nitrate causes a fractionation factor of 0.5? Also does this apply for N or O or both?

What we presented here was the values of “ $^{15}\text{e} : ^{18}\text{e}$ ratios” ($^{15}\text{e}/^{18}\text{e}$ ratios; the ratios between the enrichment factors of N and O), so that the values can, of course, be applied for both N and O. The $^{15}\text{e}/^{18}\text{e}$ ratio of the molecular diffusion of nitrate (0.5) was calculation. Because the calculation was simple and usual for many molecules, we don't think our calculation was the first one done for nitrate.

> P7240(P14)/L 3 "with respect" do you mean "in comparison"?

Yes. If the sentence is misleading, we would like to revise.

> P7240(P14)/L6 If it is approximated a “closed system” then atmospheric input cannot be accounted for.

What we concluded in this section was that assimilation by phytoplankton /periphyton was a MAJOR process to reduce nitrate during the observations, so that we can “approximate” the lake to be closed system for nitrate. As for the other minor processes (atmospheric input and remineralization), please read the lines >12 of the same page.

> P7240(P14)/L10&11 Do you have experimental evidence for $\delta^{17}\text{O}$ staying stable or at least a reference?

This is the definition of $\Delta^{17}\text{O}$.

> P7240/ L14 is a contradiction to line 6

No, as already explained you. For us, these logics (i.e. discuss major process by first order approximation and then discuss minor processes) were usual at least in Japanese. If these were misleading in English, we would like to revise.

C4136

> P7240/L 16 remove “somewhat”

OK.

> P7241(P15)/L 1 the page before you stated that $\delta^{17}\text{O}$ was stable and in the following line you also state it was uniform. It should be clearly stated what you decide for and which exceptions apply.

The $\Delta^{17}\text{O}$ value of nitrate is always stable during mass-dependent fractionation processes such as partial removal through assimilation (P7230/L18). No exceptions for this.

The $\Delta^{17}\text{O}$ value of nitrate in the lake can vary only when nitrate having different $\Delta^{17}\text{O}$ value is added. No exceptions for this as well.

> P7241/L13 to 15 contain the word “average” too often. Consider shorten sentences.

We would like to shorten the sentences in the revised manuscript.

> P7241/L 20 what would be the source material of such nitrification and could you attribute isotope end member values to them?

The ultimate source of nitrification must be organic-N, as already explained in introduction (P7229/L27). The end member $\Delta^{17}\text{O}$ value of remineralized nitrate must be zero, as already explained in introduction (P7230/L15).

> P7242(P16)/L 6 to 8 While a description of processes is ascribed to another section no mention is made for the “other sources”. Those should be identified as well.

Both processes and sources were discussed to explain the ^{15}N -depleted nitrate in section 3.5 of the submitted manuscript. We would like to revise the final sentence of this section to “These possible sources/processes are discussed in detail in Sect. 3.5.”

> P7243(P17) How did you determine initial and temporal inventories and averages?

We have explained the detail in P7238(P12) lines 9 to 21 in the submitted manuscript.

C4137

> P7244(P18)/ L21 & 22 If the authors mean that the values of 1.3 Mmol and 2.6 Mmol per two months are similar, they should explain why something twice as high can be similar.

We would like to add sentences to explain this in the revised manuscript.

> P7245(P19)/L 6 What is meant by Nos.? If the authors mean the previously described equations they should explain why they are important corrections.

The "Nos." is the abbreviation of "numbers". We would like to add sentences to explain the reason of the importance in the revised manuscript.

> P7247(P21)/L 6 if you assume that lake Mashu and the Rishiri Island have similar water isotope values the same latitude is not the only driving factor. There are continental, altitude and source effects to be considered. The best would be to state similar isotope values of the water in both locations.

We would like to add the data of water isotopes ($\delta^{18}\text{O}$) in the revised manuscript. We would like to add following reference as the data source:

Yasuhara, M., Inamura, A., Chikita, K., and Hamada, H.: Water chemistry and isotopic composition of meteoric waters in Mashu caldera volcano with a special emphasis on the leakage from Lake Mashu, J. Jpn. Ground Water Technol. Assoc., 47, 13-20, 2005 (in Japanese).

> P7249(P24)/L19 Presumably N-uptake is also controlled by temperature and daily availability of light. Can you provide data for these two parameters at least for the period of investigation?

The temperature during each observation was presented in Fig.3. No data for light in 2007. All the data available have been presented in CGER NIES et al. (2004), as well as the online water quality database GEMStat (<http://www.gemstat.org>). Concerning to the sampling/monitoring on the lake water, please note that all the instruments must be carried to the lake on hand through a small, steep path on the caldera wall, which

C4138

has resulted in lake water sampling/monitoring that requires heavy instruments or high power electricity being difficult, as presented in the submitted manuscript (P7233/L 2-4)

> P7250/L25 Are there really no phosphate data?

Phosphate were under the detection for these 20 years (P7232/L9; CGER NIES et al., 2004). The detection limit, however, was ca. 0.003 mg/L (ca. 0.1 $\mu\text{mol/L}$), so that it had been difficult to decide the limiting nutrients in the lake.

> P7253(P27) Conclusions Should contain an outlook for future studies with combined application of techniques and inventory of sediment samples.

Inventory of N is also attractive for us so we can add this in section 3.7. Actually, however, most of us don't want to do such severe task as sampling sediment in the lake.

> Overall the conclusion is a little thin and should take up undisputable facts and findings that need further research and debate. It also should refer to objectives in the introduction and how they were achieved. A clear statement about the controlling factors of lake clarity with depth is missing? How could these be controlled?

As already explained to you, clarifying the cause of the decreasing transparency in the lake water was not the goal of this paper, as presented in introduction of the submitted manuscript. The goal of this paper is to clarify nitrate dynamics in the lake, using the new tool ($\Delta^{17}\text{O}$ of nitrate). We trust our study made a significant contribution by introducing a new methodology to study nitrate dynamics in a lake and must be useful for broad readers of Biogeosciences, without direct contribution to the problem of transparency in the lake.

> Table 2: use same number of digitals at least within columns

The number of digitals corresponds to the approximate significant figure of each number. Because the significant figures are different between the numbers, it is impossible to use a same number of digitals in a column.

C4139

> Fig 3 What is the explanation for DO remaining so stable over the depth of the lake?

That's because the lake was highly oligotrophic. Even if all the nitrate in a water mass (ca. 1.5 $\mu\text{mol/L}$ in June) would have been assimilated through photosynthesis (primary production), DO increase is only +11 $\mu\text{mol/L}$ (calculated assuming the Redfield ratio), which corresponds to ca. +3% of air saturation of 4 °C water, and vice versa for the respiration (remineralization). Even if nitrate would increase from zero to 1.5 $\mu\text{mol/L}$, DO decrease is -3%. Besides, DO level could become more closer to air saturation through gas exchange if the water mass is located closer to surface. In conclusion, the maximum extent of variation from air saturation is around 3% for DO in the lake, so that we can find the almost stable values (i.e. close to air saturation level at the temperature of hypolimnion) over the depth.

> Fig 5 & 7 Do you mean permille on the x and y axes?

Yes. These are the recent expressions of permille on axes, recommended in IUPAC. See the reference listed below:

Coplen, T. B.: Explanatory glossary of terms used in expression of relative isotope ratios and gas ratios, in: IUPAC Provisional Recommendations, 2008. http://old.iupac.org/reports/provisional/abstract08/coplen_310508.html

We would like to thank you for the helpful comments and suggestions. We trust that the answers are satisfactory responses to your comments and questions.

Sincerely, Urumu

Cc: S. Daita, D. D. Komatsu, F. Nakagawa and A. Tanaka

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