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Biogeosciences Discussions

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

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Thank you very much for your comments on our manuscript. We would like to reply to you by citing each of your comment.

> First, it is in places difficult to follow, and needs to be substantially revised for clarity, organization and length.

We would like to revise the paper as suggested.

>-It would be very useful to provide data for NH4 and TP data in the introduction. TP gives a better indication of phosphorus availability than SRP, and the size of the NH4 pool is critically important toward assessing some of the later assumptions. Additionally, while nitrogen limitation seems plausible it would be useful to provide further sup-

port for this, given the possibility of P limitation in a lake with such a small catchment and large water volume. NO3:TP ratios would be useful in this regard too.

We have a same opinion with you for the importance of the other nutrients (ammonium and P) in the lake. However, both TP and ammonium in the lake analyzed by a local institute (Hokkaido Institute of Environmental Sciences) were always "under the detection" for these 20 years (CGER NIES et al., 2004). This is probably due to the high detection limits (ca. 0.1 umol/L for TP and 3 umol/L for ammonium) of their analyses, based on those used for eutrophic/mesotrophic lakes/rivers. Thus, we proposed to study P and ammonium in future studies (section 3.7). We would like to clarify that both TP and ammonium were under the detection in section 2.1, where we noted that phosphate was always under the detection.

> -The trends in nitrate isotope values presented in Fig. 4 are a little puzzling. The 15N and 18O data suggest strong effects of assimilatory processes through most depths, consistent with the NO3 drawdown observed. However, the deepwater 17O data indicates substantial inputs from nitrification, despite the drop in concentration, which suggests assimilation.

Our interpretation concerning to those in this manuscript (described in the second paragraph of page 7240) was the combination of both (removal through assimilation and production through nitrification) for nitrate in the lake. That is to say, the residual nitrate of assimilation that had been in progress in the depths around 50-100m mixed with nitrate produced through nitrification that had been in progress in hypolimnion, through both vertical advection and/or eddy diffusion in the water column. The vertical mixing was also supported by the uniform temperature profile within hypolimnion in the lake (Fig. 3).

Our interpretation (mixing of two different nitrate) was also supported by the observed low 15e/18e ratio in the depth. If assimilation would be the only process to control nitrate, the ratio must be close to 1, while 0.3 at 200m (P7240/L16), where Δ17O was minimum.

The detailed discussions for the vertical mixing within the lake water column have been made in Nojiri et al. (1990) in the reference list, by calculating density profiles in the lake, including their temporal variations.

> -Given the extremely low concentrations of NO3 in the system, what is the sensitivity of the natural abundance isotopic estimate of N cycling to error? Some additional error analyses or explanation is necessary for estimates of NO3 removal and nitrification.

All the possible errors were included in the estimated flux. Most of the errors in the estimated values of flux (ΔNnit and ΔNup) were derived from that in deposition rate of nitrate (ΔNatm), not from the error in Δ17O analysis, under the observed Δ17O values around +2.5 per mille. On the other hand, the error from Δ17O would be significant when Δ17O value of lake water was less than +0.5 per mille. If the value was less than +0.1 per mille, for instance, we could hardly estimate accurate values for both ΔNnit and ΔNup in the lake. We would like to clarify these in the revised manuscript.

> It would be very useful to support these estimate with some independent measurements of nitrification and/or uptake, which could be done with a tracer addition, even with the logistical constraints mentioned earlier. Despite the objections raised about tracer additions (pg 7253), many of them valid, the tracer approach would provide some very useful data. In addition, while the authors have clearly pushed the O17 method forward in this manuscript, this type of application is novel, with many untested or poorly known assumptions. Therefore, verification by other means will be very useful.

Prior to the sampling, we had planed to incubate adding 15N tracer in the lake water simultaneously with natural sampling. However, we suspended this to avoid contamination from the tracer to the natural samples. Instead, we compare the results with the primary production (i.e. 13C tracer addition incubation) in a literature in section 3.4 (page 7244).

We would like to compare Δ17O results directly with 15N tracer results in future in other lakes, where such logistical constraints are minimum.

> -I do not completely understand the calculations and use of fractionation data (pg 7240, line 1-5, and previous page); this section should be clarified and there is quite a bit of text that could be removed or moved to the discussion.

Our purpose to calculate the kinetic isotope effects (15e and 18e) is to verify our hypothesis that the MAJOR process to reduce nitrate from June to August was assimilation by phytoplankton/periphyton in the lake (P7238/L2-8). We would like to clarify this in the revised manuscript.

> Also, it's unclear to me how is the PON data is being used. N uptake is typically dominated by ammonium uptake, so the PON data cannot be to assess N sources without additional information.

Our purpose to determine d15N of PON was to verify that total fixed-N in the lake was also depleted in 15N, besides to nitrate. Of course PON+nitrate was somewhat different from total fixed-N in the lake, we used them as representative for those of fixed-N in the lake, because they must occupy major portion of them.

> Finally, looking at Table 1, NO3 15N and 18 isotopes don't appear to vary linearly- does this contradict statements on pg 7239?

While the data on Fig. 5 were plotted for each depth, the discussion on p7239 was that for the whole lake average. While we discussed the MAJOR process to control nitrate during the observations on p7239, the "contradictions" found in some depths (0-20m and 200m) were derived from some additional minor processes. All these minor processes were discussed in P7240 and quantified in section 3.3.

> -For Fig. 7, why is so little of the data used in this plot?

The figure was presented to show the whole lake averages ("avg.(Jun)" and "avg.(Aug)") were plotted close to the mixing line between NO3-re and NO3-atm, especially for that of June. Besides to the averages, those of surface layer (0m) were plotted for comparison, because they were reasonably deviated from the averages due to the elevated mixing ratio of NO3-atm in the surface. If we plot all the data obtained in this study, however, they were plotted almost the same region with the averages so that we could not distinguish them each other. Thus, we did not plot them on the figure .

> -Pg 7244, line 25-26, the term "reducing" is confusing here. Perhaps for example for #1, "subtracting the contribution of NH4 to total N uptake" or something similar.

We would like to revise as suggested.

> -Pg 7244-45. The corrections described here should act to lower the estimates of nitrate uptake based on primary production substantially. Application of a 10x correction factor seems a little arbitrary here without some consideration of the similarities or differences between the lake mentioned to support it (i.e. Castle Lake). How much periphyton production can occur in this system? From the description (steep walled, deep, soft bottomed), I'm guessing much less than Castle Lake. Also NH4 uptake is likely to contribute greater than 50% of uptake. This assumption needs to be better referenced. Without further justification, I don't agree with the statement that the primary production data support the reliability of the isotope based measurements to a very large degree (pg 7245, line 14)

Most of the conversion factors used in this section to estimate nitrate assimilation rate from the primary production rate were based on those of Castle lake where the data were abundant. Thus, alternative corrections can be applicable to lake Mashu, as you suggested. To do this, however, much more references and much more detailed discussions will be needed. Furthermore, even if we would do this, only the error of the nitrate assimilation rate will be larger while we could hardly obtain more precise value for the nitrate assimilation rate.

The main object of this paper was to estimate nitrate cycling in the lake using Δ17O tracer of nitrate. Thus, we didn't want to make further discussions for this in this paper.

Further discussions concerning to the reliability should be done elsewhere, by adding the data of 15N tracer incubation simultaneously with monitoring Δ17O of nitrate. Because the lake Mashu is not suitable for the 15N tracer incubation as already mentioned, we would like to do this in other lakes, under a framework of different project.

We would like to emphasis this in the revised manuscript.

> -Is the mean presented in Table 1 based on the water volume or a simple average? Some examples of text that should be revised for clarity or removed:

That was estimated from the water volume and its nitrate concentration and its isotopic compositions, as presented in P7238, lines 9-21, in the submitted manuscript.

> -Pg 7232, line 25 pg 7233 line 4. Awkward phrasing, and an example of text that should be removed unless there is a specific point to be made.

Most of them were just the citations. We would like to revise them, instead of removing, because most of them are indispensable for those who are not familiar with the lake,.

> -Pg 7236, line 23-24. Meaning is unclear here.

Two different definition have been used for Δ17O of nitrate in the world. If we use the linear approximation instead of Eq. (1), the Δ17O values would be lower than the values reported. We would like to add several sentences to clarify these for those who are not familiar with this.

> -I am also confused by the statement that the lake is a closed system "from internal/external sources". If I understand this correctly, it seems that the authors own measurement contradict this statement. Please clarify.

Our purpose to calculate the kinetic isotope effects (15e and 18e) was to verify our hypothesis that the MAJOR process to reduce nitrate from June to August was assimilation by phytoplankton/periphyton in the lake (P7238/L2-8).

We calculated kinetic isotope effects (15e and 18e) for the observed nitrate decrease between June and August (P7240/L2), assuming closed system for the lake and found that the kinetic isotope effects were reasonable values for those during assimilation of nitrate. Thus, we concluded that the MAJOR process to reduce nitrate from June to August as assimilation. This was also supported by the uniform average Δ17O of nitrate in the lake.

Of course the other minor processes (nitrification and atmospheric deposition) should also control nitrate distribution in the lake, so that we discussed them in section 3.1 (P7240/L12-P7241/L10) and then quantified them in sections 3.3. Through these quantification, we further verified that the major process that controlled nitrate was assimilation during the observations.

Because the same confusion have been pointed out by the referee #2, we would like to clarify the logic in pages 7234-36.

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

Interactive comment on Biogeosciences Discuss., 7, 7227, 2010.