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

### **Anonymous Referee #1**

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General Comments: This paper presents N<sub>2</sub>/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 levels of N<sub>2</sub>/Ar. I think the authors knew this but did not realize that a profile of N<sub>2</sub>/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 N<sub>2</sub>/Ar over time. However, the authors almost ignore the high N<sub>2</sub>/Ar concentrations in the sulfidic zone. As this includes most of the biologically produced N<sub>2</sub> in the Cariaco, I think it deserves more attention.

Specific Comments: 1. N<sub>2</sub>/Ar background First of all, the authors need to take the background into account with their N<sub>2</sub>/Ar data. The N<sub>2</sub>/Ar ratio in all oceanic deep water is supersaturated due to undersaturation of argon (Hamme et al., 2007). Deep

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water from BATS (representing Atlantic deep water) has a 1% supersaturation in N<sub>2</sub>/Ar (Nicholson et al., 2010) while at 150 m at BATS, the depth of source waters for the Cariaco Basin, N<sub>2</sub>/Ar is 0.6% supersaturated (Nicholson et al, 2010). The authors should try to estimate the background N<sub>2</sub>/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) N<sub>2</sub>/Ar ratio, the authors can better examine the excess N<sub>2</sub> both in the sulfidic zone and the oxic/anoxic transition.

2. N<sub>2</sub>/Ar in the sulfidic layer The N<sub>2</sub>/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 N<sub>2</sub>/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 N<sub>2</sub> production from intrusions is the most important form of N<sub>2</sub> 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 N<sub>2</sub> production occurs in the suboxic zone, N<sub>2</sub>/Ar supersaturation decreases with depth below the suboxic zone (Fuchsman et al., 2008) even though the deep water is quite old. The authors address N<sub>2</sub> concentration at depth in one sentence in the first paragraph of page 10561 by saying that “Excess N<sub>2</sub> might be expected to continue to increase below the oxic/anoxic interface since waters below the sill have accumulated N<sub>2</sub> from denitrification supported by nitrate-rich sill-depth Caribbean Sea waters that filled the basin (Richards and Benson, 1961). In contrast, however, N<sub>2</sub> excess decreased by 1-3  $\mu\text{mol/kg}$  below this depth.” Can the authors walk the reader thru this a little more? Richards and Benson (1961) calculate that there should be 22  $\mu\text{M}$  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 N<sub>2</sub> excess is approximately what you see here—less than the N<sub>2</sub> excess seen at the interface. The authors should cite and explain this calculation more explicitly. Richards and Benson (1961) act as if the N<sub>2</sub>

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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 N<sub>2</sub> 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 N<sub>2</sub> (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 N<sub>2</sub>/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 N<sub>2</sub> excess include values from the sulfidic zone?

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 N<sub>2</sub>” [page 10563], which is likely true. However, they 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 meters—bit higher than the maximum N<sub>2</sub> 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.

4. Comparison to older data The authors compare their measurements from 2008–2009 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  $\mu\text{mol/kg}$  N<sub>2</sub> is real and not just due to changes in technique over time?

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.

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

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.

Discussion: The first paragraph discusses N<sub>2</sub> fixation and how it is not important here. Is this paragraph necessary given that the authors explain the N<sub>2</sub> undersaturation in surface waters as due to temperature in the results section (10559 lines 12-13)? I would cut it.

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.

Figure 5. Hard to see individual N<sub>2</sub>/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?

Page 10561 first paragraph and figure 5 – The authors discuss a decrease in excess N<sub>2</sub> below 400m in figure 5, but it is very difficult to see in the figure.

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**BGD**

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