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

Anonymous Referee #2

Received and published: 17 November 2010

The study presents natural abundance nitrate N and O isotope ratios (15N/14N and 18O/16O) to infer sources and cycling of N in an oligotrophic mountain lake, as well as measurements of $\Delta^{17O}/^{16O}$ 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.
(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 recompartmentalized 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 N2 gas. Input of newly nitrified NO3 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 NO3. 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 NO3 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 O2 peak associated with the chlorophyll maximum in August? How come there is no O2 depletion due to remineralization at depth, which is evidenced by the decrease in the d18O of nitrate and the Δ17O?

(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 d15N and d18O of nitrate? While assimilation enriches the d18O of NO3, in situ nitrification in the deeper layers will tend to decrease the d18O of NO3 toward the d18O of ambient water (what is the d18O of ambient water?). Denitrification occurring in sediment will tend to reduce the concentration of NO3- without necessarily altering the d15N and d18O of NO3 in the water column. Addition of atmospheric NO3- will increase the d18O substantially in the surface layer, and will modify the d15N in the
direction of the d15N of atmospheric NO3 (What is the d15N of atmospheric NO3-deposited on the lake??). Similarly, nitrification of NH4 deposited on the lake from the atmosphere will lower of the d18O and of the d15N relative to the enrichment from assimilation (assuming a low d15N of atmospheric NH4+). Drainage of NO3- from the catchment can also modify the d15N and d18O of water column NO3 in a direction that cannot be anticipated without actually measuring it. In short: the reviewer cannot see how the 15ε and 18ε estimates put forth are meaningful or accurate in any way.

(5) Why is the d15N of PN substantially more elevated than the d15N of the nitrate from which the PN derives? The authors make no mention of this flagrant disconnect.

(6) p. 7244, 1st Âuu: 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 NO3 but NOT necessarily a source of fixed N to the lake mass balance (depending on whether PN is allochtonous or autochtonous, 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 ΔPN and Δd15N 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” NO3, and no longer sequestered as particles. Because there is no estimate of the ΔPN or alternatively, the [NO3] delivered from the catchment, it is IMPOSSIBLE to construct an accurate mass balance here.
The contention that the relatively low d15N NO3 found in the lake is 15N-deplete due to nitrification is absurd. First of all, the reader is provided with no constraint of the d15N of atmospheric N (NO3 and NH4), which determines the d15N 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 NH4+ that is fractionated by nitrification. Nitrification is COMPLETE such that the d15N of NO3 will be like that of the original NH4+ substrate. The d15N of NH4+, in turn, derives from the “reactive” PN, and will have nearly the SAME d15N as the PN from which it derives, because the ammonification of organic material does NOT implicate significant N isotope discrimination (< 3‰). An important caveat here is that it is unclear why the d15N of PN is 15N-enriched relative to its NO3 source, which evokes either (a) the contribution of allochtonous PN to the lake and/or (b) the existence of a highly recalcitrant PN pool that has been 15N-enriched trough time, much like the suspended PN pool in the deep ocean. Thus, the d15N of the “reactive” PN pool is not necessarily reflected by the measurements of the d15N of PN. However, a reasonable assumption that the authors could make is that the d15N of the labile PN derives from incomplete consumption of NO3 in the lake, and will therefore be 15N-deplete relative to the d15N of NO3. In turn, the NO3 becomes 15N-enriched by assimilation, yet this is countered by remineralization of the 15N-deplete PN. Therefore in June, if one assumes that the “reactive” PN pool is negligible compared to the total NO3 pool, the low d15N of NO3 in the lake likely reflects the d15N of the fixed N sources to the lake, which appears to be dominated by atmospheric deposition of NO3 and NH4 – nothing to do with nitrification. If atmospherically derived fixed N were 15N-enriched, then so would the NO3 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 refrig-
erated, which would fractionate PN due to NH3 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 H2O 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 Δ17O 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 Δ17O. p. 7239 line 24: it should be the ratio of the square root of the REDUCED masses p. 7242: The difference between eq(2

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