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Biogeosciences
Discussions

Interactive comment on "Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin, Venezuela" *by* E. Montes et al.

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We find comments from our reviewers accurate and very helpful, and will undoubtedly allow us improve the quality of our observations. Both reviewers showed concerned about two major areas: background N2/Ar ratios and the potential effects of phosphate adsorption by reduced metals on DIN deficit calculations we present in this study. We will carefully address these and all comments as described in detail below, and are confident that the revised version of our manuscript will have responded effectively to our reviewers' concerns.

Comments from Anonymous Referee #1 General Comments: This paper presents N2/Ar data from the Cariaco Basin. The data and analysis presented in this paper are interesting, but calculations need to be redone to take into account background

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Interactive Discussion

Discussion Paper

levels of N2/Ar. I think the authors knew this but did not realize that a profile of N2/Ar from BATS had been published (Nicholson et al., 2010), which can be used to estimate the background. The paper has interesting discussion about variability of N2/Ar over time. However, the authors almost ignore the high N2/Ar concentrations in the sulfidic zone. As this includes most of the biologically produced N2 in the Cariaco, I think it deserves more attention.

Specific Comments: 1. N2/Ar background First of all, the authors need to take the background into account with their N2/Ar data. The N2/Ar ratio in all oceanic deep water is supersaturated due to undersaturation of argon (Hamme et al., 2007). Deepwater from BATS (representing Atlantic deep water) has a 1% supersaturation in N2/Ar (Nicholson et al., 2010) while at 150 m at BATS, the depth of source waters for the Cariaco Basin, N2/Ar is 0.6% supersaturated (Nicholson et al, 2010). The authors should try to estimate the background N2/Ar either using the data from BATS (Nicholson et al., 2010) as the background or as an end member in some sort of mixing model (see Fuchsman et al., 2008 or Manning et al., 2010). With a better idea of the background (abiotic) N2/Ar ratio, the authors can better examine the excess N2 both in the sulfidic zone and the oxic/anoxic transition.

Response: We will use normalized N2/Ar ratios from BATS presented by Nicholson et al. (2010) and unpublished data from this time-series location collected by Altabet's group to estimate background concentrations of excess N2 in Cariaco. Although we have some evidence that the basin's source water is from the eastern subtropical North Atlantic, we think that BATS waters can serve as a good reference for this analysis. Under the assumption that the normalized N2/Ar ratio in bottom waters in Cariaco (∼17 degrees C waters) is ∼0.6% supersaturated, we expect an abiotic excess N2 of ∼4 micromoles N kg-1 in the deepest portion of the water column. This approach will allow us to provide a more accurate balance between the DIN deficit and the concentration of biogenic N2 in the basin. We believe, however, that including background excess N2 concentrations will not drastically change our biogenic N2 estimates in Cariaco, or at least not as importantly as in Pacific Ocean or Arabian Sea's oxygen minimum zones, since the basin is essentially filled with surface waters.

2. N2/Ar in the sulfidic layer: The N2/Ar depth profile comes to a maximum around 300 meters, but remains greatly elevated at depth. Notably, deep sulfidic water in the Cariaco Basin has 2.5% supersaturation in N2/Ar– much higher than the input of 0.6% supersaturation (Nicholson et al, 2010). Thus, it is quite likely that the majority of the 2.5% supersaturation in sulfidic waters is from biological processes. The volume of sulfidic water is large, meaning that N2 production from intrusions is the most important form of N2 production in the Cariaco Basin. This depth profile is markedly different from the Black Sea, another permanently stratified sulfidic basin. In the Black Sea, where most of N2 production occurs in the suboxic zone, N2/Ar supersaturation decreases with depth below the suboxic zone (Fuchsman et al., 2008) even though the deep water is quite old. The authors address N2 concentration at depth in one sentence in the first paragraph of page 10561 by saying that "Excess N2 might be expected to continue to increase below the oxic/anoxic interface since waters below the sill have accumulated N2 from denitrification supported by nitrate-rich sill-depth Caribbean Sea waters that filled the basin (Richards and Benson, 1961). In contrast, however, N2 excess decreased by 1-3 umol/kg below this depth." Can the authors walk the reader thru this a little more? Richards and Benson (1961) calculate that there should be 22 uM N excess in the sulfidic zone by assuming that the water in the Cariaco was originally from the Caribbean and had nitrate concentrations similar to the Caribbean. That calculated N2 excess is approximately what you see here, less than the N2 excess seen at the interface. The authors should cite and explain this calculation more explicitly. Richards and Benson (1961) act as if the N2 in the sulfidic zone was formed when the Cariaco Basin first went anoxic. It is more likely to be a constant process. How much is the nitrate input from Caribbean waters on a yearly basis? Can the authors create a more complete conceptual model of N2 production in the Cariaco basin including production in the sulfidic zone? The authors assumed in this paper that heterotrophic denitrification and anammox were the only sources of biogenic N2 (page 10554 line 18). This is

not a good assumption given that the Cariaco Basin has sulfide. The authors did not measure sulfide, and the presence of sulfide is greatly underplayed in the paper. Do nitrate rich Caribbean waters intrude into the sulfidic zone of the Cariaco basin? If so, it seems quite likely that the elevated N2/Ar at depth is due to thiodenitrification at depth. The authors need to specifically address this. Does this scenario make sense? Does Figure 10, comparing the DIN deficit and N2 excess include values from the sulfidic zone?

Response: The discussion on the accumulation of excess N2 in the sulfidic portion of the water column will be expanded in the context of Richard and Benson's work and the processes mentioned here, namely nitrate influx from intrusions of Caribbean intermediate waters and thiodenitrification, in addition to the mechanisms already outlined in the manuscript. We will also add sulfide data from the time-series location during 2008 and 2009 to support this discussion. Figure 10 does include excess N2 values from the sulfidic layer.

3. Additional information on anammox and denitrification from other sources. The authors say that "we cannot determine what specific pathways (denitrification or anammox) dominate the conversion of DIN to biogenic N2" [page 10563], which is likely true. However, the can compare their data to other published data about anammox and denitrification in the Cariaco. For example Wakeham et al (2012) find a sharp peak of ladderane lipids (anammox) around 225 meter, a bit higher than the maximum N2 peak shown here. Profiles in Wakeham (2012) look like nitrate and sulfide overlap at the suboxic/sulfidic boundary, a situation conducive to thiodenitrification. There is also evidence for extensive autotrophic production at the oxic/anoxic interface in Wakeham (2012). All of the mentioned data seems relevant to this paper.

Response: We will elaborate on potential biological sources of excess N2 other than canonical denitrification and anammox in the revised version of the manuscript.

4. Comparison to older data: The authors compare their measurements from 2008-

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Interactive Discussion

Discussion Paper

2009 to measurements by Richards and Benson in 1957. I thought this section was interesting. However, I would like more information. Can you explain better how Richards and Benson took and analyzed their samples, so that the reader believes that the difference between 20.7 and 25.0 umol/kg N2 is real and not just due to changes in technique over time?

Response: We will carefully revise Richard and Benson's methodology to ensure an accurate comparison of our data with theirs and to determine whether analytical differences could lead to discrepancies between these author's N2/Ar measurements and ours.

Technical comments: Introduction page 10553 starting line 5: The authors discuss the imbalance of the global N budget. I doubt the Cariaco basin is big enough to affect the global N budget. Is it important to mention the imbalance anyway? If you keep this section, add in DeVries et al (2012) who find a balanced budget as well as a new paper by Dalsgaard et al (2012) that accounts for "gap" between denitrification rate estimates (pg10553 line 17). They find that denitrification is patchy and easily missed.

Response: We will merge this and the following paragraphs so that readers can understand how N2/Ar ratios can be used to determine the magnitude of the nitrogen sink in the ocean.

Methods page 10556 line 12-15: more samples for DIN are shown in figure 4 than mentioned here.

Response: This section will be corrected. Nitrate and ammonium samples were collected from the surface down to 400 m (8 samples), while nitrite and phosphate were measured in samples collected from the surface to 100 m depth (4 samples).

Can the authors add in sulfide profiles from the monthly Cariaco station at the relevant months to give us an idea of the sulfide profile? The authors do note that sulfide was at 250m in the 1990s (10555 pg 11). But more recent and relevant data would be useful.

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Interactive Discussion

Discussion Paper

Response: We will include sulfide data from the CARIACO Time-series site from 2007 to 2009.

Discussion: The first paragraph discusses N2 fixation and how it is not important here. Is this paragraph necessary given that the authors explain the N2 undersaturation in surface waters as due to temperature in the results section (10559 lines 12-13)? I would cut it.

Response: This paragraph will be removed from the manuscript.

Figure 4. Add a line indicating the suboxic or sulfidic zones. Nitrite and phosphate data is quite sparse in the low oxygen/anoxic water. Can you add in data from the monthly sampling station? Is there a second nitrite max? The phosphate data from the monthly sampling is used in Nstar calculations but we never see the data. It would be nice to see the phosphate data to see how much the phosphate profile is affected by adsorption to manganese and iron.

Response: We will include nitrate and phosphate data from the CARIACO Time-series site during 2008 and 2009. We will also modify figure 4 and 5 accordingly. There is typically a measureable second nitrite maximum near the oxic-anoxic interface, which should be identifiable in the nutrient plots we will add to the manuscript.

Figure 5a: Hard to see individual N2/Ar profiles. A lot of the spatial information is lost with this graph. The authors carefully explain why every station was chosen (riverine influence, affect of the influx of Caribbean waters etc; page 10555 end to 10556 line 5) but do not use this information in the discussion. It is hard for the reader to pull this information out of the graph as well. Does the influx of Caribbean waters affect the profile at the appropriate station?

Response: N2/Ar ratios and excess N2 concentration profiles (figure 5) will be shown as average values with one standard deviation bars. We did not identify a connection between biogenic N2 concentrations and the distance of each station from the open

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Interactive Discussion

Discussion Paper

Caribbean or from areas of riverine discharge. This will be clarified in the manuscript.

Page 10561 first paragraph and figure 5a: The authors discuss a decrease in excess N2 below 400m in figure 5, but it is very difficult to see in the figure.

Response: The apparent decrease in excess N2 below 400 m should be clearer in the revised version of figure 5.

Comments from Anonymous Referee #2 Montes et al. used measurements of excess nitrogen gas above atmospheric equilibrium to investigate N loss in the Cariaco Basin. They concluded that the excess N2 varied seasonally in response to changes in POC/PON export. The authors also found the excess N2 was comparable to the DIN deficit, which substantiated the hypothesis that the N2 excess is mainly of biological origin. Overall this manuscript is well written and suitable for publication after revisions. âĂČ Specific comments: Section 3.2: In the introduction the authors state that waters were sulfidic below ∼250m which is also where most of the N2/Ar measurements were taken. They do not specify in the method whether sulfide was removed, corrected for, or did not affect N2/Ar. Granted, one would not expect good agreement between the excess N2 and DIN deficit if this were a major problem, however interfering gases are a well-known problem experienced by other researchers using IRMS (e.g. Emerson et al. 1999). For the information of other researchers please specify.

Response: Our analytical methods for N2/Ar ratio determinations include several traps for removing interfering gases before samples are carried into the mass spectrometer. Specifically, H2S is removed from the sample with a liquid nitrogen trap. This will be explicitly outlined in the methods section.

pp. 10559, line 13; pp. 10560, lines 3, 17. “Negative anomalies in N2…”, “…undersaturated in dissolved N2”. It is misleading to state that N2 is undersaturated due to heating. The author’s sufficiently explain how, due to the differing solubility curves of N2 and Ar, heating coupled to incomplete equilibration can give rise to a normalized N2/Ar < 1, and thus a negative excess N2. However, heating sans equilibration would lead to a supersaturation of the absolute concentration of N2 gas. For instance, pp. 10559, line 13 should more accurately state "Negative anomalies in excess N2. . . ", or pp. 10560, line 16-17 ": : :in situ heating is the most likely cause for the negative values of excess N2. . . "

Response: We will reword these sentences accordingly.

pp. 10562, lines 13 – 17. "We did not observe a difference. . . higher in March 2009 and September 2008". It hard to reconcile the two statements that 1) there was no difference between March 2009 and September 2008 in the average nutrient concentrations of the stations sampled for excess N2, and 2) DIN was significantly higher between the two seasons at the CARIACO Time-Series station, especially given that the Time-Series station IS one of the stations at which excess N2 was determined. This apparent incongruity seems to arise from the fact that the authors averaged all the nutrient data from all 6 of the stations sampled for N2/Ar. It would help if the authors showed the Time-Series nutrient data that was used to calculate the DIN deficit on Figures 4 and 9 (include data with O2 < 65 umol/kg) given that subsequent analyses and conclusions rely on this data from the Time-Series.

Response: We will reword these sentences so that these statements are consistent. Nutrients data from the CARIACO Time-series station will be added to the revised version as well.

pp. 10564, section 5.3. I am surprised that the excess N2 matched the DIN deficit because: 1) The authors did not subtract the preformed normalized N2/Ar from the measured value (Devol et al., 2006; Chang et al. 2010). Normalized N2/Ar > 1 due to physical processes have been observed at BATS, which this study is using as its source waters. This requires more discussion given previous work using normalized N2/Ar. 2) DIN deficits have been difficult to determine in anoxic waters due PO43- reacting with reduced metals, which must also happen in the Cariaco Basin. How did the authors determine this did not occur? As I already commented above, it would remarkable for the DIN deficit to match the excess N2 if the above issues were significant, however I do believe they warrant consideration.

Response: Background (or abiotic) N2/Ar ratios is an important concern that will be addressed as suggested in detail by Referee #1(see specific comment "1"). Phosphate adsorption by reduced metals does not likely impact the DIN deficit in Cariaco. Benitez-Nelson's group has observed that there is a clear peak of labile and oxide-associated P at the oxic-anoxic interface, but it does not seem to erode the PO43- depth profile. These forms of P have nanomolar concentrations while phosphate is in the micromolar range. We will add PO43- data to our manuscript and discuss the work of Benitez-Nelson et al.

pp. 10566, lines 8 – 10. "…where 0.86 is a factor that removed the effect of SRP production from organic matter… " The factor of 0.86 was used in the past when it was unknown if organic N remineralized during denitrification was converted to N2 and thus the loss of fixed N was simply a NO3- deficit. However, the authors are assuming the anammox process occurs and so the factor of 0.86 is unnecessary.

Response: We will remove this factor from our DIN deficit calculations.

Figure 5. In many of the other figures the authors present average values for each season (nutrients, N2 excess, DIN deficit). They should be consistent and present the average for each season in this figure.

Response: We will change this figure accordingly.

Figure 7. What is the variability of the POC/PON flux? Please add error bars to this plot or indicate range of values.

Response: We chose to plot median values due to the high variability of POC/PON fluxes in Cariaco. We will add average values with one standard deviation bars to this figure.

Figure 8. This schematic is not useful and should either be removed or significantly al-

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Interactive Discussion

Discussion Paper

tered. First, there are undefined abbreviations (Ez, SUW). Secondly, other than changing the width of the arrows to represent increased fluxes, the authors make no attempt to illustrate the other differences they describe in the text between “upwelling” and “relaxation”. In the text they hypothesize that an intrusion of water from the Caribbean Sea could lead to a deepening of the oxic-anoxic interface and higher O2 in the upper water column, neither of which are represented in the schematic. In fact, contrary to the text, they show NO3- rich (and O2 laden) water intruding directly into the zone of N-loss, which, if this were actually occurring, would DECREASE anaerobic N loss due to the introduction of O2.

Response: We will include the definition of all acronyms in the figure captions. We will also revise the content of the figure to ensure that all of the processes described in the discussion are accurately represented in the model. Indeed, oxygenated Caribbean waters intruding into the basin’s sub-oxic layer should inhibit denitrification within this portion of the water column. We have observed, however, that such ventilation events are short and that oxygen levels return to sub-oxic concentrations within weeks (See Taylor et al. [2001] and Scranton et al. [2006]), and once sub-oxic conditions are re-established the nitrate injected by the intrusion should then consumed by denitrification.

Interactive comment on Biogeosciences Discuss., 9, 10551, 2012.