**Biogeosciences
Discussions**

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Interactive comment on "An oceanic fixed nitrogen sink exceeding 400 Tg N a^{-1} vs the concept of homeostasis in the fixed-nitrogen inventory" *by* L. A. Codispoti

L. A. Codispoti

Section II: Response to Dr. N. Gruber's (NG) Comments

This reviewer (NG) suggested that the paper should be published with minor revision, but he also had a number of comments that I must address.

He points out that portions of the paper are redundant. I will do my best to eliminate any redundancies in my revision.

NG questioned the need for Fig. 2, but I opt to leave it in for the following reasons: 1) It gives an example of "luxury consumption" which is discussed in my text, and 2) It juxtaposes fairly extreme Atlantic "type" and Pacific "type" N:P relationships that

Full Screen / Esc

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Interactive Discussion

Discussion Paper

EGU

co-occur in the Canadian Basin of the Arctic Ocean, thereby giving me something to hang my hat on when I discuss the different N:P relationships that can occur in the world ocean. 3) The "march" of phosphate values in the summer data raise interesting questions about ice-melt, luxury consumption of phosphate, and maybe even nitrogen fixation at low temperatures.

NG also questioned the cited results of Li et al. (2006). NG has his doubts about this analysis. SWAN's review, on the other hand, suggests that Li et al.'s analysis may help explain a deep signal. I will revise my paper to indicate that some have questioned the conclusions of Li et al. (2006). The major points of my paper do not depend on this analysis, but I would like to leave the reference in my paper to encourage more discussion.

NG suggests that I have made too big an issue of "luxury consumption" insofar as it effects oceanic N:P ratios since the ratios and slopes of N:P scatter diagrams are largely determined by subsurface values. I think that he has a point, although I am guessing that some of the plots in the literature have a plethora of surface and near-surface values lying on top of each other, and that luxury consumption will have some impact on the nitrate and phosphate intercepts. I will de-emphasize this portion of the paper but retain the larger point that we do not really know to what extent the ocean biota *control or respond* to N:P ratios.

This reviewer suggests that the potential net phosphate removal from the ocean, mentioned in my budget will have only a minor impact. I suggest that when multiplied by a N:P ratio of 16:1 (by atoms), the net removal of P from the oceanic water column suggested by one recent budget would "mask" the removal of up to ~ 30 Tg N a^{-1} if one were determining changes via N:P ratios. This term is small when compared to the overall source and sink terms for fixed-N, but it is not trivial. Plus, we really do not have a good fix on the oceanic P budget (sound familiar?), and I would like to stimulate more thinking about the relationship between the P and N budgets. I choose to retain this portion of the manuscript.

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Discussion Paper

NG asks why nitrogen fixation could be important below the photic zone since nitrate is generally abundant. This comment was in response to my mention of a study suggesting that shipworms harbor bacteria that fix-nitrogen and to genetic studies suggesting that crustacean guts also harbor heterotrophic nitrogen fixers. Since at least some heterotrophic bacteria can assimilate nitrate, this comment has merit. I should point out, however, that Mehta et al. (2003) suggest that some hydrothermal fluids have low nitrate and ammonium concentrations, and contain nitrogen-fixing (nifH genes), so this criticism is not universally applicable. A recent edition of *Science* has a commentary (Capone, 2006) and a paper entitled "Nitrogen fixation at 92° C by a hydrothermal vent archaeon" (Mehta and Baross, 2006) that demonstrates that nitrogen fixation can occur in low fixed-N, high temperature fluids associated with hydrothermal vents. In addition, we do not know enough about the microbial environments of crustacean guts to assert that N-fixation does not occur in the presence of significant quantities of nitrate in the ambient water. Zehr et al. (1998) point out that reduced oxygen concentrations and high Fe concentrations should make conditions more favorable for N-fixation in copepod guts than it would be in ambient water. Zehr et al. (2006) suggest that it is clear that nitrogen fixation activity is suppressed by ammonium, but a strong case for suppression by nitrate cannot be made with available data, and they further point out the higher energetic cost of assimilating nitrate vs ammonium. Since ammonium concentrations are quite low in most of the sub-100 m ocean, we do not know, at this moment, whether high nitrate concentrations in the deep ocean would suppress fixation in crustacean guts. A possibility that I did not mention was the occurrence of nitrogen fixation in zooplankton guts in oligotrophic water. One might ask, for example, what happens when copepods are grazing on re-cycled post-bloom organic matter in oligotrophic waters? Also, while it is often suggested that oceanic water column nitrogen fixation is restricted to tropical and subtropical waters, I note that nitrogen fixation has been found in the water/aggregate patches found in an Antarctic Dry Valley Lakes (Paerl and Priscu, 1998). Can the "march towards 0 phosphate" seen in the summertime nitrate vs phosphate plot for the Chukchi and eastern Beaufort seas, (Fig. 2b), be

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Interactive Discussion

Discussion Paper

EGU

evidence of cold-water nitrogen fixation instead of "luxury consumption of phosphate and ice melt? Probably not, but nobody has looked very hard for water column nitrogen fixation in the subpolar and polar ocean. I will rewrite this section to emphasize the more generic point that, if we look harder and at more diverse environments, we are quite likely to find significantly more oceanic nitrogen fixation echoing the following comment of Zehr et al. (1998): "This report shows that there are far more diverse nitrogen-fixing populations and diverse habitats which can support nitrogen fixation in the open ocean than previously documented." To date, most oceanic studies of nitrogen fixation have been focused on the photic zone and on autotrophs, and to a lesser extent on shelf sediments.

NG suggests that the higher sink terms that I employ arise to a large extent from the observation of N_2 *supersaturations* in the Arabian Sea and "that there are many methodological and interpretation questions that have not been fully resolved". I will return to that methodology in a following paragraph. Here, I want to point out that these N_2 *excesses* are not the only reason for my suggested increase in the water column sink term. Please note that the new nitrate deficit equation (Codispoti et al., 2001; Devol et al., 2006a&b) suggests that traditional estimates of nitrate deficits in the Arabian Sea were too low with the new method yielding a water column nitrate deficit content $\sim$ twice as great as suggested by older methods. Because the excess N_2 values are even higher (by about 75%) than the new nitrate deficit values, they add weight to the suggestions that a significant portion of the N_2 in suboxic water columns may arise from the oxidation of organic-N and ammonium, but they are not the only source of such information. For example, there is experimental evidence suggesting that denitrifiers prefer nitrogen-rich substrates (Van Mooy et al., 2002) and that the anammox reaction that produces half of its N_2 from ammonium oxidation is significant in suboxic water masses (e.g. Kuypers et al., 2005 and 2006). Van Mooy et al's. stoichiometry for canonical denitrification predicts a yield of free N_2 that is 27% greater than would arise from nitrate reduction to N_2alone. Codispoti et al. (2001), Kuypers et al. (2006), and this paper mention processes that could increase the yield of free N_2 from ammonium

Interactive
Comment

Full Screen / Esc

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Interactive Discussion

Discussion Paper

to even higher levels. One of these would be a high ammonium flux from sediments, and Devol et al. (2006a) suggest that ammonium/phosphate flux ratio from sediments in the Arabian Sea can be expected to have an N/P ratio exceeding the Redfield ratio. Kuypers et al. (2006) suggest that consortia of microaerophilic nitrifiers that can produce NO_2^- on the outer surface of particles and anammox bacteria within could produce yields of N_2 far higher than predicted by Redfieldian stoichiometry. They note that this process has been observed in oxygen-limited bioreactors and can occur at ambient oxygen concentrations as high as 10 μM. Thus, without invoking the *excess* N_2 data, it would not be unreasonable to suggest that the Codispoti et al. (2001) nitrate deficit should be multiplied by at least 1.3 to obtain the excess N_2 production. This is because the Arabian Sea nitrate deficit method outlined by Codispoti et al. (2001) and described further by Devol et al. (2006a &b) is a true *nitrate deficit* and does not account for any N_2 produced by the oxidation of organic matter or ammonium. Thus, the N_2burden in the quasi-permanent suboxic zone in the Arabian Sea could be 2.6 times higher than estimated by older nitrate deficits and exports of these "old" deficits have been used to obtain a denitrification rate for the Arabian Sea of $\sim$ 30 Tg N a^{-1}(Bange et al., 2005). Multiplying 30 by 2.6 yields a rate of 78 Tg N a^{-1}. The ETS based estimates of denitrification in the Arabian Sea and Eastern Tropical Pacific also did not assume any oxidation of ammonium or organic nitrogen to N_2. The ETS based denitrification rate estimate for the quasi-permanent, pelagic suboxic zone in the Arabian Sea ranges from 32-44 (Devol et al., 2006a), and multiplying by 1.3 gives a range of 42 to 57 Tg N a^{-1}. Multiplying the total Eastern Tropical Pacific (total for the suboxic zones north and south of the equator of $\sim$ 50 Tg N a^{-1} estimated from ETS determinations (Codispoti and Richards, 1976; Codispoti and Packard 1980; Codispoti et al., 1986) by 1.3 would raise the rate for these regions to 65 Tg N a^{-1}. Thus, **without invoking the *excess* N_2data** I could make a case for a total denitrification rate in the three major suboxic zones of $\sim$120 Tg N a^{-1}. To this we must add contributions from the water column off Namibia where Kupers et al. (2005, suggest a value of 1.4 $\pm$ 1 Tg N a^{-1} and the West Indian Shelf where Naqvi et al. (2006) estimate a *conservative rate based on nitrate*

consumption of 1.3-3.8 Tg N a^{-1}. Then there are the contributions from, the Cariaco Basin, the Baltic, the Costa Rica Dome, California Border Land Basins, the Black Sea (Kuypers et al., 2006 estimate a rate of $\sim$0.3 Tg N a^{-1}), and the Mississippi Delta "dead zone". In addition, there are episodic outbreaks of low oxygen concentrations in coastal waters, episodic outbreaks of suboxia off the Arabian Peninsula that can be seen in the USJGOFS Arabian Sea data and that are not included in the ETS and N^{15} incubation based Arabian Sea estimates discussed by Devol et al. (2006b). Then we have the contributions from "unusual" denitrifying environments for which there are, as yet, no overall rate estimates. These have been mentioned in the manuscript and include brine pockets in sea ice. We know that denitrification occurs in some of these environments, but we have no idea of what the total contribution from some of these regions might be. We do know that it is not zero! Penultimately, there are all of the geographic regions where suboxic or near-suboxic water occurs but which have not been adequately sampled. I would include the Gulf of Oman and the Gulf of California in this category as well as the Bay of Bengal. Finally, I still think we should try to design experiments to see if significant denitrification occurs (albeit at very low rates), in the 99.8% of the ocean volume that is not suboxic, particularly in particles suspended in low oxygen sea water (see Wolgast et al., 1998) . Thus, I can make a decent case for 150 Tg N a^{-1} as the water column denitrification rate without recourse to the *excess* N_2 values. NG suggests that my litany of these additional sights will not add up to much, and he may be correct vis a vis some of them. For others, such as sea ice, I think that surprises may lie in store (see next paragraph).

NG had some specific comments about denitrification in sea ice. I need to make it clear that my estimate for ice cover area (20 x 10^6 km^2) was an annual average ice cover, so it takes into account the seasonal waxing and waning of ice cover. Kuypers et al. (2006) suggest that rates of anammox in the lower 0.5 m of sea ice to range from 100-300 nmoles N L^{-1} d^{-1}, and that anammox can account for up to 19% of total N_2 production. These values would suggest an annual N_2 production rate in brine pockets in sea ice of up to $\sim$ 100 Tg N a^{-1}. I would be surprised if the actual value

Full Screen / Esc

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Discussion Paper

EGU

is that high, but I would not be shocked by a value of > 10 Tg N a^{-1}. With respect to NG's comments about the ability of sea ice to support denitrification, this would be related to the organic matter that can accumulate in sea-ice. I can only say that, at times, I have been astounded by the accumulation of organic material in sea ice. For example, in spring 2002, we observed drifting remnants of *Melosira*, a chain-forming diatom that was apparently released by melting ice in the oligotrophic Canada Basin. On page 73, of the *Arctic Sea Ice Ecosystem*, (Melnikov, 1977) one can see a photo of *Melosira* strands ~ 2 m long extending from the bottom of sea ice at 81° N, 138° E. in the Amundsen Basin. On my last trip to the Ross Sea, I was impressed by how much algae was present in the sea-ice even though we were there so early in spring that convection was still occurring, and many of the TS diagrams collapsed to a single dot down to ~ 500m. Let us not discount denitrification in sea ice without taking a more comprehensive look! Keep in mind that much of the ice found in the interior of the Arctic Ocean has been formed at the margins under conditions that allow it to incorporate particulate material (e.g. Bischof, 2000).

Another little surprise may await us if we take a closer look at the denitrification associated with the hydrothermal circulations associated with mid-ocean ridges/flanks. Mehta and Baross (2006) point out that some of the vent fluids are associated with low inorganic-N

concentrations, thereby helping to account for their observations of high temperature nitrogen fixation. John Christensen pointed out to me many years ago that significant denitrification might be associated with vent fluids. Schultz and Elderfield suggest that the annual hydrothermal flow associated with ridges and ride-flanks is 2.4 x 10^{16} kg. If one assumes that

denitrification occurs in this entire flow and that the original nitrate concentration is 30 μM, a denitrification rate of ~ 10 Tg N a^{-1} results. Is this a wild over-estimate? Maybe, but perhaps we should take a systematic look. If we find significant denitrification associated with hydrothermal circulations, we will then have to argue about whether it

Full Screen / Esc

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Discussion Paper

EGU

should be considered as water column or sedimentary.

An additional factor that I have already alluded to (see Section I) is that to the extent that nitrogen fixation occurs in proximity to suboxic water masses (e.g. Deutsch et al., 2007; Naqvi, in press), there will be a tendency for estimates based on N*, and nitrate deficit gradients and transports to be estimates of *net* rather than *gross* denitrification rates. This complication could introduce a low bias in the *gross rates* estimates used in our budgets.

With respect to the *excess* N_2 values, NG mentioned the possibility that some of the excess may come from sediments, and that mixing of waters of different temperatures can cause N_2 *supersaturations*. There have been two recent papers (Devol et al. 2006a &b) that do a much better job of explaining how the *excess* N_2 values were obtained than I apparently did. I guess that my papers do not make it clear that the *excess* N_2 *values are calculated from nitrogen/argon ratios by difference from nitrogen/argon ratios found just outside of the Arabian Sea denitrification zone.* Argon saturations will also be increased by bubble injection and by mixing between water masses with different temperatures, so using nitrogen to argon ratios would greatly reduce such errors as does looking at the changes *just outside* vs inside the denitrification zone. With respect to a sedimentary contribution, to these excesses I can offer the following rebuttals. 1) Since the *excess* N_2 estimates are based on changes within the regions of the low oxygen water masses, it is only *local* sedimentary denitrification that should impact these values. 2) Estimates of denitrification in sediments in contact with the three major suboxic denitrification zones are low relative to the water column rates. Codispoti and Packard (1980) suggest a rate of 2 Tg N a^{-1} for sediments in proximity to the suboxic waters found in the Eastern Tropical South Pacific. Codispoti (1973) points out the small area of sediment in contact with suboxic waters in the ETNP. Devol et al. (2006a) suggest a potential sedimentary denitrification rate in sediments in contact with the suboxic waters in the Arabian Sea of 3.9 Tg N a^{-1}. 3) Maximum N_2 excesses occur at the same depths as the ^{15}N-nitrate maxima that are a signal of water column

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU

denitrification as noted in SWAN's review. Thus, it is unlikely that sedimentary denitrification contributes more than $\sim$ 10% to the *excess* N_2 signal observed in the Arabian Sea. I think that what is most important about the Arabian Sea's *excess* N_2 data is that the values reported in Codispoti et al. (2001) and additional values reported by Devol et al. (2006b) are even higher than the revised nitrate deficit method of Codispoti et al. (2001) discussed in the paragraph above. As already noted, they suggest an *excess* N_2 burden $\sim$ 75% greater than would be inferred from the Codispoti et al. (2001) nitrate deficit method. If we assume that $\sim$ 10% of the "extra" *excess* N_2 signal arises from sedimentary denitrification, then these results suggest that we should take the Arabian Sea ETS based estimates and multiply them by 1.65. However, local nitrogen fixation may be similar or greater than the sedimentary signal (Brandes et al., 1998) and of the opposite sign, so I will assume that these terms cancel. If I have complete faith in the *excess* N_2 values, I really should multiply the ETS based estimates for the Arabian Sea by $\sim$1.75 instead of 1.3, and this would give a range for the ETS based estimates for the quasi-permanent zone of 56-77 Tg N a^{-1}. The pelagic denitrification rate of $\sim$ 30 Tg N a^{-1} based on nitrate deficit exports (e.g. Bange et al., 2005) would have to be multiplied by 2 to account for "errors" in the old nitrate deficit method and then by 1.75 to account for the *excess* N_2 data. It would then become 105 Tg N a^{-1} (30 x 2 x 1.75). What I am trying to say here is that if I took the *excess* N_2 values from the Arabian Sea into full account, I could make the case that my estimate of 60 Tg N a^{-1} for the quasi-permanent suboxic zone is low. So I guess I have to say that it is a bit unfair for one reviewer, NG, to say that I am so dependent on *excess* N_2 values, and another, JS, to say that I have a propensity to choose the highest values. I think that I can make a reasonable case for choosing 80 Tg N a^{-1} for the rate for the quasi permanent suboxic zone in the Arabian Sea, and I could have multiplied the ETS based rates for the Eastern Tropical Pacific by a higher factor based on the published *excess* N_2 data. Overall, I think that when we learn more, my choice of 150 Tg N a^{-1} for water column denitrification is going to be parsimonious, but I recognize that there is room for debate.

NG suggests that in suboxic waters, the nitrate/nitrite involved in anammox can be

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Interactive Discussion

Discussion Paper

EGU

supplied by the water column, and therefore may have an isotope fractionation factor similar to that for nitrate during canonical denitrification. I agree with this, but apparently did not make this point clear enough. I need to re-write this section of the paper to clarify my present thinking about this matter. Basically, I think that all or most of the organic-N/ammonium oxidized during canonical denitrification is converted to N_2, and I assume that this process proceeds with little isotope fractionation on the assumption that the supply of labile organic-N/ammonium is limited. So, with these assumptions, the question becomes what is the ratio of N_2 produced by organic-N/ammonium oxidation to the total N_2 produced during water column denitrification or to the N_2 arising from nitrate/nitrite reduction that we assume to undergo significant fractionation? I will call the unfractionated/total ratio, R1, and the unfractionated/fractionated ratio, R2. With Gruber and Sarmiento's (1997) stoichiometry for canonical denitrification, R1 = 0.13, and R2 = 0.15. With Van Mooy et al's. (2002) stoichiometry R1 = 0.21, and R2 = 0.27. The upper limit for these ratios is probably represented by the direct oxidation of ammonium with nitrate, for example, in the Mn mediated reactions reported by (Luther et al., 1997). In this case, R1 = 0.62 and R2 =1.7 (see also, Codispoti et al., 2001), but, as yet, there is no evidence for this reaction being significant in the oceanic water column. During the anammox reaction in which nitrite oxidizes ammonium to N_2 R1 = 0.5., and R2 = 1.0, leaving aside unsettled questions about the sources of nitrite and ammonium. While it is true that the water column burden of N_2 in the Arabian Sea is about 1.75 times higher than predicted by the Codispoti et al. (2001) nitrate deficit (R1 = 0.43; R2 = 0.75) fully honoring these data would suggest a water column rate for the pelagic Arabian Sea higher than the 60 Tg N a[1] that I chose. In this work, I will assume that the water column N_2 burden in the Arabian Sea is 1.5 times higher than suggested by the Codispoti et al. (2001) nitrate deficit values and that the ETS and nitrate deficit based rates should therefore be raised by a factor of 1.5. With this assumption I can support my selected water column rate for the Arabian Sea of 60 Tg N a[1] as I have described above, and, in my opinion, using this assumption introduces a conservative bias to the estimate. With this assumption, R1 becomes 0.33. I assumed a lower proportion

of unfractionated N_2 during water column denitrification in the Eastern Tropical Pacific Ocean. In a preceding paragraph, I arrived at a value of 65 Tg N a^{-1} by multiplying the ETS values for this region by 1.3. R1 in this case would be 0.23 suggesting that about one fourth of the water column excess N would be associated with processes that do not fractionate. One could argue therefore that I should split the difference and assume in Table 1 that 28% or 42 Tg N a^{-1} of the total water column denitrification behaves like sedimentary denitrification and is "unfractionated" rather than the 50 Tg N a^{-1} originally indicated. I will make this correction, but given the uncertainties, this is a trivial difference. I will re-write the offending sections of this paper to clarify these issues. I need to make it clear that when talking about processes that could create N_2 in the water column with little or no isotope fractionation, I am basically considering the oxidation of ammonium and organic-N during canonical denitrification, anammox, and the other ammonium and organic-N oxidations suggested in Fig. 1

NG points out that Deutsch et al. (2004) suggested that an isotopic dilution effect, reduces the ratio between sedimentary and water column denitrification from the 3.7 suggested by Brandes and Devol (2002) to $\sim$ 2.7. Altabet (2006, this journal) suggests that the ratio could be much lower, maybe as low as $\sim$ 1, but he includes the water column N_2 arising from ammonium and organic N oxidation in his ratio whereas I lump this with sedimentary denitrification when speaking of what I prefer to call the "unfractionated/fractionated ratio" (Codispoti et al., 2001). When I wrote this portion of the paper, I was blissfully unaware of the discussion surrounding this ratio, ***but note that my denitrification rate estimates do not depend on this ratio.*** I do have a section of the paper that assumes a ratio and considers what variations in the unfractionated vs fractionated (ammonium and organic-N oxidation) ratio in the water column would imply for the proportions of total (fractionated + unfractionated) water column denitrification to sedimentary denitrification and what would emerge as the total sedimentary + water column rate. Given the uncertainty over what the ratio of sediment (unfractionated) to water column rate (fractionated) might be, I fear that this portion of the paper merely muddied the water, plus it really boils down to the fact that increases in "unfraction-

ated" water column denitrification would lower sedimentary denitrification by the same amount, ***assuming a constant ratio.*** I will re-write this section of the manuscript, and I will re-visit this matter in my response to JS's review (see below). ***The main point of putting the unfractionated/fractionate ratio in Table 1 is to show that, even in a steady-state ocean, a large total water column denitrification rate does not necessitate a $>$ 3X larger sedimentary rate because a significant fraction of the N_2 produced may arise from processes in the water column that may mimic the isotopic effect on N of sedimentary denitrification.*** Of course, if the ocean is going through a decadal to century scale transition, the ratios of sedimentary to water column denitrification arising from large-scale isotope budgets may not apply to the present-day ocean, as suggested by Altabet (2006, this web site), Codispoti et al. (2001) and SWAN's review. In my revision, I will attempt to clarify the notion that if the fixed-N budget has a large imbalance, then it is a likely effect of the Holocene-Anthropocene transition.

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