

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.

Anonymous Referee #1

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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 $\delta^{15}\text{N}$ -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.

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

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simply say “. . . in lieu of oxygen (O₂) for respiration.”

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.

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

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 The citations used here are pretty outdated at this point.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.

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?

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?

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.

p. 7265, lines 20-21: I think you mean that the maximum biogenic N₂ observed in this study was 20 μM , 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 μM , the error associated with the calculation becomes too high?

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

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- 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?
- p. 7271, line 18: I thought the background was closer to 500 μ M, as stated on p. 7265.
- p. 7272, lines 27-28: This sentence should also cite Buchwald and Casciotti, 2013 for T dependence of the equilibrium isotope effect.
- p. 7273, lines 18-19: The $\delta^{18}\text{O}$ 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).
- 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 $\delta^{18}\text{O}$ 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).
- p. 7276, lines 1-2: I think the critical point here is that the $\delta^{18}\text{O}$ -NO₃- added back is lower than the ambient $\delta^{18}\text{O}$ -NO₃- at these high $\delta^{18}\text{O}$ levels, not that the $\delta^{15}\text{N}$ is high due to the inverse kinetic isotope effect. Even with the inverse fractionation, the low $\delta^{15}\text{N}$ of NO₂- should produce NO₃- with a low $\delta^{15}\text{N}$. You state this more clearly in your conclusions (p. 7280, line 15).
- p. 7276, lines 2-4: This was also argued in Casciotti et al., 2013.

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- 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 $\delta^{15}\text{N}$ of organic matter is relatively high in this area.
- p. 7277, line 12: I think you mean when $f=1$, not when $f=0$, as $\ln(0)$ is undefined while $\ln(1) = 0$.
- 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?
- p. 7278-7279: What would be the uncertainty on this estimate of % sedimentary denitrification from your analysis?
- 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.
- 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.
- Figure 7: The significance of this figure, and the relationship between $\Delta\delta^{15}\text{N}$ and f_{bioN_2} was not clear. Please clarify or remove the figure.
- Figure 10: I didn't think this figure was necessary as the information is more clearly presented in tables 1 and 2.

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

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