

## Review of “Inter-annual variation in summer N<sub>2</sub>O concentration in the hypoxic region of the northern Gulf of Mexico” by Kim et al.

The manuscript by Kim et al., presents a model estimate of the interannual variability of summertime bottom N<sub>2</sub>O (a powerful greenhouse gas) from the northern Gulf of Mexico. Shallow, productive regions like the nGOM are important players in the global N<sub>2</sub>O budget, and are particularly susceptible to eutrophication and deoxygenation, so it is important to characterize the sensitivity of these N<sub>2</sub>O source regions to both natural and human-induced variations. The model by Kim et al. suggests that the N<sub>2</sub>O concentrations correlate with the area of hypoxia, and the Authors suggest that increasing hypoxia in the future might enhance the release of N<sub>2</sub>O from the region to the atmosphere. These are potentially interesting results, however limitations in the model approach, validation, and sensitivity study, as well as the limited number of observations reduce the usefulness of the results. I feel that the paper needs substantial improvements and clarifications on the methodological side, and possibly a more thorough comparison with observations to be relevant.

### Major points:

1. While I see the rationale of the model formulation (Section 2.2) I think the Authors could improve the section, by explaining in more detail the model choice and its derivation. My interpretation is that the model can be derived by expressing a small change in N<sub>2</sub>O in a water parcel due to nitrification/denitrification as:

$$dN_2O = dN_2O_{nitr} + dN_2O_{prod} + dN_2O_{sink}$$

where *nitr* stands for nitrification, *prod* for production by denitrification and *sink* for consumption by denitrification.

This can be approximate using a Taylor-like linear expansion as:

$$dN_2O = \frac{\partial N_2O}{\partial O_2} \Big|_{nitr} \cdot dO_2 + \frac{\partial N_2O}{\partial NO_3} \Big|_{prod} \cdot dNO_{3_{deni}} + \frac{\partial N_2O}{\partial NO_3} \Big|_{sink} \cdot dNO_{3_{deni}}$$

where the partial derivative terms should include some dependency on environmental factors, for example O<sub>2</sub> concentration. This is not dissimilar from the model of N<sub>2</sub>O production by nitrification described in Nevison et al. 2003. A tricky part is that if one knew an analytical expression for these dependencies (as in Nevison et al., 2003), it could be possible to integrate each dN<sub>2</sub>O component along the water mass oxygenation/denitrification history (e.g. from O<sub>2</sub> saturation and zero denitrification to given O<sub>2</sub> and ΔN<sub>deni</sub> values).

If one assumes that the partial derivative terms are constant in the different oxygen concentration regimes (e.g. anoxia-suboxia, suboxia-hypoxia, etc.) the equation could be expressed as:

$$\Delta N_2O \approx \frac{\partial N_2O}{\partial O_2}|_{nitr} \cdot \Delta O_2 + \frac{\partial N_2O}{\partial NO_3}|_{prod} \cdot \Delta NO_{3_{deni}} + \frac{\partial N_2O}{\partial NO_3}|_{sink} \cdot \Delta NO_{3_{deni}}$$

Which is analogous to Kim's et al. equation (1), once the partial derivative are approximated by finite differences.

However, in equation (1) Kim et al. include both the coefficients  $\alpha$ ,  $\beta$ ,  $\gamma$  and the partial derivative terms. This is confusing, and in fact I would argue that  $\alpha$ ,  $\beta$ ,  $\gamma$  actually do correspond to the approximate partial derivatives, for example:

$$\alpha = \frac{\partial N_2O}{\partial O_2}|_{nitr} \approx \frac{\Delta N_2O}{\Delta O_2}$$

In fact the model as expressed in equation (1) is not consistent with what is discussed in lines 13-23 of page 6319, where the terms involving  $\Delta N_2O/\Delta O_2$  are no longer included.

So while In principle I think the model (1) has some theoretical basis, I feel that its derivation and description could be clarified.

I also think that  $[N_2O]_{est}$  in equation (1) should be  $\Delta N_2O$  (where  $\Delta N_2O = N_2O - N_{2O_{sat}}$ ). For example for a water mass close to surface properties, for which AOU and  $\Delta N_{deni}$  are close to zero, the  $[N_2O]_{est}$  resulting from equation (1) would also be zero, while it should instead be close to  $N_{2O_{sat}}$  (so that it is  $\Delta N_2O$  that is in fact close to 0).

2. Somewhat more worrisome is the lack of any dependence of the coefficients  $\alpha$ ,  $\beta$ ,  $\gamma$  on oxygen concentration within each of the oxygen intervals considered. Although I can not comment on this choice for the denitrification terms, as I am not aware of a simple functional dependence on  $O_2$  concentration for  $N_2O$  production/consumption by this process, it is well established that  $N_2O$  production by nitrification increases as  $O_2$  decreases (e.g. Nevison et al., 2003). Thus, I found it puzzling that this dependence is not included. According to equation (1) the production of  $N_2O$  is linearly proportional to AOU, while non-linearities are in fact observed (Nevison et al., 2003). Since production by nitrification dominates the  $N_2O$  budget, as shown in Fig. 4, the possibility non-linear effects should be included, or at least carefully considered and discussed before discarding it. A non-linear dependence of  $N_2O$  production on  $O_2$  could indeed amplify the relationship between hypoxic area and  $N_2O$  inventories shown in Fig. 5. In fact I am not surprised by the linear proportionality between hypoxic area and  $N_2O$  inventories - my impression is that this result is a direct response to the model assumption of linearity.

Another somewhat worrisome choice is to allow denitrification sources of  $N_2O$  in the hypoxic-suboxic regime. However this regimes spans a wide rage of  $O_2$  concentrations (2 to 0.13 mg/L, or  $\sim 60$  to 4 mmol/m<sup>3</sup>), most of which seem too high to actually allow for significant denitrification. For example, Codispoti et al. (2001) or Bulow et al., (2010) suggest that denitrification is inhibited by  $O_2$  larger than  $\sim 5$  mmol/m<sup>3</sup>. However, I realize that these thresholds are far from well established in the literature, and might depend on additional environmental factors. As a note, I will mention here the results of Farias et al. ( 2009 L&O) who actually report a net *consumption* of  $N_2O$  by denitrification at oxygen levels up to 40 mmol/m<sup>3</sup> - a quite higher threshold than reported elsewhere, albeit still significantly smaller than 60 mmol/m<sup>3</sup> used by Kim et al. for denitrification *production*.

3. Equation (2) and the derivation of the denitrification N deficit ( $\Delta N_{deni}$ ) need to be clarified. Section 2.2 does not give enough information on how  $\Delta N_{deni}$  was determined, and the only reference (Kim, 2012, PhD Thesis) unfortunately is not a peer-reviewed reference that I could check. Methods such as the eOMP have been widely applied, but the results depend on assumptions such as the number of end-member water-masses, their properties, the treatment of seasonality, the stoichiometric ratios for remineralization and denitrification, etc. These assumptions should be discussed in the paper, and I think that the format of a journal like Biogeosciences should allow the Authors to add all the relevant information, in particular for a short manuscript like this one.
4. Despite the problems described above, if the model did a good job in reproducing observed data, it could be acceptable on a purely empirical basis. However, at this stage, the paper lacks any model validation. Before any prediction (e.g. Fig. 5) is done with the model, I would expect it to be tested against a set of observation - even if they were from a limited time span or region. This would greatly increase the reach of the paper, and the confidence on its conclusions. At this stage, I am not sure that the results of a modeling exercise that is not constrained by observations can be taken at face value.
5. The only actual  $N_2O$  data shown by the Authors are presented in Table 1 and Fig. 3. However I find them confusing, and I am worried that they might be including effects of physical processes that would limit their reliability to determine the value of  $\alpha$ . In particular, I am confused by the fact that moving from the pre-storm to the post-storm periods, the  $N_2O$  concentration does not change significantly, while the oxygen shows a dramatic increase in bottom waters. This is surprising, because both  $N_2O$  and  $O_2$  should follow a similar behavior while exchanging with the atmosphere through air-sea interactions and mixing through the water column. The fact that we see a notable  $O_2$  replenishment but not the expected  $N_2O$  drawdown suggests that some source of  $N_2O$  is offsetting its equilibration with the atmosphere.

I doubt that this could be a biogeochemical source, as the time-frame considered is probably short (although this should be added to the discussion - when exactly were the pre- and post-storm measurements taken?), and  $O_2$  is actually increasing, possibly limiting  $N_2O$  production by nitrification. I wonder if physical exchange with water masses richer in  $N_2O$  (e.g. advection of offshore waters?) could be responsible for the lack of apparent  $N_2O$  drawdown during the storm phase. Alternatively, the bottom and surface measurements might not be indicative of the bulk of the water column properties. These points should be addressed, as they are critical to the determination of the coefficient  $\alpha$ . Certainly, if a larger number of concomitant  $N_2O/O_2$  observations were used, that would increase the confidence on any empirical relationship between the two tracers.

Overall, I feel that it's hard to take the relationship in Fig. 3 as a robust basis for the nitrification part of the empirical model of equation (1). Ideally, more data-points should be used, as well as a more careful consideration of the physical sources/sink terms by gas exchange and circulation. Perhaps this could be done by constraining an eOMP model which includes  $N_2O$  production and near-saturation (with respect to  $O_2$  and  $N_2O$ ) surface end-members. I realize that data availability might be the limiting factor for such an effort. If this is the case I feel that some more in-depth discussion of the approach limitation should be considered, and how these would impact the quantitative results of the modeling exercise.

6. With respect to the quantitative results, I think a better job could be done in estimating and discussing the resulting uncertainty. I am not sure the spatial standard deviation shown in Table 2 is the best measure of the resulting  $N_2O$  uncertainty. In fact, such uncertainty does not arise from model uncertainties, but rather from spatial variability in the hydrographic properties that drive the model, and by the sampling distribution of these properties. Since the model is so simple, it could be possible to attach an uncertainty to its parameters  $\alpha$ ,  $\beta$  and  $\gamma$ , as well as the  $O_2$  concentration thresholds chosen for the three  $N_2O$  production/consumption regimes, and do a more rigorous estimate of the model's true uncertainty, for example by adopting a Montecarlo approach, or an error propagation approach. This would allow to address the impacts of the uncertainty surrounding the value of  $\alpha$ ,  $\beta$ ,  $\gamma$  discussed in section 3.1. I also think it could be valuable to add uncertainty bounds to Figure 5 (they are in fact presented in Table 2), even though the large values provided by the spatial standard deviations would make these appear quite large. In fact, looking at Table 2, the uncertainty is often large enough that it's hard to tell if one year is statistically different from another.
7. Regarding the model results, I was somewhat puzzled by the low values obtained. The  $N_2O$  concentrations shown in Table 2 and Fig. 5-6 seem to be quite small compared to observations from other hypoxic and suboxic regions. For example Nevison et al. (2003) show values up to  $> 100$  nM in typical open ocean OMZs. The relatively low values from

equation (1) clearly depend on the choice of  $\alpha$  (and to a lesser extent  $\beta$ ,  $\gamma$ ), so it is critical that such parameter is constrained with as many observations as possible (more than the two data points of Fig. 3 that were finally chosen!), or, put it another way, that the model results are validated against a larger number of observations, as discussed in points 4. and 5.

**Minor points:**

- Abstract: “we present evidence...”. I would consider actual observations as evidence, not model results - given the rather severe limitations of the model that I discussed in points 4, 5 and 7. This sentence should be rephrased.
- Abstract: Temporal variation is very general. Given that the seasonal cycle is ignored, I would clarify this as interannual variations in summertime  $N_2O$ .
- Section 1 (ll. 4-20, p. 6317). It would be useful to put the  $N_2O$  emission estimate in a global context. For example, of the  $\sim 6$  Tg N/year suggested by Nevison et al. 2003 (or similar estimates) how much would be coming from the nGOM? How much come from similar shallow water regions subjected to hypoxia?
- The use of summer data and of bottom data alone should be put in a more general context. While I understand that these choices might stem from data availability, it would be very useful to add a discussion on how summertime  $N_2O$  concentrations compare to year-round concentrations, and how bottom  $N_2O$  concentrations relate to the bulk of the water column  $N_2O$  values. Similarly, are summertime and bottom  $O_2$  and  $\Delta N_{deni}$  values indicative of the whole year, and of the whole water column? This is important given that these properties are the only drivers of the model.
- Page 6320, ll.25-26, and page 6321, lines 1-2. I think the use of the term “solubility” in this sentence is confusing. The way I’m reading it is that the solubilities at saturation of  $O_2$  and  $N_2O$  are disproportionally affected by changes in water mass properties (T, S). However I’m not sure that this is true - it could be easily shown by calculating the changes in saturation concentrations of the two gases - but I doubt that the differences would be dramatic. Maybe the Authors are just referring to the actual  $O_2$  and  $N_2O$  concentrations?
- page 6321, lines 3-5. This sentence is confusing and should be rephrased. Also, please clarify what sensitivity tests were performed, and what results they yielded.
- The Authors should add more details on how the model was applied to the observations to yield the results in Figs. 5-6 and in Table 2. Was equation (1) applied on a point-by-point basis, and the results spatially averaged? Was the spatial distribution of the points considered in this averaging (e.g. through some mapping procedure - see Fig. 6)? Similarly, how were the standard deviations in Table 2 determined?

- Figure 1 is not needed. I found it confusing, and I had to read the text carefully before I could make sense of it. Overall it does not add any information to the text itself.
- Table 1: why does the table only reports two N<sub>2</sub>O values (one at the surface and one at the bottom), while there are 4 values for all other properties, including ΔN<sub>2</sub>O, corresponding to pre-storm and post-storm periods? Wouldn't it make sense to show the corresponding 4 values for N<sub>2</sub>O as well?

**Technical comments:**

- Fig 3. The term “simulation” is confusing, maybe change it to “estimate”?
- Table 2, year 1998: the N<sub>2</sub>O should not be allowed to take negative values.

**References:**

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