

## ***Interactive comment on “Constraints on global oceanic emissions of N<sub>2</sub>O from observations and models” by Erik T. Buitenhuis et al.***

**Anonymous Referee #3**

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The manuscript by Buitenhuis and Coauthors describes the results of simulations with an ocean biogeochemical model that includes different parameterizations of N<sub>2</sub>O production, constrained with available N<sub>2</sub>O observations. The main finding is a net N<sub>2</sub>O outgassing to the atmosphere of  $2.4 \pm 0.8$  TgN/year, which is substantially lower than many of the estimates previously reported, and also less uncertain. A very small proportion of the N<sub>2</sub>O production comes from denitrification-associated pathways in sub-oxic waters. The estimate also appears robust to the choice of the parameterization of N<sub>2</sub>O production.

This is a short and potentially useful paper, although not particularly original. But I think that, if better supported, the results will push other scientists to reconsider estimates of N<sub>2</sub>O emissions from the ocean (as well as from other sources) in light of the low val-

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ues suggested. That said, I also think the paper is poorly written, in particular when it comes to the description of the methods employed - for example the model equations, the rational and choices behind the parameterizations, the steps behind the optimization. Furthermore, I have some additional concerns about the results that prevent me from fully supporting publication of the manuscript as is.

Specific comments:

- The model formulation is quite hard to follow, partly because equations are not shown. This makes it difficult at times to judge the validity of the model's assumption. I strongly encourage the Authors to show all the pertinent equations, either in the main text, or in an appendix.

- The choice of some of the model equations and parameterization is unclear and could be better justified. The Authors could do a much better job explaining why certain functional forms have been utilized, and what consequences these choices may have, if any. For example, looking at Table 1, line 3 lists an equation that uses the logarithm of  $O_2$ . Is there any reason for this form? The logarithm will expand the range at very low  $O_2$  concentration - do we trust  $O_2$  measurements there? Further, this form breaks down at  $O_2=0$ ; does this ever happen in the model/observations, and is there any limit applied to prevent it? Finally, all of these equations should represent a process ultimately limited by  $O_2$ . Is there any limitation as  $O_2$  goes to zero?

- I found the distinction between the prognostic and diagnostic model (for  $N_2O$ ) somewhat confusing. In both models  $N_2O$  is carried as a prognostic tracer - except in the first model it does not depend on other N-cycle tracers, and is not consumed, but only produced and passively advected until it outgassed from the surface. What makes one model diagnostic and another prognostic?

- Regarding the prognostic model - the Authors say that it explicitly represents the redox transformations that lead to the conversion of  $NH_4^+$  to eventually  $N_2O$  (actually only a subset, as for example, the model does not include  $NO_2^-$ ), but the model seems to

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still parameterize them heavily. For example the current understanding is that N<sub>2</sub>O is an obligate intermediary during heterotrophic denitrification, so that one should expect a gross N<sub>2</sub>O production comparable to the denitrification rate (i.e.  $\sim 70$  Tg N/year). However, the Authors indicate a suboxic gross production of only 0.33 Tg N year<sup>-1</sup> - a very small rate in comparison. This may be explained by the use of “slopes” in the prognostic model that relates N<sub>2</sub>O to other tracers (more on these slopes in the next comment). This implicitly assumes a tight coupling between production and consumption at suboxic levels, with only a fraction of the N cycled by denitrification escaping to the water column. It may be fine as a parameterization - especially since it is one that is optimized against observations. However it may be problematic if the model is to be used under varying circulation or climate - the coupling between production and consumption may vary, and given the large gross N<sub>2</sub>O fluxes this may impact net production and accumulation of N<sub>2</sub>O.

- It is unclear what “slopes” are used in the prognostic model. Are these slopes actual yields (e.g. N<sub>2</sub>O production per NH<sub>4</sub><sup>+</sup> oxidized), relationships with O<sub>2</sub> consumed, or just empirical relationships based on data syntheses? And what is then the slope of the third step of N<sub>2</sub>O cycling (consumption of N<sub>2</sub>O by denitrification)? Is it a relationship with O<sub>2</sub>, with NH<sub>4</sub><sup>+</sup> or with NO<sub>3</sub><sup>-</sup>? (and specifically, is there explicit denitrification in the model, so that one could relate N<sub>2</sub>O production to NO<sub>3</sub><sup>-</sup> deficit?).

- The lack of spinup in the model is worrisome: the model was apparently initialized in 1965 and run for 49 years through 2014. This is a short running time, and it completely misses a spinup phase. It may very well be the case that the N<sub>2</sub>O inventory of the ocean over the last 5 years is still adjusting from the initial condition, in a way that could bias the outgassing estimates. For example, there seems to be a substantial accumulation of N<sub>2</sub>O in the deep ocean - if this is still ongoing after 49 years, then the outgassing estimated by the Authors could be a lower estimate. A comparison between the total net production in the interior and the outgassing could give a sense of any disequilibrium. Note that a similar modeling study by Martinez Rey et al., 2013,

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BGS (incidentally finding about 4Tg/year emissions) suggested a 150-year spinup was not enough to eliminate drifts in N<sub>2</sub>O and other biogeochemical variables. Any drift should be discussed in the paper, and the consequences assessed.

- I found the description of the optimization steps very unclear. It took me a while to figure out what steps the Author follow and how the model is actually compared to the data, and I'm still not sure about them. Now my understanding is that a first optimization is carried out for the NH<sub>4</sub>-cycle using nitrification rates and NH<sub>4</sub><sup>+</sup> concentrations; then a second optimization is performed with interior N<sub>2</sub>O data to determine parameters for low-O<sub>2</sub> pathways (but does this apply to both the prognostic and diagnostic model?); and finally a third optimization (presumably with some parameters fixed by the previous steps?) using surface Delta-pN<sub>2</sub>O data for the global source terms, used to determine the final air-sea fluxes. That's my understanding but I am still not sure I got it right, and some aspects remain puzzling. I think this could be much better explained from the start, for example by a method section outlining the optimization strategy in more detail.

- Related to the previous comment, the equations for the optimization are absolutely opaque and unclear. They need to be substantially clarified: ideally anyone should be able to apply them after reading the paper, which is not the case. For example equation (1) is not very specific: instead of "average", "model", "observations" the actual mathematical form could be given - this would also help knowing how the average was done, whether the in situ or gridded data were used, how the model was sampled etc. Similarly I am completely at loss with section 2.8, and I could not trace back the steps applied by the Authors based on this description alone. How is RSS/RRS<sub>min</sub> (equation 3) used, how does it relate to the quantities shown in Fig. 8 and 10, and why does it only contain the number of observations but no information on the actual variables? What does the "phi" term (equation 4) represent, and how is it actually used?

- Regarding the final estimate of N<sub>2</sub>O air-sea flux, I think it could be couched much better into the context of previous estimates (also, a table would help), and what could be

behind the potential discrepancies in light of the substantially lower revision. This could be especially interesting given that many modeling studies use a similar approach. The Authors also present an “observational” estimate of N<sub>2</sub>O production whose central value (4.6 TgN/year) is quite different than the final model estimate - this discrepancy could be added to the discussion. I am not particularly surprised by the lack of sensitivity of N<sub>2</sub>O production to the choice of diagnostic and prognostic models, since both are optimized versus observations. Surface pN<sub>2</sub>O should be a quite powerful constraint to outgassing fluxes. However, one may still expect different sensitivities to interannual variability and climate change, so this is not a strong argument in favor of not resolving complex pathways that characterize the low-O<sub>2</sub> N<sub>2</sub>O cycle.

- The model is biased in its representation of export and remineralization, as well as N<sub>2</sub>O distribution. The discussion of the effect of these biases (e.g. lines 289-300) is not especially thorough - so the conclusion, in particular regarding the narrower range of the new estimate, is not very convincing. Furthermore, there are hidden resolution biases. For example, the model can not resolve low-O<sub>2</sub> coastal upwelling regions, which have been shown to be powerful conduits to N<sub>2</sub>O outgassing (e.g. Arevalo Martinez et al., 2015, Nature Geosciences). The abstract/conclusions could be more cautious with respect to the real uncertainties.

- Line 43: The reference to Klawonn et al., 2015 is missing.

- Line 95, equation 2: More information should be given on this equation, and how it was used in the model/observation comparison. Does using this equation mean that the N<sub>2</sub>O flux is calculated for a specific period, or that it varies in time? This is unclear. Also, the number of significant digits in the various coefficients is way larger than any believable uncertainty associated with the measurements the equations should fit.

- Section 2.4, Table 1. Maybe some effort can be done to evaluate the improvements associated with each model: by adding terms the cost function decreases minimally - is the improvement significant? Does it justify the increase in the model degrees of

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freedom?

- Line 133-134. The equation could be shown.
- Section 2.6. The slopes (of what, with respect to what?) and relationships used for the model should be clarified with equations, and maybe with corresponding figures (e.g. the observational constraints used). Also, what is the range from which the various slopes were drawn in order to run the different model versions for the optimization? How were they determined? What values were actually used? Finally, there must be concentration thresholds associated to the transitions between different slopes (e.g. O<sub>2</sub>). How were these thresholds determined? Were they also optimized for?
- Line 211-212. The reasoning is unclear: an increase in outgassing for a given atmospheric concentration should be driven by a parallel increase in surface concentrations, since the flux is proportional to the concentration (or pN<sub>2</sub>O) difference. For example, in the limit of removing the saturation N<sub>2</sub>O concentration, a doubling of the interior production of N<sub>2</sub>O should double both the outgassing and the surface concentration.
- Lines 242-247. This entire paragraph is very unclear, please clarify.
- Lines 270-271. Constraining remineralization backwards from N<sub>2</sub>O production seems a bit far-fetched, given how hard it is to even constrain processes like denitrification alone.
- Lines 279-281. Please clarify.
- Lines 294-297. The issue of biases in model circulation could be assessed by using ventilation tracers, e.g. CFCs. Are they available for this mode?
- Line 308: do the Authors really think their model can capture coastal N<sub>2</sub>O dynamic, and the massive air-sea fluxes observed there (see Arevalo Martinez et al., 2015), especially in eastern boundary upwellings?

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