

Interactive comment on “Oceanic N₂O emissions in the 21st century” by J. Martinez-Rey et al.

We wish to thank the referees for the thorough assessment of our study. Remarks and suggestions put forward important discussion points. We considered them carefully and provide a point by point answer below. Three topics are common to the three reviews. In order to avoid further redundancies in the reply, we address them first and then proceed with the individual remarks.

These three major topics are:

- The choice of the N₂O parameterizations used in NEMO-PISCES.*
- NEMO-PISCES model performance in the context of the CMIP5 models.*
- Model-data intercomparison, using Nevison et al., 2004.*

We would also like to take the opportunity for updating the reference of the data product to Nevison et al., 2004, as suggested by the author herself via personal communication.

1. The choice of the N₂O parameterizations used in NEMO-PISCES

The decision about the parameterizations used in our experiments has been commented by the three reviewers, demanding additional explanations on different issues. For example, among many other remarks:

- "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 $\mu\text{mol/L}$ 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." (Reviewer #1)*
- "A second concern relates to the choice of the two N₂O production parameterizations, which seem somewhat arbitrary. (...) What is confusing is that the Author use two alternative parameterization of N₂O production (P.TEMP and P.OMZ) where decline in nitrification is compensated by either process. This makes it hard to compare the two parameterizations, and assess which one is more representative of the real ocean - where perhaps all factors are at play. As a sensitivity study, two simulations only are not enough to bracket the range of possibilities of the mechanisms proposed, and separate their effects." (Reviewer #2)*
- "One of the conclusions that they make is that we need to better understand the processes leading to N₂O production under low oxygen conditions. I agree with this statement, but I do think we know more about N₂O production than is represented in their parameterization.(...) Moreover, it is not clear to what extent they tested their assumptions about the N₂O initial condition and production parameterization. A range of values is possible for the N₂O yields for low and high O₂ proceses, and I'm curious how the values used here were chosen." (Reviewer #3)*

We acknowledge the simplistic representation of N cycle processes within the global NEMO-PISCES model. However, as pointed out by the reviewers, the contribution of different microbial reaction pathways to N₂O production is still under debate. While waiting for significant advances in process understanding and availability of data, a global biogeochemical model projection contributes a 'what if' study to the debate. Fully acknowledging the limitation of our approach and biases inherent to NEMO-PISCES, we like to emphasize that the model is not a statistical outlier in the greater ensemble of coupled Earth System Models that contributed to the IPCC's 5th assessment report (e.g. Bopp et al., 2013). Our objective was to evaluate changes in N₂O production and storage over the 21st century in response to climate change, assuming that nitrification would indeed be the dominant production pathway. We feel that this is a valid working hypothesis, albeit not the only one. Our choice is coherent with the current lack of skill of the NEMO-PISCES model in reproducing observed volumes of low oxygen waters. Having said this, we agree that consequences of our working hypothesis need to be addressed in greater detail throughout the manuscript. For this, the manuscript will change accordingly to reflect this additional information.

The choice of parameterizations follows from the scope of our study, which is to explore the consequences of a major assumption, i.e., if most of the N_2O production comes from nitrification what would happen with global N_2O production and emissions in 2100. We implemented two parameterizations: the first one, *P.TEMP*, is based on Butler et al. (1989), the second one, *P.OMZ*, on Jin and Gruber (2003). A sensitivity analysis on the relative contribution of high-, respectively low-oxygen N_2O production pathways on a global scale by Suntharalingam et al. (2000) points towards a higher contribution of nitrification (75%) than denitrification (25%). Using sea-air fluxes by Nevison et al. (1995) to constrain the contribution of nitrification versus denitrification, balanced 50/50 contributions lead to poorer results than the 75/25 share. The relative contribution of nitrification/denitrification of 75/25 in *P.OMZ* in the model follows therefore Suntharalingam et al. (2000). *P.TEMP* can be considered as 100% nitrification, testing in this way the assumption, where nitrification is apparently responsible of 93% of the total N_2O production on a global scale (Freing et al., 2012). These parameterizations allow the independent quantification of the two production pathways (high- O_2 due to nitrification and low- O_2 due to nitrification plus denitrification) and their evolution in time over the next century.

Coefficients used in these parameterizations were adjusted to achieve a modeled global N_2O sea-to-air flux around 3.6 TgN yr^{-1} in line with Ciais et al. (2013) and within the uncertainty interval of $1.8 - 9.4 \text{ TgN yr}^{-1}$ of the last IPCC report. Details on the original and model modified values are shown in Tables 1 and 2. For parameterization *P.TEMP*, based on Butler et al (1989), the same ratio between constants gamma and theta (the temperature effect) is used in the model as in the original formulation. The original values are twice the ones we have used. Retaining the original values would lead to an increase in the total production and flux of N_2O in the model. The overall sensitivity to changes in temperature and the sensitivity to changes in AOU or the way O_2 consumption is described in the model would remain the same.

Table 1: Original and final model derived *P.TEMP* parameterization used in NEMO-PISCES experiments, with their associated gamma and theta constants.

Parameterization	gamma	theta
Butler et al., 1989		
$\Delta N_2O = -13.5 + [0.125 + 0.00993T]AOU$	0.125	9.93×10^{-3}
<i>P.TEMP</i> (Martinez et al., 2014)	0.053	4.3×10^{-3}
$J^{P.TEMP}(N_2O) = (\gamma + \theta T)J(O_2)_{\text{consumption}}$		

For parameterization *P.OMZ*, based on Jin and Gruber (2003), the relative contribution of nitrification/denitrification of 75/25 was applied as an additional constraint. The constant alpha, modulating N_2O production associated with nitrification, is in the same order of magnitude as proposed by Jin and Gruber (2003), while beta, modulating N_2O production associated with denitrification, is two orders of magnitude smaller (Table 2). Constant beta modulates to contribution of denitrification to N_2O production. The use of the original values for alpha and beta in the model would result in a significant increase of N_2O production associated with oxygen minimum zones and, hence, in a departure from the imposed ratio of 75 to 25 for nitrification versus denitrification.

Table 2: Original and final model derived *P.OMZ* parameterization used in NEMO-PISCES experiments, with their associated alpha and beta constants.

Parameterization	alpha	beta
Jin and Gruber, 2003	mmol N_2O /mol NH_4	mmol N_2O /mol NH_4
$\Gamma(N_2O) = J^{\text{nitr}}(N_2O) + J^{\text{denitr}}(N_2O) + J^{\text{cons}}(N_2O),$	0.98	944
$J^{\text{nitr}}(N_2O) = \alpha r_{N:P} J(PO_4^{3-}),$		
$J^{\text{denitr}}(N_2O) = \beta f(O_2) r_{N:P} J(PO_4^{3-}),$		

$J^{\text{cons}}(\text{N}_2\text{O}) = -\frac{1}{\tau}\text{N}_2\text{O}$ for $\text{O}_2 \leq \text{O}_2^{\text{lim}}$,		
P.OMZ (Martinez-Rey et al., 2014)	0.90	6.2
$J^{\text{P.OMZ}}(\text{N}_2\text{O}) = (\alpha + \beta f(\text{O}_2))J(\text{O}_2)_{\text{consumption}} - k\text{N}_2\text{O}$		

2. NEMO-PISCES model performance in the context of CMIP5 models

Several comments, from all 3 reviewers, raise the fact that our estimates of N₂O emissions rely on only one Earth System Model (IPSL-CM5A-LR). While we think that this is justified as we provide here the first estimate of the impact of climate change on marine N₂O emissions, we agree with the reviewers that we should do better in presenting these results in the context of the overall evaluation of our model and in the context of CMIP5. In particular, the analysis of output from other Earth System Models can help to investigate how the drivers of N₂O emissions could change in response to anthropogenic climate change.

The comments of the reviewers converge and specifically ask for more work on the evaluation of NEMO-PISCES and on the comparison with the other ESMs:

- “the problem of (the lack of OMZs in NEMO-PISCES) needs further discussion and it would be good to provide a global map of (...) the O₂ concentration at the depth of the water column O₂ minimum” (Reviewer #1).

- “My first concern is the use of IPSL-CM5A-LR model (...).IPSL-CM5A-LR seem to predict an O₂ increase in the Atlantic tropical OMZ, and a more complex pattern in the Pacific, with overall O₂ increase above 100 m and decrease below. In the pacific OMZ, this is at odds with many other models that predict O₂ increase. Hence N₂O projections of the low-O₂ pathways could be not robust when the model is put in a larger prospective. (...). The decline in Export Production, which is indeed among the largest, and which is what really matter for subsurface nitrification and N₂O production.” (Reviewer #2).

- “a better estimate of uncertainty in the model results, with which to gauge whether the simulated decrease in oceanic N₂O emissions is significant” (Reviewer #3),

In the revised version of the manuscript, we take these comments into account. We take advantage of the recently published model projections from CMIP5. The discussion will include one sub-section in which (1) we describe the potential limitations of our study due to the large biases in representing the OMZs in NEMO-PISCES forced by IPSL-CM5A-LR, and in which (2) we add a comparison of how the model used in our study project export production and O₂ levels in low-O₂ environments in response to anthropogenic climate change

5.1 Oxygen and Export of carbon in NEMO-PISCES compared to CMIP5 models

The state variables upon which representation of N₂O in models rely, i.e., oxygen and export of carbon, are compared to the CMIP5 model ensemble to put our analysis in context of the current state-of-the-art model capabilities. We focus here our analysis on suboxic waters (<5 μmol L⁻¹) and on export production. Whereas CMIP5 models tend to have large volumes of O₂ concentrations in the suboxic (<5 μmol L⁻¹) regime, it is not the case for our NEMO-PISCES simulation, which clearly underestimates the volume of low-oxygen waters as compared to the oxygen corrected World Ocean Atlas 2005 (WOA2005*) (Bianchi et al., 2012). The fact that NEMO-PISCES forced by IPSL-CM5A-LR is highly oxygenated is confirmed by Figure 1, where the histogram of the full O₂ spectrum of WOA2005* and NEMO-PISCES is shown. The O₂ distribution in the model (Fig. 2) shows a deficient representation of the OMZs, with

higher concentrations than those from observations in WOA2005* (Bianchi et al., 2012) and the other CMIP5 models. The rest of the O_2 spectrum is well represented in our model. NEMO-PISCES is therefore biased towards the high O_2 production pathway of N_2O due to the modeled O_2 fields.

When turning to the export of organic matter, NEMO-PISCES is close to the CMIP5 average value of 6.9 PgC yr^{-1} . The overall distribution of export is also very close to the CMIP5 model mean and both show smaller values than those from the data-based estimate of 9.84 PgC yr^{-1} (Figure 2).

Figure 1: Histogram of the dissolved O_2 concentration (in $\mu\text{mol L}^{-1}$) in WOA2005* (red) and NEMO-PISCES in offline mode (black).

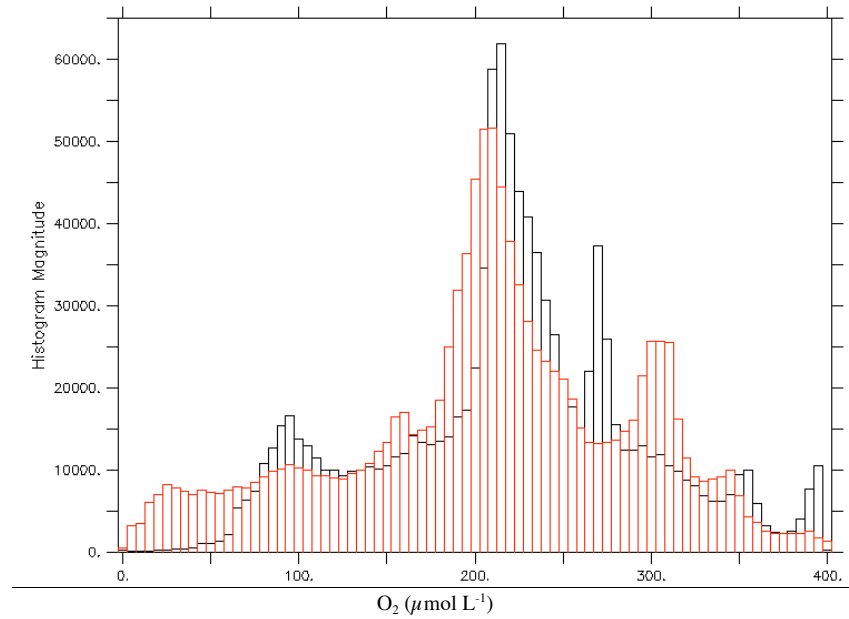
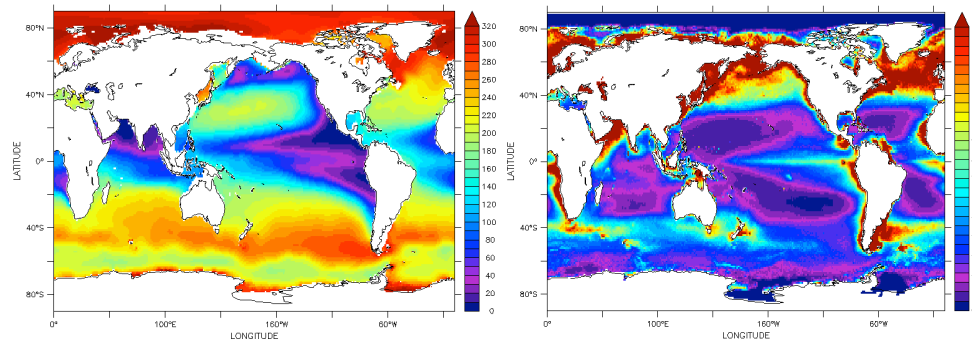
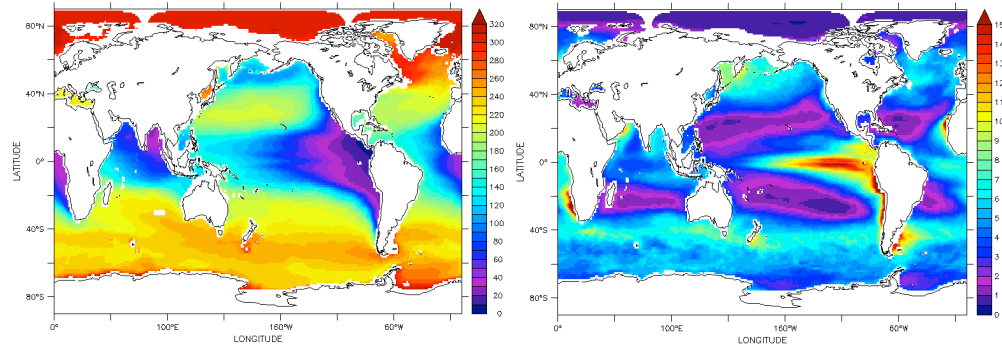


Figure 2: Averaged O_2 between 200-600m depth (in $\mu\text{mol L}^{-1}$) and Export of organic carbon (CEX) (in $\text{mmolC m}^{-2} \text{d}^{-1}$) in (a) WOA2005* and Dunne et al., 2007, (b) CMIP5 model mean (historical simulations, 1990-1999 period from Bopp et al. 2013) and (c) NEMO-PISCES for the present 1985-2005 time period.

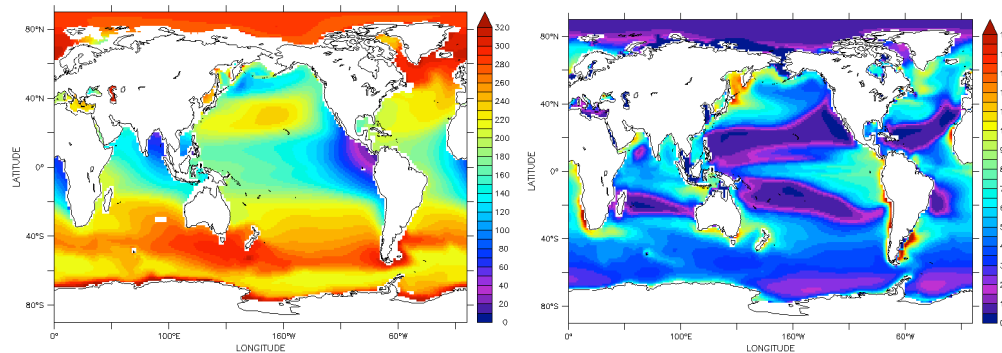
a. WOA2005* and Dunne et al., 2007



b. CMIP5 model mean



c. NEMO-PISCES



The uncertainties derived from present and future model projections can be estimated using the spread in the CMIP5 model projection of export of organic matter and assuming a linear response between nitrification (or export) and N₂O production in the subsurface, which is assumed to be quickly outgassed to the atmosphere. In NEMO-PISCES, a decrease in 13% in export leads to a maximum decrease in N₂O emissions of 12% in the P.OMZ scenario. Based on results by Bopp et al. (2013), changes in export of carbon span -7% to -18% in the CMIP5 model ensemble at the end of the 21st century and for RCP8.5. The spread would propagate to a similar range in projected N₂O emissions across the CMIP5 model ensemble. Applying these values to present N₂O emissions of 3.6 TgN yr⁻¹, uncertainties are then bracketed between -0.25 and -0.65 TgN yr⁻¹.

Regarding the low-O₂ pathway, a similar approach is of course not that straight forward. Zamora et al., (2012) found that a linear relationship between AOU and N₂O production might occur even at the OMZ of the ETP. Zamora et al. (2012) acknowledged the fact that the MEMENTO database includes N₂O advected from other regions and that mixing could play a relevant role, smoothing the fit between N₂O and AOU from exponential to linear. However, Zamora et al. (2012) quoting Frame and Casciotti (2010), suggested that regions where an exponential relationship in N₂O production is present might be rare, that other non-exponential N₂O production processes might occur and therefore the plot they presented could describe the actual linear relationship between N₂O production and oxygen consumption. Based on this hypothesis, we could refer again to the linear relationship suggested in the high-O₂ and export scenario. However, in this case the CMIP5 model projections of changes in the hypoxic and suboxic volumes differ substantially. Most models project an expansion of the OMZs in the +2% to +16% range in the suboxic volume (O₂ < 5 μmol L⁻¹). There are, however, models that project a slight reduction of 2%. Spatial variability of projections add to the spread between CMIP5 models. These discrepancies suggest that uncertainties from this spread must be interpreted with caution when estimating potential future N₂O emissions.

3 - Model-data intercomparison, using Nevison et al., 2004.

The reviewers have pointed out that the NEMO-PISCES N₂O sea-to-air flux shows more discrepancies with data from Nevison et al., 2004, than those described in the manuscript, or at least that model-data discrepancies should better explained. We acknowledge this fact, which has been suggested by all of the reviewers in their reports:

- "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 and ETNP. The Nevison et al., 2004, map, which is used to evaluate the NEMO-PISCES 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.)" (Reviewer #1).
- "Overall I'm not impressed by the model N₂O simulation (again Fig 3a-b), and I disagree that even P.OMZ has a good correlation with the model (p. 16714, l. 9). No model is perfect, but the specific shortcoming in the N₂O simulation should be clearly laid out and there should be a discussion on how they could affect the conclusions." (Reviewer #2)
- "Would tuning of these parameters lead to an improvement in the model? As it currently stands, the model/data agreement could be better (Figures 1-3), and that leads me to question the results of the future simulations." (Reviewer #3)

The choice in the parameterization constants was motivated, as explained before, by the global N₂O flux and the relative contribution of the production pathways, rather than a spatial match between the model and the data product. We aimed nevertheless at an overall agreement with a satisfying representation of major hotspots of N₂O sea-to-air fluxes reported for the Eastern Tropical Pacific, the Benguela Upwelling System, the Arabian Sea, the Bay of Bengal, the Agulhas Current and the North Pacific.

However, there is room to highlight the discrepancies in the text more clearly as follows:

*Elevated N₂O emission regions (>50mgN m⁻²yr⁻¹) are found in the **Equatorial and Eastern Tropical Pacific**, in the northern Indian ocean, in the northwestern Pacific, in the North Atlantic and in the Agulhas Current. In contrast, low fluxes (<10mgNm⁻²yr⁻¹) are simulated **in the Southern Ocean**, Atlantic and Pacific subtropical gyres and southern Indian Ocean. The large scale distribution of N₂O fluxes is coherent with Nevison et al. (2004). **This comes as a natural consequence of the relatively high contribution of nitrification and hence hotspots of N₂O emissions are associated with regions where higher export of organic matter occurs in the model.***

*There are however several discrepancies between the model and the data product (Nevison et al., 2004). **At high latitudes, the high N₂O emissions observed in the North Pacific are not well represented by the model, with a significant shift towards the western part of the Pacific basin, similar to other modeling studies. The OMZ in the North Pacific, located at approximately 600 m depth, is underestimated in the model due to the deficient representation of the Meridional Overturning Circulation (MOC) in the North Pacific in global ocean biogeochemical models, which in turn might suppress low oxygenated areas and therefore one potential N₂O source. Discrepancies between model and observations also occur in the Southern Ocean, a region whose role in global N₂O fluxes remains debated due to the lack of observations and the occurrence of artifacts (e.g., Suntharalingam and Sarmiento, 2000; Nevison et al., 2003) due to interpolation techniques reflected in data products such as that from Nevison et al., 2004. The model also overestimates the N₂O emissions in the North Atlantic. The emphasis put on the nitrification pathway suggests that hotspots of carbon export are at the origin of elevated concentrations of N₂O in the subsurface. N₂O is quickly***

outgassed to the atmosphere, leading to such areas of high N₂O emissions in the model.

Model-data discrepancies can be seen as a function of latitude in Figure 1d. The modeled N₂O flux maxima peak at around 40°S, i.e., around 10°N to that estimated by Nevison et al. (2004), although Southern Ocean data must be interpreted with caution. In the northern hemisphere the stripe in the North Pacific is not captured by the model, splitting the flux from the 45°N band into two peaks at 38°N and 55°N.

Discrepancies between model and data product prompted changes in the conclusion:

The contribution of the high-O₂ pathway that was considered in this model analysis might be a conservative estimate. Freing et al. (2012) suggested that the high-O₂ pathway could be responsible of 93 % of the total N₂O production. Assuming that changes in the N₂O flux are mostly driven by N₂O production via nitrification, that would suggest a larger reduction in the marine N₂O emissions in the future. However, the mismatch between NEMO-PISCES and the Nevison et al. (2004) spatial distribution of N₂O emissions in the western part of the basins suggests that changes in the future might not be as big as the changes projected in the model in such regions. Changes would be then distributed more homogeneously.

The assessment of the model performance compared to the MEMENTO database is also modified following the suggestions from the referees. Regarding the global depth average and the restriction in the depth bands where agreement between model and data occurs, that paragraph has been now modified as,

"In the second layer, P.OMZ shows a fairly good agreement with the observations in the 500 to 900m band, whereas P.TEMP is too low by ~10 nmol L⁻¹."

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.

We thank the reviewer for his positive evaluation.

Below are some more detailed comments.

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 μmol/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 μmol/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 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.

Please refer to first part of author's reply and revision of the main text.

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

The paragraph in the introduction has been modified as,

*The atmospheric concentration of N₂O is determined by the natural balance between sources from land and ocean and the destruction of N₂O in the atmosphere largely **by photolysis** (Crutzen, 1970; Johnston, 1971).*

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

The paragraph in the introduction has been modified as,

*Anthropogenic activities currently add an additional 6.7 Tg N yr⁻¹ to the **atmosphere, which has caused** atmospheric N₂O to increase by 18 % since pre-industrial times (Ciais et al., 2013).*

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.)

Three additional references have been added:

*There are only few studies from a limited number of specific regions such as the Arabian Sea, Central and North Pacific, **Black Sea**, the Bedford Basin and the Scheldt estuary, which can be used to derive and test model parameterizations (Mantoura et al., 1993; Bange et al., 2000; Elkins et al., 1978; **Farias et al., 2007; Frame and Casciotti, 2010; Westley et al., 2006; Yoshida et al., 1989; Punshon and Moore, 2004; De Wilde and De Bie, 2000.**)*

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

Based on Freing et al., 2012: "As marine autotrophic and heterotrophic processes display sensitivities to temperature (to varying degrees), ocean warming might result in changes of the bacterial community structure and hence in changes of N₂O production."

The paragraph has been modified accordingly as,

*"Ocean warming might **change** the rate of N₂O production during nitrification (**Freing et al., 2012**)"*

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."_____

The paragraph has been modified as,

*Finally, the expected general loss of oxygen (Keeling et al., 2010; Cocco et al., 2012; Bopp et al., 2013) could substantially affect N₂O production via **both nitrifier denitrification and classic denitrification.***

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

The paragraph has been modified as,

***Ocean biogeochemical models** used for IPCC's 4th assessment report estimated a decrease between 2 and 13 % in primary production (PP) under the business-as-usual high CO₂ concentration scenario A2 (Steinacher et al., 2010)*

P16710, 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.

Following the discussion in the introductory part of our reply, Zamora et al. (2012) acknowledges the fact that the MEMENTO database includes N₂O advected from other regions and that mixing could play a relevant role, smoothing the fit between N₂O and AOU from exponential to linear. However, Zamora et al. (2012) quoting Frame and Casciotti (2010), suggests that regions where an exponential relationship in N₂O production is present might be rare, that other non-exponential N₂O production processes might occur and therefore the plot they presented could describe the actual linear relationship between N₂O production and oxygen consumption.

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.

In the model the light inhibition on nitrification is implemented removing all N₂O production in the upper 100m for both P.TEMP and P.OMZ parameterizations, so there is only a 50m depth band difference between Zamora analysis and the model assumption. Most of the N₂O production in the model occurs right below the euphotic zone but this corresponds to highly oxygenated regions in the subsurface where the more "traditional" assumption of linear relationship between N₂O production and O₂ consumption applies, as shown by the measurements from the MEMENTO database.

A paragraph in the methodology section was added to explicitly mention the inhibition of N₂O production in the upper 100m in the model,

N₂O production is inhibited by light in the model, and therefore N₂O production in P.TEMP and P.OMZ parameterizations only occurs below a fixed depth of 100m.

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.

We acknowledge the fact that the value we have used in our simulations has been kept constant throughout the 21st century model projections. The value of 284 ppb corresponds to the early 20th century and we have not changed this value to explore future changes inherent to ocean processes and not to include the feedbacks due to the atmosphere.

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.)

Please refer to first part of author's reply.

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 and ETNP. The Nevison et al., 2004 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.

Please refer to first part of author's reply.

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.

Please refer to first part of author's reply.

p16714, line 11 and subsequent discussion. "Below 1500m, 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.

The disagreement between NEMO-PISCES and MEMENTO database below the 1500m threshold points more towards the initialization values rather than to the parameterization constants. Considering that the most of N₂O production is via nitrification, production occurs right below the euphotic zone, where remineralization is maximum and hence it is more sensitive to the values we have used in the parameterizations. We think that the prescribed N₂O concentration at depth, 20nmol L⁻¹, drives the overestimation at depth.

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

The paragraph in the model validation has been modified as,

*P.TEMP (Fig. 3a) slightly overestimates N₂O for dissolved O₂ concentrations above 100μmolL⁻¹, and does not fully reproduce **either the high N₂O values in the OMZs or the N₂O depletion when O₂ is almost completely consumed***

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 μmol/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), comparing model to WOA.

Please refer to first part of author's reply.

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.

Regarding the larger enhancement of P.TEMP compared to P.OMZ at the BUS, if we look at changes in P.OMZ high- and low-O₂ production pathways (Figure 5c and 5d), changes are negative, meaning that NEMO-PISCES projects a reduction of the OMZ at the BUS. The combined effect leads to a decrease in N₂O flux in P.OMZ, while positive changes in P.TEMP due to temperature contribute to an enhancement of flux at the BUS.

Regarding the enhanced P.OMZ emissions in the Southern Ocean, we can observe in Figure 4b and 4c that both parameterizations have the same pattern in changes in N₂O flux, and that the only difference is the intensity or magnitude of these changes, rather than regional disparities. In fact, positive and negative changes in the P.OMZ low-O₂ pathway, shown in Figure 5d, are not spatially correlated to the enhancement we have observed in the flux. Considering that both parameterizations are tied to the same changes in export and to the same changes in ocean circulation, and that low-O₂ is not driving the enhancement, the effect of temperature seems the only effect left which can potentially attenuate P.TEMP at high latitudes compared to P.OMZ. Hence the change in magnitude.

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

The paragraph in the results section has been modified as,

*The vast majority of the changes in the N₂O production in the P.OMZ parameterization is caused by the high-O₂ pathway with virtually no contribution from the low-O₂ pathway (Fig. 5a). As the N₂O production in **P.OMZ parameterization** is solely driven by changes in the O₂ consumption (Eq. 2), which in our model is directly linked to export production, the dominance of this pathway implies that primary driver for the future changes in N₂O production in our model is the decrease in export of organic matter (CEX).*

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.

Please refer to first part of author's reply.

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

The inventory in the upper 1500m in P.OMZ is 237.0 TgN at present, while in P.TEMP in the same depth band is 179.8 TgN. This means that the projected changes in the inventory in 2100 of 8.9 and 4.0 TgN represent an increase of about 4% and 2% in P.OMZ and P.TEMP respectively.

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).

The assumption of left/right of the bar is correct and, in our opinion, very intuitive. The sentence refers to flux and production, whose changes are of the same sign. Therefore the sentence "Changes in N₂O flux and N₂O production are mostly of the same sign in almost all of the oceanic regions in line with the assumption of nitrification being the dominant contribution to N₂O production" is consistent with Figure 7. It is N₂O inventory who has a different sign.

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.”

We agree with the referee that changes are more homogeneous. The paragraph has been modified as,

*The increase in inventory is particularly pronounced along the eastern boundary currents in the Equatorial and Tropical Pacific, **Indian Ocean, and also in smaller quantities in the Atlantic Ocean.** Figure 7 shows how **the decrease in N₂O production and increase in N₂O storage occurs in all oceanic basins.***

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?

The box model is designed to disentangle physics from biogeochemistry effects on N₂O emissions and to analyse the separate impact of each one of them (mixing and CEX). This separation of mixing and CEX can not be done in the transient NEMO-PISCES simulations, particularly because export and mixing are tied and unique in the specific single scenario we have considered.

The explanation of the box model has been modified as follows,

*The synergy among the driving mechanisms can be explored with a box model pursuing two objectives. **First, to separate the effect of the physical (i.e., increased stratification) and the***

biogeochemical (i.e., reduction of N₂O production in high-O₂ regions) mechanisms on N₂O emissions. In the particular NEMO-PISCES model projection we have studied, changes in mixing and export are unique and can not be explored individually. In this way we can also reproduce future projections assuming that the only mechanisms ruling the N₂O dynamics in the future were those that we have proposed in our hypothesis. Secondly, to explore a wider range of values for both mixing (i.e., degree of stratification) and efficiency of N₂O production in high-O₂ conditions.

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?

In the box model we have explored the range of mixing and export of carbon to depth (CEX), separating in this way two effects that are by construction tied to each other in the transient NEMO-PISCES model projections. The range of CEX is that from the CMIP5 model ensemble projections. The range of mixing is much more difficult to bracket. It encompasses different physical processes such as diffusion, convection, ventilation, vertical diffusion, etc... and it is more difficult to quantify from the CMIP5 model output. So we take advantage of the plasticity of the box models to explore the widest possible range, covering all the imaginable cases, event a total stagnation of the ocean circulation.

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.

We acknowledge the uncertainty in which we incur when we compare Stocker et al., 2013 results with our estimate. We think that this calculation gives however an idea in terms of order of magnitude, whether it's comparable or not to terrestrial emissions, and conclusions are drawn from this fact rather from an specific value of the precise feedback strength of oceanic/terrestrial emissions, which might be of course subject to large uncertainties. We do agree that there are many uncertainties on estimating N₂O in general, but in the extreme scenario that we have studied, where N₂O production is mainly driven by nitrification, changes in the feedback strength do not exceed those from terrestrial sources. We think it's a valuable result as an upper limit, and opens future discussions on how to evaluate/compare feedback strengths from terrestrial and oceanic models.

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.

The paragraph has been modified as follows:

*The same combination of mechanisms (i.e., change in export production and ocean stratification) have been identified as drivers of changes in oceanic N₂O emissions during the Younger Dryas by Goldstein et al. (2003), **although other studies point towards changes in the N₂O production at the OMZs as the main reason for variations in N₂O fluxes observed in the past (Suthof et al., 2001).***

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?

The hatching represents annuan mean depth. The criteria in choosing 5m is a threshold in the model to show a minimum decrease/increase in MLD in general. For clarification, the figure caption has been modified as:

"Hatched areas indicate regions where the **annual mean** mixed layer depth is reduced by more than 5m in 2080–2100 compared to 1985–2005".

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

The x symbol has been replaced by a line, which represents the univocal NEMO-PISCES decrease in export. The figure caption has been modified as follows:

Figure 8: Box model results, analysing the effect of changes in ocean circulation by reducing the mixing coefficient (μ in %) and changes in biogeochemistry by reducing export of organic matter (ϵ in %) separately in N₂O sea-to-air emissions and N₂O inventory. (a) Constant regimes in percentage of the historical N₂O sea-to-air flux: 95 % pink, 90 % blue, 85 % cyan and 80 % green, and (b) Constant regimes in percentage of the historical N₂O concentration in the deep: 90 % pink, 110 % blue, 125 % cyan and 150 % green. The line represents the univocal NEMO-PISCES model export in the context of the box model.

Anonymous Referee #2

Received and published: 14 January 2015

The manuscript by Martinez-Rey et al. uses a current-generation Earth System Model to predict changes in N₂O emissions during the 21st century under the RCP8.5 business as usual emission scenario. N₂O is an important greenhouse gas that affects the atmosphere's radiative and ozone budgets. Hence, understanding how natural sources of N₂O will evolve under a changing climate is an important question. N₂O emissions depend on biogeochemical sources, ocean circulation and air-sea exchange. ESM provide a natural framework to represent these processes in a physically consistent way.

The main findings of the paper is a (minor) decline in N₂O production and emissions and increase in N₂O inventories in the simulations, resulting from compensating changes in oceanic sources (following warming, declining export and nitrification, general deoxygenation), and a decrease in air-sea fluxes driven by increased stratification. Increased stratification dominates the overall transient response, producing the most robust results. The predicted decline in marine N₂O emissions is nearly equal to the projected N₂O increase from terrestrial sources, potentially offsetting it.

ESM projections as the ones presented by the Authors are necessary but difficult, and suffer from large uncertainties. These include model biases, shortcoming in parameterizations, and results (e.g. N₂O production changes) that often depend on the compensation between opposite but largely uncertain terms. Clearly framed simulations could help disentangle the role and magnitudes of the various mechanisms at play. In this prospective the Author's work is welcome. However, aspects of the work are not systematic enough to entirely support all the conclusions, and clarifications are necessary. I also worry that some of the conclusions might be model-dependent and hence not robust enough. On the other hand, the work highlights several aspects of N₂O cycling where additional research is needed.

The manuscript is well structured and written, and generally clear. Similarly, the figures are clear and support the analysis.

Specific comments:

- My first concern is the use of the IPSL-CM5A-LR model, mostly because of its seriously deficient O₂ simulation. The Authors clearly state that most current ESMs have a hard time getting the right O₂ patterns

(especially low-O₂ regions). However some models perform better than others. In the upper ocean (0-1000 m), IPSL-CM5A-LR strongly overestimates O₂ (on average by 50-100 mmol/m³). Hence it underrepresented quite dramatically the extent of low-O₂ waters where most of the enhancement of N₂O production in the low-O₂ pathway takes place. Similarly, anoxic waters in IPSL-CM5A-LR are almost missing, biasing the representation of the (already uncertain) N₂O dynamics related to denitrification. Finally, most low-O₂ waters in IPSL-CM5A-LR are found below 1000m in the deep North Pacific, where they would intercept very little organic matter fluxes. Figure 3C acknowledges some of these biases, but the discussion in the manuscript is lacking. The Authors should be more upfront about these biases, and should put more effort in discussing how they could affect the results, especially the claim that changes in the low-O₂ pathway are negligible. Given how small OMZ are to start with, especially in the upper ocean where most nitrification takes place, I'm not surprised that the model puts so little emphasis on this pathway.

Please refer to first part of author's reply.

- The same goes for the projections to 2100, especially related to the evolution of OMZ in the tropics. As the Authors point out, the tropics are regions of disagreement among ESMs. IPSL-CM5A-LR seem to predict an O₂ increase in the Atlantic tropical OMZ, and a more complex pattern in the Pacific, with overall O₂ increase above ~100 m and decrease below. In the Pacific OMZ, this is at odds with many other models that predict O₂ increase. Hence N₂O projections of the low-O₂ pathways could be not robust when the model is put in a larger prospective.

Please refer to first part of author's reply.

- Similarly, IPSL-CM5A-LR seem on the large side of models' NPP decrease prediction - up to twice as large as many other models (e.g. Bopp et al., 2013, Fig 9). This would overstate the role of nitrification decreases.

Please refer to first part of author's reply.

- Overall, the title and abstract should reflect the model-dependent aspects of the study - e.g. “. . . in a Earth System Model” or “. . . in IPSL Earth System Model” in the title, etc.

The following title could be proposed to the editor: "Projections of oceanic N₂O emissions over the 21st century using the IPSL Earth System Model".

- A second concern relates to the choice of the two N₂O production parameterizations, which seem somewhat arbitrary. The Authors identify 3 major processes controlling the evolution of N₂O sources. These are: decline in nitrification rates (because of less export and remineralization), warming, and deoxygenation. The first process decreases N₂O production, the last two increase it, hence opposing the first. What is confusing is that the Author use two alternative parameterization of N₂O production (P.TEMP and P.OMZ) where decline in nitrification is compensated by either process. This makes it hard to compare the two parameterizations, and assess which one is more representative of the real ocean - where perhaps all factors are at play. As a sensitivity study, two simulations only are not enough to bracket the range of possibilities of the mechanisms proposed, and separate their effects.

Please refer to first part of author's reply.

- For P.TEMP, I am not sure what the reference (and background) for equation (1) is - especially the temperature dependence, which seems a little bit ad hoc. This should be more clearly discussed, because in this simulation the temperature effect appears strong enough to almost compensate entirely for the decreases in nitrification sources by 2100. I also note that IPSL-CM5A-LR predicts a temperature increase by 2100 of around 4 K which is on the high end of ESM prediction (~2-3 K). This might overstate the role of warming in increasing N₂O emissions.

The temperature dependency was first proposed by Elkins et al., 1978, based on the effect of temperature on microbial nitrification. This formulation provided a good fit between ΔN_2O and AOU in data from the central Pacific, with temperature spanning 5 to 25°C. Butler et al., 1989, updated the coefficients when using an expanded dataset of $\Delta N_2O/AOU$.

IPSL-CM5-LR projects an increase in sea surface temperature of around 4K, which is larger than that from the CMIP5 models, i.e., 2.73K on average according to Bopp et al., 2013. This fact suggests that the temperature effect that we have observed in our study, almost compensating the decrease in export and nitrification, might be not so pronounced, leading to an additional decrease in N_2O production and hence a decrease on N_2O sea-to-air flux. However, this hypothesis must be interpreted with caution, particularly when we consider nitrification in the model to occur below the euphotic zone, and therefore changes in temperature might be different from those projected in the surface.

- Regarding P.OMZ, the Authors should write down the exact equation used for $f(O_2)$. While they say it is a step-like function, it appears more complex in Fig S1.

The explicit formulation of $f(O_2)$ has been added to the supplementary material as follows,

$$f(O_2) = \begin{cases} \frac{O_2}{O_2^{*1}} & O_2 < O_2^{*1} \\ 1 & O_2^{*1} < O_2 < O_2^{*2} \\ 0.7 \cdot \exp - 0.5(O_2 - O_2^{*2})/O_2^{*2} + \\ 0.3 \cdot \exp - 0.05(O_2 - O_2^{*2})/O_2^{*2} & O_2 \geq O_2^{*2} \end{cases}$$

- Also, how was the partitioning between 75% high-o2 pathway and 25% low-O2 pathway calibrated? I assume that was done by adjusting alpha and beta, but this seems a bit arbitrary. Don't existing parameterizations based on measurements (e.g. Nevison et al. 2003, GBC, etc.) provide a more data-based way for this partitioning?

The partitioning in data-based parameterizations, e.g., Nevison et al. 2003, are biased towards nitrification, excluding N_2O production in regions with O_2 precisely below $4\mu\text{mol L}^{-1}$, as suggested in the same study, and therefore we have excluded such approach in our analysis.

- How does the final parameterization used here compare to the existing ones? Perhaps some discussion on how these choices impact the low-pathway results and sensitivity could be added.

Please refer to first part of author's reply.

- p. 16731, ll. 27-28. These correlation coefficients seem quite small - corresponding to R^2 of 0.18-0.24, that is around 1/5th of the data variance. . . Overall I'm not impressed by the model N_2O simulation (again Fig 3a-b), and I disagree that even P.OMZ has a good correlation with the model (p. 16714, l. 9). No model is perfect, but the specific shortcoming in the N_2O simulation should be clearly laid out and there should be a discussion on how they could affect the conclusions.

Please refer to first part of author's reply.

- Part of the N_2O emission changes are transient. If the system were to stabilize (e.g. to a warmer climate), air-sea fluxes would again match interior production. Perhaps the distinction between transient and long-term responses could be discussed, as it would matter for the long-term climate effects of N_2O .

We refer in the caveats section to the potential impact of longer simulation periods. This paragraph has been now extended as follows,

Longer simulation periods could reveal additional effects on N_2O transport beyond changes in

upwelling or meridional transport of N₂O in the subsurface (Suntharalingam and Sarmiento, 2000) that have been observed in this transient simulation. Long-term responses might include eventual ventilation of the N₂O reservoir in the Southern Ocean, highlighting the role of upwelling regions as an important source of N₂O when longer time periods are considered in model projections.

- Conclusions: p. 16724, ll. 12-16. I'm confused by this sentence. Saying that differences between the P.TEMP and P.OMZ are modest and translate into non-significant differences in model projections, seems inaccurate and contradicts many of the findings discussed before. Just by looking at the trajectories of production and fluxes (Fig. 4-5) the models respond quite differently - with much larger production and flux decline in P.TEMP. I disagree that the biogeochemical differences are negligible between the two models. Rather, my take is that purely physical responses (through air-sea exchange reduction) dominate - hence the (somewhat) homogeneous response of emissions in P.TEMP and P.OMZ. This comment somewhat echoes some confusion throughout the paper of what is driven by physical changes, and what by biogeochemical changes. These are well-separated by construction in the box model, but not as well in the 3D models.

We agree on the emphasis that the referee puts on the physical processes driving the future changes rather than the biogeochemical ones. Each production pathway is tied, in addition to CEX, to ocean circulation changes, which impact either stratification in the case of the high-O₂ pathway, or stratification plus reduced ventilation and therefore changes in the OMZs in the case of the low-O₂ pathway. On top of that, ocean physics are better represented in models than biogeochemistry. This fact adds robustness to our conclusions: identified mechanisms derived from ocean circulation are more reliable than those from biogeochemistry, as pointed out in several occasions when talking about the inherent uncertainties in the representation of the N-cycle in models. And that's why we have developed the box model, as mentioned before, to disentangle physics and biogeochemistry and to analyse the separate impact of each one of them (mixing and CEX) on N₂O emissions. This separation of mixing and CEX can not be done in transient NEMO-PISCES simulations.

We emphasize this remark in the conclusions' paragraph as,

*Differences between the two parameterizations used here are **more related to biogeochemistry rather than changes in ocean circulation**. Despite sharing the high-O₂ N₂O production pathway, leading to a decrease in N₂O emissions in both cases, the role of warming in P.TEMP or higher N₂O yield at low-O₂ concentrations in P.OMZ **translate** into notable differences in the evolution of the two production pathways. **However, the dominant effect of changes in stratification in both parameterizations drives ultimately the homogeneous response of the two parameterizations considered in model projections in the next century.***

- A recent paper by Zamora and Oschlies (2014, GRL) suggests that N₂O production by nitrification in the euphotic zone could be a large and an overlooked source of uncertainty for N₂O emissions. Such a source term would respond similarly to the 'high-o₂ pathway' and decline with declining productivity, but the Authors should reference it in the paper.

We agree with the referee that the recent findings from the study by Zamora and Oschlies (2014) could indeed add value to the discussion on future changes in the high-O₂ production pathway. Discussing the results on changes in N₂O production a paragraph has been added as,

The general pattern of export changes, i.e., decreases in lower latitudes, increase in higher latitudes, is consistent generally with other model projection patterns (Bopp et al., 2013), although there exist very strong model-to-model differences at the more regional scale.

The model assumption neglecting N₂O production in the upper 100m avoids one important

source of uncertainty in estimating global oceanic N₂O fluxes. In case nitrification occurs in the euphotic layer, our results would be facing a significant uncertainty of at least ± 25% in N₂O emissions according to Zamora and Oschlies (2014) analysis using the UVic Earth System Climate Model.

- The paper by Zamora and Oschlies (2014, GRL), and others before, pointed out the large uncertainty stemming from parameterizations of N₂O sources. If uncertainties figures were attached to Martinez-Rey results, would climate-induced changes in N₂O production and emissions be distinguishable from zero? Changes in inventories might be more robust. They would also be the easiest to detect if we were to monitor N₂O over the next century and put Martinez-Rey and coauthors' predictions to a test. I have the impression that the inventory increase is the most robust result of the paper, and should be highlighted as such in the abstract.

We do agree on the robustness of our conclusions regarding changes due to ocean circulation rather than changes in ocean biogeochemistry, as mentioned before. There is no doubt that error intervals bracketed by Zamora and Oschlies (2014) would put ours -or any other model projection results- under question marks, considering the wide error interval induced by potential surface nitrification alone, spanning -25% to +50% changes in N₂O emissions in two conservative scenarios. However, it must be noticed that all the uncertainty sources associated to variables linked to OMZs (consumption rate, switch from production to consumption and suboxic volume) do not introduce such big uncertainties, or at least not as big as those from surface nitrification. This suggests that, despite the importance of the OMZs in estimating global oceanic N₂O production and N₂O flux, excessive N₂O production via nitrification is of paramount importance, and it is an scenario that must be looked carefully.

The abstract has been modified accordingly to highlight the role of changes in ocean circulation,

"The reduction in N₂O emissions is caused on the one hand by weakened nitrification as a consequence of reduced primary and export production, and on the other hand by stronger vertical stratification, which reduces the transport of N₂O from the ocean interior to the ocean surface. While there are many uncertainties in the relative contribution and changes in N₂O production pathways, the increasing storage seems unequivocal and determines largely the decrease in N₂O emissions in the future."

Technical comments:

- I'm confused by the units and values of some of the box-model parameters. k should have units of 1/time, and represent a global integral of a piston velocity, but is listed as a concentration ratio in Table S1 - this is confusing. Also Table S1 should include the value of v .

Thanks for this remark. As it states, k is misleading. Using letter k has been a very unfortunate choice for labeling this parameter, as it has nothing to do with piston velocity but just the ratio of the surface N₂O which is outgassed to the atmosphere. The parameter has been changed to π in the box model description with units of %. A description of v has been included in the same table S1.

Anonymous Referee #2

Received and published: 16 January 2015

In the 3d specific comment of my review, I stated that the IPSL model projects a NPP decline that is among the largest among CMIP5 models. This is not true, as the NPP decline is right in between other models (figure 4 in Bopp et al., 2013 BGS). What I should have referred to is the decline in Export Production, which is indeed among the largest, and which is what really matter for subsurface nitrification and N₂O production. The reference to Fig. 9 in Bopp et al., 2013 (BGS) is accurate. I apologize for any source of

confusion.

Thanks for the hint.

Anonymous Referee #3

Received and published: 15 January 2015

This paper presents a model simulation of oceanic N₂O emissions under an enhanced CO₂ level 'business as usual' future climate scenario. Their results suggest a decrease in future N₂O emissions may occur due to a reduction in export primary production and mixing between the surface and deep N₂O reservoirs. This decrease in mixing (increased stratification) would also lead to an increase in N₂O concentration in the deep ocean. They consider two model parameterizations of N₂O production, with one parameterization also including N₂O consumption at low O₂. Given the predominance of a high-O₂ production pathway, the differences between the parameterizations are relatively small. In fact, without an estimate of uncertainty, it's not even clear whether they are significant.

One of the conclusions that they make is that we need to better understand the processes leading to N₂O production under low oxygen conditions. I agree with this statement, but I do think we know more about N₂O production than is represented in their parameterization. The low-O₂ parameterization used here is derived from a Goreau et al., (1981) study based on experiments with nitrifying bacteria. It's pretty clear that denitrification is linked to organic matter supply, and more sophisticated model could include denitrification explicitly, allowing N₂O to be both produced and consumed by this process.

Please refer to first part of author's reply.

- Moreover, it is not clear to what extent they tested their assumptions about the N₂O initial condition and production parameterization. A range of values is possible for the N₂O yields for low and high O₂ processes, and I'm curious how the values used here were chosen. Would tuning of these parameters lead to an improvement in the model? As it currently stands, the model/data agreement could be better (Figures 1-3), and that leads me to question the results of the future simulations. In addition, it would be helpful to have an estimate of uncertainty in the model results, with which to gauge whether the simulated decrease in oceanic N₂O emissions is significant.

Regarding the question of whether a different choice in the parameterization values could improve the model-data comparison, in P.TEMP, nitrification hotspots are closely related to maxima in export of organic matter and therefore by changing the constants we might change the intensity but the location and the spatial pattern would remain similar. Regarding P.OMZ, N₂O production in OMZs could be boosted increasing the beta constant in order to have a higher contribution of the OMZs to the flux and quite likely to a better match of N₂O concentration at 200-500m depth band with the MEMENTO Database. It must be mentioned however, that the MEMENTO database seems biased towards measurements in the OMZs and therefore values of N₂O concentration in that depth band could be higher than the actual ones.

- Finally, I wonder what are the implications of the model spin-up procedure (only letting the N₂O model run for 150 years before perturbing the system) and proscribed initial conditions (20 nM everywhere) for the results. How do we know that the 'future scenario' is not simply the model N₂O field continuing to evolve from the proscribed initial conditions? It seems like these changes should be evaluated relative to a control simulation in which the forcing is kept constant through 2100.

We agree with the referee that special attention must be paid in general to model drifts when using ocean biogeochemical models over long time scales, and in particular when the spin-up phase has been relatively short. The model achieved equilibrium in N₂O emissions after that period, but nevertheless all the biogeochemical variables which have been presented in this study have been drift corrected using a control

simulation with pre-industrial dynamical forcing fields to remove such drift from the results.

p. 16711: The choice of 75% of N₂O production in the P.OMZ simulation via the high- O₂ pathway seems rather arbitrary. It would be helpful to know how sensitive the model results are to this assumption.

Please refer to first part of author's reply.

p. 16711-12: What are the implications of the model drift for model results described here? Were such drifts corrected for in some way? A model spin-up time of 150 years is probably too short to come to equilibrium.

As mentioned above, the model drift has been corrected using an extra control simulation.

p. 16712: “close to the subsurface” is awkward phrasing.

The paragraph has been corrected as,

*As a result, the major part of N₂O is produced **in the subsurface** via nitrification,*

p. 16714: How was the global average profile of N₂O estimated? Why not this distribution to initialize the model?

The global average profile of N₂O in the model was done sampling the model output on the data points available from the MEMENTO database, and then calculating the global depth average. The reason for not using this distribution to initialize the model is that MEMENTO might be biased towards measurements done mostly in OMZs, and therefore it might not be representative of the global open ocean.

p. 16714: “does not fully reproduce neither. . .” is a double negative.

The paragraph has been modified as,

*P.TEMP (Fig. 3a) slightly overestimates N₂O for dissolved O₂ concentrations above 100 μmolL⁻¹, and does not fully reproduce **either the high N₂O values in the OMZs or the N₂O depletion when O₂ is almost completely consumed***

p. 16715: It seems relatively easy to parameterize the high O₂ process and get distributions correct outside the OMZ, but the real trick is to get it right in the OMZ. How much tuning went into this model fit?

Please refer to first part of author's reply.

p. 16717, first paragraph: This discussion seems circular. They are seeing a model manifestation of what they parameterized it to look like. They parameterized N₂O production to primarily track O₂ consumption responding to organic matter export, and that is what it does. Would some other combination of parameters simulate the N₂O distributions and fluxes equally well, or even better?

Please refer to first part of author's reply.

p. 16719: Again, “close to the subsurface” is awkward.

The paragraph has been now modified as,

*Changes in N₂O production **in the subsurface** are translated into corresponding changes in N₂O flux.*

p. 16719: It's not clear to me from Figure 7 that all relevant changes occur in low-latitude regions? Could

you please be more specific or quantitative in this statement? The changes appear to be fairly evenly spread.

We agree on the referee statement that similar changes are widespread. The paragraph has been modified as follows,

*The increase in inventory is particularly pronounced along the eastern boundary currents in the Equatorial and Tropical Pacific, **Indian Ocean, and also in smaller quantities in the Atlantic Ocean.** Figure 7 shows how **the decrease in N₂O production and increase in N₂O storage occurs in all oceanic basins.***

p. 16723: Constant atmospheric N₂O what is the sensitivity to this assumption and the choice of atmospheric N₂O concentration?

As mentioned before, we acknowledge the fact that the value we have used in our simulations has been kept constant throughout the 21st century model projections. The value of 284 ppb corresponds to the early 20th century and we have not changed this value to explore future changes inherent to ocean processes and not to include the feedbacks due to the atmosphere.

Figures: In general, the text in the figures is very small and an increased font size would improve readability.

The text size in the figures have been increased, hopefully up to a readable size.

Figure 1: What is the reason for the mismatch between model results and observations from Nevison et al (2004)? It looks like the model simulations underestimate N₂O emission from the ocean in several regions of the ocean (Figure 1d).

Please refer to first part of author's reply.

Figure 8 legend: I assume these are the box model results, but it is not clear what is being shown.

The figure caption has been modified as follows:

Figure 8: Box model results, analysing the effect of changes in ocean circulation by reducing the mixing coefficient (μ in %) and changes in biogeochemistry by reducing export of organic matter (ϵ in %) separately in N₂O sea-to-air emissions and N₂O inventory. (a) Constant regimes in percentage of the historical N₂O sea-to-air flux: 95 % pink, 90 % blue, 85 % cyan and 80 % green, and (b) Constant regimes in percentage of the historical N₂O concentration in the deep: 90 % pink, 110 % blue, 125 % cyan and 150 % green. The line represents the univocal NEMO-PISCES model export in the context of the box model.

New references:

Frame, C. H., & Casciotti, K. L. (2010). Biogeochemical controls and isotopic signatures of nitrous oxide production by a marine ammonia-oxidizing bacterium.

Fariás, L., Paulmier, A., & Gallegos, M. (2007). Nitrous oxide and N-nutrient cycling in the oxygen minimum zone off northern Chile. Deep Sea Research Part I: Oceanographic Research Papers, 54(2), 164-180.

Westley, M. B., Yamagishi, H., Popp, B. N., & Yoshida, N. (2006). Nitrous oxide cycling in the Black Sea inferred from stable isotope and isotopomer distributions. Deep Sea Research Part II: Topical Studies in Oceanography, 53(17), 1802-1816.