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# *Interactive comment on* "Nitrogen cycling in shallow low oxygen coastal waters off Peru from nitrite and nitrate nitrogen and oxygen isotopes" *by* H. Hu et al.

**H. Hu et al.**

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Anonymous Referee #1 Received and published: 30 June 2015

This was a generally well-written paper, describing the use of nitrate and nitrite N and O stable isotopes, as well as biogenic N2 and $\delta$15N-N2 analyses to examine the cycling of N in oxygen-deficient Peruvian coastal waters. I particularly liked the variety of approaches used to estimate the isotope effect for N loss, including the measurement of the end product (N2). It is a solid contribution to the literature and I had relatively minor comments for the authors, listed below.

Our response: We thank reviewer #1 for his/her helpful comments. We generally ad-

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dressed all concerns below.

Specific comments:

p. 7259, lines 11-12: I know what you mean here, but found the wording to be a bit ambiguous, as neither NO3- or O2 donate electrons in respiration. I think you could simply say "...in lieu of oxygen (O2) for respiration."

Our response: Done.

p. 7261, lines 1-2: The wording here is also slightly ambiguous as the inverse isotope effect for NO2- oxidation is atypical of biochemical reactions, but is uniformly observed in nitrite oxidizing organisms.

Our response: We changed the sentence for: ". . . NO2- oxidation is associated with an inverse N isotope effect (Casciotti, 2009), atypical of biogeochemical reactions, . . ."

p. 7261, lines 4-6: On what basis is this "analogous relationship" expected?

Our response: We changed the sentence for: "Logically, NO2- reduction would be expected to produce a positive relationship between $\delta$15N-NO2- and $\delta$18O-NO2- though there are no quantitative observations in the literature. Analogous to NO3- reduction, it also involves enzymatic breakage of the N-O bond."

p. 7261, lines 10-12: I don't think that this is really still under discussion. Many more recent papers suggest a balanced budget. The citations used here are pretty outdated at this point. It's clear that there are still many questions regarding the mechanisms of N loss and cycling in oxygen deficient waters, but the budget seems pretty well understood, at least better than the cited 400 Tg/year imbalance.

Our response: We changed the text accordingly, citing more recent studies: "Current estimates from direct observations and models for N2 fixation, considered the primary marine N source, range from 110-330 Tg N yr-1 (Brandes and Devol, 2002; Gruber, 2004; Deutsch et al., 2007; Eugster and Gruber, 2012; Gro$\beta$kopf et al., 2012). Esti-

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mates for major marine N-sinks, i.e., denitrification and anammox in the water-column of oxygen deficient zones and sediments account for 145-450 Tg N yr-1 (Gruber, 2004; Codispoti, 2007; DeVries et al., 2012; Eugster and Gruber, 2012).”

p. 7263, lines 12-13: It is my understanding that Casciotti and Bohlke have not distributed these primary NO2- isotope standards due to the possession of limited amounts. Perhaps the Altabet lab is an exception, but is it possible that you mean that your laboratory standards were calibrated against N23, N7373 and N10219?

Our response: We have these standards in our laboratory. We changed the text, to include the $\delta$15N/$\delta$18O of these standards, as requested by reviewer #2: “In-house (i.e., MAA1, $\delta$15N = -60.6‰ $MAA2,\delta$15N = 3.9‰ $Zh1,\delta$15N = -16.4%) and other laboratory calibration standards (N23, $\delta$15N = 3.7‰ and $\delta$18O = 11.4‰ $N7373,\delta$15N = -79.6‰ and $\delta$18O = 4.5‰ $andN10219;\delta$15N = 2.8‰ and $\delta$18O = 88.5‰ $seeCasciottiandMcIlvin, 2007)wereusedforNO2-\delta$15N and $\delta$18O analysis.”

p. 7263, lines 14-16: These are not appear among the proportions tested by Granger and Sigman (2009). Do the authors have independent evidence for the removal of NO2- under these conditions?

Our response: We always use this method in Altabet’s laboratory for NO2- removal immediately following sample collection. Of course, we previously thoroughly tested that all NO2- was removed under these conditions.

p. 7265, lines 6-7: This is an interesting finding, but it might be worth emphasizing here that it is very much an effective isotope effect since it involves the expression of fractionation at several steps between NO3-, NO2- and N2.

Our response: Done.

p. 7265, lines 20-21: I think you mean that the maximum biogenic N2 observed in this study was 20 $\mu$M, but found the wording here to be a bit ambiguous since it is given parenthetically after “small levels of biogenic N2”. I think you want to say that for biogenic N2 levels less than 7.5 $\mu$M, the error associated with the calculation becomes too high?

Our response: We changed the sentence for: “greater than 7.5 $\mu$M because of increasing noise below this level due to the huge atmospheric dissolved N2 background (typically up to âĹij500 $\mu$M).”

p. 7266, lines 22-23: I like this use of biogenic N2 measurements.

p. 7267, lines 5-6: This third approach could use another sentence of clarification about the maximum [NO3-] or [DIN] used. Is this drawn from an individual profile, or elsewhere along the isopycnal?

Our response: We changed the sentence for: “. . . by observed maximum [NO3-] or [DIN] for the source of the upwelled waters (see red rectangles in Fig. 2).”

p. 7271, line 18: I thought the background was closer to 500 $\mu$M, as stated on p. 7265.

Our response: We were referring here to $\mu$M N in N2. We modified the text to express the background in $\mu$M N2 (400 to 500 $\mu$M N2) as previously, to avoid confusion.

p. 7272, lines 27-28: This sentence should also cite Buchwald and Casciotti, 2013 for T dependence of the equilibrium isotope effect.

Our response: We added this reference.

p. 7273, lines 18-19: The $\delta$18O source values as low as -8‰ as estimated by calculations in the cited papers do not appear to be representative of marine systems. Values between -1.5‰ and +1.3‰ appear to be more appropriate, as described in a more recent paper (Buchwald et al., 2012).

Our response: Noted. We changed the text accordingly.

p. 7274, lines 10-15: This is an interesting calculation of NO2- turnover time, but a few clarifications would be helpful. In particular, whether your estimates represent an upper or lower limit of turnover time. Figure 2 in Buchwald and Casciotti, 2013 results from a batch time course experiment and does not involve a steady state assumption. I would recommend calculating the rate constant for NO2- exchange at the appropriate T and pH, using equation 1 in Buchwald and Casciotti, 2013. You can then apply this to your steady-state model to calculate the NO2- turnover time. Since you don't know where you started in $\delta$18O space, the NO2- could be older than your estimate, giving you what I would consider a lower limit of turnover time (i.e., it could be longer). You state this more clearly in your conclusions (p. 7280, lines 6-7).

Our response: Using equation 1 in Buchwald and Caciotti (2013), we calculated a k, the specific rate of abiotic oxygen atom equilibration between nitrite and water, of 0.0765 day-1 and a reciprocal of 13.07 days. Considering that isotope equilibrium occurs as an exponential decay, ~100% equilibration is reached at 3 e-foldings (3/k), we can estimate an equilibration time of ~13.07 x 3 = 39 days using this method, which is equivalent to the ~40 days we estimated from Fig. 2. We also modified the text to clarify that our estimate is a lower limit of turnover time: "… we estimated an equilibration time of at least ~40 days for pH near 7.8 (estimated from equation 1 and Fig. 2 in Buchwald and Casciotti, 2013). A turnover time as low as 40 days implies a flux of N through the NO2- pool of at least 0.21 $\mu$M d-1, as estimated from the maximum NO2- concentration observed in this study divided by this estimated turnover time."

p. 7276, lines 1-2: I think the critical point here is that the $\delta$18O-NO3- added back is lower than the ambient $\delta$18O-NO3- at these high $\delta$18O levels, not that the $\delta$15N is high due to the inverse kinetic isotope effect. Even with the inverse fractionation, the low $\delta$15N of NO2- should produce NO3- with a low $\delta$15N. You state this more clearly in your conclusions (p. 7280, line 15).

Our response: We agree and changed the sentence for: "Our observed deviation toward slopes < 1 can instead be explained by the addition of newly nitrified NO3- with a lower $\delta$18O-NO3-, mostly derived from water (Andersson and Hooper, 1983), relative to the high ambient $\delta$18O-NO3- values."

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p. 7276, lines 2-4: This was also argued in Casciotti et al., 2013.

Our response: We added this reference.

p. 7277, lines 8-10: Could you elaborate on how a contribution of NH4+ derived from organic matter would raise the calculated isotope effect? It's not clear that it should have this effect since the $\delta$15N of organic matter is relatively high in this area.

Our response: In fact, we measured relatively low $\delta$15N-NH4+ values (between 3.8‰ and 6.1‰ in bottom waters at shallow stations located close to the studied area during the SFB754 M92 cruise that took place one month later, in January 2013 (unpublished results). The NH4+ concentrations at these stations ranged from 5.3 to 7.5 $\mu$M. Thus a contribution of NH4+ from organic material and consumption by anammox bacteria could theoretically raise the isotope effect derived from biogenic N2. We added two sentences to clarify this point: "Supporting this hypothesis, NH4+ accumulation (5.3-7.5 $\mu$M) associated with a relatively low $\delta$15N-NH4+ of 3.8‰ to 6.1‰ was observed at 125 and 200 m bottom water depths at shallow stations located in the studied area (âĹij12.3°S and 77.3°W) in January 2013 (unpublished results). A contribution of NH4+ from organic material and consumption by anammox could therefore supply comparatively lower $\delta$15N to the biogenic N2 pool, increasing $\varepsilon$ïĂăïĄťïĄĺïĄąïĄť must be larger to account for the observed isotopic enrichment."

p. 7277, line 12: I think you mean when f=1, not when f=0, as ln(0) is undefined while ln(1) = 0.

Our response: We meant when f=1. We corrected this in the text.

p. 7278, lines 8-22: Can you say anything about the role of anammox based on your findings in comparing the isotope effects calculated in different ways?

Our response: As explained above, anammox could raise the isotope effect derived from biogenic N2 only if the NH4+ consumed is originating from organic material with a relatively low $\delta$15N (see above). Otherwise, if the NH4+ is coming from dissimilatory nitrate reduction to ammonium (DNRA), we should still observe an isotopic balance between the DIN and biogenic N2 pools. We already previously elaborated on this (see our response to your comment regarding p. 7277, lines 8-10), where it is more in context, and though it would be repetitive to repeat it again here.

p. 7278-7279: What would be the uncertainty on this estimate of % sedimentary denitrification from your analysis?

Our response: We added uncertainties for both $\varepsilon$obs (6.77 ± 0.45‰ and $\varepsilon$wc (13.75 ± 1.3‰. We also now include a range for our estimate of % sedimentary denitrification, i.e., 48 to 64%.

p. 7281, lines 15-16: This statement about most of the N loss occurring in the ETSP is not strongly supported by other studies. For example, Devries et al., 2012 infer similar denitrification rates in ETSP and ETNP.

Our response: We removed this statement.

p. 7281, lines 16-18: I don't disagree with this statement, but it I think it is worth reiterating that you advocate using a 14-15‰ isotope effect for the water column portion of the budget (as in Bourbonnais et al., 2015), and that the 6.5‰ isotope effect you measure here already includes a contribution from sedimentary denitrification.

Our response: We added the value, ∼14‰ for the $\varepsilon$ of N-loss estimated by Bourbonnais et al. (2015) in the previous sentence (p. 7281, line 14). We already discuss that the observed $\varepsilon$ of 6.5‰ includes a contribution from sedimentary denitrification in the previous paragraph.

Figure 7: The significance of this figure, and the relationship between $\Delta\delta$15N and fbioN2 was not clear. Please clarify or remove the figure.

Our response: We removed this figure.

Figure 10: I didn't think this figure was necessary as the information is more clearly

presented in tables 1 and 2.

Our response: We also removed this figure.

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Interactive comment on Biogeosciences Discuss., 12, 7257, 2015.

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