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Comment

Interactive comment on “Interannual variation in summer N₂O concentration in the hypoxic region of the northern Gulf of Mexico, 1985–2007” by I.-N. Kim et al.

Anonymous Referee #1

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Review of Inter-annual variation in summer N₂O concentration in the hypoxic region of the northern Gulf of Mexico, 1985–2007 by I.-N. Kim, K. Lee, H. W. Bange, and A. M. Macdonald submitted to Biogeoscience.

General comments:

The authors present a modeling study whereby they looked for estimating N₂O levels in near-bottom waters of Northern Gulf of Mexico (the nGOM) for the period comprised between 1985 and 2007 (summer period). These estimates may be important for understanding the marine/estuarine N₂O cycle and its environmental controls, and thus this manuscript could be an important contribution to the field.

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My two main concerns arise from the review:

1. - Important pieces of information are omitted throughout the manuscript and there is a lack of logical sequence that triggers a series of questions throughout the whole manuscript. It had been very difficult for me to understand the used conceptual model (rationale) and the relationships among O₂, N₂O and NO₃⁻ in order to reproduce N₂O concentration in the bottom water under hypoxia condition, most of the time. I guess that the exercise was only done for bottom water to prevent further advection (vertical) and diffusion effects, but what about the role of lateral advection, resuspension, pelagic-benthic coupling, etc.?

2. - As authors mentioned, nGOM is an extended continental shelf area with hypoxic and eutrophic condition. In this kind of ecosystems, we expect a huge N₂O accumulation as a product of in situ biological production and/or discharge from rivers, estuaries; particularly as they are being affected by anthropogenic nitrogen (N) inputs. The estimated N₂O values are really low, even at levels of under saturation, making boast of:

-Lack of sensitivity and robustness in the used model - A N₂O consumption by denitrification, but as it proceeds only in anoxic environments, N₂O reduction to N₂ is unlikely because hypoxic and suboxic conditions always remain in the bottom water; - A N₂O consumption by the sediments (denitrification) but in this ms. the role of sediment is ignored.

Below I provide some question and guideline for improving this manuscript if it is possible:

1) there are inconsistencies among the presented background in introduction section, the used conceptual biogeochemical model, results and others

Since the study is focused on a hypoxic region, it precludes the existence of anaerobic process as canonical denitrification or DNRA, I wonder if the study area has represen-

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tative anoxia period. Let include information about frequency of anoxic periods. Table 1 reveals DO as low as $40 \mu\text{mol L}^{-1}$, it is far to be suboxic ($4.4 \mu\text{mol L}^{-1}$)

Introduction section only mentioned N_2O producing processes; how about N_2O consuming process? . However, conceptual model incorporates a terms of N_2O consuming,. Again, how you weigh or ponders the role of canonical denitrification in the study area?

The modeled mean N_2O concentration in the bottom water was $7.7 \pm 6.7 \text{ nmol L}^{-1}$; it means a range from 10% to 234% saturation. I wonder if there are data with under saturation levels in other eutrophicated and hypoxic ecosystems. Under saturated N_2O concentrations are usually found in suboxic/anoxic and nitrite-rich waters, as observed of the oxygen minimum zones or the sediments. This pattern has been clearly ascribed to canonical denitrification, which is, so far, the sole process known to consume N_2O through its dissimilatory reduction to N_2 under anoxic condition.

2) In my opinion the production of N_2O is very sensitive to changes in oxygenation but also depends on several factors. If authors assume that oxygen is the dominating factor (80%) controlling N_2O cycling and that there are not limitations for ammonium (electron donor for nitrification) or nitrate/nitrite (electron acceptor for denitrifies),

Thus, those assumptions should be clearly established. Regarding the scale used to separate concepts of oxia, hypoxia, suboxia and anoxia, it is confusing because authors use the same range to separate anoxic suboxia, and I think this is a mistake, because the nitrogen cycle (particularly N_2O) behaves very differently depending on O_2 traces or not exist in the environment. The authors must to include an anoxic term. I think that the best definition is those stated out by Naqvi who defined anoxia when $\text{O}_2=0 \mu\text{mol L}^{-1}$ and $\text{NO}_2^- >0$. I believe that NO_2^- distribution should really help to define O_2 ranges. Please include that data.

3) The rationale of N_2O conceptual model is very difficult to follow to me. Dynamic patterns of dissolved N_2O concentrations in marine waters emerge from complex in-

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interactions among physical, biogeochemical processes. Therefore, since the model only includes a microbiological term, it is a very biased conceptual framework.

What is ΔO_2 in the Eq. 1? and What include the term ΔN_{deni} , NO_3^- and NO_2^- loss as N_2 ?

What do you think about N-loss by anammox? Could ΔN_{deni} be being underestimated?

What kind of (lineal exponential, polynomial) relationship was used to estimate α , β , γ ?

It is widespread knowledge that relationships between O_2 (AOU) and N_2O (ΔN_2O) and even NO_3^- are not linear. For example, these relationships depend on (besides oxygen) water masses mixing, the microbial communities (functional and even phylogenetic diversity) among others. So, it is not possible to use parameterizations obtained in other ecosystems, like the OMZ of the eastern South Pacific.

Finally, N_2O cycling should comprise the conceptual model:

Oxic Condition should include aerobic ammonium and nitrite oxidation (AAO and ANO, respectively) by Bacteria and Archaea (only NH_4 oxidation) Hypoxic Condition: AAO ANO, partial denitrification, if you a priori preclude nitrifier denitrification Suboxic Condition: idem to hypoxic condition Anoxic Condition: total or canonical denitrification, if you a priori preclude DNRA

4) Regarding results, I am truly surprised with respect to the separation of data between pre or post storm, why not the authors previously present these dynamics as a background

But the existence of pre and post storm dynamics means that there was another temporal scale of variation, which overlaps with some seasonal and annual variability, etc. You should include an analysis of this perturbation each summer (July). In this regard, I could not understand how simulation of α (pre and post storm) was performed.

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Table 1 present estimated N₂O data; given the high standard deviation of the data, I see that no significant differences exist in N₂O levels among years, with a mean range from 3.7 to 13.5 and a SD range from 4.3 to 12.2. Another point, during July 1998 a value of 3.7 ± 12.2 was reproduced, it means that negative value could be estimated, I ask myself what is the sensitivity of this model?. Relative a N₂O production/consumption (Figure 4), I realize that there is not a trend in N₂O produced by nitrification, but if nitrification is main N₂O producing process, How the authors justify found correlation between estimated N₂O levels and areal hypoxia.

I found the estimated N₂O levels extremely low for an eutrophic area where ammonium levels should be high (close to sediment-water interface). If you have in mind that N₂O values in bottom water as high as 533 nM were found in the western continental shelf of India (Naqvi et al, 2000), 7.7 nM seems to be low. Finally, the authors omitted information about nutrient and the influence of river in the coastal area, such information can contribute to the discussion of this ms.

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/10/C1839/2013/bgd-10-C1839-2013-supplement.pdf>

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