

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

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One of my all-time favorite papers is Codispoti and Christensen [1985], in which the authors proposed an unbalanced fixed-N oceanic budget with sources of 90 Tg N/yr, and sinks of 158 Tg N/yr. Given my graduate education, which was similar to that described by Codispoti in Codispoti, et al. [2001], where “the principle of parsimony encouraged many to assume an ocean that was in steady-state,” (Note: Codispoti also included “limited observations” as an additional reason for assuming steady-state, but in fact my experience was that the observations tended to support the steady-state assumption), I found this analysis to be highly provocative. It was thus very exciting

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for me to be able to make a contribution to this debate with Niki Gruber in Gruber and Sarmiento [1997], where we found a much larger nitrogen fixation rate in the North Atlantic than had previously been estimated. Extrapolated globally, our pre-industrial total source estimates increased to 181 +/- 44 Tg N/yr, now roughly in balance with a slightly revised total pre-industrial sink estimate of 184 +/- 29 Tg N/yr.

In the meantime, however, there began to be indications that denitrification might be larger than we had thought. In particular, in a paper published in December of 1996 (our paper appeared in June of 1997, but we missed this earlier study), Middelburg, et al. [1996] used a sediment model to estimate a sedimentary denitrification sink of 230 to 285 Tg N/yr, as contrasted with our estimate of only 85 +/- 30 Tg N/yr based on Codispoti and Christensen [1985]. In 2001, Codispoti, et al. [2001] dramatically upped the ante with a new synthesis of the fixed-N budget in which the most important modification from earlier work was a denitrification estimate of >450 Tg N/yr! The basic elements of the 2001 synthesis of fixed-N sinks as summarized also in the new manuscript by Codispoti are the following:

CODISPOTI DENITRIFICATION BUDGET:

(1) **SEDIMENT DENITRIFICATION:** The large Middelburg, et al. [1996] model based estimate of 230-285 Tg N/yr for global sediment denitrification, supported by various and sundry in situ measurements, and revised upwards to 300 Tg N/yr to account for production of N₂ by the annamox reaction.

300 Tg N/yr

(27) **WATER COLUMN DENITRIFICATION:** The excess N₂ measurements in the Arabian Sea reported on by Codispoti, et al. [2001] and now starting to appear in various papers by Devol et al., which suggest that the N* deficit is only seeing about half the total effect of denitrification. Extrapolated globally, this increases the water column

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denitrification rate estimate to 150 Tg N /yr.

150 Tg N/yr

(3) RATIO OF NON-FRACTIONATING TO FRACTIONATING DENITRIFICATION: The oceanic ^{15}N isotopic budget analysis of Brandes and Devol [2002], which implied that the ratio of fractionating denitrification (thought to occur primarily in the water column) to non-fractionating denitrification (thought to occur primarily but not exclusively in the sediments), should be about 3.5. Assuming that ~ 50 Tg N/yr of the N_2 in the water column is produced by non-fractionating processes in the water column (per Codispoti) gives a fractionating denitrification of $(150 - 50) = 100$ Tg N/yr in the water column, and a total non-fractionating sediment plus water column denitrification of $(300 + 50) = 350$ Tg N/yr for an overall ratio of 3.5, as required by Brandes and Devol [2002].

3.5 (unitless)

The fixed-N source estimates increased modestly to ~ 250 Tg N/yr (supported by additional analyses such as that of Deutsch, et al. [2001]), which gave an imbalance of order 200 Tg N/yr in the annual budget, almost three times larger than that proposed by Codispoti and Christensen [1985]!

What has happened since 2001 that merits this new review of the problem by Codispoti? Scientifically, there have been many new measurements, but there are no breakthrough insights comparable to the sediment denitrification estimate and N_2 and isotopic measurements that formed the backbone of the Codispoti, et al. [2001] paper. From what I infer, a major motivation for this new paper is that Gruber in 2004 published another synthesis of the nitrogen cycle in which he basically stuck to our old numbers and went through a long series of arguments discounting the larger denitrification estimates of Codispoti, et al. [2001] (cf. Gruber [2004]). In this new manuscript, Codispoti comes back with a counter-analysis disagreeing with Gruber [2004] and de-

fending the Codispoti, et al. [2001] analysis.

Before proceeding with my review, I should point out in all fairness that I am squarely on the Gruber side of this disagreement (cf. Sarmiento and Gruber [2006]). My first reaction upon reading this manuscript was thus to begin marshalling all the arguments as to why the ocean denitrification rates could not be as large as claimed by Middelburg, et al. [1996] and all the other studies described by Codispoti. These will come in a moment, but before that, I think the most important message of this historical reconstruction of the debate is that we do not have sufficient constraints on the fixed-N budget of the ocean. What we really need in order to solve this problem are some breakthrough insights and/or new measurements.

From this point of view, I must confess to being somewhat disappointed in Codispoti's paper in that I think the most appropriate emphasis in the end would have been on what we could do in the future in order to truly resolve these disagreements other than by arguments that tend to degenerate into hand-waving. I have a few suggestions: (1) model simulations of how the oceanic and atmospheric distribution of properties would change in time if the fixed-N budget were as far out of balance as Codispoti's budget shows it to be. I have a feeling that this will prove highly instructive, and I am doing this right now with Curtis Deutsch. (2) A global scale map of the dissolved N₂ distribution. In combination with tracers and ocean model simulation analyses, such observations should prove to be a powerful constraint on denitrification in the ocean. While we are at it, I would think that a global scale map of del15N would also prove useful. I note that GEOTRACES includes del15N measurements, but not N₂. (3) Improved quantitative rate estimates from tracers like N* and del15N and N₂ including a more thorough exploration of uncertainties especially using models as testing grounds. I am certain others could come up with better suggestions. (Note: I personally tend to be skeptical of our ability to get global estimates from in situ rate measurements due to the large spatio-temporal variability of biological processes in the ocean, which is why I have chosen to emphasize large scale observational and modeling constraints.)

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Does this paper add anything constructive or new to the disagreement over the fixed-nitrogen budget? Yes, in some respects. This is not a discussion that has been resolved, and anything that stimulates continued research on this important problem is good. Codispoti's speculations on how the budget might be closed are stimulating. This paper is fun to read and gets the adrenaline flowing; as I am sure Codispoti intended it to do. However, I believe that it is possible for reasonable people to disagree with him on his budget, and in particular with his assertion that "reducing the sink term is not the answer." Rather than go into a detailed review of all of Codispoti's arguments, I will confine my comments below to what I see as the most important points of his analysis.

As regards Codispoti's budget, I feel that his propensity to pick the highest estimate for denitrification in every case gives an unfair impression of how great the uncertainties are. His Table 1 gives a single number with no estimate of uncertainty or of the range of estimates. Before this paper is accepted for publication, there should be some attempt made to rectify this problem. Furthermore, the table should include all estimates for fixed-N addition, not just nitrogen fixation. It is confusing that the total shown in the table is not equal to the sum of the numbers given above.

As regards Codispoti's assertion that "reducing the sink term is not the answer," I offer the following thoughts on the total denitrification estimate, hoping that perhaps this will lead to a more flexible view if not a change of mind.

ALTERNATIVE TO CODISPOTI BUDGET:

(1) **SEDIMENT DENITRIFICATION:** One thing that reading this manuscript of Codispoti's made me realize is how strongly his argument depends on the Middelburg, et al. [1996] model-based sediment denitrification estimate. This is perhaps a bit ironic, considering that Codispoti, et al. [2001] et al. were moved to criticize "...the tendency to call mathematical outputs, 'data'" (a tendency which I also deplore despite being a modeler myself).

In recent work that is reported on in Sarmiento and Gruber [2006], John Dunne and I with others have re-done the Middelburg, et al. [1996] meta model estimate of global denitrification (a paper by Dunne et al., with further details is in preparation). We obtain 0.165 Pg C/yr, equivalent to a denitrification rate of 154 Tg N/yr using the Middelburg, et al. [1996] N₂:C ratio of 0.8, 190 TgN/yr if we use a ratio of ~1, which assumes that all ammonium gets converted to N₂. Our global total benthic remineralization of 2.5 Pg C/yr, is comparable to other estimates.

This result falls well below the Middelburg, et al. [1996] curve of global denitrification versus total benthic remineralization (their Figure 5). I suspect that our lower denitrification estimate arises from a different frequency distribution of total carbon fluxes. Figure 8 from Middelburg, et al. [1996] shows that the % of organic matter that gets remineralized by denitrification varies considerably (though systematically) with the per unit area organic carbon flux. If the frequency distribution of our fluxes is different than theirs, the mean % will also be different. Middelburg, et al. [1996] use a flux distribution based on the oceanic hypsometric curve and a relationship between the organic matter flux and ocean depth, whereas we use satellite based estimates of ocean biological production together with remineralization curves based on sediment trap observations in a spatially resolved calculation.

~190 Tg N/yr (Scenario 1 & 2b)

~127 Tg N/yr (Scenario 2a)

(see item (3) for scenario descriptions).

(2) RATIO OF NON-FRACTIONATING TO FRACTIONATING DENITRIFICATION: The ratio drops to <3 when corrected for the Deutsch, et al. [2004] dilution effect to Brandes and Devol [2002] (cf. Gruber [2004]).

<3 (unitless)

(3) WATER COLUMN DENITRIFICATION: If we assume that all “true” water column

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denitrification is fractionating, then the water column denitrification implied by the sedimentary denitrification must be $\sim 190/3 = 63$ Tg N/yr. This number is consistent with the water column denitrification estimates of Deutsch, et al. [2001] and Howell, et al. [1997], but about a factor of 2 lower than implied by the excess N₂ measurements in the Arabian Sea reported on by Codispoti, et al. [2001]. Two extreme scenarios for resolving this issue are:

SCENARIO 1: The most conservative assumption is that half the water column N₂ signal must be due to sediment denitrification. In that case, the total denitrification will sum to $190 + 63 = 253$ Tg N/yr, and the fixed-N budget will be in balance. Note: as regards why the sediment denitrification signal does not also show up in the N* data used in some of the water column denitrification estimates, there are several lines of evidence suggesting that this is due primarily to dilution by remineralization of high N:P organic matter produced by nitrogen fixers, e.g., paragraph 46 of Sigman, et al. [2005]. Overall, this is the scenario that I tend to favor. Given that most of the sediment signal of denitrification has to appear in the water column somewhere and that a high fraction of this occurs in high productivity continental margin regions, it seems reasonable to assume that much of it will appear in the oxygen minimum zones where the big water column denitrification signals occur.

SCENARIO 2: Codispoti raises a valid question as to whether there is enough sediment exposure of the corresponding density surfaces to account for such a large N₂ excess. This should be possible to test with models. He also provides a series of other arguments as to why the conservative assumption might be incorrect. If we assume for the sake of this discussion that all the N₂ excess is in fact due to non-fractionating water column denitrification, as does Codispoti, then the total water column denitrification must be ~ 126 Tg N/yr. However, this violates the N-15 budget because the ratio of non-fractionating to fractionating denitrification in this case would be $(190+63)/63=4.0$.

Two possible ways to resolve this problem are: **SCENARIO 2a:** reduce the sediment denitrification by 63 to 127, giving a non-fractionating to fractionating ratio of $(127 +$

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63)/63 \sim 3, with the same total denitrification as in Scenario 1 of 127 + 126 = 253 Tg N/yr. This is a big reduction in the sediment denitrification rate, but while I do not tend to favor this scenario, I am not confident enough in the sediment denitrification estimates to totally eliminate this possibility. SCENARIO 2b: increase the fractionating water column denitrification to 95 Tg N/yr, and the total water column denitrification to 190 Tg N/yr. This gives a non-fractionating to fractionating ratio of (190 in sediments + 95 in water column)/95 = 3, and a total denitrification rate of 380 Tg N/yr. The fixed-N budget will then be out of balance, though only about half as much as claimed by Codispoti.

\sim 63 Tg N/yr (Scenario 1)

\sim 126 Tg N/yr (Scenario 2a)

\sim 190 Tg N/yr (Scenario 2b)

I tend to favor Scenario 1 whereas Codispoti, in addition to going for the larger Mid-delburg, et al. [1996] sediment denitrification estimate, favors a variant of Scenario 2b. However, the overall evidence in favor of or against any one of these scenarios is I think insufficient to assert that any one of them is anything more than marginally more or less likely. I reiterate: what we truly need to resolve this controversy are new observational and modeling constraints.

REFERENCES

Brandes, J. A., and A. H. Devol (2002), A global marine fixed nitrogen isotopic budget: Implications for Holocene nitrogen cycling, *Global Biogeochemical Cycles*, 16, 67.61-67.14, doi:10.1029/2001GB001856.

Codispoti, L. A., J. A. Brandes, J. P. Christensen, A. H. Devol, S. W. A. Naqvi, H. W. Paerl, and T. Yoshinari (2001), The oceanic fixed nitrogen and nitrous oxide budgets: Moving targets as we enter the anthropocene?, *Scientia Marina*, 65, 85-105.

Codispoti, L. A., and J. P. Christensen (1985), Nitrification, denitrification and nitrous oxide cycling in the Eastern Tropical South Pacific Ocean., *Marine Chemistry*, 16, 277-300.

Deutsch, C., N. Gruber, R. M. Key, and J. L. Sarmiento (2001), Denitrification and N₂ fixation in the Pacific Ocean, *Global Biogeochem. Cycles*, 15, 483-506.

Deutsch, C., D. M. Sigman, R. C. Thunell, A. N. Meckler, and G. H. Haug (2004), Isotopic constraints on glacial/interglacial changes in the oceanic nitrogen budget, *Global Biogeochemical Cycles*, 18, GB4012, doi:4010.1029/2003GB002189.

Gruber, N. (2004), The dynamics of the marine nitrogen cycle and its influence on atmospheric CO₂ variations, in *Carbon Climate Interactions*, edited by T. Oguz and M. Follows, Kluwer Academic, Rotterdam.

Gruber, N., and J. L. Sarmiento (1997), Global patterns of marine nitrogen fixation and denitrification, *Global Biogeochemical Cycles*, 11, 235-266.

Howell, E. A., S. C. Doney, R. A. Fine, and D. B. Olson (1997), Geochemical estimates of denitrification in the Arabian Sea and the Bay of Bengal during the WOCE, *Geophysical Research Letters*, 24, 2549-2552.

Middelburg, J. J., K. Soetaert, P. M. J. Herman, and C. H. R. Heip (1996), Denitrification in marine sediments: A model study, *Global Biogeochemical Cycles*, 10, 661-673.

Sarmiento, J. L., and N. Gruber (2006), *Ocean Biogeochemical Dynamics*, Princeton University Press, Princeton.

Sigman, D. M., J. Granger, P. J. DiFiore, M. M. Lehmann, R. Ho, G. Cane, and A. Van Geen (2005), Coupled nitrogen and oxygen isotope measurements of nitrate along the eastern North Pacific margin, *Global Biogeochemical Cycles*, 19, GB4022, doi:10.1029/2005GB002458.

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