Biogeosciences Discuss., 3, S1006–S1014, 2007
www.biogeosciences-discuss.net/3/S1006/2007/

Biogeosciences
Discussions

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

Received and published: 30 January 2007

Section III: Response to Drs. Jorge Sarmiento and S.W.A. Naqvi and Conclusion

Response to Dr. Jorge Sarmiento’s (JS) review:

The first several paragraphs of JS’s review give a synopsis of the papers/ideas/ and literature “conversations” that may be pertinent. Amongst some complimentary comments for which I thank him, he has two major critiques, 1) where are the new data and new break-through insights, and 2) it seems to have been written mostly as a counter to Gruber (2004). I gave an answer to 1) in my general comments at the beginning of this response. 2) I plead guilty, **in part,** to 2), as I think that the arguments about the sedimentary contribution to the water column signal in the vicinity of suboxic regions in

Gruber (2004) are incorrect and that the implications of the *excess* N_2 values in Codispoti et al. (2001) were not interpreted properly. I do apologize, however, if any of my comments seemed unfair, and I acknowledge that more information on the *excess* N_2 values in Codispoti et al. (2001) might have helped prevent mis-interpretation. This problem has since been alleviated with the publications of Devol at al. (2006a &b). More importantly, I think that this contribution is more than a rebuttal of Gruber (2004). I strongly believe that a review of all of the pathways and potential sites for denitrification and nitrogen fixation is in order and that I was in a good position to synthesize the results of recent studies involving a wide-range of disciplines. I am guessing that this is one of the reasons why I was asked to speak at the SPOT-ON meeting and to submit this manuscript.

JS expresses disappointment that I did not emphasize what we could do in the future to resolve these disagreements. I thought that I at least strongly implied, that we should expand the range of environments in which we look for nitrogen fixation and denitrification and attempt to estimate rates in these environments based on experiment. I think that, here, we come to the nub of our differing views (although there is much we agree about). JS suggests a number of worthwhile activities, but most involve looking at global scale distributions. There is nothing wrong with what he suggests (but please include the Arctic), but in the general comments portion of this response, I have given reasons why we still need studies that directly measure the separate gross rates of denitrification and nitrogen fixation even if such studies are not capable of integrating over large temporal and spatial scales. In addition, knowing some of the details of the distribution of denitrification rates vs depth in different regions and the extent to which nitrogen fixation and denitrification may be juxtaposed have a bearing on what ratio is appropriate for unfractionated to fractionated denitrification.

JS had problems with the budget, as presented in Table 1. He suggests that I have picked the “highest estimate for denitrification in every case”. I think that my answer to NG’s comments (see Section II) shows that I could have picked higher estimates, so I dispute this statement. JS asks for uncertainty estimates. In asking for error estimates to be added to the values in Table 1 *a la* Gruber and Sarmiento (1997), I think that we see, once again, a difference in outlook between JS and myself. I really don't have faith in such error estimates, since we have not yet even begun to obtain a comprehensive picture of potentially important sites and pathways such as anammox, and denitrification in sea ice, suspended aggregates, etc. My view is that the estimates that I have made in Table 1 are likely to prove to be too low, that is why I have added the plus signs after them. To describe Table 1 as a "Pro Forma" budget was a bit tongue in cheek, but it had a serious purpose. I assumed that the reader has some acquaintance with financial jargon. To base an investment on a "pro forma" financial statement is a bit like buying the Brooklyn Bridge! I thought that I had explained this in the footnote to Table 1, but I will clarify this matter in the revision. With respect to JS's request to add all of the sources and sinks, I purposely left them out of this budget in Table 1 to concentrate on the issues where I believe that the battle is joined. Here is a compromise on how I will revise Table 1; 1) I will add the error estimates given by Gruber and Sarmiento and Gruber for their budgets; 2) I will add a footnote that mentions the uncertainties; and 3) I will discuss/include the other source and sink terms in footnotes to this table.

In the next portion of this review, JS comments on the range of estimates for sedimentary denitrification. It is true that, as written, Codispoti et al.'s 2001 sedimentary denitrification rate estimate relied heavily on the results of Middleburg, et al. (1996) amplified by the emerging knowledge vis a vis anammox and iodate and trace metal mediated pathways to N_2 that might occur in sediments, and undergirded by our own observations (e.g. Devol et al., 1997). But oh how it must have warmed the cockles of JS's heart to write his comments about our reliance on a modeling study for the Codispoti et al. (2001) sedimentary denitrification rate estimate! Actually, I think that we both agree that models can be useful, and that no matter how useful a model is, it is perhaps not the best terminology to refer to model output as data! As I remember, Middelburg et al. (1996) provided one of the few estimates for denitrification in slope and deeper sediments, but in assessing his results, we had some of our results from shallower sediments to hang our hats on. Moreover, Middelburg et al. (1996) took the trouble to compare their model outputs to data. Interestingly, their estimate for sedimentary denitrification in the Arctic is similar to a value that I arrived at in a preliminary analysis based on nutrient distributions. So, the estimate of Codispoti et al. (2001) was not totally reliant on model output.

JS outlines Middleburg's modeling results (230-285 Tg N a^{-1}) based on a N_2:C ratio of 0.8, and gives the values from a model that he and colleagues are working on. Based on a N_2:C ratio of 0.8, he and his colleagues suggest an oceanic sedimentary denitrification rate of 154 Tg N a^{-1}. Based on a ratio of 1.0, JS suggests a rate of 190 Tg N a^{-1}, but this ratio could be a lot higher. The stoichiometry of Van Mooy et al. (2002) suggest a ratio of N_2 produced to C oxidized of 1.25. In addition, the strong ammonium gradients in sediments may be analogous to the strong ammonium gradients that underlie the suboxic zone in the Black Sea, and such a situation is favorable for anammox which could lead to even higher ratios (see Kuypers et al., 2006). Multiplying 190 by 1.25 gives a sedimentary rate of 238 Tg N a^{-1}. This type of consideration, by the way, is one of the reasons that Codispoti et al. (2001) suggested a sedimentary denitrification rate somewhat higher (300 Tg N a^{-1}) than suggested by Middelburg et al.(1996, 230-285 Tg N a^{-1}). Indeed, Middelburg et al. (1996) explicitly addressed this issue and suggest that including ammonium oxidation by nitrate in their standard run would have increased the estimate of sedimentary denitrification from 285 to 318 Tg N a^{-1}. I think that their correction is parsimonious (285x1.25/0.8 = 445 Tg N a^{-1}, but they were prescient enough to consider the possibility. Direct determination of N_2evolution from sediments gives higher rates than would be inferred from older studies and several recent studies. Devol (1991) suggested that direct measurements of nitrogen gas fluxes from the Washington State shelf and upper slope were 4-5 times greater than those estimated by indirect methods prevailing at that time. His shelf values ($<$ 150 m), when scaled up to the world-wide shelf area, yield a shelf-sediment denitrification rate of $\sim$ 500 Tg N a^{-1}. Similar values from the Arctic Ocean shelf taken in late summer and early spring (heavy ice, pre-bloom) scale up to a world-wide shelf estimate of 170 Tg N a^{-1}(Devol et al., 1997). The 0-200 m (shelf) sedimentary area comprises only 7.5% of the total area of oceanic sediments (Menard and Smith, 1966). Devol (1991) gives a 600 m rate that when scaled up to the world wide area of sediment between 200 and 2000 m gives a rate of $\sim$120 Tg N a^{-1}. Lehmann et al. (2005) give a rate of 1.3 Tg N a^{-1} for the abyssal Bering Sea based on nitrate deficits in the water column. They suggest that their rate is more than 3x higher than high end estimates of abyssal sedimentary denitrification, but I am guessing that these prior estimates are probably low-biased because of N_2:C ratios that are too low (see above). It is possible that direct determinations of the N_2 flux out of the sediments might yield a rate several times higher *a la* Devol (1991). If we assume that the "true" denitrification rate at depths $>$ 2000m in the Bering Sea is 2 Tg N a^{-1} and divide this value by 5 to obtain an average rate for sediments at depths greater than 2000m, we obtain a global rate of 118 Tg N a^{-1}. I will take a closer look at the modeling results and the data on sedimentary denitrification rate in my revision. This preliminary foray through the literature suggests that an estimate of 300 Tg N a^{-1} for the global oceanic sedimentary rate can be defended without reference to the models, but wait, there's more!

I think that there are several reasons why the traditional modeling and data approaches outlined in the preceding paragraph may be low-biased. It is not clear to me for example, that the existing models, satellite data, and sediment trap observations adequately account for boundary processes such as bed-load transport and turbidity currents, canyon dynamics, etc. that occur over outer shelves, and slopes. Lehmann et al's. (2005) paper gives an example of how downward transport of organic matter may enhance abyssal sedimentary denitrification near a slope. In the Chukchi Sea, my Shelf Basin Interactions project colleagues have data demonstrating that the export of organic matter is focused in Barrow Canyon (e.g. Moran et al., 2005). I also think that there are productivity hotspots not included in satellite data. For example, canonical estimates of primary production in the Arctic have been too low (e.g. Codispoti et al., 1991) and hard to determine via satellite observations. For example, recent observations suggest highest rates of primary productivity in subsurface layers embedded in the pycnocline of the Chukchi Sea with a hitherto under appreciated “hotspot” at the head of Barrow Canyon with maximum productivity of $\sim$ 10 g C m^{-2} d^{-1} (Hill and Cota, 2005). The Arctic represents only a small portion of the earth’s surface, but the Arctic Ocean and its marginal and adjacent seas contain about 25% of the global shelf sediments. By the way, have we sufficiently considered that anammox bacteria may be chemo**autotrophs** (e.g. Kuypers et al., 2006) thereby providing an extra challenge to models based on the carbon/organic matter supply to sediments? Penultimately, there are the non-traditional sites of sedimentary denitrification mentioned in my manuscript, and finally I have to ask if we have thought enough about the possible enhancement of abyssal denitrification in sediments near mid-ocean ridges and flanks, and near cold-seeps due to the chemoautotrophic communities that exploit the redox gradients. All in all, I think that I can defend the proposition that the rate of sedimentary denitrification is at least 300 Tg N a^{-1}, and I will bring additional rate data to bear in the revised manuscript.

The next portion of JS’s review involves the ratio of unfractionated to fractionated denitrification and scenarios that involve this ratio. I have already stated in my response to NG (see Section II) that this ratio is not vital to any of my estimates for source and sink terms, and that if the ocean is going through a transition, there is reason to think that the ratios obtained from isotope budgets may not apply. I will beat my breast, however, and acknowledge that I muddied the water as I became entranced about how things would proportion themselves given different amounts of fractionated vs unfractionated denitrification in the water column. SWAN rightly points out that we are really just guessing as to what the isotope signature of anammox is at the present moment, adding another source of uncertainty with respect to this ratio. I have already noted that Altabet’s (2006) ratio of $\sim$1 is a sedimentary to water column ratio, not an unfractionated to fractionated ratio, so changing the terminology would raise his suggested ratio to $\sim$1.5. In addition, there are strong suggestions that some of the organic-N supplied to the suboxic waters in the Arabian Sea are produced by nitrogen fixation

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

(e.g. Brandes et al., 1998, Naqvi, in press) and therefore isotopically light. I think that including this feature might raise the unfractionated/fractionated ratio in Altabet's analysis. With respect to the arguments about lowering the 3.7 ratio suggested by Brandes and Devol (2002) based on the concentrations of nitrate associated with the export of "heavy" nitrate, a lot depends on the average weighted nitrate concentration over which denitrification occurs. Therefore, please note that Codispoti et al's. (2001) nitrate deficit method, and the excess N_2 values suggest that the denitrification zone may extend deeper than initially thought and therefore include higher nitrate concentrations. Similarly, some of the denitrification that occurs in the Eastern Tropical North Pacific is associated with nitrate concentrations of 40 μM or more. So, given the uncertainties in what this ratio should be, I am going to assume that the "real ratio" for unfractionated to fractionated denitrification for several hundred year or longer periods is somewhere between $\sim$ 2-4. Since, there is no requirement that this ratio to apply over a transition period, the main value of this ratio for my analysis is that it suggests that one should expect sedimentary and water column denitrification to have similar magnitudes. Once we have a better handle on all of the factors that make up this ratio, it has the potential to impose a much stricter constraint during the Holocene.

JS's scenarios may be moot at this point since the revision will de-emphasize the unfractionated/fractioned denitrification ratio. Nevertheless, I would like to note the following:

Scenario 1: This scenario seems to suggest that JS thinks that the *excess* N_2 signals contain a global sedimentary denitrification signal rather than a local one. I have dealt with this in my response to NG. I think that this scenario must be rejected on this basis, as well as on the basis of a unfractionated/fractionated ratio that is poorly known.

Scenario 2: JS chooses a total water column rate of 126 Tg N a^{-1} for this scenario that results from a calculation that starts with his modeled sedimentary denitrification rate of 190 Tg N a^{-1}. He also assumes an unfractionated/fractionated ratio of 3, and that the water column rate is evenly divided between fractionated and unfractionated denitrification. I note that starting out with a lower sedimentary rate will just about guarantee a lower total oceanic denitrification rate, and I have given my reasons for thinking that a sedimentary rate of 190 Tg N a^{-1} is too low. I can understand how JS assumed that my water column rate in this manuscript assumes that half of the water column rate is fractionating and half non-fractionating based upon what was stated in Codispoti et al (2001). We were just starting to deal with these concepts (before publication of Brandes and Devol, 2002), but, in fact, in this paper I assume that 28% of the water column denitrification rate is non-fractionating as stated in my response to NG. I will clarify this point in the revision.

If we assume a constant unfractionated/fractionated ratio, just for fun, we can come up with the following types of scenarios based on the assumption that 28% of water column denitrification is unfractionated. a) If we take the "true" sedimentary denitrification rate to be $\sim$ 300 Tg N a^{-1} and assume that 28% of the water column denitrification is unfractionated, then to obtain an unfractionated/ fractionated ratio of 3 would require, 160 Tg N a^{-1} of water column denitrification of which 45 Tg N a^{-1} is unfractionated. This would give a total denitrification rate of 460 Tg Na^{-1}. If we start with a water column denitrification rate of 150 Tg N a^{-1} as the "true" value, the sedimentary denitrification rate would be 282 Tg N a^{-1} and there would be 42 Tg N a^{-1} of unfractionated denitrification in the water column, with a total oceanic denitrification rate of 432 Tg N $^{-1}$. Taking, Deutsch et al.'s (2004) suggested unfractionated/fractionated ratio of 2.7 and a "true" sedimentary rate of 250 Tg N a^{-1}, total water column denitrification would be 150 Tg N $a^{-1}$of which 42 Tg N a^{-1} would be unfractionated, and the total oceanic denitrification rate would be 400 Tg N a^{-1}. Taking the "true" water column rate to be 150 Tg N a^{-1} would, of course, give us the same answer. If I were a theoretical physicist obtaining the same answer with the last two selections would give me pause for thought (He said, tongue in cheek!). Note that taking 400 Tg N a^{-1} from denitrification and adding the depositional and nitrous oxide sinks would still justify the title of this paper.

Response to Dr. S.W.A. Naqvi's (SWAN) Review:

This reviewer was in general agreement with the main points of the paper, and recommended publication with minor revision. He noted a few minor technical/proof reading errors that I will correct, and made a further argument for the possibility of accelerations in the water column rate by pointing out that the Bay of Bengal contains a sizeable body of water that is close to suboxic.

SWAN also added to the arguments suggesting that the constraints of isotope budgets on the ratio of sedimentary to water column denitrification are probably weak over several-decade or shorter time-scales. In addition, he noted that there is considerable uncertainty about what the unfractionated/fractionated ratio should be over longer periods. As stated earlier, I am going to de-emphasize the significance of this ratio in my revision, and this ratio never formed the main basis for my estimates of sedimentary or water column denitrification.

Conclusion:

This response to the reviewers has been both exhausting and exhilarating! It has convinced me to take another stab at obtaining some funding to investigate the questions that we are debating! I thank the reviewers for their stimulating comments, and look forward to further exchanges. ***Lay on McDuff, and damned be he who cries Hold, Enough!*** (with apologies to the Bard).

Interactive comment on Biogeosciences Discuss., 3, 1203, 2006.