

Review of Inter-annual variation in summer N<sub>2</sub>O 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 N<sub>2</sub>O 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 N<sub>2</sub>O cycle and its environmental controls, and thus this manuscript could be an important contribution to the field.

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 O<sub>2</sub>, N<sub>2</sub>O and NO<sub>3</sub><sup>-</sup> in order to reproduce N<sub>2</sub>O concentration in the bottom water under hypoxia 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 N<sub>2</sub>O 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 N<sub>2</sub>O values are really low, even at levels of under saturation, making boast of:

-Lack of sensitivity and robustness in the used model

- A N<sub>2</sub>O consumption by denitrification, but as it proceeds only in anoxic environments, N<sub>2</sub>O reduction to N<sub>2</sub> is unlikely because hypoxic and suboxic conditions always remain in the bottom water;

- A N<sub>2</sub>O 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 representative

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  $\text{N}_2\text{O}$  producing processes; how about  $\text{N}_2\text{O}$  consuming process? . However, conceptual model incorporates a terms of  $\text{N}_2\text{O}$  consuming,. Again, how you weigh or ponders the role of canonical denitrification in the study area?

The modeled mean  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  through its dissimilatory reduction to  $\text{N}_2$  under anoxic condition.

- 2) In my opinion the production of  $\text{N}_2\text{O}$  is very sensitive to changes in oxygenation but also depends on several factors. If authors assume that oxygen is the dominating factor (80%) controlling  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$ ) behaves very differently depending on  $\text{O}_2$  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  $\text{NO}_2^-$  distribution should really help to define  $\text{O}_2$  ranges. Please include that data.

- 3) The rationale of  $\text{N}_2\text{O}$  conceptual model is very difficult to follow to me. Dynamic patterns of dissolved  $\text{N}_2\text{O}$  concentrations in marine waters emerge from complex interactions among physical, biogeochemical processes. Therefore, since the model only includes a microbiological term, it is a very biased conceptual framework.

What is  $\Delta\text{O}_2$  is the Eq. 1 ? and What include the term  $\Delta\text{N}_{\text{deni}}$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  loss as  $\text{N}_2$ ?

What do you think about N-loss by anammox? Could  $\Delta\text{N}_{\text{deni}}$ , be being underestimated?

What kind of (lineal exponential, polynomial) relationship was used to estimate  $\alpha$ ,  $\beta$ ,  $\gamma$ ?

It is widespread knowledge that and relationships between  $\text{O}_2$  (AOU) and  $\text{N}_2\text{O}$  ( $\Delta\text{N}_2\text{O}$ ) and even  $\text{NO}_3^-$  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 no possible to use parameterizations obtained in other ecosystems, like the OMZ of the eastern South Pacific.

Finally, N<sub>2</sub>O 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<sub>4</sub> oxidation)

Hypoxic Condition: AAO ANO, partial denitrification, if you a priori preclude nitrifier denitrification

Suboxic Condition: idem to hypoxic condition

Anoxic Condition: total o canonical denitrification, if you a priori preclude DNRA

- 4) Regarding results, I am truly surprising 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  $\alpha$  (pre and post storm) was performed.

Table 1 present estimated N<sub>2</sub>O data; given the high standard deviation of the data, I see that no significant differences exist in N<sub>2</sub>O 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  $3,7 \pm 12.2$  was reproduced, it means that negative value could be estimated, I ask myself what is the sensitivity of this model?. Relative a N<sub>2</sub>O production/consumption (Figure 4), I realize that there is not a trend in N<sub>2</sub>O produced by nitrification, but if nitrification is main N<sub>2</sub>O producing process, How the authors justify found correlation between estimated N<sub>2</sub>O levels and areal hypoxia.

I found the estimated N<sub>2</sub>O levels extremely low for an eutrophic area where ammonium levels should be high (close to sediment-water interface). If you have in mind that N<sub>2</sub>O 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.