Biogeosciences Discuss., 4, S655–S661, 2007
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Biogeosciences
Discussions

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Interactive comment on "Nitrous oxide distribution and its origin in the central and eastern South Pacific Subtropical Gyre" *by* J. Charpentier et al.

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Received and published: 14 June 2007

Review of: Nitrous oxide distribution and its origin in the central and eastern South Pacific Subtropical Gyre

By: J. Charpentier, L. Farias, N. Yoshida, N. Boontanon, and P. Raimbault

General Comments: This contribution examines and interprets the distributions of nitrous oxide, and its isotopic and isopotomeric composition at three stations along a gradient extending from the highly productive waters off Chile to the highly oligotrophic subtropical gyre of the South Pacific Ocean. Supporting data such as dissolved oxygen, nitrate, and particle concentrations are also discussed. The fundamental data are likely to prove highly valuable, since isotope and particularly isopotomeric data are scarce, and data from the South Pacific Ocean,of any kind, are relatively scarce.

Overall, I believe that this paper requires moderate revision before it is published. For one thing, it needs a thorough "scrubbing" by an editor well-versed in English so that it will be more easily read. For example, Fig. 1 clearly suggests that nitrous oxide may be produced during both primary and secondary denitrification, but I found the textual description of these processes very confusing although I am not sure if this is a translation problem or fuzzy thought. I have made numerous changes on my copy of the manuscript in order to improve the English, and I am happy to pass them on to the authors if someone will send me a Word version of the text. In the interest of brevity, I will not make any purely grammatical comments in this review.

More importantly, I find much of the data analysis unconvincing for the following reasons.

1. The authors tend to neglect the fact that the nitrous oxide composition at any particular location, is not solely (and often not even significantly!) a function of local processes, but represents the combined history of the nitrous oxide producing and consuming processes, and the atmospheric source term and sink terms that a water parcel has experienced. In this regard, I bemoan the fact that the authors say little about the possible sources and paths of the waters that they have examined. Since they claim, that their Gyre station is one of the most oligotrophic regions in the world ocean, why should one think that the isotopic signals at this station are significantly influenced by local biological processes rather than being a memory of happier days when the water parcels were experiencing more productive conditions? By the way, I had always thought that the Eastern Mediterranean was the most oligotrophic portion of the world ocean. Who is correct? The crux of my problem may be exemplified by the opening statement of their results and discussion section (page 1680, lines17&ff. "The three studied stations are representative of three characteristic environments and allow us to compare the nitrous oxide sources for these different oceanographic regimes". In fact, the major sources may not always be local and much of the local nitrous oxide is

probably mixed or advected into the region approximately along isopycnal (isentropic?) surfaces! Remember that, once produced, nitrous oxide persists except when consumed by denitrification or lost to the atmosphere. On page 1683, the authors implicitly acknowledge this possibility by pointing out that SP (site preference) minima occur at 40 m, at UPX, 250m at EGY amd 350m at GYR, just what I would expect if a signal was produced along the productive/low oxygen Peru/Chile margin, and propagated along an ˜ isopycnal surface into the ocean's interior. Looking at the potential densities of their 3 stations, I see that the density at 100 m at UPX roughly corresponds to the density at 250 m at the two offshore stations, but given variability in the strength of upwelling and the fact that mixing of water masses produces water masses with slightly higher densities, I see no reason to discard my hypothesis without a more-detailed analysis. Similarly, minimum SP values tend to be a bit higher at UPX, and the del18O values tend to be higher there as well (a signal of nitrous oxide consumption by denitrification?), but I am wondering what conditions a bit further from shore would look like. My competing hypothesis would be as follows: "At the boundaries, of the Peru/Chile low oxygen/upwelling zone, there exists a region where nitrifier denitrification is intensified, and the signals of this region propagate into the interior of the ocean." So, I am guessing that if one collects enough data between stations UPX and EGY, one will find a region of particularly low SP. Nitrifier denitrification may indeed be the source of the SP mininum, but I am guessing that it occurs mainly in the Peru/Chile margin and that the signal is then advected and mixed offshore.

2. On page 1682, the authors suggest that approximately Redfieldian behavior between nitrate and phosphate at their offshore stations means that nitrification is the main source of nitrous oxide at these stations. Once again, I demur. Nitrous oxide is a trace gas with extreme variability in production versus nitrification to nitrate. Moreover, any nitrogen fixation in overlying waters could drive the overall relationships towards Redfield, even if the waters contained elevated nitrous oxide as a result of transiting oxygen deficient/denitrifying regions. Finally, a strong nitrous oxide signal produced along the Peru/Chile margin with a somewhat weaker nitrate removal signal (remem-

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ber those $>$ 400 % nitrous oxide saturations), can be associated, via mixing. with a return to Redfieldian nitrate/phosphate ratios without completely destroying the nitrous oxide signal.

3. Like others before them, the authors make a great deal of the correlation between AOU and nitrous oxide to imply that nitrification is the main source of nitrous oxide. This may be true, but the r2 of their correlation is only 0.48. More fundamentally, since nitrous oxide is a trace constituent whose production may be greatly enhanced at low oxygen concentrations, there is no fundamental reason why there should be a good correlation in water masses that have experienced oxygen deficient or near oxygen deficient conditions. In addition, why do the authors cite the AOU/nitrous oxide regressions of Cohen and Gordon, but omit those of Elkins? Elkins found different correlations depending on the oxygen history of the water masses, if my memory is correct.

4. It is a bit confusing, that at the top of page 1683, the authors discount the importance of dentrification in particles as contributing to their signals, but later on make a point of nitrifier denitrification within particles as having some significance, without giving a clear explanation of this. While on this subject, I should mention that I find their explanation of nitrifier denitrification in particles at their offshore stations unconvincing, and unnecessarily confusing. With respect to the confusion issue, their Gaussian fit of the Brunt-Vaisala frequency data creates features that don't exist, as one can see by taking a careful look at the potential density data. This is an example of over-smoothing of data.

5. On page 1688, lines 8-10, the authors state categorically that their results demonstrate that nitrifier denitrification can be an important source of nitrous oxide in oligotrophic well-oxygenated waters. I believe that I have made the case that their analysis is entirely unconvincing with respect to this statement. To prove their case, they would have to discuss local rates, vs residence times, vs signals transported into the region. They have no data on rates, no data on particle velocities, no data on oxygen gradients

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in their particles, etc., etc.

6. The authors's description of nitrification does not take into account that some recent studies suggest that Archaea may be important microbes for primary nitrification. See Mincer et al. (2007, Environmental Microbiology, 9:1162-1175) and Ingalls et al. (2006, PNAS, 103:6442-6447).

Specific Quibbles: On page 1674, line 18, the authors suggest that oxygen deficient conditions existed at station UBX. I do not think that oxygen deficiency exists until oxygen concentrations fall below about 5 micromolar, and the minimum concentrations that they show in their figure (Fig. 4) are significantly higher.

On page 1675, line 17, the authors give the classical definition of denitrification which is o.k., but I am sure that they know that ammonium can be oxidized to N2 such that the classical definition of denitrification does not include all processes that can convert fixed-N to N2.

On page 1675, line 24: It is curious to me that the authors do not refer to the work of Wollast that suggests that denitrification might occur within particles.

On page 1676, line 10 & ff, the authors' description of the association of nitrous oxide with oxygen and nitrate seems a bit loose. The relationships are not linear, and I would guess that the association is more with AOU than oxygen.

On page 1678, lines 5 & ff, the authors' listing of latitudes and longitudes needs reformatting into standard units, and I had to chuckle that they felt bold enough to express the latitudes and longitudes with a precision of 1 m! I would like to meet the captain and hydrographic crew who were able to navigate to 1 m accuracy, and keep the hydro wire in position with an accuracy of 1m. Were they on a very tiny ship, with tiny people, no ship drift, no wire angle, etc.

On page 1679 & ff, the authors cite a nitrate method whose range does not include their higher concentrations. Presumably, they used a modified version of this method.

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It would also be nice to see a reference for the equations used to calculate AOU.

On page 1683, lines17-23, the authors come up with a “deus ex machina” to explain high SP variability, “non-bacterial nitrous oxide production” and cite Delwich (1981). I did not remember Delwich (1981) discussing this matter in that paper, and when I went back and took a look at this book chapter, I still could not find any mention of “non-bacterial nitrous oxide production”. Even if this process was present, there is no explanation of how it might contribute to the high SP variability!

On page 1685, lines 13-15, we find another “deus ex machina”, “the sudden loss of speed in the pycnocline”. Poth and Focht (1985) are cited without clearly stating that their paper was about the detoxification mechanism only (if my memory is correct). I doubt that they said anything about variations in the sinking speed of particles. I might add the query, what particles? The authors’ data on particle distributions suggests that the concentrations are quite low at their offshore stations, particularly in comparison to their coastal station. Once again, I am more inclined to think that their offshore signals are heavily influenced by processes at the ocean margin.

On page 1686, lines 20 and ff, the authors’ finally hint that the origins of water masses might be important when discussing conditions near 600m in an advective oxygen maximum are discussed (subantarctic water?). So, I have to say, it seems like they just throw out the first explanation that comes to mind. Why are water mass origins are important here, but not in one of the most oligotrophic parts of the ocean?

On page 1686-1687, the authors’ discussion of how particles might accumulate to produce the signals that they discuss at their offshore stations is entirely unaccompanied by any quantitative foundation.

Bottom Line: The data in this paper are highly valuable, but I think that the authors have to give their data interpretation more thought which should result in a moderate revision of the paper that should be worthy of publication.

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Respectfully submitted,

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Interactive comment on Biogeosciences Discuss., 4, 1673, 2007.