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Discussions

Interactive comment on "Nitrous oxide dynamics in low oxygen regions of the Pacific: insights from the MEMENTO database" *by* L. M. Zamora et al.

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1 Summary

Zamora et al. use a global database of marine N_2O observations to determine three uncertainties associated with the parameterization of N_2O dynamics in ocean biogeochemical models: i) the N_2O yield by nitrification/denitrification at low oxygen concentration, ii) the O2 concentration below which N_2O is consumed on net rather than produced, and iii) the rate of N_2O consumption at low O_2. They find (i) that the N_2O yield appears to increase linearly at low O_2 concentrations rather than exponentially, that (ii) N_2O may be consumed, on net, starting at O_2 concentrations as high as 10 μmol kg^{-1}, and that N_2O is being consumed at rates of the order of 0.1 mmol N_2O m^{-3}

yr^{-1}.

2 Evaluation

Interest in the marine modeling of N_2O has surged in the past few years, largely in response to the growing recognition that global warming will tend to decrease the ocean's oxygen content, i.e., deoxygenate the ocean. Although the exact impact of ocean deoxygenation on the low oxygen regions remains highly uncertain and is currently intensively debated, a wide-spread deoxygenation will likely increase the marine N_2O production, thereby leading to a positive feedback owing to N_2O's strong greenhouse gas properties. The magnitude of this N_2O response and consequently of the ocean warming-deoxygenation-N_2O production feedback depends critically on the processes governing N_2O production and consumption in the ocean. Hence, this careful data-based analysis is a much welcomed addition to the field, and will help to better constrain ocean models that aim to simulate this feedback. Indeed, the primary audience of this paper are model developers, as the study focuses on three critical elements in the currently employed parameterizations for N_2O.

The study is overall well executed, the data and analyses generally solid, and the conclusions well supported by the provided evidence. The topic is clearly relevant, so that I am overall very much in favor of seeing this study published.

I have a number of overarching comments that I would like the authors to consider when revising this paper. However, none are of a nature that would prevent me from supporting this paper.

- (i) The approach taken is very much driven by the current ways how the N_2O cycle is parameterized in biogeochemical models. This is useful on the one hand, but on the other hand, it is missing the opportunity to better connect the modeling of N_2O to the underlying biological processes. For example, the question of whether the yield of N_2O production increases exponentially or not, and the O2 concentration below which N_2O will be consumed, on net, are connected to the actual processes producing and consuming N_2O, i.e., nitrification and denitrification. There is a growing literature on how N_2O is really produced and consumed in low oxygen environments, but virtually none of this is discussed in the context of the presented results. This is accentuated by the fact that the processes are analyzed and presented in terms of N_2O/AOU ratios, while the actual processes need to be understood in terms of N_2O/NH_4^+ or N_2O/NO_3^- yields.

- ii) I would submit that the conclusion that the N_2O yield at low oxygen concentration increases exponentially rather than linearly is not tenable. The reason is that mixing and consumption at low oxygen concentrations will tend to flatten the curve quite substantially, quite likely making it impossible to statistically distinguish between a linear and an exponential model. The reason I conclude this is because we happened to have looked at this issue in our N_2O modeling study (Jin and Gruber, 2003). In this study, we modeled N_2O production following two separate pathways, i.e., a nitrification pathway with constant yield, and a "low oxygen" pathway with an exponentially increasing yield. When we investigated how well the data fit the observations in a plot similar to that in Figure 5 of this paper, even a case where all N_2O was produced following the "low oxygen" pathway, i.e., following solely an exponential function, gave a distribution that wasn't as steep as the blue-dashed line in Figure 5. The more realistic case, where only part of the N_2O was produced following the "low oxygen" pathway, gave a rather linear relationship of N_2O with oxygen (a detailed description of the Jin and Gruber model approach as well as this figure is available in the supplementary material section of that paper - available from http://www.up.ethz.ch/people/ngruber/publications/jin_grl_03_supporting_material.pdf. The Jin and Gruber model is also described in illustrated in Sarmiento and Gru-

ber (2006), on pages 197ff). I therefore recommend that the authors revisit their conclusion with a model that does include mixing and N_2O consumption at low O2 concentration. In addition, it is also not really realistic to assume that the exponential model of yield goes to zero at high O2 levels, but rather asymptote to some background rate, as suggested by the fact that in Jin and Gruber, we found the best fit was obtained by the model with a 50/50 contribution from the two considered pathways. Translated into a yield function, gamma, this means: gamma = alpha + beta * f(O_2).

- iii) The N_2O consumption rate value of 0.129 mmol N_2O m^{-3} yr^{-1} in the abstract is rather misleading, in my opinion, as the actually computed values differ by an order of magnitude. Thus, I recommend to provide a range in the abstract rather than a number. Furthermore, it is not quite clear to me why the authors estimated this rate as a zeroth order process. Wouldn't it be more defensible to model this as a first order process, i.e., as $-k$ [N_2O] or perhaps even with a Michaelis-Menten type kinetics? N_2O is used as a substrate in this process, so its consumption rate should depend on the substrate concentration.

- (iv) The MEMENTO database is referenced by a publication that is essentially a proposal to build the database. Given the prominence and importance of this database in this paper, this is not really tenable. Either the underlying data need to be better described in this paper, or a better reference needs to be used. Of course, my favorite solution would be to make the database publicly accessible.

3 Recommendation

I recommend acceptance of this manuscript after moderate revision. I particularly recommend that the authors put their discussion into the context of the underlying biological processes.

4 Minor comments

p10022, method section: I recommend to rearrange the method section. I found it a bit odd to start with the description of the models, given the fact that the models play only a very minor role in this paper. I recommend the following sequence: - MEMENTO database - calculating N_2O production rates - calculating N_2O consumption rates and add the model description as part of this section

p10022, UVIC model: Given the very limited application and relevance of this model for this paper, I don't think that deserves such a long section in the methods.

p10026, equation 4: I think it is critical to point out that N_2O_PR is the MEAN N_2O production rate for a water parcel since it lost contact with the atmosphere. It is not the instantaneous production rate.

p10026, section 2.3: reference to Bange et al., 2009. This reference does not suffice, in my opinion, to describe the data base. Bange et al. (2009) discuss the proposal to develop this database, but they do not describe the content of the database, nor the quality control procedures employed. As mentioned above, I recommend to either use a better reference or to describe the data better in this manuscript.

p10026, line 26: "necessary to exclude additional data". This is likely confusing for the reader - at least it confused me at my first reading of the article. I suggest to write this differently. After flagging all "bad" data, you then selected only those data that have a TTD age older than 15 years. Then you separated these data into two bins: One where O_2 is > 10 μmol kg^{-1} and where O_2 is < 10 μmol kg-1. The former will be used for the analysis of the N_2O production rate, whereas the second will be used to determine N_2O consumption rates.

p10029, lines 10-18 and subsequent paragraph: "obtained similar distributions". In a somewhat indirect manner, the authors admit here themselves that it is difficult to differentiate in the data between a linear and exponential increase in the yield at low O_2

concentrations. So they support my scepticism with regard to how firm their conclusion is with regard to linear vs exponential models. One can turn this argument also on its head and argue that given the inability of the data to distinguish between these two models, it might not be that important overall. Then, it is perhaps more important to know the integrated value and not the particular shape of the curve, no?

p10029, lines 19ff: The results are discussed solely on the basis of the N_2O/AOU ratio. This is relevant for simple parameterizations in ocean biogeochemical models, but it is much less relevant for the underlying processes. A change in this apparent yield can simply be generated by changes in the relative contributions of nitrification and denitrification to the production of N_2O, with each process having a constant yield relative to nitrogen. As mentioned above, I think it will be beneficial to open up the discussion here.

p10030, consumption rate: Although I agree that the uncertainty of this estimate is high, I don't think that the level of uncertainty is that large. The highest value stems from a single instantaneous estimate and is really driven by a low volume and high ventilation rate. I cannot judge this particular estimate, but I am quite confident that one can estimate the volume of PCUC better than to within a factor of 10 through careful water mass analyses. So I would be prepared to dismiss the highest value. The remaining range is still high, and therefore the whole subsequent discussion (as well as the abstract) should be done in terms of a range and not a single value for which way too many significant digits are provided.

p10032, line 18: Modeling consumption: Note that Jin and Gruber (2003) modeled N_2O loss by a first order reaction. I am still of the opinion that this is a more sensible way of modeling N_2O loss than assuming a zeroth order loss rate.

p10033, line 13ff: NO_2^- as a proxy for denitrification and the onset of N_2O consumption. This discussion would benefit from a better connection with the underlying processes. The challenge is that denitrification is a both a source and a sink for N_2O. So the appearance of higher NO_2^- may indeed be an indicator of the onset of (canonical) denitrification, but this does not mean that the net balance for N_2O must have switched sign as well. I thus remain sceptical about the arguments that the switching point to net consumption occurs already at concentrations as high as 10 μmol kg^{-1}.

p10034, lines 4-11: depth and temperature dependency of N_2O production: In my opinion, it is not meaningful to present the data as is done here. The N_2O production estimated from equation 4 is a flux weighted mean of the production along the entire pathway from the surface to the depth where the parcel was sampled. So you can't plot it against depth and infer anything about the depth dependency. It works perhaps slightly better for temperature, but also here, it is is problematic. The only way out is the estimation of more instantaneous rates, which would require the evaluation of gradients in N_2O_xs and age.

Figures: I suggest to combine figures 7 and 8 into one figure.

Nicolas Gruber October 3, 2012

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