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

### **Anonymous Referee #2**

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The study presents natural abundance nitrate N and O isotope ratios ( $^{15}\text{N}/^{14}\text{N}$  and  $^{18}\text{O}/^{16}\text{O}$ ) to infer sources and cycling of N in an oligotrophic mountain lake, as well as measurements of  $\Delta^{17}\text{O}/^{16}\text{O}$  of nitrate relative to the ratio expected for mass dependent behaviour of nitrate, to gauge the contribution of atmospheric nitrate to the current nitrate pool. I was excited to review this study, as such tracer measurements hold promise for significant insight in N biogeochemical cycling. However, I found the manuscript obtuse, disjointed and difficult to follow. The interpretations of the data are often contradictory in and amongst themselves. And the authors make numerous implicit but erroneous assumptions to justify their conclusions. While I outline some short-comings below, my review is by no means comprehensive and does not address all of the problems that need to be addressed.

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(1) The study suffers from the confusion of interchanging concepts between source and sink terms to the entire lake system vs. internal N cycling in the water column: Atmospheric deposition consists of a source of fixed N to the lake, in the form of nitrate, ammonium, or organic N. Assimilation is not a net sink of fixed N but rather part of the lake's internal cycle, as fixed N is neither created or loss but rather recompartimentalized by assimilation. Assimilation could be construed as an internal sink for nitrate, atmospheric or other, not to be confused with a net sink of fixed N from the lake. Denitrification represents a net a sink of fixed N to the lake system, as fixed N is literally lost as N<sub>2</sub> gas. Input of newly nitrified NO<sub>3</sub> from the catchment is a net source of fixed N to the lake, whereas nitrification of N remineralized within the lake is NOT a net source of fixed N, but rather an internal source of NO<sub>3</sub>. These important distinctions are never considered in the text and result in flawed interpretation of the inherent isotope dynamics.

(2) How did the concentration of NO<sub>3</sub> decrease below the pycnocline due to assimilation by phytoplankton? To which depth does light penetrate given a Secchi depth of 45 m? Penetration to 200 m seems unlikely.

(3) How come there is no O<sub>2</sub> peak associated with the chlorophyll maximum in August? How come there is no O<sub>2</sub> depletion due to remineralization at depth, which is evidenced by the decrease in the d<sub>18</sub>O of nitrate and the  $\Delta^{17}\text{O}$ ?

(4) How do the authors calculate an isotope effect for assimilation in the lake? First, which assumptions are made? Is the lake treated as a closed system or an open system? Second, how do the authors account for co-incident biological transformations that can alter the d<sub>15</sub>N and d<sub>18</sub>O of nitrate? While assimilation enriches the d<sub>18</sub>O of NO<sub>3</sub>, in situ nitrification in the deeper layers will tend to decrease the d<sub>18</sub>O of NO<sub>3</sub> toward the d<sub>18</sub>O of ambient water (what is the d<sub>18</sub>O of ambient water?). Denitrification occurring in sediment will tend to reduce the concentration of NO<sub>3</sub>- without necessarily altering the d<sub>15</sub>N and d<sub>18</sub>O of NO<sub>3</sub> in the water column. Addition of atmospheric NO<sub>3</sub>- will increase the d<sub>18</sub>O substantially in the surface layer, and will modify the d<sub>15</sub>N in the

direction of the  $\delta^{15}\text{N}$  of atmospheric  $\text{NO}_3$  (What is the  $\delta^{15}\text{N}$  of atmospheric  $\text{NO}_3$  deposited on the lake??). Similarly, nitrification of  $\text{NH}_4$  deposited on the lake from the atmosphere will lower the  $\delta^{18}\text{O}$  and of the  $\delta^{15}\text{N}$  relative to the enrichment from assimilation (assuming a low  $\delta^{15}\text{N}$  of atmospheric  $\text{NH}_4^+$ ). Drainage of  $\text{NO}_3^-$  from the catchment can also modify the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of water column  $\text{NO}_3$  in a direction that cannot be anticipated without actually measuring it. In short: the reviewer cannot see how the  $15\epsilon$  and  $18\epsilon$  estimates put forth are meaningful or accurate in any way.

(5) Why is the  $\delta^{15}\text{N}$  of PN substantially more elevated than the  $\delta^{15}\text{N}$  of the nitrate from which the PN derives? The authors make no mention of this flagrant disconnect.

(6) p. 7244, 1st  $\hat{\text{A}}\hat{\text{U}}$ : Very confusing. The authors make no distinction here between net and gross, internal vs. external sources of nitrate from the catchment vs. in situ nitrification. For instance, the authors state that “0.52 Mmoles of remineralized nitrate had been fed into the lake water through nitrification.” First of all, “remineralized” nitrate means “newly nitrified,” such that nitrification of remineralized nitrate is nonsensical. Second, does this statement mean that remineralized nitrate enters the lake from the catchment, in which case it is an external source of fixed N to the lake, or does that mean that it is remineralized in situ from organic material (PN), in which case it is an internal source of  $\text{NO}_3$  but NOT necessarily a source of fixed N to the lake mass balance (depending on whether PN is allochthonous or autochthonous, which is unclear)?

(7) The authors contend that: “2.6 Mmol of nitrate has been removed from the lake water through assimilation during the period between sampling events.” First of all, the authors do not have the  $\Delta\text{PN}$  and  $\Delta\delta^{15}\text{N}$  PN to justify this claim, but apparently forgot to sample PN in June. Second, is that NET or GROSS PN production? One could imagine that much of the fixed N assimilated into particles at the surface since June had been remineralized since, thus contributing to the “newly nitrified”  $\text{NO}_3$ , and no longer sequestered as particles. Because there is no estimate of the  $\Delta\text{PN}$  or alternatively, the  $[\text{NO}_3]$  delivered from the catchment, it is IMPOSSIBLE to construct an accurate mass balance here.

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(8) p. 7245, line 24: The contention that the relatively low  $\delta^{15}\text{N}$   $\text{NO}_3$  found in the lake is  $^{15}\text{N}$ -deplete due to nitrification is absurd. First of all, the reader is provided with no constraint of the  $\delta^{15}\text{N}$  of atmospheric N ( $\text{NO}_3$  and  $\text{NH}_4$ ), which determines the  $\delta^{15}\text{N}$  of the dominant reactive N source to the lake assuming no other sources of fixed N from the catchment. Second, given that the lake is highly oligotrophic, there is no residual  $\text{NH}_4^+$  that is fractionated by nitrification. Nitrification is COMPLETE such that the  $\delta^{15}\text{N}$  of  $\text{NO}_3$  will be like that of the original  $\text{NH}_4^+$  substrate. The  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$ , in turn, derives from the “reactive” PN, and will have nearly the SAME  $\delta^{15}\text{N}$  as the PN from which it derives, because the ammonification of organic material does NOT implicate significant N isotope discrimination ( $< 3\text{‰}$ ). An important caveat here is that it is unclear why the  $\delta^{15}\text{N}$  of PN is  $^{15}\text{N}$ -enriched relative to its  $\text{NO}_3$  source, which evokes either (a) the contribution of allochthonous PN to the lake and/or (b) the existence of a highly recalcitrant PN pool that has been  $^{15}\text{N}$ -enriched through time, much like the suspended PN pool in the deep ocean. Thus, the  $\delta^{15}\text{N}$  of the “reactive” PN pool is not necessarily reflected by the measurements of the  $\delta^{15}\text{N}$  of PN. However, a reasonable assumption that the authors could make is that the  $\delta^{15}\text{N}$  of the labile PN derives from incomplete consumption of  $\text{NO}_3$  in the lake, and will therefore be  $^{15}\text{N}$ -deplete relative to the  $\delta^{15}\text{N}$  of  $\text{NO}_3$ . In turn, the  $\text{NO}_3$  becomes  $^{15}\text{N}$ -enriched by assimilation, yet this is countered by remineralization of the  $^{15}\text{N}$ -deplete PN. Therefore in June, if one assumes that the “reactive” PN pool is negligible compared to the total  $\text{NO}_3$  pool, the low  $\delta^{15}\text{N}$  of  $\text{NO}_3$  in the lake likely reflects the  $\delta^{15}\text{N}$  of the fixed N sources to the lake, which appears to be dominated by atmospheric deposition of  $\text{NO}_3$  and  $\text{NH}_4$  – nothing to do with nitrification. If atmospherically derived fixed N were  $^{15}\text{N}$ -enriched, then so would the  $\text{NO}_3$  in lake water, regardless of nitrification.

More comments:

Line 27: nitrate is not technically “decomposed” by denitrification but it is respired/reduced. p. 7235, line 13: why was PON refrigerated rather than frozen? How long after collection? Could there have been decomposition of PN while refig-

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erated, which would fractionate PN due to NH<sub>3</sub> volatilization? P. 7235, line 5: what is “an original automatic reaction line?” p. 7235, line 20: Were the nitrate isotope standards used in the same low concentration and in similar matrix as the samples? p. 7236, line 18: “using another aliquot”... replicate samples? Does that mean that the measurements were only replicated for low nitrate samples? p. 7236, eq (3) is wrong. See McIlvin and Altabet 2005. Rather than repeating all the methods, the authors could simply cite McIlvin and Altabet. However, in such a case the reviewer would never have known that the d18O data were calculated incorrectly. And what is the d18O H<sub>2</sub>O of the lake samples? How were these measured? p. 7237, line 20: 15N-depletion relative to what? Give d15N value range here. p. 7238, lines 1 – 8: refer to a figure... p. 7238, line 10: the d15N, d18O, and  $\Delta^{17}\text{O}$  were NOT vertically uniform in June: d15N had a 2‰ range (which the authors never discuss), d18O was uniform to 25 m up from which it increased by 3‰. a did  $\Delta^{17}\text{O}$ . p. 7239 line 24: it should be the ratio of the square root of the REDUCED masses p. 7242: The difference between eq(2

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