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Interactive comment on "Oceanic N_2O emissions in the 21st century" *by* J. Martinez-Rey et al.

Anonymous Referee #1

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This paper presents a model simulation, using NEMO-PISCES, aimed at predicting how oceanic N2O emissions and storage will change over the next century in the face of decreasing export production, increasing water column stratification, and declining interior O2 content. I enjoyed the introductory discussion, which raised important issues and motivated the current study in a compelling way. My main concern is whether the framework of the 2 major N2O production pathways used here, O2-independent ammonia oxidation, and the low O2 pathway at levels < 5 umol/L is adequate to describe the complexity of the oceanic N2O cycle, especially considering that the extent of oxygen minimum zones in the global ocean is poorly captured by NEMO-PISCES. There is essentially no discussion of nitrifier denitrification, which can be important at more modestly depleted O2 levels well above 5 umol/L and may be responsible for the bulk of oceanic N2O production. For those who believe that much of oceanic N2O production occurs in and around OMZs (e.g., see work by Codispoti), the P.TEMP and

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P.OMZ formulations are unsatisfactory as independent parameterizations that encompass the full range of possible future oceanic N2O response. Both parameterizations are heavily weighted toward nitrification, with at least 75% of total N2O production occurring via ammonia oxidation. As a result, there is a lack of significant variability in some aspects of the results, e.g., in Figure 1d.

That said, given the current state of knowledge, the authors have done a reasonable job with the information and modeling tools available, and it seems unreasonable to insist upon a complete overhaul of the modeling approach. I therefore recommend publication with minor editorial revisions, aimed primarily at acknowledging the uncertainty associated with the potentially incomplete and overly simplified representation of the oceanic N2O cycle in the model. In particular, I would like to see some discussion of the fact that the current model is unable to predict what might happen to future N2O emissions if much of N2O production does indeed occur in association with the OMZs. While the Conclusion does acknowledge some of these points already, they could be emphasized more strongly throughout the paper.

Below are some more detailed comments.

p16705, line 10. N2O is destroyed about 90% by photolysis, 10% by O(1D), but not really by the OH radical.

p16705, line 13. Change “atmosphere that caused” to “atmosphere, which has caused”

p16706, line 2. The most recent of these citations is from 2004. It would be good to include more recent work, e.g., by Westley, Farias, Frame, etc.)

p16707, line 24. Please support this statement with a reference: "Ocean warming might increase the rate of N2O production during nitrification"

p16707, line 29. “could substantially affect denitrification and the N2O production.” Better as something like, “could substantially affect N2O production via both nitrifier denitrification and classic denitrification.”

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P16708, line 1. Instead of “Models” it might be better to use a more specific term like “Ocean biogeochemistry models”

P16709, line 10. A concern about the Zamora et al. analysis, which is used to justify the near-linear N2O yield (gamma) in the P.TEMP formulation, is that this analysis was based on deltaN2O vs. AOU relationships at depth, representing the integrated effects of N2O production and O2 consumption in old water parcels. However, in the NEMO-PISCES model, the relationship is applied to JN2O = f(JO2), i.e., the instantaneous production and consumption rates, which may be significantly more nonlinear. Further, the Zamora analysis excluded all data above 150m depth, but this may be where the bulk of N2O production is actually occurring, i.e., at the base of the euphotic zone, much of which may quickly ventilate to the atmosphere (see, e.g., Popp et al., GBC, vol.16, no.4, 2002). Please acknowledge or discuss this point.

p16711 line 15. “We assume a constant atmospheric N2O concentration of 284 ppb in all simulations.” It would be good to add a clause clarifying that this value is only slightly above the natural, preindustrial N2O concentration. Also, perhaps explain why 284 ppb was chosen, considering that this paper deals with 21st Century projections, in which N2O may rise well above 325 ppb, approaching 350 or even 400 ppb.

P16712, lines 1-4. “This assumption is based on growing evidence that nitrification is the dominant pathway of N2O production on a global scale, based on estimations considering N2O production along with water mass transport (Freing et al., 2012).” I don’t think this can be taken as an accepted fact. Other lines of evidence, e.g., based on isotopes, suggest that denitrification (including nitrifier denitrification) is responsible for most N2O production (e.g., Park et al., Nature Geoscience, DOI: 10.1038/NGEO1421, 2012.)

p16712-13, Section 3.1. Some further discussion of model shortcomings would be useful. Figure 1 shows a tendency to overestimate the N2O flux in the North Atlantic and to underestimate the N2O flux in hot spots of N2O production such as the ETSP

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and ETNP. The Nevison et al., 1995 map, which is used to evaluate the NEMO results, also tends to underestimate the flux in the ETSP and ETNP, due to lack of surface pN2O data in these regions in the original Weiss dataset, but even so, captures substantially higher N2O emissions from the ETNP than the NEMO model, as shown in Figure 1d. (See Nevison et al., GBC, vol. 18, 2004 for further discussion.) Collectively, the NEMO results could be interpreted to show an overestimate of N2O production from widely distributed nitrification (i.e., ammonia oxidation) sources and an underestimate of N2O production from nitrifier denitrification and denitrification sources in lower O2 regions.

p16714, line 9. "P.OMZ shows a good correlation with the observations" doesn't seem like an accurate statement. The shape of the depth profile is considerably off from MEMENTO, although the maximum values in the 500-900 m depth range are in fairly good agreement.

p16714, line 11 and subsequent discussion. "Below1500m, both parameterizations simulate too high N2O compared to the observations." An alternative explanation from those given is that the coefficient assigned to N2O production at high O2 is too high.

P16714, line 22-23. Neither/nor should be either/or

Figure 3 and Section 3.2. It seems from this analysis, esp. the bar graph comparing to WOA, that NEMO-PISCES doesn't capture any of the OMZs in the world oceans – there is almost no volume with O2 < 50 umol/L !! This is mentioned only briefly as a "deficient representation of the OMZs" in a way that downplays the potential scope of the problem. Given that the jury is still out on the question of how important the OMZs are to global N2O production, the lack of OMZs in NEMO-PISCES raises serious questions about whether this model can be trusted to predict N2O emissions in the present let alone the future. This problem needs further discussion, and it would be good to provide a global map either in the supplement or main text of the O2 concentration at the depth of the water column O2 minimum (or else at some appropriate fixed depth),

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comparing model to WOA.

P16716, lines 5-7 “In particular, the P.TEMP parameterization projects a larger enhancement of the flux than P.OMZ at the BUS, whereas the emissions in the Southern Ocean are enhanced in the P.OMZ parameterization.” Please explain further why this happens, since the Southern Ocean is far removed from the OMZs.

P16717, line 3 “As the N2O production in THIS pathway” I am confused about which pathway is being discussed. I prresume high, but this is unclear as written.

P16718, line 7-9, “Overall these changes are negative, and happen to nearly completely compensate the increase in production in the OMZs, resulting in the near constant global N2O production by the low-O2 production pathway up to year 2100” Yes, but please put this in the context that NEMO-PISCES strongly underestimates the global volume of the OMZs.

p. 16718, section 4.2.2. Please state the absolute value of the inventory to put these changes into context.

p. 16719, lines 6-8. This sentence seems at odds with Figure 7, in which inventory is mainly increasing while production decreases. If this is not the case, then please explain more clearly in the caption whether a bar to left of center = decrease and a bar to right of center = increase (which is what I assumed for lack of other information).

p. 16719, lines 11-14, This sentence also seems at odds with Figure 7. “Figure 7 shows how almost all the relevant changes in N2O production and storage are related to low-latitude processes, with little or no contribution from changes in polar regions.”

p. 16720, discussion of box model. It would be helpful to provide a better explanation of why this model is presented and whether it’s really worth including in the paper. What questions does it address that cannot be answered with the 3D NEMO-PISCES model? Also, in Figure 8, what criteria are used to define the range of the box model parameters? Are some 3D models really predicting decreases of up to 80% in mixing?

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P16723, Section 6. I found this section confusing and am not sure it adds to the value of the paper. The back-of-the-envelope calculations presumably reflect the indirect result of temperature on stratification and export production, but they also could be interpreted as a direct response of N2O production as a function of temperature, given the formulation of P.TEMP. Overall, the calculation is fraught with so much uncertainty that it in my opinion should be deleted.

P16724, line 27. For balance, it might be worth mentioning that other studies (e.g., Suthof, GBC, Vol 15., no.3, 2001.) have explained ice core variations in N2O with mechanisms driven primarily by changes in OMZ-related production.

p. 16740, Figure 6 caption. Please provide more details on the MLD 5m change criteria. Is hatching drawn when the summertime mixed layer depth, the annual mean depth or some other time average changes by 5m?

P16742 Figure 8. Please explain in the figure caption what the x's are.

Interactive comment on Biogeosciences Discuss., 11, 16703, 2014.