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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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General impression This manuscript presents a suite of what appears to be high quality N-isotopic data from the Peru margin OMZ. From these data they draw conclusions that seem relatively sound. However, right now the discussion is rather unfocused and sometimes redundant and their data is not put into the context of the larger global data set on N-isotopes in OMZs. For example. Although they note the difference between the epsilon values calculated from their data and Bourbonnais et al. and briefly mention values from the ETNP and Arabian Sea, there is no thoughtful discussion of these as

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a whole. Elaboration of these points follows below. Consequently, my opinion is that the manuscript needs revision before publication.

Our response: We thank the reviewer for its helpful comments. We generally addressed all concerns below. We tried to improve the discussion section and better use background information from previous studies to support our results.

Scientific

Page 7265. On this page they give the equations for open and closed system calculation of epsilon. They say “The fraction of remaining DIN is a better estimation of the overall isotope effect for N-loss (Bourbonnais et al., 2015), while using NO₃⁻ as the basis to calculate ϵ specifically targets NO₃⁻ reduction.” I agree DIN is better. OK, so on line 2 they give the equation for $\delta^{15}\text{N-NO}_3^-$ which has no equation number and then on line 3 for $\delta^{15}\text{N-DIN}$ which is equation (1) and they use the corresponding values for f for each equation. If I have this correct, the $\delta^{15}\text{N-NO}_3^-$ equation is the one they say is specifically for NO₃⁻ reduction. It seems to me that almost all of their samples have NO₃⁻ and NO₂⁻ and some N-deficit. In that case then this equation is not NO₃⁻ reduction to NO₂⁻ because some went to N-deficit and it's not denitrification because some remains as NO₂⁻. Why do this calculation? What does it mean?? The same comment applies to the open system equation (line 15).

Our response: We fixed the equations numbering, the equation on line 2 is now equation 1 and the equation on line 3, equation 2, etc. . . Equation 1 is to determine ϵ as associated with NO₃⁻ reduction, regardless of whether the produced NO₂⁻ accumulates or is further reduced to N₂. This equations has been widely used in other studies for this purpose, for example, see Granger et al. (2009) (Limnol. Oceanogr.). Note that Granger et al. (2009) specifically removed NO₂⁻ before determining ϵ for NO₃⁻ reduction using equation 1, as we also did. Equation 2 ($\delta^{15}\text{N-DIN}$) is appropriate to estimate ϵ for total N-loss, as it considers both $\delta^{15}\text{N-NO}_3^-$ and $\delta^{15}\text{N-NO}_2^-$ (weighted average). Another way to estimate ϵ for global N-loss is to use $\delta^{15}\text{N-biogenic N}_2$ (previously

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equations 2 and 4). In practice, if the source of biogenic N₂ is solely from NO₃⁻ and NO₂⁻, then the two estimates should converge, but it is also possible to have generally small contributions from organic matter remineralization to NH₄⁺ and conversion to N₂ through anammox, as discussed in our manuscript, p. 7277, lines 8 to 10.

Page 7267 line11-13. Why do they say the upwelled water appears to be a single water mass originating from the offshore OMZ? Why can't it be a coastal undercurrent? Do they have evidence for stronger wind forcing at station 63?

Our response: We accordingly modified this section: “During the study period, there was active coastal upwelling as seen by relatively low satellite sea surface temperatures, higher chlorophyll α concentrations, and a shallow oxycline along the shore, and especially at station 63 (Fig. 1). A common relationship and narrow range for T and S were found, comparable to T/S signatures for offshore ODZ waters between ~100 and 200 m depths (Bourbonnais et al. (2015), indicating a common source of water upwelling at these inner shelf stations (Fig. 2). This is expected as in these coastal, shallow waters, upwelling of the Peru Coastal Current, with low O₂, high nutrients and a typical depth of ~200 m, play a dominant role (Penven et al., 2005).”

Page 7271 line15. $\delta^{15}\text{N-N}_2$ anomaly..... ranged from -0.2 to +0.1.” Figure 8c shows that most anomalies are negative and only highest biogenic N₂s have positive anomalies. What would cause a negative N₂ anomaly? I don't think this is ever discussed.

Our response: We added the following sentence after line 15 (page 7271) to better discuss this point: “Negative $\delta^{15}\text{N-N}_2$ anomaly (i.e., lower $\delta^{15}\text{N}$ -biogenic N₂) is produced at the onset of N-loss, because extremely depleted $\delta^{15}\text{N-N}_2$ is first produced. At a more advanced N-loss stage, we expect $\delta^{15}\text{N-N}_2$ anomaly and $\delta^{15}\text{N}$ -biogenic N₂ to increase, as we observed in this study, as heavier ^{15}N is added to the biogenic N₂ pool.” We think that only referring to $\delta^{15}\text{N-N}_2$ anomaly here, which is the difference between the $\delta^{15}\text{N-N}_2$ observed and at equilibrium, might be confusing because we later only refer to $\delta^{15}\text{N}$ of biogenic N₂. We thus also added the corresponding

$\delta^{15}\text{N}$ -biogenic N_2 range after line 15 (page 7271): “The corresponding range in $\delta^{15}\text{N}$ biogenic N_2 , calculated from the $\delta^{15}\text{N}$ - N_2 anomaly as in Bourbonnais et al. (2015), was from -9.0 to 3.2‰”

Specific.

Page 7259 line 27, $\text{DIN}=\text{NO}_3^-$, NO_2^- and NH_4^+ should be $\text{DIN}=\text{NO}_3^-+\text{NO}_2^-+\text{NH}_4^+$

Our response: Corrected!

Page 7260 line 11. The sentence starting with “Canonical” says epsilon associated with NO_3^- reduction. NO_3^- reduction is the reduction of NO_3^- to NO_2^- . Do they mean NO_3^- reduction or canonical denitrification, which is NO_3^- to N_2 ? The studies by Brandes et al and Voss et al and Granger et al that they cite are actually equivalent to their DIN because they measured $\text{NO}_3^-+\text{NO}_2^-$.

Our response: We meant NO_3^- reduction, as in other cited studies. See our response to your comment for page 7265. Regarding your comment about these other cited studies. In older studies, e.g., Brandes et al. (1998) and Voss et al. (2001), the authors always used NO_3^- concentrations only when calculating their isotope effects and although they claim also measuring NO_2^- concentrations in their method sections, there is no further mention of NO_2^- anywhere in their papers afterward. I agree that since they did not removed NO_2^- before using the alkaline Devardas alloy method for the conversion of NO_3^- (and NO_2^-) to NH_4^+ , their measured $\delta^{15}\text{N}$ - NO_3^- must also include $\delta^{15}\text{N}$ - NO_2^- . The fact that they then calculated their isotope effects using only NO_3^- concentrations (and assuming that they only measured the $\delta^{15}\text{N}$ of NO_3^-) is thus a bit problematic. However, I assume that the contribution from NO_2^- should have been be minimal since their isotopes effects are comparable with Granger et al. (2009). In a most recent study, using the denitrifier method for analysis of $\delta^{15}\text{N}$ - NO_3^- (Granger et al., 2009), the authors specifically removed NO_2^- before $\delta^{15}\text{N}$ - NO_3^- analysis, as we also did. I am citing from their paper here: “Consequently, we proceeded to remove nitrite from samples within a few weeks of their collection. Isotope ratios measured for

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experiments that had been stored for approximately 6 months or more prior to nitrite removal showed sporadic and haphazard isotope behavior at lower nitrate concentrations when the proportion of nitrite was relatively high. Data generated from these experiments were discarded.”

Page 7260 line 13 “are ranging” should be “range”

Our response: Corrected.

Page 7260 line 15 “...sedimentary denitrification is highly suppressed in the water column.” This is confusing (although I think I know what they are trying to say). Delete “in the water column”.

Our response: We changed the sentence for: “In contrast, the expression of the isotope effect of sedimentary denitrification is highly suppressed as compared to the water-column. . .”

Page 7261 line 22 Ryabenko et al. not in References

Our response: We added this reference.

Page 7262 Line 20 name of the manufacturer of the CTD/Rosette and O₂ sensor and type? This is important because we are talking about processes that take place at the limit of detection of O₂ sensors. How were the O₂ sensors calibrated?

Our response: We added the following sentence (page 7261, after line 21): “O₂ concentrations were determined using a Seabird sensor, calibrated using the Winkler method (precision of 0.45 $\mu\text{mol L}^{-1}$) with a lower detection limit of 2 $\mu\text{mol L}^{-1}$.”

Page 7262 line 1. They say “NO₂- samples were collected and stored in ...HDPE bottles” but on the previous page they say the samples were collected in Niskin bottles. Delete the word “collected”.

Our response: Done.

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Page 7262 line 14. Same for NO₃- samples change collected to stored.

Our response: Done.

Page 7263 line 21. I assume for nutrient analysis that DIN=NO₃- +NO₂- was done by Cd reduction and NO₂- was done colorometrically and NO₃- was determined by difference. How do their concentrations measured by their methods compare with the hydrographic ones?

Our response: Yes, this is the method that was used to measure nutrient concentrations (NO₃- and NO₂-). Concentrations were measured onboard during the M91 cruise (SFB 754 Project), as described in Stramma et al. (2013). We did not independently measured nutrient concentrations in our laboratory.

Page 7265 Line 20-22. “..... increasing noise with small levels of biogenic N₂ (up to 20 μ M in this study)” This makes it seem like 20 is the small level with increased noise. Why not just say something like “..... greater than 7.5 μ M because of increasing noise below this level”

Our response: We changed the sentence for: “... greater than 7.5 μ M because of increasing noise below this level due to the huge atmospheric dissolved N₂ background (typically up to \sim 500 μ M).”

Line 7268 line1. “.... below this value.” What value? Does this refer to undetectable or 10 μ M? And then on line 4 “...such low concentrations..” Again, what are such low concentrations. Any good O₂ sensor should be able to go somewhat below 10. Then on line 14 “O₂-depleted zone”. Is there a difference between OMZ and O₂-depleted zone? What oxygen values define the OMZ and O₂-depleted zone?

Our response: Line 1: We changed “below this value” for “10 μ M”. Line 4: The full sentence reads: “Whereas a recent study indicates that denitrification and anammox are reversibly suppressed at nanomolar O₂ levels (Dalsgaard et al., 2014), CTD deployed Seabird O₂ sensors are not sufficiently sensitive to detect such low concentrations

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and hence our choice of a 10 μM threshold.” “Such low concentrations” is thus referring to nanomolar O₂ levels. Line 14: The current accepted view in the community is that OMZs are regions where oxygen saturation in the water columns is at its lowest, whereas ODZs are where oxygen concentrations are zero, within O₂ sensor errors. In our case, we meant ODZ. We accordingly changed OMZ for ODZ throughout the text.

Page 7269 Line 3 is the slope of 0.86 statistically different from 1.0?

Our response: Yes, the slope was statistically different than 1.0 (p-value < 0.05, confidence intervals for the slope = 0.84 to 0.89). We clarified this in the text.

Page 7269 Line 20. They are using the biogenic N₂ data before they present it. Shouldn't they present the data first. Also in this section that present results of epsilon calculation for changes in $\delta^{15}\text{N}$ -DIN and $\delta^{15}\text{N}$ -NO₃⁻ using equations 1-4. However the equations for $\delta^{15}\text{N}$ -NO₃⁻ have no equation numbers. Shouldn't they have numbers?

Our response: We changed the sub-section order, sections 3.5 and 3.6 now come before section 3.4. We present biogenic N₂ data in section 3.6 (now 3.5). We also renumbered the equations, such that the equation for $\delta^{15}\text{N}$ -NO₃⁻ is now equation 1.

Page 7220. Lines 8-11. Again, they say for “NO₃⁻ reduction alone” but Brandes et al., Voss et al., Granger et al and Cline and Kaplan did their studies with N+N not nitrate alone.

Our response: See our response to your comment above (Page 7260, Line 11).

Page 7220. Line 21. What are $\delta^{15}\text{N}$ -N₂ anomalies. I think this means the deviation from atmospheric equilibrium but I'm not sure. If that is indeed what they are, how do they compare to those given by Brandes et al., and Chang et al.?

Our response: We clarified this in the text: “The $\delta^{15}\text{N}$ -N₂ anomaly, i.e., the difference between the $\delta^{15}\text{N}$ -N₂ observed and at equilibrium and derived as in Charoenpong et al. (2014). . .”. We cannot compare our values to Brandes et al., and Chang et al., as they do not report $\delta^{15}\text{N}$ -N₂ anomalies.

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Page 7272 Paragraph starting on line 6. Much of this is a repeat of a previous paragraph. Condense this into a single paragraph.

Our response: We reorganized this section according to reviewer #2 comments. We tried to condense and remove repetitive information. We however think it is important to remind the reader about background information here, providing a framework to explain our results.

Page 7272 line 14. “have” should be “has”

Our response: Corrected.

Page 7273. Paragraph starting on line 4. There is a lot of background here but it is generally not summed up as to how it might explain their data. One is left with the general feeling that we don’t really understand much more than we did before. Is there a conclusion they can draw?

Our response: Again, we reorganized this section according to reviewer #2 comments. The background information is now more in context with our results.

Page 7273 line 3. “M90” In the methods you say this paper is from M91. Is this just a typo. If not you need a reference for this.

Our response: The data we present in Fig. 5 C are new data from the M90 cruise. We added the following sentence in the method section, Page 7262, Line 18: “We additionally sampled deep offshore stations during the M90 cruise in November 2012.”

Page 7273 line 9. Sentence starting with NO₂- oxidation. First, use the word Nitrite at the beginning of a sentence. Second, is this sentence really necessary, all this has been explained before?

Our response: We now start the sentence with “Nitrite”. This is briefly mentioned in the introduction, but we think it is important to remind the reader about this background information in the discussion, as it is important to explain our results.

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Page 7273 line 26. Delete the word “presumably”.

Our response: Done.

Page 7275 Lines 16-18. “our data suggests (sic) NO₂- oxidation up to only up to 80% of total NO₃- reduction.” On the bottom of page 7272 they said “the dominance of NO₂- reduction over oxidation. 80% to 100% doesn’t seem like dominance to me. Also, it should be “our data SUGGEST”.

Our response: We corrected for “suggest”. We think 80% to 100% implies a dominant process.

Page 7276 lines 13-15. I’m not sure how this tests the assumptions in the balance. What is the result of this test, and what do they think is correct. They then go on on line 19 of this page to say that relationships are not sensitive to the method of calculating epsilon. This seems that it’s not much of a test.

Our response: We are referring to two different things. Lines 13-15, we say that by calculating the different ϵ using either $\delta^{15}\text{N}$ of DIN or $\delta^{15}\text{N}$ of biogenic N₂, we can test whether there is isotopic mass balance between the substrate ($\delta^{15}\text{N}$ -DIN) and the product ($\delta^{15}\text{N}$ -biogenic N₂). If there is perfect isotopic mass balance, the ϵ calculated either ways should be equal. Differences can be explained by the contribution from other source(s) than DIN to the $\delta^{15}\text{N}$ biogenic N₂ pool. We discuss this point on Page 7277, Lines 8 to 10. On Line 19, we say that ϵ values are not sensitive to choice of method for calculating f (see Page 7267, Lines 3 to 6 for the different methods employed to calculate f).

Page 7279 line 25. Concentrations of what were “relatively low? Concentrations of oxygen or concentrations of the different N species?

Our response: N species. We clarified this in the text.

Page 7280 lines 23-25. Again in the T/S plot I see a surface mixed layer (above 14 degrees C) and a deeper mixing line pointing at some unresolved water mass (points

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in the box). So I would like to see their choice of epsilon of 7 better supported.

Our response: Reviewer #2 also raised this concern. If we compare with data for offshore waters from Bourbonnais et al. (2015), we observe a similar T/S signature for the source of the upwelled waters. However, given the narrow range in T and S, further mixing between different water masses on the shelf is unlikely, favoring a closed system. We discuss this on Page 7277, Lines 25 to 28: “Closed system estimates of ε are likely more reliable in our setting because of low likelihood of mixing between water masses of contrasting characteristics on the shelf. Temperature and salinity in the OMZ at our stations narrowly ranged from 13.5 to 15 oC and 34.88 to 34.98 (Fig. 2), similar to T/S signatures from offshore source waters (Bourbonnais et al., 2015), and suggestive of a single water mass.”

Table 2. What does “error on slope” mean? Is it S.D. or confidence limits on slope or at what level of significance?

Our response: We meant standard error of the slope. We added this information in the Table 1 and 2 legends.

Figure 5. The x-axis in panel C should be smaller, i.e. from -30 to zero, so we can see the scatter better. Also, for this figure and others, are all regressions significant at the 0.05 level?

Our response: We changed the x-axis in Figure 5, as suggested. We also added a sentence in Figure legends (Figures 5, 6 and 9): “Significant correlation coefficients at a 0.05 significance level are denoted by *.”

Figure 7. is the regression line for the >30 m data only or for all data?

Our response: We removed this figure, as suggested by reviewer #1.

Again, I think it is important that all the data be available as supplementary information to this proposal.

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Our response: Regarding data availability: we uploaded these data on the Data Management Portal for Kiel Marine Sciences hosted at GEOMAR: <https://portal.geomar.de/>. The data are also available upon request to the corresponding author. We added this information in the acknowledgement section.

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