

## ***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 #2**

Received and published: 1 July 2015

General comments:

Hu et al. examine the N- and O isotopic signatures of nitrite, nitrate, and biogenic N<sub>2</sub> to assess the importance of various N-cycling processes in the Peruvian coastal OMZ. They provide a fairly comprehensive set of isotopic data, including measurements of <sup>15</sup>N on N<sub>2</sub>, a relatively novel approach in deriving water column N-loss estimates. And, while I would like to see those data published, in its current state the manuscript does not clearly convey the main goals, outcomes, and implications of the study. Particularly the introduction and the discussion section are not very concise and lack structure that guides the (non-expert) reader through the manuscript. Various parts of the introduction do not connect very well and contain unnecessary details that distract from the

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broader framework, in which the study should be viewed. In the discussion part, the authors' conclusions are not well integrated into the presentation of prior work. What I am particularly missing is a more thorough discussion of the here presented results in light of recent, extensive rate measurements of N-cycling processes in the Peruvian OMZ. Also, a number of statements/conclusions are not backed up by references or are highly speculative and not supported by the data shown.

Specific comments:

Abstract

The abstract is missing any statement on the (novel) implications of your study.

Page 7258 – line 4f. All oceanic OMZs subject to water column N-loss are coupled to regions of high productivity. Please rephrase.

Page 7258 – line 13f. Do you mean nitrate assimilation (uptake)? Assimilatory reduction would refer to the cell internal reduction for N-incorporation into biomolecules following nitrate uptake.

Introduction

Page 7259 – line 2 Please change “Chemically combined nitrogen (N, e.g. NO<sub>3</sub>-)” to: “Chemically combined nitrogen (N), e.g. NO<sub>3</sub>-,”

Page 7259 – line 10ff. Please specify below which oxygen level nitrate respiration can be expected and provide some reference(s).

Page 7259 – line 12ff. It currently reads: “successive reduction of NO<sub>3</sub>-, . . . and finally N<sub>2</sub>”. Please rephrase.

Page 7259 – line 14ff. Maybe you could find a more suitable term for “considerable evidence”, which suggests that anammox still awaits final proof to actually occur in the oceans. Same sentence: Which are those “other pathways for N-loss” besides anammox and denitrification? Further, Lam et al. (2009) is not an appropriate refer-

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ence here. The N-loss rates presented in the former study were originally published in Hamersley et al. (2007).

Page 7259 – line 16ff. You should probably also refer to recent studies by Dalsgaard et al. (2012) and Kalvelage et al. (2013) examining the large-scale distribution of N-loss processes in the ETSP OMZ.

Page 7259 – line 18ff. These two sentences remain fairly vague. Please rephrase and provide references.

Page 7259 – line 23-26 Again, there are no references provided here.

Page 7260 – line 4f. This is not well phrased. N- and O-isotopes are not useful because of their reaction rate but because they can provide information on the time-integrated activity of N-cycling processes.

Page 7260 – line 17-28 This section needs some clarification. Particularly for the non-specialist reader, the underlying cause for the difference in  $18\epsilon:15\epsilon$  between nitrate consumption and nitrification is not well explained (e.g. there is no mentioning of N-isotope fractionation during nitrification).

Page 7261 – line 4 Please add “during denitrification” after “NO<sub>2</sub>- reduction”, as there is also NO<sub>2</sub>- reduction to NH<sub>4</sub><sup>+</sup>.

Page 7261 – line 6 “NO<sub>2</sub>- O” looks odd. Maybe change to: “O-isotope exchange of NO<sub>2</sub>- with water”

Page 7261 – line 10ff. These numbers don't seem quite up to date. E.g. compare with Bianchi et al. (2009), who list a number of (more balanced) oceanic N-budget estimates.

Page 7261 – line 16 Maybe change “N-loss” to “denitrification”, which back then was considered the sole N-loss process.

Page 7261 – line 17 Please provide some numbers for the accepted range of  $\epsilon$  during

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denitrification.

Page 7261 – line 24ff. Results and conclusions don't belong here. Please remove.

Material and Methods

Page 7262 – line 10ff. Please delete unnecessary information that are anyways found in the acknowledgements.

Page 7262 – line 16ff. Please move to results section.

Page 7263 – line 11f. Please delete “resulting in a final concentration...”. That is unnecessary information.

Page 7263 – line 12f. & line 20 Please provide  $\delta^{15}\text{N}/\delta^{18}\text{O}$  values for nitrite and nitrate isotope standards.

Page 7263 – line 25ff. I don't think those details on the purge and trap system, e.g. sample run time, are necessary. Please shorten.

Page 7264 – line 11 Please add “samples” after “warming”.

Page 7264 – line 23f. Some words seem to be missing here. Please check.

Page 7265 – line 4f. There is a large number of abbreviations, symbols, and formulas, which, particularly for the non-expert reader, is challenging enough to remember. Unnecessary abbreviations, such as “[NO<sub>3</sub>-]” instead of “NO<sub>3</sub>- concentrations”, should thus be avoided. It also assists readability. Please check throughout the manuscript.

Page 7266 – line 5f. Please move the sentence to the results/discussion section.

Page 7266 – line 10 Please define “Npdef/expected”.

Page 7266 – line 22 Noffke et al. (2012), who quantified benthic iron and phosphate fluxes along the Peruvian margin, would be a more suitable reference here than the study by Reed et al. in the Baltic Sea.

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## Results

Page 7276 – line 9ff. From your T/S plots it is not evident that the sampled waters originate from further offshore (there are no offshore data for comparison). Further, you suggest that originally all waters are oxygen deplete and only become oxygenated once they reach the surface and there is exchange with the atmosphere. That contradicts your statement that surface currents dominate the shallow coastal waters (any references?). These waters are originally oxic and become oxygen deplete below the euphotic zone (which near the coast can be very shallow due to high phytoplankton densities) as a result of oxic microbial respiration of organic matter. Also, I don't quite agree with your interpretation of the observed north-south temperature increase. Is it not more likely, that sea surface temperatures increase towards st. 67 because of the indentation of the Peruvian coastline at  $\sim 14^{\circ}\text{S}$  combined with the sheltering effect of the Paracas National Park peninsula near Pisco, impeding the advection of cold surface waters from the south? In my understanding, upwelling (vertical water mass transport) is very slow compared to lateral advection of (surface) water masses.

Page 7267 – line 19f. See previous comment

Page 7267 – line 21ff. You also examine possible effects of nitrite oxidation, an aerobic process (at least an alternative electron acceptor has not been identified, yet, in OMZs), on the isotopic composition of nitrite and nitrate.

Page 7268 – line 3 Please specify “CTD deployed O<sub>2</sub> sensors”. A STOX sensor, which can resolve nanomolar changes in oxygen concentration, can be mounted to a CTD rosette system, too.

Page 7268 – line 8f. I do not think “intense local upwelling” is a likely reason for elevated phosphate and/or silicate levels in the shelf bottom waters. The very high concentrations of ammonium, which typically does not accumulate at such high levels in the OMZ, clearly indicate benthic release.

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Page 7268 – line 13ff. I agree that nitrate depletion indicates N-loss, but you did not measure actual N-removal. Please rephrase accordingly.

Page 7268 – line 24 According to Fig. 4c,  $\delta^{15}\text{N-NO}_3^-$  was  $\sim 40$  ‰ at stations 65 + 67. Please check those numbers.

Page 7268 – line 25f. Maybe move this to methods section (e.g., “samples down to xx  $\mu\text{M N}$  were analyzed for their isotopic composition”).

Page 7269 – line 1 Maybe substitute “N-loss” with “NO<sub>3</sub><sup>-</sup> reduction”, to be more specific.

Page 7270 – line 4f. Please provide reference.

Page 7270 – line 18f. How does this observation align with actual rate measurements of nitrite oxidation in the Peruvian coastal OMZ?

Page 7271 – line 1ff. In my understanding, N deficit and excess P express exactly the same and are mutually interchangeable. Hence, does “excess PO<sub>4</sub><sup>3-</sup>” refer to benthic P release here? That is only obvious at station 63, but not at the remaining sampling sites. Please clarify.

## Discussion

Page 7271 to 7273 – line 19 This is largely a summary of previous studies on the effects of microbial activity on DIN isotopic compositions and is not well tied in with the discussion of the here presented data.

Page 7271 – line 21f. I disagree that micromolar levels of nitrite as found in OMZs are “low concentrations”. Also, later in the same paragraph you write: “Accordingly, relatively high [NO<sub>2</sub><sup>-</sup>] was observed. . .”.

Page 7272 – line 3 There are more fitting references here, e.g. Lipschultz et al. (1990), Lam et al. (2009), and Kalvelage et al. (2013), all of which provide actual rate measurements of nitrate reduction in the Peruvian OMZ.

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Page 7272 – line 3ff. Are you suggesting that the observed nitrite is actually not formed in the shallow shelf waters but originates in deeper OMZ waters and is simply advected (upwelled)? Previous studies have shown that nitrite is produced at those shallow, oxygen depleted depths (see also above).

Page 7272 – line 22ff. This needs better explanation and should be discussed in the context of the preceding sections. By describing observations made in previous studies and your own ones in separate sections, the non-expert reader has a hard time to follow your line of argumentation here.

Page 7273 – line 25ff. Although high rates of N-loss have been measured on the Peruvian shelf that alone does not explain rapid nitrite turnover. The nitrite pool in these waters is affected by aerobic ammonium and nitrite oxidation, nitrate reduction to nitrite, as well as further reduction to either ammonium or N<sub>2</sub> (see Lam et al. (2009) and Kalvelage et al. (2013)).

Page 7274 – line 14ff. Are these rates calculated based on your own data or do you refer to previously results?

Page 7275 – line 11ff. I would like to see a more thorough discussion of how the estimates of nitrite oxidation vs. nitrate reduction compare to previous rate measurements of these processes. Anammox bacteria (in culture) only oxidize a minor fraction of nitrite to nitrate. At the same time, rates of nitrite oxidation mostly exceed those of N-loss via anammox several fold on the Peruvian shelf (Kalvelage et al. (2013)), clearly indicating non-anammox related nitrite oxidation.

Page 7275 – line 21 see comment Page 7258 – line 13f.

Page 7276 – line 2ff. This sentence is not very clear and needs some rewording.

Page 7276 – line 6f. Is this your own observation or an observation made in the cited study?

Page 7276 – line 16ff. This paragraph is again very hard to digest for any non-expert  
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reader. Maybe you could expand here a bit on the different approaches used to calculate  $\epsilon$ .

Page 7277 – line 4ff. Please specify those “mass balance considerations”.

Page 7277 – line 25ff. As mentioned before, your T/S data merely indicate a relatively homogeneous water mass over the shelf, but that does not necessarily exclude any mixing with waters further offshore. Could you provide data from neighboring, offshore stations that show a significantly different T/S signature for those waters?

Page 7278 – line 21f. Please specify how potential effects of contributions from organic N to N<sub>2</sub> formation were taken into account.

Page 7279- line 12ff. This is too simple a conclusion. One could also argue that N-flux measurements over a relatively short time span and at relatively few locations overestimate benthic N-loss. And, there are hot spots of water column N-loss, too.

Page 7279 – line 21f. Not only N-loss processes, but, as you have demonstrated in previous sections, also nitrification and incomplete denitrification determine the isotopic compositions of nitrite and nitrite. Please revise.

Page 7280 – line 6f. How does your estimate of nitrite turnover time compare to recently published N-fluxes and N-inventories for the Peruvian costal OMZ by Kalvelage et al. (2013)?

Page 7281 – line 4f. Please include some reference for benthic N-loss on the Peruvian shelf, e.g. Bohlen et al. (2011).

#### Tables and Figures

Table 1 and 2 For non-expert readers it may not be obvious that  $\epsilon$  corresponds to the slope of the linear regression. Hence, instead of listing  $\epsilon$  and the error of the slope of the linear regression separately, I suggest to delete the “Error on slope” column and include the error in the  $\epsilon$  column (e.g. N<sub>2</sub> biogenic = 14.27 ± 0.86).

Figure 1 Panel A is not labeled as such. Further, the inserted ODV map is very small and provides little extra information. I suggest removing it.

Figures 3, 4 and 8 A cosmetic detail: ODV allows plotting bathymetry using station bottom depths. Those grey sediment boxes look somewhat arbitrarily drawn.

Figures 5, 6 and 9 Please increase figure size.

Figure 7 The axis label looks somewhat skewed (aspect ratio not locked during increase/decrease of plot size). Please correct.

Figure 10 The figure does not add any information, all values are given in Table 1 and 2. Please remove.

Technical corrections:

Page 7258 – line 11 Please add comma after “10  $\mu\text{M}$ ”.

Page 7259 – line 12 Please add comma after “nutrient”.

Page 7259 – line 17 Please change to: “dominant pathway for N-loss”

Page 7262 – line 17 “temperatures” instead of “temperature”.

Page 7265 – line 4 “parcels” instead of “parcel”.

Page 7267 – line 9 Please add comma after “found”.

Page 7268 – line 20 Please add comma after “[NO<sub>2</sub>-]”.

Page 7269 – line 20 Please add comma after “N<sub>2</sub>”

Page 7269 – line 24 Please add “ones” after “canonical”.

Page 7270 – line 2f This should probably read: “The Rayleigh equations’ y-intercepts, where  $f = 1$  represents the initial  $\delta^{15}\text{N}$  of NO<sub>3</sub>- or DIN, varied from. . .”

Page 7274 – line 1 Change to: “Kalvelage et al., 2013”

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Page 7275 – line 1 “average” instead of “avering”

Page 7277 – line 4 Please add comma after “two”.

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

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