***Interactive comment on* "Oceanic N_2O 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 N_2O 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 N_2O 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 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." (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-O2 due to nitrification and low-O2 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 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 N2O in the model. The overall sensitivity to changes in temperature and the sensitivity to changes in AOU or the way O2 consumption is described in the model would remain the same.

Table 1: Original and final model derived P.TEMP parameterization used in NEMO-PISCES experiements, 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 x 10^{-3}
P.TEMP (Martinez et al., 2014) $J^{P.TEMP}(N_2O) = (\gamma + \theta T)J(O_2)_{consumption}$	0.053	4.3 x 10^{-3}

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 N2O production associated with nitrification, is in the same order of magnitude as proposed by Jin and Gruber (2003), while beta, modulating N2O production associated with denitrification, is two orders of magnitude smaller (Table 2). Constant beta modulates to contribution of denitrification to N2O 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 experiements, with their associated alpha and beta constants.

Parameterization	alpha	beta
Jin and Gruber, 2003	$mmolN_2O/molNH_4$	$mmolN_2O/molNH_4$
$\Gamma(N_2O) = J^{nitr}(N_2O) + J^{denitr}(N_2O) + J^{cons}(N_2O),$	0.98	944
$J^{nitr}(N_2O) = \alpha\, r_{N:P}\, J(PO_4^{3-}),$		
$J^{denitr}(N_2O) = \beta\, f(O_2)\, r_{N:P}\, J(PO_4^{3-}),$		

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

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 O_2 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 O_2 spectrum of WOA2005* and NEMO-PISCES is shown.*
The O_2 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 μmol L^{-1}) in WOA2005* (red) and NEMO-PISCES in offline mode (black).

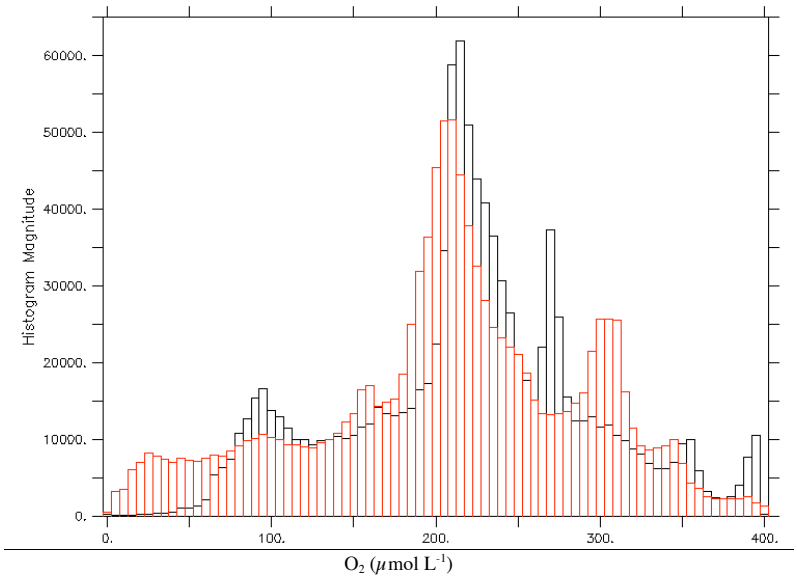
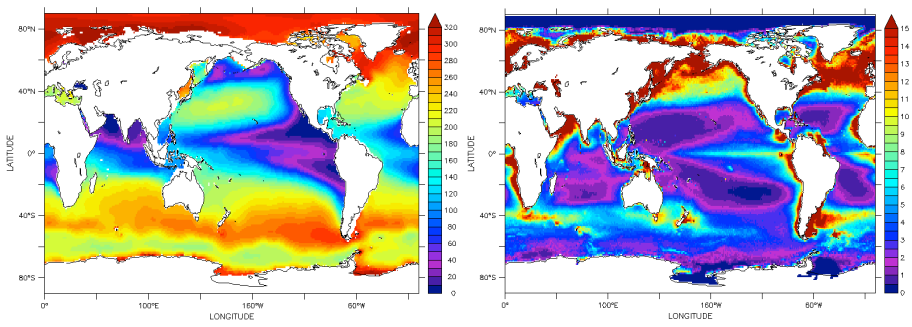
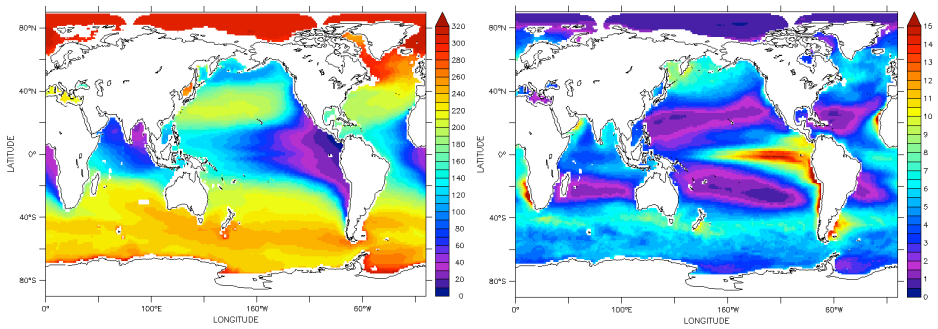


Figure 2: Averaged O_2 between 200-600m depth (in μmol L^{-1}) and Export of organic carbon (CEX) (in mmolC m^{-2} d^{-1}) in (**a**) WOA2005* and Dunne et al., 2007, (**b**) CMIP5 model mean (historical simulations, 1990-1999 period from Bopp et al. 2013) and (**c**) NEMO-PISCES for the present 1985-2005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

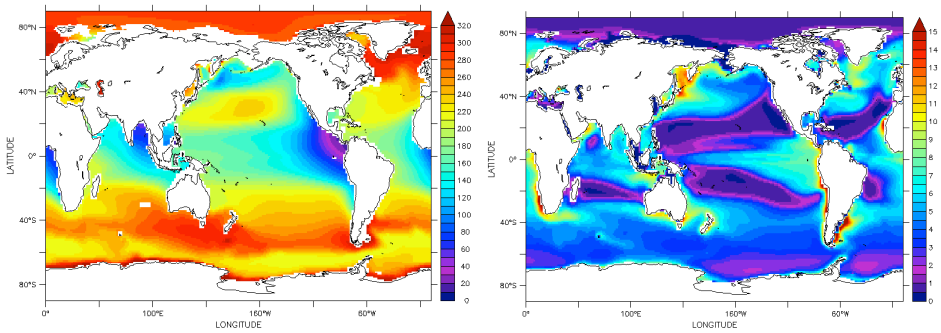
a. WOA2005* and Dunne et al., 2007



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 were 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 N_2O 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 N_2O emission regions (>50mgN $m^{-2}yr^{-1}$) 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 N_2O 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 N_2O 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 N_2O 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 N_2O 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 N_2O in the subsurface. N2O is quickly***

outgassed to the atmosphere, leading to such areas of high N_2O emissions in the model.

Model-data discrepancies can be seen as a function of latitude in Figure 1d. *The modeled N_2O 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 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 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 N_2O advected from other regions and that mixing could play a relevant role, smoothing the fit between N_2O and AOU from exponential to linear. However, Zamora et al. (2012) quoting Frame and Casciotti (2010), suggests that regions were an exponential relationship in N_2O 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 N_2O 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,

> ***N_2O production is inhibited by light in the model, and therefore N2O production in P.TEMP and P.OMZ paramterizations 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. "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.

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 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), 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 paramterizations 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 disentagle 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 N_2O production in high-O_2 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 ex- port 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 ΔN2O 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 ΔN2O/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 N2O production and hence a decrease on N2O 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(O2). While they say it is a step-like function, it appears more complex in Fig S1.

The explicit formulation of f(O2) has been added to the supplementary material as follows,

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

- 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 N2O production in regions with O2 precisely below 4µmol 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 R2 of 0.18-0.24, that is around 1/5th of the data variance. . . 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.

Please refer to first part of author's reply.

- Part of the N2O 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 N2O.

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 N2O 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 finding 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 disentagle 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 N_2O production in the upper 100m avoids one important***

source of uncertainty in estimating global oceanic N_2O 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 where 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 proceses, 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 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*

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.

Farías, 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.

"Projections of oceanic N_2O emissions in the 21st century using the IPSL Earth System Model"

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0. Abstract

The ocean is a substantial source of nitrous oxide (N_2O) to the atmosphere, but little is known on how this flux might change in the future. Here, we investigate the potential evolution of marine N_2O emissions in the 21st century in response to anthropogenic climate change using the global ocean biogeochemical model NEMO-PISCES. Assuming nitrification as the dominant N_2O formation pathway, we implemented two different parameterizations of N_2O production, which differ primarily at low oxygen (O_2) conditions. When forced with output from a climate model simulation run under the business-as-usual high CO_2 concentration scenario (RCP8.5), our simulations suggest a decrease of 4 to 12 % in N_2O emissions from 2005 to 2100, i.e., a reduction from 4.03 / 3.71 to 3.54 / 3.56 TgN yr^{-1} depending on the parameterization. The emissions decrease strongly in the western basins of the Pacific and Atlantic oceans, while they tend to increase above the Oxygen Minimum Zones (OMZs), i.e., in the Eastern Tropical Pacific and in the northern Indian Ocean. The reduction in N_2O 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 N_2O from the ocean interior to the ocean surface. The higher emissions over the OMZ are linked to an expansion of these zones under global warming, which leads to increased N_2O production associated primarily with denitrification. While there are many uncertainties in the relative contribution and changes in the N_2O production pathways, the increasing storage seems unequivocal and determines largely the decrease in N_2O emissions in the future. From the perspective of a global climate system, the averaged feedback strength associated with the projected decrease in oceanic N_2O emissions amounts to around -0.009 W $m^{-2}K^{-1}$, which is comparable to the potential increase from terrestrial N_2O sources. However, the assesment for a compensation between the terrestrial and marine feedbacks calls for an improved representation of N_2O production terms in fully coupled next generation of Earth System Models.

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1 Introduction

Nitrous oxide (N_2O) is a gaseous compound responsible for two key feedback mechanisms within the Earth's climate. First, it acts as a long-lived and powerful greenhouse gas (Prather et al., 2012) ranking third in anthropogenic radiative forcing after carbon dioxide (CO_2) and methane (CH_4) (Myrhe et al., 2013). Secondly, the ozone (O_3) layer depletion in the future might be driven mostly by N_2O after the drastic reductions in CFCs emissions start to show their effect on stratospheric chlorine levels (Ravishankara et al., 2009). The atmospheric concentration of N_2O is determined by the natural balance between sources from land and ocean and the destruction of N_2O in the atmosphere largely by photolysis (Crutzen, 1970; Johnston, 1971). The natural sources from land and ocean amount to ~6.6 and 3.8 TgN yr^{-1}, respectively (Ciais et al., 2013). Anthropogenic activities currently add an additional 6.7 TgN yr^{-1} to the atmosphere, which has caused atmospheric N_2O to increase by 18% since pre-industrial times (Ciais et al., 2013), reaching 325 ppb in the year 2012 (NOAA ESRL Global Monitoring Division, Boulder, Colorado, USA, http://esrl.noaa.gov/gmd/).

Using a compilation of 60,000 surface ocean observations of the partial pressure of N_2O (pN_2O), Nevison et al. (2004) computed a global ocean source of 4 TgN yr^{-1}, with a large range of uncertainty from 1.2 to 6.8 TgN yr^{-1}. Model derived estimates also differ widely, i.e., between 1.7 and 8 TgN yr^{-1} (Nevison et al., 2003; Suntharalingam et al., 2000). These large uncertainties are a consequence of too few observations and of poorly known N_2O formation mechanisms, reflecting a general lack of understanding of key elements of the oceanic nitrogen cycle (Gruber and Galloway, 2008; Zehr and Ward, 2002), and of N_2O in particular (e.g., Zamora et al., 2012, Bange et al., 2009 or Freing et al., 2012, among others). A limited number of interior ocean N_2O observations were made available only recently (Bange et al., 2009), but they contain large temporal and spatial gaps. Information on the rates of many important processes remains insufficient, particularly in natural settings. 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 parameterisations (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

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and Moore, 2004; De Wilde and De Bie, 2000).

N_2O is formed in the ocean interior through two major pathways and consumed only in oxygen minimum zones through denitrification (Zamora et al., 2012). The first production pathway is associated with nitrification (conversion of ammonia, NH_4^+, into nitrate, NO_3^-), and occurs when dissolved O_2 concentrations are above 20 µmol L^{-1}. We subsequently refer to this pathway as the high-O_2 pathway. The second production pathway is associated with a series of processes when O_2 concentrations fall below ~5 µmol L^{-1} and involve a combination of nitrification and denitrification (hereinafter referred to as low-O_2 pathway) (Cohen and Gordon, 1978; Goreau et al., 1980; Elkins et al., 1978). As nitrification is one of the processes involved in the aerobic remineralization of organic matter, it occurs nearly everywhere in the global ocean with a global rate at least one order of magnitude larger than the global rate of water column denitrification (Gruber, 2008). A main reason is that denitrification in the water column is limited to the OMZs, which occupy only a few percent of the total ocean volume (Bianchi et al., 2012). This is also the only place in the water column where N_2O is being consumed.

The two production pathways have very different N_2O yields, i.e., fractions of nitrogen-bearing products that are transformed to N_2O. For the high-O_2 pathway, the yield is typically rather low, i.e., only about 1 in several hundred molecules of ammonium escapes as N_2O (Cohen and Gordon, 1979). In contrast, in the low-O_2 pathway, and particularly during denitrification, this fraction may go up to as high as 1:1, i.e., that all nitrate is turned into N_2O (Tiedje, 1988). The relative contribution of the two pathways to global N_2O production is not well established. Sarmiento and Gruber (2006) suggested that the two may be of equal importance, but more recent estimates suggest that the high-O_2 production pathway dominates global oceanic N_2O production (Freing et al., 2012).

Two strategies have been pursued in the development of parameterizations for N_2O production in global biogeochemical models. The first approach builds on the importance of the nitrification pathway and its close association with the aerobic remineralization of organic matter. As a result the production of N_2O and the consumption of O_2 are closely tied to each other, leading to a strong correlation between the concentration of N_2O and the apparent oxygen utilization (AOU). This has led to the development of two sets of parameterizations, one based on concentrations, i.e., directly

as a function of AOU (Butler et al., 1989) and the other based on the rate of oxygen utilization, i.e. OUR (Freing et al., 2009). Additional variables have been introduced to allow for differences in the yield, i.e., the ratio of N_2O produced over oxygen consumed, such as temperature (Butler et al., 1989) or depth (Freing et al., 2009). In the second approach, the formation of N_2O is modeled more mechanistically, and tied to both nitrification and denitrification by an O_2 dependent yield (Suntharalingam and Sarmiento, 2000; Nevison et al., 2003; Jin and Gruber, 2003). Since most models do not include nitrification explicitly, the formation rate is actually coupled directly to the remineralization of organic matter. Regardless of the employed strategy, all parameterizations depend to first order on the amount of organic matter that is being remineralized in the ocean interior, which is governed by the export of organic carbon to depth. The dependence of N_2O production on oxygen levels and on other parameters such as temperature only acts at second order. This has important implications not only for the modeling of the present-day distribution of N_2O in the ocean, but also for the sensitivity of marine N_2O to future climate change.

Over this century, climate change will perturb marine N_2O formation in multiple ways. Changes in productivity will drive changes in the export of organic matter to the ocean interior (Steinacher et al., 2010; Bopp et al., 2013) and hence affect the level of marine nitrification. Ocean warming might change the rate of N_2O production during nitrification (Freing et al., 2012). Changes in carbonate chemistry (Bindoff et al., 2007) might cause changes in the C:N ratio of the exported organic matter (Riebesell et al., 2007), altering not only the rates of nitrification, but also the ocean interior oxygen levels (Gehlen et al., 2011). Finally, the expected general loss of oxygen (Keeling et al., 2010; Cocco et al., 2012; Bopp et al., 2013) could substantially affect N_2O production via both nitrifier denitrification and classic denitrification.

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 CO_2 concentration scenario A2 (Steinacher et al., 2010). A more recent multi-model analysis based on the models used in IPCC's 5th assessment report also suggest a large reduction of PP down to 18% by 2100 for the RCP8.5 scenario (Bopp et al., 2013). In these simulations, the export of organic matter is projected to decrease between 6% and 18% in 2100 (Bopp et al., 2013), with a spatially distinct pattern: in general, productivity and

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export are projected to decrease at mid- to low-latitudes in all basins, while productivity and export are projected to increase in the high-latitudes and in the South Pacific subtropical gyre (Bopp et al., 2013). A wider spectrum of responses was reported regarding changes in the ocean oxygen content. While all models simulate decreased oxygen concentrations in response to anthropogenic climate change (by about 2 to 4% in 2100), and particularly in the mid-latitude thermocline regions, no agreement exists with regard to the hypoxic regions, i.e., those having oxygen levels below 60 µmol L^{-1} (Cocco et al., 2012; Bopp et al., 2013). Some models project these regions to expand, while others project a contraction. Even more divergence in the results exists for the suboxic regions, i.e., those having O_2 concentrations below 5 µmol L^{-1} (Keeling et al., 2010; Deutsch et al., 2011; Cocco et al., 2012; Bopp et al., 2013), although the trend for most models is pointing towards an expansion. At the same time, practically none of the models is able to correctly simulate the current distribution of oxygen in the OMZ (Bopp et al., 2013). In summary, while it is clear that major changes in ocean biogeochemistry are looming ahead (Gruber, 2011), with substantial impacts on the production and emission of N_2O, our ability to project these changes with confidence is limited.

In this study, we explore the implications of these future changes in ocean physics and biogeochemistry on the marine N_2O cycle, and make projections of the oceanic N_2O emissions from year 2005 to 2100 under the high CO_2 concentration scenario RCP8.5. We analyze how changes in biogeochemical and physical processes such as net primary production (NPP), export production and vertical stratification in this century translate into changes in oceanic N_2O emissions to the atmosphere. To this end, we use the NEMO-PISCES ocean biogeochemical model, which we have augmented with two different N_2O parameterizations, permitting us to evaluate changes in the marine N_2O cycle at the process level, especially with regard to production pathways in high and low oxygen regimes. We demonstrate that while future changes in the marine N_2O cycle will be substantial, the net emissions of N_2O appear to change relatively little, i.e., they are projected to decrease by about 10% in 2100.

2. Methodology

2.1 NEMO-PISCES Model

Future projections of the changes in the oceanic N_2O cycle were performed using the PISCES ocean biogeochemical model (Aumont and Bopp, 2006) in offline mode with physical forcings derived from the IPSL-CM5A-LR coupled model (Dufresne et al., 2013). The horizontal resolution of NEMO ocean general circulation model is 2° x 2° cos Ø (Ø being the latitude) with enhanced latitudinal resolution at the equator of 0.5°. PISCES is a biogeochemical model with five nutrients (NO_3, NH_4, PO_4, Si and Fe), two phytoplankton groups (diatoms and nanophytoplankton), two zooplankton groups (micro and mesozooplankton), and two non-living compartments (particulate and dissolved organic matter). Phytoplankton growth is limited by nutrient availability and light. Constant Redfield C:N:P ratios of 122:16:1 are assumed (Takahashi et al., 1985), while all other ratios, i.e., those associated with chlorophyll, iron, and silicon (Chl:C, Fe:C and Si:C) vary dynamically.

2.2 N_2O parameterizations in PISCES

We implemented two different parameterizations of N_2O production in NEMO-PISCES. The first one, adapted from Butler et al. (1989) follows the oxygen consumption approach, with a temperature dependent modification of the N_2O yield (P.TEMP). The second one is based on Jin and Gruber (2003) (P.OMZ), following the more mechanistic approach, i.e., it considers the different processes occurring at differing oxygen concentrations in a more explicit manner.

The P.TEMP parameterization assumes that the N_2O production is tied to nitrification only with a yield that is at first order constant. This is implemented in the model by tying the N_2O formation in a linear manner to O_2 consumption. A small temperature dependence is added to the yield to reflect the potential impact of temperature on metabolic rates. The production term of N_2O, i.e., $J^{P.TEMP}(N_2O)$, is then mathematically formulated as:

$$J^{P.TEMP}(N_2O) = (\gamma + \theta\, T\,)\, J(O_2)_{consumption} \quad (1)$$

where γ is a background yield (0.53 x 10^{-4} mol N_2O/mol O_2 consumed), θ is the temperature dependency of γ (4.6 x 10^{-6} mol N_2O (mol O_2)$^{-1}$ K^{-1}), T is temperature (K),

and $J(O_2)_{consumption}$ is the sum of all biological O_2 consumption terms within the model. The same ratio between constants γ and θ is used in the model as in the original formulation from Butler et al. (1989). Although this parameterization is very simple, a recent analysis of N_2O observations supports such an essentially constant yield, even in the OMZ of the Eastern Tropical Pacific (Zamora et al., 2012).

The P.OMZ parameterization, formulated after Jin and Gruber (2003), assumes that the overall yield consists of a constant background yield and an oxygen dependent yield. The former is presumed to represent the N_2O production by nitrification, while the latter is presumed to reflect the enhanced production of N_2O at low oxygen concentrations, in part driven by denitrification, but possibly including nitrification as well. This parameterization includes the consumption of N_2O in suboxic conditions. This gives:

$$J^{P.OMZ}(N_2O) = (\alpha + \beta f(O_2))J(O_2)_{consumption} - k\,N_2O \quad (2)$$

where α is, as in Eq.(1), a background yield ($0.9 \cdot 10^{-4}$ mol N_2O/mol O_2 consumed), β is a yield parameter that scales the oxygen dependent function ($6.2 \cdot 10^{-4}$), $f(O_2)$ is a unitless oxygen-dependent step-like modulating function, as suggested by laboratory experiments (Goreau et al., 1980) (Fig. S1, Supplementary Material), and k is the 1st order rate constant of N_2O consumption close to anoxia (zero otherwise). For k, we have adopted a value of 0.138 yr^{-1} following Bianchi et al. (2012) while we set the consumption regime for O_2 concentrations below 5 µmol L^{-1}. The constant α is in the same order of magnitude as the one proposed by Jin and Gruber (2003), while β is two orders of magnitude smaller. The use of the original value would result in a significant increase of N_2O production associated with OMZs and, hence, in a departure from the assumption of dominant nitrification.

The P.OMZ parameterization permits us the independent quantification of the N_2O formation pathways associated with nitrification and those associated with low-oxygen concentrations (nitrification/denitrification) and their evolution in time over the next century. Specifically, we consider the source term $\alpha\, J(O_2)_{consumption}$ as that associated with the nitrification pathway, while we associated the source term $\beta f(O_2)\, J(O_2)_{consumption}$ with the low-oxygen processes (Fig. S2, Supplementary Material).

N_2O production is inhibited by light in the model, and therefore N_2O production in P.TEMP and P.OMZ parameterizations only occurs below a fixed depth of 100m.

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We employ a standard bulk approach for simulating the loss of N_2O to the atmosphere via gas exchange. We use the formulation of Wanninkhof et al. (1992) for estimating the gas transfer velocity, adjusting the Schmidt number for N_2O and using the solubility constants of N_2O given by Weiss and Price (1980). We assume a constant atmospheric N_2O concentration of 284 ppb in all simulations to explore future changes inherent to ocean processes without feedbacks due to changes in the atmosphere.

2.3 Experimental design

NEMO-PISCES was first spun up during 3000 years using constant pre-industrial dynamical forcings fields from IPSL-CM5A-LR (Dufresne et al., 2013) without activating the N_2O parameterizations. This spin-up phase was followed by a 150-yr long simulation, forced by the same dynamical fields now with N_2O production and N_2O sea-to-air flux embedded. The N_2O concentration at all grid points was prescribed initially to 20 nmol L^{-1}, which is consistent with the MEMENTO database average value of 18 nmol L^{-1} below 1500m (Bange et al., 2009). During the 150-yr spin-up, we diagnosed the total N_2O production and N_2O sea-to-air flux and adjusted the α, β, γ and θ parameters in order to achieve a total N_2O sea-to-air flux in the two parameterizations at equilibrium close to 3.85 TgN yr^{-1} (Ciais et al., 2013). In addition, the relative contribution of the high-O_2 pathway in the P.OMZ parameterization was set to 75% of the total N_2O production based on Suntharalingam et al. (2000), where a sensitivity model analysis on the relative contribution of high- and low-O_2 production pathways showed that a higher contribution of nitrification (75%) than denitrification (25%) achieved the best model performance compared to the data product from Nevison et al. (1995). P.TEMP can be considered as 100% nitrification, testing in this way the hypothesis of nitrification as the dominant pathway of N_2O production on a global scale. Nitrification could contribute with up to 93% of the total production based on estimations considering N_2O production along with water mass transport (Freing et al., 2012).

Projections in NEMO-PISCES of historical (from 1851 to 2005) and future (from 2005 to 2100) simulated periods were done using dynamical forcing fields from IPSL-CM5A-LR. These dynamical forcings were applied in an offline mode, i.e. monthly means of

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temperature, velocity, wind speed or radiative flux were used to force NEMO-PISCES. Future simulations used the business-as-usual high CO_2 concentration scenario (RCP8.5) until year 2100. Century scale model drifts for all the biogeochemical variables presented, including N_2O sea-to-air flux, production and inventory, were removed using an additional control simulation with IPSL-CM5A-LR pre-industrial dynamical forcing fields from year 1851 to 2100. Despite the fact that primary production and the export of organic matter to depth were stable in the control simulation, the air-sea N_2O emissions drifted (an increase of 5 to 12% in 200 yr depending on the parameterization) due to the short spin-up phase (150 yrs) and to the choice of the initial conditions for N_2O concentrations.

3. Present-day oceanic N_2O

3.1 Contemporary N_2O fluxes

The model simulated air-sea N_2O emissions show large spatial contrasts, with flux densities varying by one order of magnitude, but with relatively small differences between the two parameterizations (Fig. 1a and 1b). This is largely caused by our assumption that the dominant contribution (75%) to the total N_2O production in the P.OMZ parameterization is the nitrification pathway, which is then not so different from the P.TEMP parameterization, where it is 100%. As a result, the major part of N_2O is produced jn the subsurface via nitrification, contributing directly to imprint changes into the sea-to-air N_2O flux without a significant meridional transport (Suntharalingam and Sarmiento, 2000).

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Elevated N_2O emission regions (> 50 mgN m^{-2} yr^{-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 (< 10 mgN m^{-2} yr^{-1}) are simulated in the Southern Ocean, Atlantic and Pacific subtropical gyres and southern Indian Ocean. The large scale distribution of N_2O fluxes is coherent with Nevison et al. (2004) (Fig. 1c). This comes as a natural consequence of the relatively high contribution of nitrification and hence hotspots of N_2O 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. At high latitudes, the high N_2O emissions observed in the North Pacific are not well represented in our model, with a significant shift towards the western part of the Pacific basin, similar to other modeling studies (e.g., Goldstein et al., 2003; Jin and Gruber, 2003). The OMZ in the North Pacific, located at approximately 600m deep, 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 N_2O source. Discrepancies between model and observations also occur in the Southern Ocean, a region whose role in global N_2O fluxes remains debated due to the lack of observations and the occurrence of potential artifacts due to interpolation techniques reflected in data products such as that from Nevison et al., 2004. (e.g., Suntharalingam and Sarmiento, 2000, and Nevison et al, 2003). The model also overestimates N_2O 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 N_2O in the subsurface. N_2O is quickly outgassed to the atmosphere, leading to such areas of high N_2O emissions in the model.

Model-data discrepancies can be seen as a function of latitude in Figure 1d. The modeled N_2O flux maxima peak at around 40°S, i.e., around 10° north 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 in not captured by the model, splitting the flux from the 45°N band into two peaks at 38°N and 55°N.

3.2 Contemporary N_2O concentrations and the relationship to O_2

The model results at present day were evaluated against the MEMENTO database (Bange et al., 2009), which contains about 25,000 measurements of co-located N_2O and dissolved O_2 concentrations. Table 1 summarizes the standard deviation and correlation coefficients for P.TEMP and P.OMZ compared to MEMENTO. The standard deviation of the model output is very similar to MEMENTO, i.e., around 16 nmol L^{-1} of N_2O. However, the correlation coefficients between the sampled data points from MEMENTO and P.TEMP / P.OMZ are 0.49 and 0.42 respectively. Largest

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discrepancies are found mostly in the deep ocean and in the OMZs.

Figure 2 compares the global average vertical profile of the observed N_2O against the results from the two parameterisations. The in-situ observations show three characteristic layers: the upper 100m layer with low (~10 nmol L^{-1}) N_2O concentration due to gas exchange keeping N_2O close to its saturation concentration, the mesopelagic layer, between 100 and 1500m, where N_2O is enriched via nitrification and denitrification in the OMZs, and the deep ocean beyond 1500m, with a relatively constant concentration of 18 nmol L^{-1} on average. Both parameterizations underestimate the N_2O concentration in the upper 100 meters, where most of the N_2O is potentially outgassed to the atmosphere. 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}. Below 1500m, both parameterizations simulate too high N_2O compared to the observations. This may be caused by the lack or underestimation of a sink process in the deep ocean, or by the too high concentrations used to intialize the model, which persist due to the rather short spin-up time of only 150 yrs.

The analysis of the model simulated N_2O concentrations as a function of model simulated O_2 shows the differences between the two parameterizations more clearly (Fig. 3a and 3b). Such a plot allows us to assess the model performance with regard to N_2O (Jin and Gruber, 2003), without being subject to the strong potential biases introduced by the model's deficiencies in simulating the distribution of O_2. This is particularly critical in the OMZs, where all models exhibit strong biases (Cocco et al., 2012; Bopp et al., 2013) (see also Fig. 3c). P.TEMP (Fig. 3a) slightly overestimates N_2O for dissolved O_2 concentrations above 100 µmol L^{-1}, and does not fully reproduce either the high N_2O values in the OMZs or the N_2O depletion when O_2 is almost completely consumed. P.OMZ (Figure 3b) overestimates the N_2O concentration over the whole range of O_2, with particularly high values of N_2O above 100 nmol L^{-1} due to the exponential function used in the OMZs. There, the observations suggest concentrations below 80 nmol L^{-1} for the same low O_2 values, consistent with the linear trend observed for higher O_2, which seems to govern over most of the O_2 spectrum, as suggested by Zamora et al. (2012). The discrepancy at low O_2 concentration may also stem from our choice of a too low N_2O consumption rate under essentially anoxic conditions. Finally, it should be considered that most of the MEMENTO data points are from OMZs and therefore N_2O

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measurements could be biased towards higher values than the actual open ocean average, where our model performs better.

4. Future oceanic N_2O

4.1 N_2O sea-to-air flux

The global oceanic N_2O emissions decrease relatively little over the next century (Fig. 4a) between 4% and 12%. Namely, in P.TEMP, the emissions decrease by 0.15 TgN yr^{-1} from 3.71 TgN yr^{-1} in 1985-2005 to 3.56 TgN yr^{-1} in 2080-2100 and in P.OMZ, the decrease is slightly larger at 12%, i.e., amounting to 0.49 Tg N yr^{-1} from 4.03 to 3.54 TgN yr^{-1}. Notable is also the presence of a negative trend in N_2O emissions over the 20th century, most pronounced in the P.OMZ parameterization. Considering the change over the 20th and 21st centuries together, the decreases increase to 7 and 15%.

These relatively small global decreases mask more substantial changes at the regional scale, with a mosaic of regions experiencing a substantial increase and regions experiencing a substantial decrease (Fig. 4b and 4c). In both parameterizations, the oceanic N_2O emissions decrease in the northern and south western oceanic basins (e.g., the North Atlantic and Arabian Sea), by up to 25 mgN $m^{-2}yr^{-1}$. In contrast, the fluxes are simulated to increase in the Eastern Tropical Pacific and in the Bay of Bengal. For the Benguela Upwelling System (BUS) and the North Atlantic a bi-modal pattern emerges in 2100. As was the case for the present-day distribution of the N_2O fluxes, the overall similarity between the two parameterizations is a consequence of the dominance of the nitrification (high-O_2) pathway in both parameterizations.

Nevertheless there are two regions where more substantial differences between the two parameterizations emerge: the region overlying the oceanic OMZ at the BUS and the Southern Ocean. 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.

4.2 Drivers of changes in N_2O emissions

The changes in N_2O emissions may stem from a change in net N_2O production, a change in the transport of N_2O from its location of production to the surface, or any combination of the two, which includes also changes in N_2O storage. Next we determine the contribution of these mechanisms to the overall decrease in N_2O emissions that our model simulated for the 21st century.

4.2.1 Changes in N_2O production

In both parameterizations, global N_2O production is simulated to decrease over the 21st century. The total N_2O production in P.OMZ decreases by 0.41 TgN yr^{-1} in 2080-2100 compared to the mean value over 1985-2005 (Fig. 5a). The parameterization P.OMZ allows to isolate the contributions of high- and low-O_2 and will be analysed in greater detail in the following sections. N_2O production via the high-O_2 pathway in P.OMZ decreases in the same order than total production, by 0.35 TgN yr^{-1} in 2080-2100 compared to present. The N_2O production in the low-O_2 regions remains almost constant across the experiment. In P.TEMP parameterization, the reduction in N_2O production is much weaker than in P.OMZ due to the effect of the increasing temperature. N_2O production decreases by 0.07 TgN yr^{-1} in 2080-2100 compared to present (Fig. 5b).

The vast majority of the changes in the N_2O production in the P.OMZ parameterization is caused by the high-O_2 pathway with virtually no contribution from the low-O_2 pathway (Fig. 5a). As the N_2O production in P.OMZ parameterization is solely driven by changes in the O_2 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 N_2O production in our model is the decrease in export of organic matter (CEX). It was simulated to decrease by 0.97 PgC yr^{-1} in 2100, and the high degree of correspondence in the temporal evolution of export and N_2O production in Fig. 5a confirms this conclusion.

The close connection between N_2O production associated with the high-O_2 pathway and changes in export production is also seen spatially (Fig. 5c), where the spatial pattern of changes in export and changes in N_2O production are extremely highly correlated (shown by stippling). Most of the small deviations are caused by lateral advection of organic

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carbon, causing a spatial separation between changes in O_2 consumption and changes in organic matter export.

As there is an almost ubiquitous decrease of export in all of the major oceanic basins except at high latitudes, N_2O production decreases overall as well. Hotspots of reductions exceeding -10 mgN $m^{-2}yr^{-1}$ are found in the North Atlantic, the western Pacific and Indian basins (Fig. 5c). The fewer places where export increases, are also the locations of enhanced N_2O production. For example, a moderate increase of 3 mgN m^{-2} yr^{-1} is projected in the Southern Ocean, South Atlantic and Eastern Tropical Pacific. 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.

Although the global contribution of the changes in the low-O_2 N_2O production is small, this is the result of regionally compensating trends. In the model's OMZs, i.e., in the Eastern Tropical Pacific and in the Bay of Bengal, a significant increase in N_2O production is simulated in these locations (Fig. 5d), with an increase of more than 15 mgN m^{-2} yr^{-1}. This increase is primarily driven by the expansion of the OMZs in our model (shown by stippling), while changes in export contribute less. In effect, NEMO-PISCES projects a 20% increase in the hypoxic volume globally, from 10.2 to 12.3 x 10^6 km^3, and an increase in the suboxic volume from 1.1 to 1.6 x 10^6 km^3 in 2100 (Fig. 5e). Elsewhere, the changes in the N_2O production through the low-O_2 pathway are dominated by the changes in export, thus following the pattern of the changes seen in the high-O_2 pathway. Overall these changes are negative, and happen to nearly completely compensate the increase in production in the OMZs, resulting in the near constant global N_2O production by the low-O_2 production pathway up to year 2100.

4.2.2 Changes in storage of N_2O

A steady increase in the N_2O inventory is observed from present to 2100. The pool of oceanic N_2O down to 1500m, i.e., potentially outgassed to the atmosphere, increases by 8.9 TgN from 1985-2005 to year 2100 in P.OMZ, whereas P.TEMP is less sensitive to changes with an increase of 4.0 TgN on the time period considered (Fig. 6a). 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 represent an increase of about 4% and 2% in P.OMZ and P.TEMP respectively.

This increase in storage of N_2O in the ocean interior shows an homogeneous pattern for P.TEMP, with particular hotspots in the North Pacific, North Atlantic and the eastern boundary currents in the Pacific (Fig. 6b). The spatial variability is more pronounced in P.OMZ (Fig. 6c), related in part to the enhanced production associated with OMZs. Most of the projected changes in storage are associated with shoaling of the mixed layer depth (shown by stippling), suggesting that increase in N_2O inventories is caused by increased ocean stratification. Enhanced ocean stratification, in turn, occurs in response to increasing sea surface temperatures associated with global warming (Sarmiento et al., 2004).

4.2.3 Effects of the combined mechanisms on N_2O emissions

The drivers of the future evolution of oceanic N_2O emissions emerge from the preceding analysis. Firstly, a decrease in the high-O_2 production pathway driven by a reduced organic matter remineralization reduces N_2O concentrations below the euphotic zone. Secondly, the increased N_2O inventory at depth is caused by increased stratification and therefore to a less efficient transport to the sea-to-air interface, leading to a less N_2O flux. The global changes in N_2O flux, N_2O production and N_2O storage for P.OMZ are presented in Fig. 7. Changes in N_2O flux and N_2O production are mostly of the same sign in almost all of the oceanic regions in line with the assumption of nitrification begin the dominant contribution to N_2O production. Changes in N_2O production in the subsurface are translated into corresponding changes in N_2O flux. There is only one oceanic region (Sub-Polar Pacific) where this correlation does not occur. N_2O inventory increases in all of the oceanic regions. The increase in inventory is particularly pronounced at low latitudes 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 N_2O production and increase in N_2O storage occurs in all oceanic basins.

The synergy among the driving mechanisms can be explored with a box model pursuing

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two objectives. First, to separate the effect of physical (i.e., increased stratification) and the biogeochemical (i.e., reduction of N_2O production in the high-O_2 regions) mechanisms on N_2O emissions. In this way we can reproduce future projections assuming that the only mechanisms ruling the N_2O dynamics in the future were those that we have proposed in our hypothesis, i.e., increased stratification and reduction of N_2O production in high-O_2 regions. Secondly, to explore a wider range of values for both mixing (i.e., degree of stratification) and efficiency of N_2O production in high-O_2 conditions. In the particular NEMO-PISCES model projection we have studied, changes in mixing and export are unique and can not be explored individually.

To this end, a box model was designed to explore the response of oceanic N_2O emissions to changes in export of organic matter (hence N_2O production only in high-O_2 conditions) and changes in the mixing ratio between deep (> 100m) and surface (< 100m) layers. We divided the water column into two compartments: a surface layer in the upper 100m where 80% of surface N_2O concentration is outgassed to the atmosphere (Eq. (3)), and a deeper layer beyond 100m, where N_2O is produced from remineralization as a fraction of the organic matter exported in the ocean interior (Eq. (4)). The N_2O reservoirs in the surface and in the deep layer are allowed to exchange. The exchange is regulated by a mixing coefficient v:

$$\text{surface } N_2O\ ; \quad \frac{dN_2O^s}{dt} = -v \cdot (N_2O^s - N_2O^d) - \kappa \cdot N_2O^s \tag{3}$$

$$\text{deep } N_2O\ ; \quad \frac{dN_2O^d}{dt} = v \cdot (N_2O^s - N_2O^d) + \varepsilon \cdot \Phi^{POC} \tag{4}$$

where N_2O^s is N_2O in the surface, N_2O^d is N_2O in the deep reservoir, Φ^{POC} is the flux of POC into the lower compartment, v is the mixing coefficient between both compartments, k is the fraction of N_2O^s outgassed to the atmosphere and e the fraction of POC leading to N_2O^d formation (Fig. S3 and Table S1, Supplementary Material). Equations (3) and (4) are solved for a combination of POC fluxes and mixing coefficients, reflecting the increasing stratification and the decrease in export production projected by year 2100 (Sarmiento et al., 2004; Bopp et al., 2013).

A decrease in the N_2O flux is observed for a wide range of boundary conditions simulating reduced mixing and export of POC (Fig. 8a). The most extreme scenario explored with the box model suggests a -20% decrease in N_2O flux, although these

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associated values of mixing and export are clearly unrealistic, from a nearly total stagnation of ocean circulation between the deep and surface layers to an attenuation of export of -20% in the global ocean.

The projected increase in N_2O storage in the deep reservoir is reproduced by the box model (Fig. 8b) at a wide range of changes particularly in mixing. Changes in mixing dominate over changes in export as drivers of the increase in the N_2O reservoir at depth. A 25% decrease in mixing leads to an increase in storage similar to the one projected with NEMO-PISCES (+10%), independently of changes in export of organic matter.

In general, the interplay between mixing and export of organic matter operates differently when N_2O flux or N_2O inventory are considered. The box model experiment suggests that the evolution of the N_2O reservoir is driven almost entirely by changes in mixing, while changes of mixing and export of organic matter have similar relevance when modulating N_2O emissions.

5. Caveats in estimating N_2O using ocean biogeochemical models

The state variables upon which representation of N_2O 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 ($O_2 < 5$ µmol L^{-1}) and on export production. Whereas CMIP5 models tend to have large volumes of O_2 concentrations in the suboxic 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 9, where the histogram of the full O_2 spectrum of WOA2005* and NEMO-PISCES is shown. The O_2 distribution in the model shows a deficient representation of the OMZs, with higher concentrations than those from observations. The rest of the O_2 spectrum is well represented in our model.

The O_2 distribution in the model (Fig. 10) shows a deficient representation of the OMZs, with higher concentrations than those from observations in WOA2005* and the other CMIP5 models. NEMO-PISCES is therefore biased towards the high O_2 production pathway of N_2O due to the modeled O_2 fields.

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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 similar to the CMIP5 model mean and both show smaller values than those from the data-based estimate of 9.84 PgC yr^{-1} from Dunne et al., 2007 (Fig. 10).

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 N_2O 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 N_2O 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 N_2O emissions across the CMIP5 model ensemble. Applying these values to present N_2O emissions of 3.6 TgN yr^{-1}, uncertainties are then bracketed between -0.25 and -0.65 TgN yr^{-1}.

Regarding the low-O_2 pathway, a similar approach is not that straight forward. Zamora et al., (2012) found that a linear relationship between AOU and N_2O production might occur even at the OMZ of the ETP. Zamora et al. (2012) acknowledged the fact that the MEMENTO database includes N_2O advected from other regions and that mixing could play a relevant role, smoothing the fit between N_2O and AOU from exponential to linear. However, Zamora et al. (2012) quoting Frame and Casciotti (2010), suggested that regions were an exponential relationship in N_2O production is present might be rare, that other non-exponential N_2O production processes might occur and therefore the plot they presented could describe the actual linear relationship between N_2O production and oxygen consumption. Based on this hypothesis, we could refer again to the linear relationship suggested in the high-O_2 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 (O_2 < 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 N_2O emissions.

The use of O_2 consumption as a proxy for the actual N_2O production plays therefore a pivotal role in the uncertainties in N_2O model estimations. Future model development should aim at the implementation of mechanistic parameterizations of N_2O production based on nitrification and denitrification rates. Further, in order to determine accurate O_2 boundaries for both N_2O production and N_2O consumption at the core of OMZs additional measurements and microbial experiments are needed. The contribution of the high-O_2 pathway that was considered in this model analysis might be a conservative estimate. Freing et al. (2012) suggested that the high-O_2 pathway could be responsible of 93% of the total N_2O production. Assuming that changes in the N_2O flux are mostly driven by N_2O production via nitrification, that would suggest a larger reduction in the marine N_2O emissions in the future. However, the mismatch between NEMO-PISCES and the Nevison et al. (2004) spatial distribution of N_2O emissions in the western part of the basins suggests that changes in the future might not be as big as those projected in the model in such regions. Changes would be then distributed more homogeneously.

The model assumption neglecting N_2O production in the upper 100m avoids one important source of uncertainty in estimating global oceanic N_2O fluxes. In case nitrification occurs in the euphotic layer, our results would be facing a significant uncertainty of at least ±25% in N_2O emissions according to Zamora and Oschlies (2014) analysis using the UVic Earth System Climate Model. Finally, Zamora et al. (2012) observed a higher than expected N_2O consumption at the core of the OMZ in the Eastern Tropical Pacific, occurring at an upper threshold of 10 μmol L^{-1}. The contribution of OMZs to total N_2O production remains an open question. N_2O formation associated with OMZs might be counterbalanced by its own local consumption, leading to the attenuation of the only increasing source of N_2O attributable to the projected future expansion of OMZs (Steinacher et al., 2010; Bopp et al., 2013).

The combined effect of climate change and ocean acidification has not been analyzed in this study. N_2O production processes might be altered by the response of nitrification to increasing levels of seawater pCO_2 (Huesemann et al., 2002; Beman et al. 2011). Beman et al. (2011) reported a reduction in nitrification in response to decreasing pH. This result suggests that N_2O production might decrease beyond what we have estimated only due to climate change. Conversely, negative changes in the ballast effect could potentially

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reinforce nitrification at shallow depth in response to less efficient POC export to depth and shallow remineralization (Gehlen et al., 2011). Regarding N_2O formation via denitrification, changes in seawater pH as a consequence of higher levels of CO_2 might not be substantial enough to change the N_2O production efficiency, assuming a similar response of marine denitrifiers as reported for denitrifying bacteria have in terrestrial systems (Liu et al., 2010). Finally, the C:N ratio in export production (Riebesell et al., 2007) might increase in response to ocean acidification, potentially leading to a greater expansion of OMZs than simulated here (Oschlies et al., 2008; Tagliabue et al., 2011), and therefore to enhanced N_2O production associated with the low-O_2 pathway.

Changes in atmospheric nitrogen deposition have not been considered in this study. It has been suggested that due to anthropogenic activities the additional amount of reactive nitrogen in the ocean could fuel primary productivity and N_2O production. Estimates are however low, around 3-4% of the total oceanic emissions (Suntharalingam et al., 2012).

Longer simulation periods could reveal additional effects on N_2O transport beyond changes in upwelling or meridional transport of N_2O in the subsurface (Suntharalingam and Sarmiento, 2000) that have been observed in this transient simulation. Long-term responses might include eventual ventilation of the N_2O reservoir in the Southern Ocean, highlighting the role of upwelling regions as an important source of N_2O when longer time periods are considered in model projections. Additional studies using other ocean biogeochemical models might also yield alternative values using the same parameterizations. N_2O production is particularly sensitive to the distribution and magnitude of export of organic matter and O_2 fields defined in models.

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6. Contribution of future N_2O to climate feedbacks

Changes in the oceanic emissions of N_2O to the atmosphere will have an impact on atmospheric radiative forcing, with potential feedbacks on the climate system. Based on the estimated 4 to 12% decrease in N_2O sea-to-air flux over the 21st century under RCP8.5, we estimated the feedback factor for these changes as defined by Xu-Ri et al. (2012). Considering the reference value of the pre-industrial atmospheric N_2O concentration of 280 ppb in equilibrium, and its associated global N_2O emissions of 11.8 TgN yr^{-1}, we quantify the resulting changes in N_2O concentration per degree for the two

projected emissions in 2100 using P.TEMP and P.OMZ. The model projects changes in N_2O emissions of -0.16 and -0.48 TgN yr^{-1} respectively, whereas surface temperature is assumed to increase globally by 3°C on average according to the physical forcing used in our simulations. These results yield -0.05 and -0.16 TgN yr^{-1} K^{-1}, or alternatively -1.25 and -3.80 ppb K^{-1} for P.TEMP and P.OMZ respectively. Using Joos et al. (2001) we calculate the feedback factor in equilibrium for projected changes in emissions to be -0.005 and -0.014 W $m^{-2}K^{-1}$ in P.TEMP and P.OMZ.

Stocker et al. (2013) projected changes in terrestrial N_2O emissions in 2100 using transient model simulations leading to feedback strengths between +0.001 and +0.015 W $m^{-2}K^{-1}$. Feedback strengths associated with the projected decrease of oceanic N_2O emissions are of the same order of magnitude as those attributable to changes in the terrestrial sources of N_2O, yet opposite in sign, suggesting a compensation of changes in radiative forcing due to future increasing terrestrial N_2O emissions. At this stage, potential compensation between land and ocean emissions is to be taken with caution, as it relies of a single model run with constant atmospheric N_2O.

7. Conclusions

Our simulations suggest that anthropogenic climate change could lead to a global decrease in oceanic N_2O emissions during the 21st century. This maximum projected decrease of 12% in marine N_2O emissions for the business-as-usual high CO_2 emissions scenario would compensate for the estimated increase in N_2O fluxes from the terrestrial biosphere in response to anthropogenic climate change (Stocker et al. 2013), so that the climate-N_2O feedback may be more or less neutral over the coming decades.

The main mechanisms contributing to the reduction of marine N_2O emissions are a decrease in N_2O production in high oxygenated waters as well as an increase in ocean vertical stratification that acts to decrease the transport of N_2O from the sub-surface to the surface ocean. Despite the decrease in both N_2O production and N_2O emissions, simulations suggest that the global marine N_2O inventory may increase from 2005 to 2100. This increase is explained by the reduced transport of N_2O from the production zones to the air-sea interface.

Differences between the two parameterizations used here are more related to

biogeochemistry rather than changes in ocean circulation. Despite sharing the high-O_2 N_2O production pathway, leading to a decrease in N_2O emissions in both cases, the role of warming in P.TEMP or higher N_2O yields at low-O_2 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 parameterizations considered in model projections in the next century.

The N_2O production pathways demand however a better understanding in order to enable an improved representation of processes in models. At a first order, the efficiencies of the production processes in response to higher temperatures or increased seawater pCO_2 are required. Second order effects such as changes in the O_2 boundaries at which nitrification and denitrification occur must be also taken into account. In the absence of process-based parameterizations, N_2O production parameterizations will still rely on export of organic carbon and oxygen levels. Both need to be improved in global biogeochemical models.

The same combination of mechanisms (i.e., change in export production and ocean stratification) have been identified as drivers of changes in oceanic N_2O emissions during the Younger Dryas by Goldstein et al. (2003). The N_2O flux decreased, while the N_2O reservoir was fueled by longer residence times of N_2O caused by increased stratification. Other studies point towards changes in the N_2O production at the OMZs as the main reason for variations in N_2O observed in the past (Suthhof et al., 2001). Whether these mechanisms are plausible drivers of changes beyond year 2100 remains an open question that needs to be addressed with longer simulations.

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8. Acknowledgements

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1008 Table 1: Standard deviation and correlation coefficients between P.TEMP and P.OMZ
1009 parameterizations with respect to MEMENTO database observations (Bange et al., 2009).
1010

	P.TEMP	P.OMZ	OBS
Standard deviation (in nmol N_2O L^{-1})	12	18	16
Correlation coefficient with obs.	0.49	0.42	-

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Table S1: Box model boundary conditions and parameters. NEMO-PISCES model output values are taken from the historical averaged 1985 to 2005 time period and the future averaged 2080 to 2100 time period.

parameter	quantity	units	source
surface N_2O	10	TgN	PISCES model output
deep N_2O	1000	TgN	PISCES model output
yield N_2O produced from POC (e)	0.0025	mol N_2O /mol C	Nevison et al. (2003)
ratio of surface N_2O outgassed (π)	0.8	mol N_2O air/mol N_2O surface	assumption that most of the surface N_2O is outgassed.
ratio of surface N_2O exchanged with the deep N_2O compartment (v)	0.4	mol N_2O surface/ mol N_2O deep	box model assumption
export POC @100m in 2005	6.22	PgC yr^{-1}	PISCES model output
export POC @100m in 2100	5.30	PgC yr^{-1}	PISCES model output

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Fig.1: N_2O sea-to-air flux (in mgN m^{-2} yr^{-1}) from (a) P.TEMP parameterzation averaged for the 1985 to 2005 time period in the historical simulation, (b) P.OMZ parameterization over the same time period, (c) data product of Nevison et al. (2004) and (d) latitudinal N_2O sea-to-air flux (in TgN $deg^{-1}yr^{-1}$) from Nevison et al. (2004) (black), P.TEMP (blue) and P.OMZ (red).

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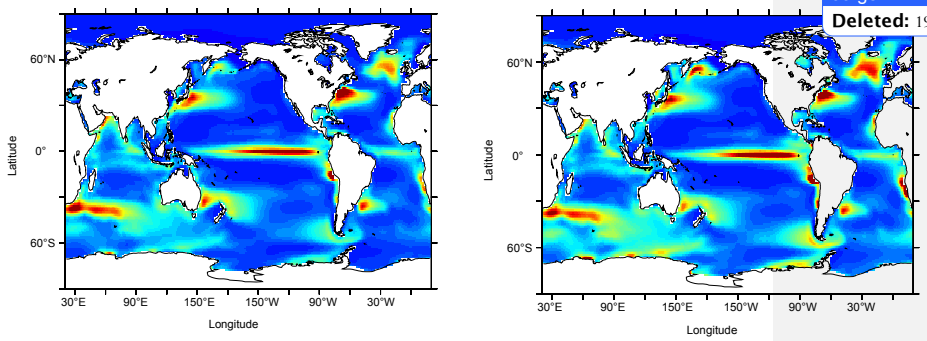
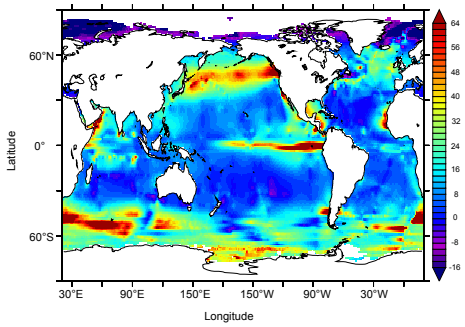


(a)

(b)



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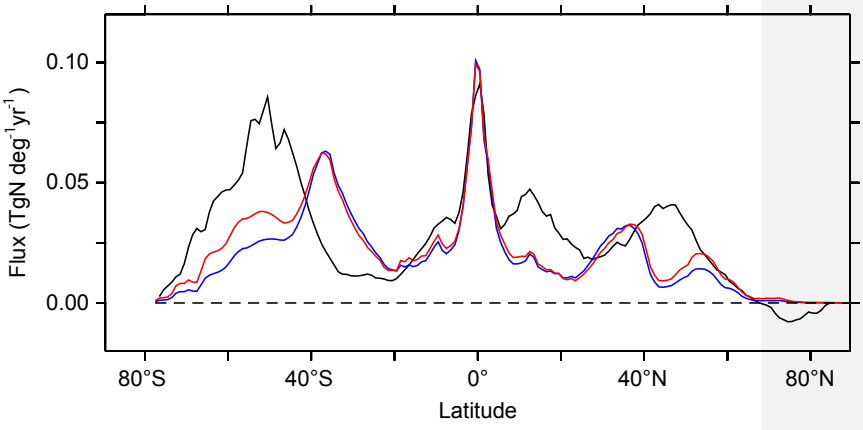


(d)

Fig.2: Global average depth profile of N_2O concentration (in nmol L^{-1}) from the MEMENTO database (dots) (Bange et al., 2009), P.TEMP (blue) and P.OMZ (red). Model parameterizations are averaged over the 1985 to 2005 time period from the historical simulation.

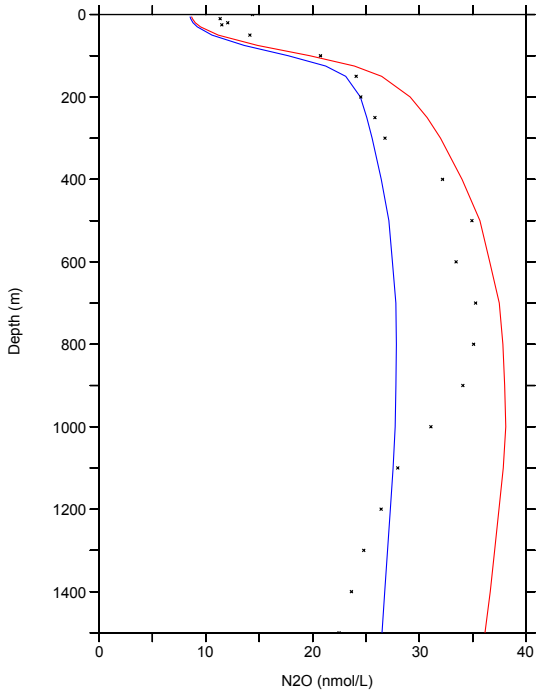
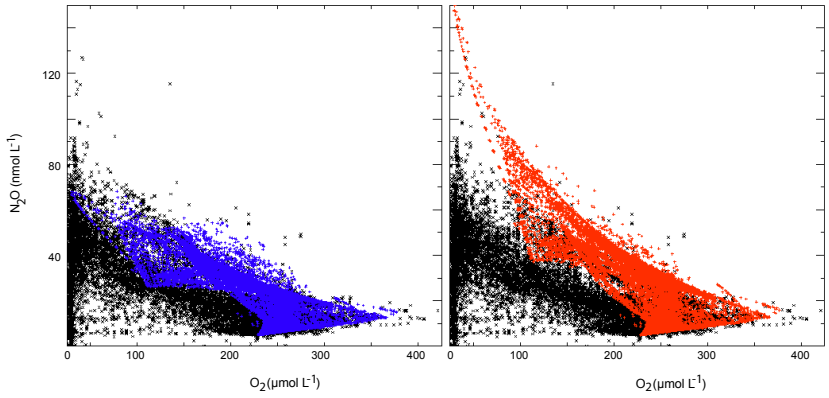


Fig.3: Relationship between O_2 concentration (in µmol L^{-1}) and N_2O concentration (in nmol L^{-1}) in the MEMENTO database (black) (Bange et al., 2009), compared to model (a) P.TEMP (blue) and (b) P.OMZ (red) parameterizations averaged over the 1985 to 2005 time period from the historical simulation.



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Deleted: (c) Distribution of O_2 concentration in NEMO-PISCES 1985 to 2005 averaged time period (blue) compared to the oxygen corrected World Ocean Atlas (grey) from Bianchi et al. (2012).

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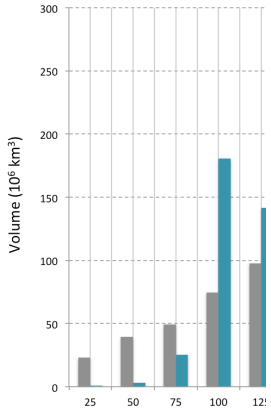

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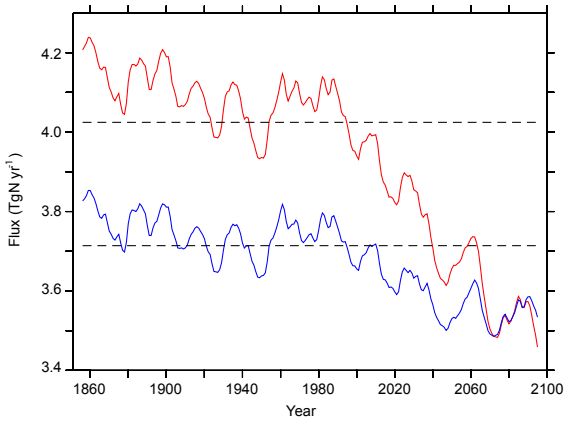
Fig 4: (a) N_2O sea-to-air flux (in TgN yr^{-1}) from 1851 to 2100 in P.TEMP (blue) and P.OMZ (red) using the historical and future RCP8.5 simulations. Dashed lines indicate the mean value over the 1985 to 2005 time period. Change in N_2O sea-to-air flux (mgN $m^{-2}yr^{-1}$) from the averaged 2080-2100 to 1985-2005 time periods in future RCP8.5 and historical simulations in (b) P.TEMP and (c) P.OMZ parameterizations.



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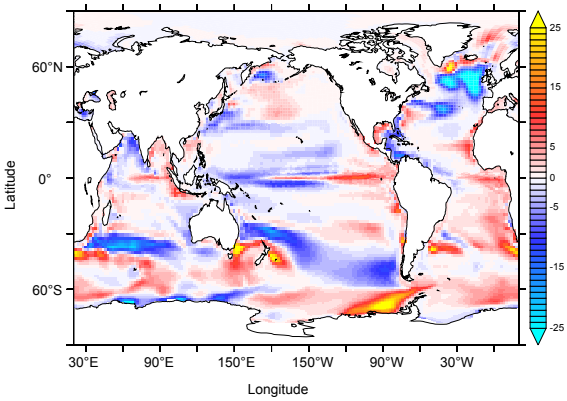
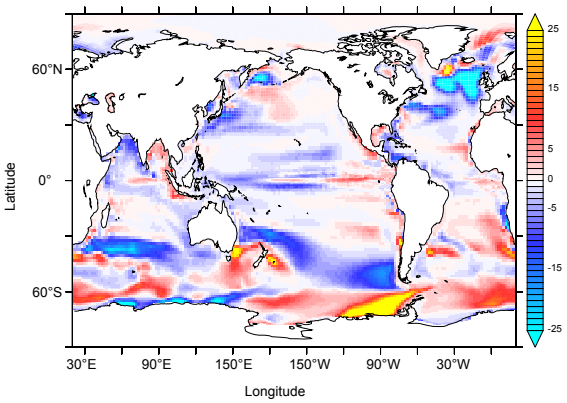


(b)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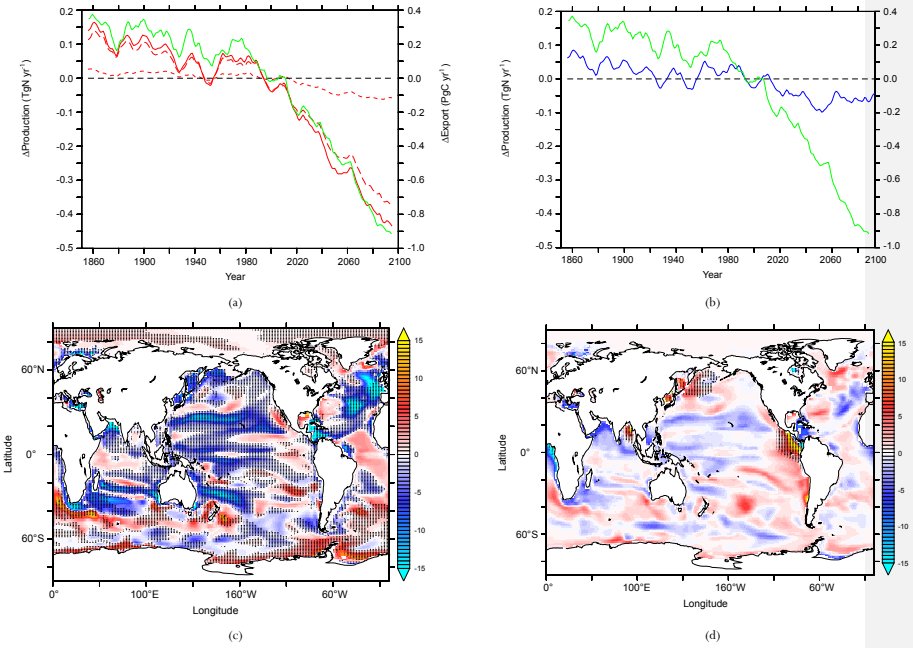
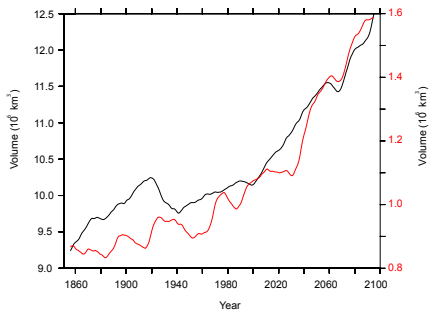
(c)

Fig 5: (a) Anomalies in export of organic matter at 100m (green), low-O_2 production pathway (short dashed red), high-O_2 production pathway (long dashed red) and total P.OMZ production (red) from 1851 to 2100 using the historical and future RCP8.5 simulations. (b) Anomalies in export of organic matter at 100m (green) and P.TEMP production (blue) over the same time period. (c) Change in high-O_2 production pathway of N_2O (in mgN m^{-2} yr^{-1}) in the upper 1500m between 2080-2100 to 1985-2005 averaged time periods. Hatched areas indicate regions where change in export of organic matter at 100m deep have the same sign as in changes in high-O_2 production pathway. (d) Change in low-O_2 production pathway of N_2O (in mgN m^{-2} yr^{-1}) in the upper 1500m between 2080-2100 to 1985-2005 averaged time periods. Hatched areas indicate regions where oxygen minimum zones (O_2 < 5 µmol L^{-1}) expand. (e) Volume (in 10^6 km^3) of hypoxic (black, O_2 < 60 µmol L^{-1}) and suboxic (red, O_2 < 5 µmol L^{-1}) areas in the 1851 to 2100 period in NEMO-PISCES historical and future RCP8.5 simulations.

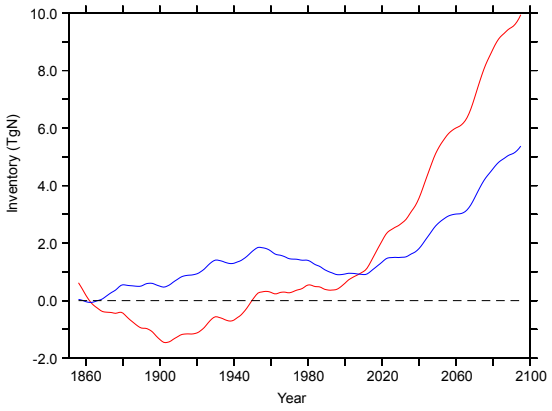



12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
Volume (10^6 km^3)
1.6
1.4
1.2
1.0
0.8
Volume (10^6 km^3)
1860
1900
1940
1980
2020
2060
2100
Year

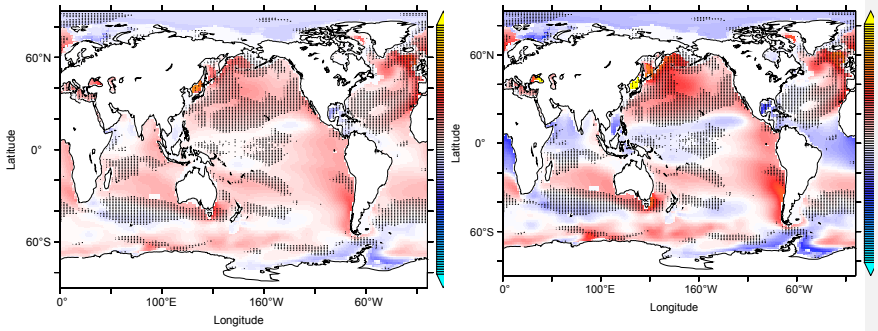
(e)

1076
1077

Fig 6: (a) Anomalies in N_2O inventory (in TgN) from 1851 to 2100 in P.TEMP (blue) and P.OMZ (red) using the historical and future RCP8.5 simulations in the upper 1500m. Change in vertically integrated N_2O concentration (in mgN m^{-2}) in the upper 1500m using NEMO-PISCES model mean from the averaged 2080-2100 to 1985-2005 time periods in future RCP8.5 and historical scenarios respectively in (b) P.TEMP and (c) P.OMZ. Hatched areas indicate regions where the annual mean mixed layer depth is reduced by more than 5m in 2080-2100 compared to 1985-2005.

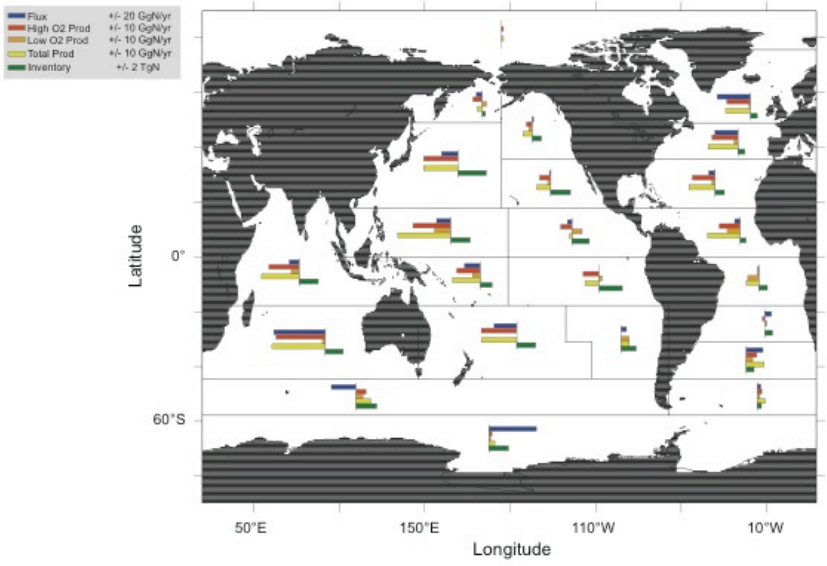


(a)



(b) (c)

Fig. 7: Change in the whole water column in N_2O sea-to-air flux (blue), high-O_2 production pathway (red), low-O_2 production pathway (orange), total N_2O production (yellow) and N_2O inventory (green) for P.OMZ from the averaged 2080-2100 to present 1985-2005 averaged time period in the NEMO-PISCES historical and future RCP8.5 simulations (based on Mikaloff-Fletcher et al. (2006) oceanic regions).



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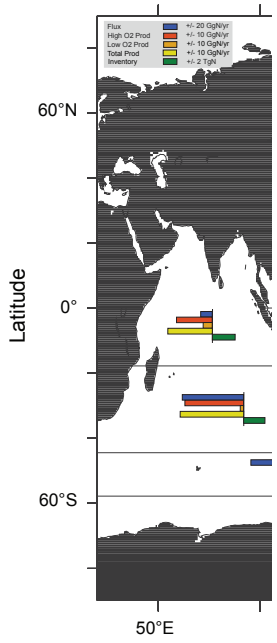

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Fig. 8: Box model results, analyzing the effect of changes in ocean circulation by reducing the mixing coefficient (μ in %) and changes in biogeochemistry by reducing export of organic matter (in %) separately in N_2O sea-to-air emissions and N_2O inventory in 2100. (**a**) Constant regimes in percentage of the historical N_2O sea-to-air flux: 95% pink, 90% blue, 85% cyan and 80% green, and (**b**) Constant regimes in percentage of the historical N_2O concentration in the deep: 90% pink, 110% blue, 125% cyan and 150% green.

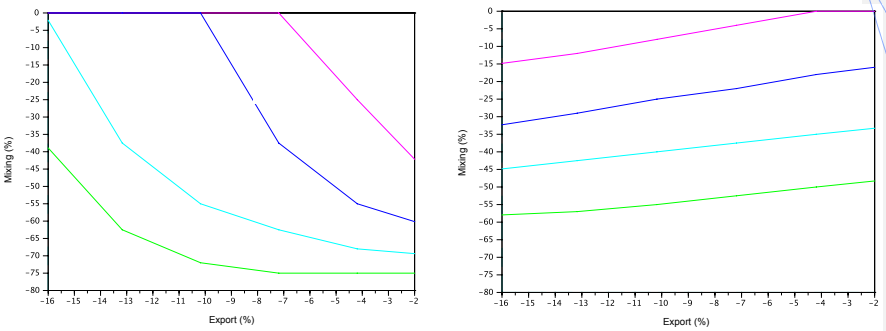

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Figure 9: Distribution of O_2 concentration in NEMO-PISCES 1985 to 2005 averaged time period (black) compared to the oxygen-corrected World Ocean Atlas (red) from Bianchi et al. (2012). Interval widths are O_2 concentrations at steps of 5 µmol L^{-1}.

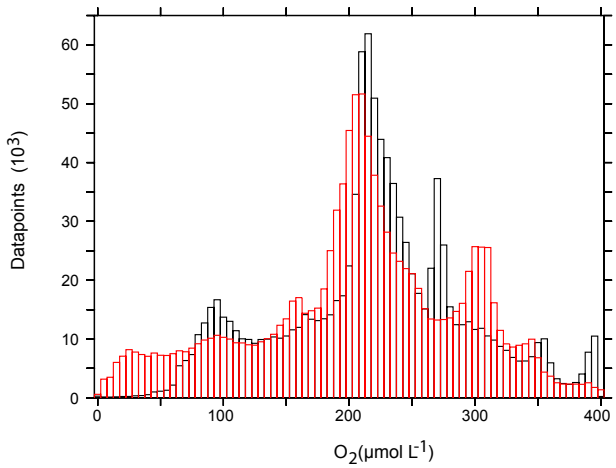
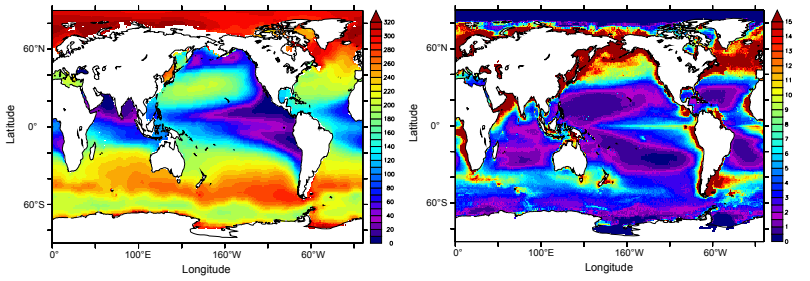
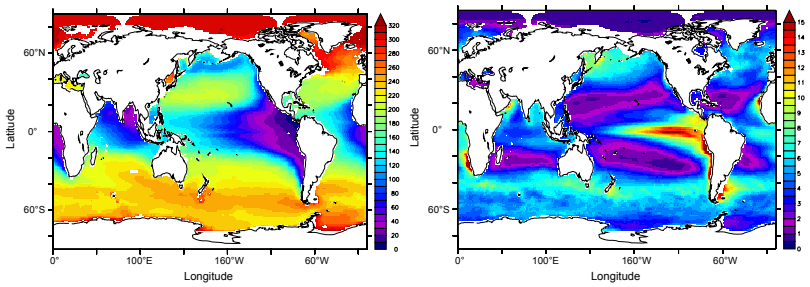


Figure 10: Averaged O_2 concentration between 200-600m depth (in µmol L^{-1}) (left) and export of carbon (in mmolC m^{-2} d^{-1}) (right) in (**a**) WOA2005* and Dunne et al. (2007), (**b**) CMIP5 model mean historical simulations over the 1985-2005 time period and (**c**) NEMO-PISCES for the present 1985-2005 time period.

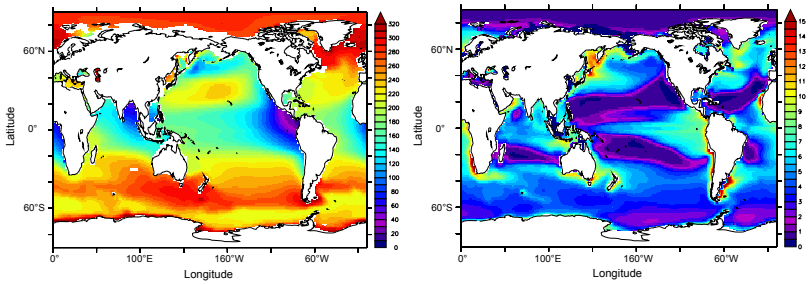
a. WOA2005* and Dunne et al., 2007



b. CMIP5 model mean



c. NEMO-PISCES



SUPPLEMENTARY MATERIAL

The O_2 modulation fuction $f(O_2)$ in P.OMZ is defined as,

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

where O_2^{*1} is 1 µmol L^{-1} and O_2^{*2} is 5 µmol L^{-1}. The shape of the function is shown in Fig. S1.

Fig. S1: Oxygen modulating function $f(O_2)$ in the low-O_2 production pathway term included in P.OMZ from Goreau et al. (1980).

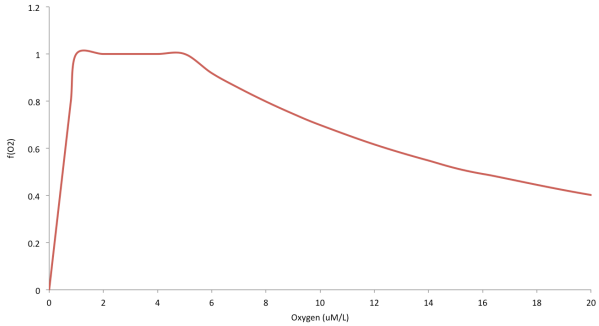


Fig. S2: Vertically integrated (a) high-O_2 and (b) low-O_2 production pathways (in gN m^{-2} yr^{-1}) in P.OMZ for the averaged 1985 to 2005 historical simulation.

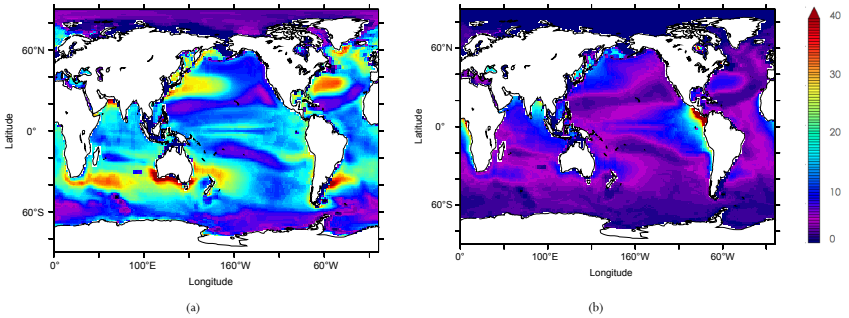


Fig. S3: Diagram of the box model. N_2O inventory is separated into surface and deep concentrations above and below 100m. The fraction of N_2O outgassed to the atmosphere (*k*), mixing ratio (*v*) between deep and surface and the rate of N_2O production from the export of organic matter to depth (*e*) regulate the N_2O budget in the ocean interior.