

## ***Interactive comment on “An oceanic fixed nitrogen sink exceeding 400 Tg N a<sup>-1</sup> vs the concept of homeostasis in the fixed-nitrogen inventory” by L. A. Codispoti***

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### **Summary:**

In this thundering review, Lou Codispoti muses about the state of the current marine nitrogen budget, with a focus on the consequences of his suggestion that the losses of fixed nitrogen in the ocean may exceed 400 Tg N yr<sup>-1</sup>. Accepting this high level of fixed nitrogen loss, Codispoti argues that either current estimates of the sources of fixed nitrogen, especially N<sub>2</sub>-fixation, are biased low, or that the marine nitrogen cycle is currently undergoing a temporary phase characterized by net losses, perhaps as a consequence of the anthropogenic perturbation of the global nitrogen cycle.

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## Assessment:

This manuscript is interesting to read, particularly since Codispoti contrasts his view with that postulated by myself and others that the net loss of fixed nitrogen is smaller and of the order of 200 to 300 Tg N yr<sup>-1</sup>. Although I am not (yet) convinced of the presented arguments, there are only a few small issues that I can point at being truly questionable. Perhaps the most important weakness of this manuscript is that it is rather unquantitative as it fails to present new quantitative estimates for the different processes and it also tends to push for the high-end estimates without considering that the uncertainties equally permit low-end estimates. As discussed in more detail below, the most important new constraint on the problem comes from the recent observation of N<sub>2</sub> supersaturations that are larger than expected based on the analysis of nutrient deficiencies. These observations come from one place only (Arabian Sea), and there are many methodological and interpretational questions that have not been fully resolved yet in the scientific literature. This is particularly an issue because the underlying papers by Devol and colleagues have either just been published or are in press (the data were shown in Codispoti et al. (2001) but without much explanation). If the extrapolation of these observations from the Arabian Sea proves questionable, the other (mostly unquantitative) arguments lose much of their weight. I don't have evidence against the validity of such an extrapolation, but I remain sceptical. All of this, in the end, is just an illustration of our current state of ignorance about many key aspects of the marine nitrogen cycle, and as such, I highly welcome the publication of this article. It is a position paper, but an interesting and stimulating one! I therefore recommend its publication with a few caveats.

The first one is that I think the article would benefit from a more detailed consideration of the uncertainties, including the fact that given an uncertainty estimate, it is equally likely that the true value lies at the lower end as it lies at the upper end. I also think that the article would benefit from some careful pruning. As it is, the article gives the impression of having been written rapidly, and there are a few redundancies that should

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be eliminated.

In addition I provide also a couple of major comments, which I ultimately may write down as an official comment to the paper rather than expect Lou Codispoti to respond to in his paper.

## Recommendation:

I recommend publication of this manuscript after minor revision. The major comments below are points of contention and do not necessarily require a response by the author.

## Major Comments:

I have three major comments: One pertains to the interpretation of the  $N_2$  excess in the Arabian Sea, one to the interpretation of the  $^{15}N$  isotopic balance, and the third one to the phosphate balance.

### $N_2$ excess:

A key argument for the very substantial increase in the estimated loss rate is the observation that the  $N_2$  excess in the Arabian Sea is much larger than inferred from traditional estimates based on nutrient stoichiometry. In an earlier critique, I argued that the direct interpretation of  $N_2$  excesses as a signal of denitrification is dangerous, since  $N_2$  supersaturations can also be produced physically, either near the surface through bubble entrainment and sub-surface solar heating, or as a result of mixing of waters with differing temperature, due to the non-linearity of the temperature dependence of the  $N_2$  solubility. Codispoti points out correctly that the former problem was taken care of in the Arabian Sea by just considering  $N_2$  excesses relative to inflowing waters (although this wasn't explained in the Codispoti et al. (2001) paper). However, mixing still leads to  $N_2$  supersaturations, and in a regime with relatively strong temperature gradients this can cause a substantial supersaturation of  $N_2$ .

Even if the  $N_2$  excess is correctly identified as being of biological origin, one needs to worry about the separation between water column and benthic denitrification. In the

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case of the Arabian Sea, this is a particularly difficult problem, as the ratio of sediment interface to water column is relatively high (and for  $N_2$  excess, the argument presented on page 1213 (lines 34) that "the sediments in contact with suboxic water masses compromise less than 3% of the total oceanic sedimentary area" is not relevant, as  $N_2$  produced by denitrification (irrespective of whether it is produced by canonical denitrification or Anammox or...) will escape into the overlying water regardless of whether the bottom water is anoxic or not. Therefore, the distribution of  $N_2$  excess in the water column reflects the sum of water column and benthic denitrification, and given the fact that benthic denitrification is thought to be at least twice as large as water column denitrification, poses not a small problem to correctly associate a given  $N_2$  excess to a particular source in the water column.

#### *Isotopic balance:*

The isotopic balance arguments of Brandes and Devol (2002) and Deutsch et al. (2004) built on the assumption that water column denitrification fractionates strongly (-20 permil), while benthic denitrification leaves only a small net signal, as the reactants are entirely used up. Codispoti now argues that Anammox likely fractionates very differently, and therefore Anammox in the water column may look isotopically much more like benthic denitrification. Although not much is known yet about the isotopic fractionations of Anammox bacteria, Codispoti's conclusion depends strongly on where the nitrite for the Anammox bacteria is coming from. In the water column, for example, the only major source of this nitrite I can think of is partial denitrification of nitrate. As this step is the step that leads to the strong isotopic fractionation during canonical denitrification, one doesn't see - from the perspective of the  $^{15}N/^{14}N$  ratio of nitrate - a difference of whether nitrate is denitrified canonically or through anammox.

#### *Phosphate sink:*

Codispoti argues at a few places that the N to P nutrient anomaly analyses ( $N^*$  or similar) could be biased because of their neglect of phosphate removal in anoxic sediments.

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It is undeniably correct that anoxic sediments represent a major sink for phosphate, but if the estimated total removal rate of phosphate is considered (Delaney, 1998) (stoichiometrically, the total loss rates of P compared to those of N are more than a factor of 10 smaller), it is difficult to conceive how N to P anomalies would be biased by a factor of two by neglecting the losses of P.

## Minor comments:

p: page; l: line

p1213, l1 and elsewhere: "N<sub>2</sub>-fixation in sub-euphotic zone etc." From an physiological point of view, it is difficult to conceive why organisms would spend much energy to fix nitrogen when they live in a nitrogen rich environment. I therefore would argue that it is highly unlikely that N<sub>2</sub>-fixation rates in thermocline waters are significant. Furthermore, the presence of a genetic capacity is certainly relevant, but not an evidence.

p1212, l26: "at variance": Although the direct rate measurements are a strong constraint, the integrated rates depend extremely strongly on the assumptions made about the spatial (and temporal) extent of the active denitrification region. I therefore don't think that one easily dismiss a 15 Tg N yr<sup>-1</sup> reduction (less than 20%) on the basis of these point measurements.

p1213, l24: "Li et al.": I have many problems with the stoichiometric ratio analysis method of Li et al. In my opinion, this method starts from a wrong perspective, and produces erroneous results.

p1214, l5ff: "Outmoded stoichiometries": In my opinion, this argument is not entirely correct. As discussed above for N-15, the impact of the different pathways on the inorganic nutrient ratios very much depends on the ultimate source of the N in N<sub>2</sub>. Fundamentally, one has only two possibilities as all other reservoirs are too small: NO<sub>3</sub> and organic nitrogen. Only if Anammox and the other non-canonical denitrification pathways have a different ultimate source of N will their impact on the inorganic nutrient

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ratios be fundamentally different. I argued above that the most likely source of nitrite for Anammox is nitrate, hence its impact on  $\text{NO}_3^-$  and the  $^{15}\text{N}$  of nitrate would ultimately be identical to that of canonical denitrification. Given the fact that N in nitrate is in many places much more abundant than organic N, it is not easily conceivable that more than 50% of the N in  $\text{N}_2$  ultimately comes from organic matter. In my view, it is much more likely that most of the N in  $\text{N}_2$  ultimately comes from nitrate.

p1214, line12ff (section undersampling): Although these are all interesting special sites of denitrification, I strongly doubt that they add up to a substantial number. Denitrification in brine pockets is a very interesting observation, but I don't think one can extrapolate these measurements to the global sea-ice area. First, in order for denitrification to occur, a substantial amount of organic matter must be present. This is likely the case only in very productive near-shore regions - i.e. unlikely the case in open ocean sea-ice fields. Second, these rates can only occur during a fraction of the year, hence one cannot take the ratio between sea-ice and sediments during the active period and extrapolate this in time and space.

p1216, l20ff: Note that Deutsch et al. (2004) showed that a "dilution" effect not considered by Brandes and Devol (2003) is quite important when considering the  $^{15}\text{N}$  isotopic balance of nitrate in the ocean. This "dilution" stems from the fact that denitrification and  $\text{N}_2$ -fixation are spatially separated.

p1216, l22ff: "differences in isotopic fractionation factor": see major comment above. I don't think that one can easily say that Anammox will have a very different overall fractionation from that of canonical denitrification.

p1217, l19: "The weight of the evidence..." This is subjective, of course, but to me, the weight is not that large. There are many arguments, but each one has its problems or is of small magnitude. Only time will tell...

p1219, l25ff (section 3.6.2): I found this section confusing and adding little weight to the arguments. The plots from the Chucki Sea show to me primarily the interplay

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of denitrification and mixing, without providing new insights. It is incorrect to argue that these figures show that one cannot use intercept analyses to say something about "homeostasis". First, the argument about homeostasis is based on the global intercept, determined from fitting a straight line to data from around the globe and from all depth. This means it is determined by the data from the ocean interior and not from the data at the near surface, where some decoupling and luxury uptake indeed can occur. Second, the homeostasis argument requires also information about the N:P input ratio. Only in this context, does the near-zero intercept of the global relationship say anything about the existence of a possible homeostasis. I suggest to delete this section.

p1226, section 3.7: Maybe I was getting tired, but I had the impression that several arguments presented in this section were dealt with already before.

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