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Interactive comment on “Nitrous oxide dynamics in low oxygen regions of the Pacific: insights from the MEMENTO database” by L. M. Zamora et al.

L. M. Zamora et al.

lzamora@geomar.de

Received and published: 30 October 2012

2 Evaluation

Interest in the marine modeling of N_2O has surged in the past few years, largely in response to the growing recognition that global warming will tend to decrease the ocean's oxygen content, i.e., deoxygenate the ocean. Although the exact impact of ocean deoxygenation on the low oxygen regions remains highly uncertain and is currently intensively debated, a wide-spread deoxygenation will likely increase the marine N_2O production, thereby leading to a positive feedback owing to N_2O 's strong greenhouse gas properties. The magnitude of this N_2O response and consequently of the ocean warming-deoxygenation- N_2O production feedback depends critically on the processes governing N_2O production and consumption in the ocean. Hence, this careful

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data-based analysis is a much welcomed addition to the field, and will help to better constrain ocean models that aim to simulate this feedback. Indeed, the primary audience of this paper are model developers, as the study focuses on three critical elements in the currently employed parameterizations for N_2O .

The study is overall well executed, the data and analyses generally solid, and the conclusions well supported by the provided evidence. The topic is clearly relevant, so that I am overall very much in favor of seeing this study published.

Thank you

I have a number of overarching comments that I would like the authors to consider when revising this paper. However, none are of a nature that would prevent me from supporting this paper.

* (i) The approach taken is very much driven by the current ways how the N_2O cycle is parameterized in biogeochemical models. This is useful on the one hand, but on the other hand, it is missing the opportunity to better connect the modeling of N_2O to the underlying biological processes. For example, the question of whether the yield of N_2O production increases exponentially or not, and the O_2 concentration below which N_2O will be consumed, on net, are connected to the actual processes producing and consuming N_2O , i.e., nitrification and denitrification. There is a growing literature on how N_2O is really produced and consumed in low oxygen environments, but virtually none of this is discussed in the context of the presented results. This is accentuated by the fact that the processes are analyzed and presented in terms of N_2O /AOU ratios, while the actual processes need to be understood in terms of N_2O / NH_4 or N_2O / NO_3 —yields.

We agree that adding in this discussion would benefit the paper and have made substantial revisions regarding this suggestion. Within the introduction we have added several paragraphs discussing the various microbial processes that produce and consume N_2O . We have also made an effort to tie these processes into our discussion through-

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out the paper. For a complete list of the changes made, please see our response to the first referee's first comment above (which was very similar) and our responses to the 'Minor comments' below. Also, please note our related revisions/responses regarding exponential N₂O production in the comment directly below.

* ii) I would submit that the conclusion that the N₂O yield at low oxygen concentration increases exponentially rather than linearly is not tenable. The reason is that mixing and consumption at low oxygen concentrations will tend to flatten the curve quite substantially, quite likely making it impossible to statistically distinguish between a linear and an exponential model. The reason I conclude this is because we happened to have looked at this issue in our N₂O modeling study (Jin and Gruber, 2003). In this study, we modeled N₂O production following two separate pathways, i.e., a nitrification pathway with constant yield, and a 'low oxygen' pathway with an exponentially increasing yield. When we investigated how well the data fit the observations in a plot similar to that in Figure 5 of this paper, even a case where all N₂O was produced following the 'low oxygen' pathway, i.e., following solely an exponential function, gave a distribution that wasn't as steep as the blue-dashed line in Figure 5. The more realistic case, where only part of the N₂O was produced following the 'low oxygen' pathway, gave a rather linear relationship of N₂O with oxygen (a detailed description of the Jin and Gruber model approach as well as this figure is available in the supplementary material section of that paper - available from http://www.up.ethz.ch/people/ngruber/publications/jin_grl_03_supporting_material.pdf. The Jin and Gruber model is also described in illustrated in Sarmiento and Gruber (2006), on pages 197ff). I therefore recommend that the authors revisit their conclusion with a model that does include mixing and N₂O consumption at low O₂ concentration. In addition, it is also not really realistic to assume that the exponential model of yield goes to zero at high O₂ levels, but rather asymptote to some background rate, as suggested by the fact that in Jin and Gruber, we found the best fit was obtained by the model with a 50/50 contribution from the two considered pathways. Translated into a yield function, gamma, this means: $\gamma = \alpha + \beta \cdot f(O_2)$.

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We address the above comment together with a related comment from the ‘Minor comments’ section:

* p10029, lines 10-18 and subsequent paragraph: ‘obtained similar distributions’. In a somewhat indirect manner, the authors admit here themselves that it is difficult to differentiate in the data between a linear and exponential increase in the yield at low O₂ concentrations. So they support my skepticism with regard to how firm their conclusion is with regard to linear vs. exponential models. One can turn this argument also on its head and argue that given the inability of the data to distinguish between these two models, it might not be that important overall. Then, it is perhaps more important to know the integrated value and not the particular shape of the curve, no?

Thank you for directing us to the Jin and Gruber (2003) study, which we have now compared and contrasted with our findings. Before we discuss the question of an exponential vs. linear increase in N₂O production, we think it is important to first clarify several things. First, by an ‘integrated’ fit to production rates in the discussion below, we mean that the history of O₂ utilization in the water mass is taken into account so that the production rate models (be they linear or exponential) can be comparable to actual data. In contrast, an ‘instantaneous’ production rate is the rate of production in a water mass at any given moment. The ‘instantaneous’ production rate is what a model would use as input; the model output would then reflect the integrated value.

We also want to clearly describe the three fits to the N₂O production data that are discussed by the referee in his comment above and by us in our paper’s ‘N₂O production rate’ section:

(1) An exponential increase in instantaneous N₂O production rate at low O₂ as described by the Goreau et al. laboratory study. By the blue dashed line in our Fig. 5, we show the corresponding integrated fit derived from the Goreau et al. data by Nevison et al. in their equation 6.

(2) A nearly linear model with only a mild exponential component fit by Nevison et

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al. in their equation 9 to a dataset largely overlapping ours (note that they used a less complete previous version of what is now the MEMENTO database). This slightly exponential fit is shown in their Fig. 12 and appears to be most similar to the 50/50 nitrification/low O_2 scenario in the Jin and Gruber study. Both the Nevison et al. and Jin and Gruber model results discussed here in (2) refer to integrated values that are comparable to ocean observations.

(3) A cubic smoothing spline fit to the MEMENTO data, shown in our Fig. 5 by the solid blue line. A line overlaying the spline would represent our estimate of a linear integrated model of the data. The instantaneous linear fit we propose for use in models is a line with twice the slope of the nearly linear spline and is not shown in our Fig. 5.

Having clarified these points, let us address the referee's concerns. The referee is entirely correct that (2) and (3) approximate the results similarly well. Quantitatively, the r^2 values were 0.16 for the straight line and 0.12 for the functional form of (3) when fit to our data after removing two outliers ($p < 0.01$). We considered the simpler and slightly better fitting linear model to be the more parsimonious description.

In contrast with (2) and (3) the Goreau laboratory study (1) suggested a severe nonlinearity at low O_2 concentrations. As previously mentioned, the dashed thick blue line in our Fig. 5 is Nevison et al.'s approximation of the Goreau et al. laboratory data when integrated with respect to water mass historical O_2 consumption (to proxy how the laboratory data would appear in the real ocean). What we intended to convey in our Fig. 5 was that this strong exponential relationship between N_2O_{xs} /AOU ratios and O_2 from the Goreau results is not supported by the bulk ocean data. We believe this point is important because the switching point between net N_2O production and consumption occurs at O_2 concentrations where (1) is highly non-linear but (2) and (3) are not, and model output based on (1) vs. (2)/(3) would be very different.

Regarding the referee's comment that 'it is also not really realistic to assume that the exponential model of yield goes to zero at high O_2 levels, but rather asymptote to some

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background rate, ...', we totally agree. This is what we were trying to suggest with our Fig. 5: that the Goreau laboratory data do not approximate the actual data very well. The Jin and Gruber study indicated that consumption does dampen the signal that the Goreau integrated function (our blue dashed line) would present in the real ocean. However, after taking consumption into account, their study still supports our conclusion that a scenario totally based on the Goreau findings alone was not realistic.

To avoid potential confusion, we have clarified the purpose of the blue dashed line in Fig. 5 (with changes in bold):

‘For comparison in figure 5, we plot the expected exponential relationship between $\text{N}_2\text{O}_{\text{xs}}$ /AOU ratio and O_2 based on Goreau et al. (1980) as defined in equation 6 in Nevison et al. (2003). Nevison et al. (2003) hypothesized that the lack of observed in situ exponential behavior might have been due to mixing with N_2O -depleted waters from OMZs, **a hypothesis that is supported by modeling work by Jin and Gruber (2003)**. In addition to mixing, it is also possible that the lack of observed exponential behavior could be explained by a smaller than previously expected volume of water in which conditions exist where exponential behavior would be observable (as the data of Frame and Casciotti (2010) seem to suggest). It is also worthwhile to emphasize that the Goreau et al. (1980) study was limited to bacterial nitrification. Therefore, it is possible that N_2O production from other sources, such as denitrification (e.g., Farías et al. (2009)) or archaeal nitrification, is larger than previously thought and that these sources do not exponentially increase as O_2 declines (although laboratory data do suggest some sort of increase in yields of N_2O at low O_2 levels from these processes (Knowles et al., 1981; Loescher et al., 2012; Payne et al., 1971)). Independent of mechanism, it appears that the best description of net N_2O production in the ETP is a linear **or nearly linear function of decreasing O_2 (as opposed to the severely non-linear exponential function suggested by the Goreau et al. (1980) laboratory study.**’

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Next, we will address the referee's concerns about the impacts of mixing on the data.

Just to avoid any potential misunderstandings, we would like to point out that the plots referenced by the referee above are for N_2O vs. O_2 and N_2O vs. AOU, making them not directly comparable to our Fig. 5 (which is $\text{N}_2\text{O}_{\text{xs}}$ /AOU vs. O_2). Another difference is that we have very carefully excluded data from Fig. 5 that had any indication of active N_2O consumption (i.e., O_2 levels had to be $>10 \mu\text{M}$ and NO_2 concentrations, when available, had to be below $0.1 \mu\text{M}$). While we clearly cannot ensure that some of the data shown in Fig. 5 had not recently been advected out of N_2O consuming regions, we did not see evidence that this has affected the data by way of a significant drop in $\text{N}_2\text{O}_{\text{xs}}$ /AOU ratios or an increase in ratio variability at low O_2 (e.g., between $10\text{-}50 \mu\text{M}$). The spline shown in Fig. 5 is the best fit to these data, and this spline closely approximates a linear fit.

That clarified, the Jin and Gruber work does indicate that mixing may be more important than we initially accounted for. Thus, we have added a note on this uncertainty that the referee pointed out (see changes to the text below).

We still believe, however, that a linear fit provides the best description of currently existing data. While the Jin and Gruber study demonstrates that mixing interference might be substantial, due to uncertainties in model representations of O_2 concentrations, the interference from mixing might be very minor as well, and it is difficult to know with certainty. Jin and Gruber used a $1 \mu\text{M}$ O_2 cutoff for the start of N_2O consumption, and we propose a $10 \mu\text{M}$ O_2 cutoff. Particularly at low O_2 concentrations such as $1\text{-}10 \mu\text{M}$, it is notoriously difficult to get O_2 concentrations correct in models. Thus, the regions in which N_2O is consumed in both our model and that of Jin and Gruber may severely misrepresent actual locations of consumption, not to mention mixing of waters from such locations. Our Fig. 6a indicates that the switching point and therefore the volumes of O_2 within them are vital for obtaining correct N_2O production levels. Additionally, while there is laboratory evidence to support an exponential increase (e.g. the Goreau et al. study), there is also laboratory data indicating that an exponential increase is not

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realistic (e.g. Frame and Casciotti, 2010) and there is very much that we do not know about how the various microbial processes actually work together in situ.

Based on the many uncertainties of how N₂O production functions in the real ocean, we still think the best course is to simply continue to describe the data as they appear. We have changed the text and Fig. 5 in the paper to reflect our now less certain take on the dynamics of N₂O production at low O₂ (see changes below) but we stick by our original point that a linear fit provides the best description of currently existing data, and that the data do not provide evidence for an exponential increase. The changed text reads:

‘For comparison in figure 5a, we plot the expected exponential relationship between N₂O_{xs} /AOU ratio and O₂ based on Goreau et al. (1980) as defined in equation 6 in Nevison et al. (2003). Nevison et al. (2003) hypothesized that the lack of observed in situ exponential behavior might have been due to mixing with N₂O-depleted waters from OMZs, a hypothesis that is supported by modeling work by Jin and Gruber (2003), **who were able to reproduce observed N₂O vs. O₂ concentrations in the ETP using a model that included an exponential function at low O₂ levels.** In addition to mixing, it is also possible that the lack of observed exponential behavior could be explained by a smaller than previously expected volume of water in which conditions exist where exponential behavior would be observable (as the data of Frame and Casciotti (2010) seem to suggest). It is also worthwhile to emphasize that the Goreau et al. (1980) study was limited to bacterial nitrification. Therefore, it is possible that N₂O production from other sources, such as denitrification (e.g., Farías et al. (2009)) or archaeal nitrification, is larger than previously thought and that these sources do not exponentially increase as O₂ declines. Laboratory data suggest greater yields of N₂O at low O₂ levels from these processes (Knowles et al., 1981; Loescher et al., 2012; Payne et al., 1971), but the shape of the relationship is not currently conclusive (although laboratory data do suggest some sort of increase in yields of N₂O at low O₂ levels from these

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processes (Knowles et al., 1981; Loescher et al., 2012; Payne et al., 1971)). Independent of mechanism, it appears that the best description of net N_2O production in the ETP is a linear or nearly linear function of decreasing O_2 (as opposed to the severely non-linear exponential function suggested by the Goreau et al. (1980) laboratory study. **Note however, that substantial uncertainties exist for the role particularly of mixing in determining the observations shown in Fig. 5.**

* iii) The N_2O consumption rate value of $0.129 \text{ mmol N}_2\text{O m}^{-3} \text{ yr}^{-1}$ in the abstract is rather misleading, in my opinion, as the actually computed values differ by an order of magnitude. Thus, I recommend providing a range in the abstract rather than a number. Furthermore, it is not quite clear to me why the authors estimated this rate as a zeroth order process. Wouldn't it be more defensible to model this as a first order process, i.e., as $-k [\text{N}_2\text{O}]$ or perhaps even with a Michaelis-Menten type kinetics? N_2O is used as a substrate in this process, so its consumption rate should depend on the substrate concentration.

We have changed consumption rate to a range as suggested. Regarding estimating N_2O consumption as a zeroth order process, while N_2O consumption is more O_2 - dependent than other processes, it is also more energetically favorable. Thus, at low enough O_2 concentrations, organisms that are able to consume N_2O will do so in preference of NO_3 because it is a more energetically favorable process. Therefore, we question whether a NO_3 -based substrate consumption model really would be the best formulation for consumption rates. Regardless, the model output shown in our Fig. 6b indicate that N_2O production is not very sensitive to consumption rate anyways, so it is likely that adding in a substrate-based consumption would not greatly impact the results either way.

* (iv) The MEMENTO database is referenced by a publication that is essentially a proposal to build the database. Given the prominence and importance of this database in this paper, this is not really tenable. Either the underlying data need to be better

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described in this paper, or a better reference needs to be used. Of course, my favorite solution would be to make the database publicly accessible.

We have better described these data as suggested. Please see our response to the same point in the 'Minor comments' section below for further details for a list of exact changes.

3 Recommendation

I recommend acceptance of this manuscript after moderate revision. I particularly recommend that the authors put their discussion into the context of the underlying biological processes.

4 Minor comments

* p10022, method section: I recommend to rearrange the method section. I found it a bit odd to start with the description of the models, given the fact that the models play only a very minor role in this paper. I recommend the following sequence: - MEMENTO database - calculating N₂O production rates - calculating N₂O consumption rates and add the model description as part of this section.

We have rearranged this section as suggested.

* p10022, UVIC model: Given the very limited application and relevance of this model for this paper, I don't think that deserves such a long section in the methods.

We have reduced the material in this section substantially. Because we believe that some of this information is necessary for others to reproduce our results and because the first referee thought that we actually needed more detail in this section, we did not delete this information completely but instead moved portions of it to an appendix (see new Appendix B).

* p10026, equation 4: I think it is critical to point out that N₂OPR is the MEAN N₂O production rate for a water parcel since it lost contact with the atmosphere. It is not the

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instantaneous production rate.

Note that this actually had been pointed out just below equation 4. As this was not clear, we have added to this note with new text in bold:

‘where . . . N_2OPR is the average production rate the water parcel has experienced since last contact with the atmosphere (as opposed to the instantaneous rate)’

* p10026, section 2.3: reference to Bange et al., 2009. This reference does not suffice, in my opinion, to describe the database. Bange et al. (2009) discuss the proposal to develop this database, but they do not describe the content of the database, nor the quality control procedures employed. As mentioned above, I recommend to either use a better reference or to describe the data better in this manuscript.

To address this point, we have expanded upon the Methods section, giving more details on content and quality control methods for the database. Co-authors H. Bange and A. Kock intend on archiving the MEMENTO database in a publically available open access format within about 1 year, but at this point the database is still in development and is thus not yet in a publically available format. However, we will mention that if people want to obtain the preliminary database used here, they can contact H. Bange. The revised Methods text is below (with changes in bold).

‘2.1 MEMENTO observations N_2O observations were obtained from **a preliminary version of** the MEMENTO database (version as of September 2011, see Fig. 2) **currently in development** (Bange et al., 2009). The **version of the** Pacific MEMENTO database **used here** includes 10 subsurface datasets gathered between 1976-2009 (station locations are shown in Fig. 2). Most of these N_2O datasets have been comprehensively described previously (Cohen and Gordon, 1978; Pierotti and Rasmussen, 1980; Friederich et al., 1992; Dore and Karl, 1996; Dore et al., 1998; Popp et al., 2002; Nevison et al., 2003; Charpentier et al., 2007; Farías et al., 2007;

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Ryabenko et al., 2012), with the exception of **two** cruises in the ETP (A. Kock and C. Löscher, unpublished data **and H. Bange, unpublished data**). N_2O values for all cruises were obtained by gas chromatography coupled with electron capture detectors. **Precision for N_2O measurements for all datasets was $<3.4\%$.** For most datasets, O_2 was determined by modified Winkler method (the exception being that of Charpentier et al. (2007), where O_2 was determined by CTD measurements calibrated with the Winkler method). Measurements of NO_2^- , NO_3^- and PO_4^{3-} were determined spectrophotometrically. **Note that only 5 of the 11 datasets used in this study include NO_2^- measurements (see Fig. 7).**

Salinity/ temperature were obtained from CTD casts, with the exception of Pierotti and Rasmussen (1980) where temperature was measured by expendable bathythermograph and salinity was not measured. **For this cruise, salinity was interpolated from the nearest World Ocean Atlas 2009 data (and was used only to calculate the $\text{N}_2\text{O}_{\text{eq}}$ value and apparent oxygen utilization of the water mass as presented in section 2.2).** Because the data from which the WOA 2009 salinity data were gathered were not sampled in exactly the same locations or times as the Pierotti and Rasmussen (1980) data, this generates some very minor uncertainty in our interpretation of $\text{N}_2\text{O}_{\text{xs}}$ /AOU ratios in Figs. 5 and 9 and N_2OPR values presented in Fig. 7. Even assuming a major salinity difference of one salinity unit, this uncertainty is expected to be $<1\%$ of the values of the ratio and rate, respectively.

We additionally instituted quality control measures to ensure that the data entered into the MEMENTO dataset were entered correctly. This included checking whether N_2O concentrations and other seawater components/properties were consistent with expected values from surrounding cruises and checking whether surface values were consistent with atmospheric N_2O concentrations expected for the year of sampling (to check for calibration issues). Data with quality flags were not included in the analysis. The data

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presented here (a preliminary version of the MEMENTO database, which is still in development), can be requested from H. Bange (hbange@geomar.de).'

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* p10026, line 26: 'necessary to exclude additional data'. This is likely confusing for the reader - at least it confused me at my first reading of the article. I suggest writing this differently. After flagging all 'bad' data, you then selected only those data that have a TTD age older than 15 years. Then you separated these data into two bins: One where O_2 is $> 10 \mu\text{mol kg}^{-1}$ and where O_2 is $< 10 \mu\text{mol kg}^{-1}$. The former will be used for the analysis of the N_2O production rate, whereas the second will be used to determine N_2O consumption rates.

Thanks for your suggestion on rewording. We changed this text as recommended.

* p10029, lines 19: The results are discussed solely on the basis of the N_2O /AOU ratio. This is relevant for simple parameterizations in ocean biogeochemical models, but it is much less relevant for the underlying processes. A change in this apparent yield can simply be generated by changes in the relative contributions of nitrification and denitrification to the production of N_2O , with each process having a constant yield relative to nitrogen. As mentioned above, I think it will be beneficial to open up the discussion here.

As suggested, in this section we now discuss the sensitivity of the N_2O_{xs} /AOU ratio at low O_2 concentrations to changes in the relative contribution of processes such as nitrification and denitrification. We do not, however, expect that this relationship to actually be very sensitive to future changes in the relative ratio of these two processes (for a greater discussion on this point, see our reply to the final point in referee 1's general comments). Newly added text on this point is as follows:

'Also note that although we proxy N_2O production via the N_2O_{xs} /AOU ratio, in reality the production would ideally be described by the relationship between N_2O production and NH_4 and NO_3^- loss, because the N_2O_{xs} /AOU ratio masks

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changes in the relative contribution of nitrification and denitrification at a given oxygen concentration. Different relative contributions of these multiple processes may contribute to the scatter shown in Fig. 5 as well. Note, however, that the MEMENTO data span a wide range of in situ temperature, mixing, geographic, and temporal conditions. Thus, it seems unlikely that future changes in the relative contribution of nitrification and denitrification will cause noticeable change in N_2O production from its current relationship as indicated in Fig. 5.’

p10030, consumption rate: Although I agree that the uncertainty of this estimate is high, I don’t think that the level of uncertainty is that large. The highest value stems from a single instantaneous estimate and is really driven by a low volume and high ventilation rate. I cannot judge this particular estimate, but I am quite confident that one can estimate the volume of PCUC better than to within a factor of 10 through careful water mass analyses. So I would be prepared to dismiss the highest value. The remaining range is still high, and therefore the whole subsequent discussion (as well as the abstract) should be done in terms of a range and not a single value for which way too many significant digits are provided.

As suggested, we have changed the single value in the text for a range and have also reduced significant digits on this range down to one. We agree that the bounds on the uncertainty might be reduced though an in-depth water mass analysis. However, our Fig. 6b shows that even at the uppermost range of consumption rates, there is little difference in net N_2O concentrations. Thus, lowering the bounds probably does not matter too much.

* p10032, line 18: Modeling consumption: Note that Jin and Gruber (2003) modeled N_2O loss by a first order reaction. I am still of the opinion that this is a more sensible way of modeling N_2O loss than assuming a zeroth order loss rate.

Please see our response to ‘Evaluation’ point 3 above.

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* p10033, line13: NO_2^- – as a proxy for denitrification and the onset of N_2O consumption. This discussion would benefit from a better connection with the underlying processes. The challenge is that denitrification is both a source and a sink for N_2O . So the appearance of higher NO_2^- – may indeed be an indicator of the onset of (canonical) denitrification, but this does not mean that the net balance for N_2O must have switched sign as well. I thus remain skeptical about the arguments that the switching point to net consumption occurs already at concentrations as high as $10\ \mu\text{mol kg}^{-1}$.

As suggested, we will add in some further discussion of the underlying processes (see below). We also agree that clearly there is substantial uncertainty in the exact switching point between net N_2O production and consumption and will make that more clear in our discussion. However, we believe we have sound evidence for an association of observable NO_2^- concentrations with net N_2O consumption in this region. We also stand by our position that a cutoff at $10\ \mu\text{M}$ is the best geochemical estimate for the switching point that can currently be made.

We explain our position and address the referee's comment in two parts: 1) by showing that N_2O consumption is associated with NO_2^- accumulation in this region, and 2) by arguing that due to this association, even though NO_2^- is an indirect proxy for N_2O consumption, the switching point for net N_2O consumption has to occur at O_2 concentrations at least as high as $10\ \mu\text{M O}_2$.

1) The association of N_2O consumption with NO_2^- accumulation

Because the referee seemed skeptical of our original argument that N_2O consumption is associated with NO_2^- consumption in this region, here we delve a little deeper into the data in an attempt to convince him. Our reasoning for standing by our position is as follows. As seen previously in our Fig. 7, we related N_2O production rates to NO_2^- concentrations. The data exhibit a distinct L-shaped pattern: when NO_2^- is low there is a relatively large range in N_2O production rates; when NO_2^- accumulates, the mean values of N_2O production rates are substantially diminished, as is the range of

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these rates. It is useful to note that NO_2^- was only measured at ocean sites where it was expected to be above detection limits (primarily sites to the far east of the tropical Pacific between 97- 70 oW, see Fig. 7). Because the samples without NO_2^- data have a large range of N_2O production rates (interquartile range from 0.2-0.6) and near zero expected NO_2^- , we would thus expect that the L-shaped distribution in Fig. 7 would be more pronounced if the rest of the MEMENTO data with missing NO_2^- measurements were included.

Now we separate out the data in Fig. 7 into the locations and cruises they represent. Of the cruises in which NO_2^- was measured, only five cruises have NO_2^- levels above $0.5 \mu\text{M}$ (i.e., NO_2^- levels well above detection limits). For each of these 5 cruises, the N_2OPR (and $\text{N}_2\text{O}_{\text{xs}}$ concentrations) in water with NO_2^- at observable levels is significantly lower than the N_2O PR and $\text{N}_2\text{O}_{\text{xs}}$ in water without NO_2^- accumulation ($p \ll 0.01$, t -test), indicating the likely influence of N_2O consumption in these waters. Two of these cruises are either in the PCUC (an area of active N_2O consumption, see our section 3.2) or surrounding the PCUC with water mass exchange into and out of the PCUC (see Fig. 7). Note that the L-shaped trend shown in Fig. 7 remains the same for these 2 cruises if we separately analyze the data along isopycnal surfaces where the water masses sampled are mixing with each other (field and modeling studies indicate that there is strong mixing in the region) (Czeschel et al., 2011; Montes et al., 2010). Thus in order for $\text{N}_2\text{O}_{\text{xs}}$ and N_2OPR to be lower at higher NO_2^- in this region of high mixing (i.e., in order to reproduce Fig. 7), N_2O consumption must be occurring. Therefore, NO_2^- accumulation is associated with N_2O consumption, at least at these 2 sites.

Previous studies have directly related NO_2^- accumulation with N_2O consumption in two of the other sites where NO_2^- accumulates as well. One of the cruises is located in the same location as the Cornejo and Farias 2012 study in the eastern tropical South Pacific, which they show by bacterial cultures and field observations to be a region where N_2O consumption is also associated with NO_2^- accumulation. The two remaining cruises are located in eastern tropical North Pacific. One of these sites has not

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been described previously (H. Bange, unpublished data), but in the other (referenced in Cohen and Gordon (1978)), the authors tied NO_2^- accumulation to N_2O consumption based on coinciding NO_2^- maxima and N_2O minima in the stations sampled. Thus, we believe that NO_2^- accumulation is consistently associated with net N_2O consumption in the data presented in our Fig. 7, although the mechanism for the association is not understood.

2) Why we believe the switching point for net N_2O consumption has to occur at O_2 concentrations at least as high as $10 \mu\text{M O}_2$.

The referee's related concern was that NO_2^- is still an indirect proxy for N_2O consumption and thus even if the two are associated, the point at which NO_2^- accumulates is not necessarily the point at which N_2O consumption begins. In response to this- we partially agree. The distribution of data in Fig. 7 could exist if N_2O consumption began before NO_2^- accumulated (meaning that the switching point could be GREATER than $10 \mu\text{M O}_2$). However, the distribution observed in Fig. 7 is unlikely to exist if the switching point were less than $10 \mu\text{M O}_2$, because of the demonstrated link between NO_2^- accumulation and N_2O consumption at these sites.

Based on our work, a value of $10 \mu\text{M O}_2$ for the switching point between net N_2O production and consumption represents the best geochemical estimate for the study region. Unfortunately, no existing method for estimating this important model parameter is perfect. Given the difficulties in extrapolating laboratory results involving individual species and artificial conditions to bulk processes in the ocean, we believe that our geochemical approach provides an important contribution to the understanding of N_2O dynamics in the ETP region.

We have made the following changes in the text to reflect our response to the reviewer (with new text in bold):

‘Cornejo and Farías (2012) recently proposed using the development of subsurface

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nitrite (NO_2^-) as a proxy for N_2O consumption for the coastal eastern tropical South Pacific. NO_2^- is frequently associated with N_2O depletion; also, both NO_2^- reduction and N_2O production are inhibited at very low O_2 levels (Farías et al., 2007). As indicated in figure 7, subsurface NO_2^- accumulation in the ETP is also associated with low N^* and O_2 , both indicators of denitrification. Based on NO_2^- concentrations $>0.75 \mu\text{M}$, Cornejo and Farías (2012) identified the beginning of net N_2O consumption at $8 \mu\text{M}$ O_2 in the coastal eastern tropical South Pacific; **NO_2^- accumulation has also been related to N_2O consumption in the eastern tropical North Pacific (Cohen and Gordon, 1978).**

One problem with applying this approach to a scale is that NO_2^- may not be a good indicator of denitrification in all circumstances, even when the NO_2^- is accompanied by low N^* and low O_2 (Nicholls et al., 2007; Naqvi et al., 2010; Lam et al., 2011). Although NO_2^- , N_2O , low O_2 , and low N^* can all be associated with water column denitrification, other processes such as anammox, sedimentary denitrification, **dissimilatory nitrate reduction to ammonia, stand-alone NO_3^- reduction to NO_2^-** , and nitrification can affect the concentrations of these species as well. Additionally, accumulation of each can occur on different timescales, and each can also be passively transported.

Therefore, we use the MEMENTO database to test if NO_2^- is a good proxy for N_2O consumption over a larger region of the ETP than that described in Cornejo and Farías (2012) (the region in the MEMENTO database that includes NO_2^- data spans between 20°N – 21°S and 70 – 110°W , Fig. 7). We find that when NO_2^- is low, N_2O production rates cover a range of values; conversely, when NO_2^- is above detection limits ($0.1 \mu\text{M}$), N_2O production rates are almost always $<0.25 \text{ nmol kg}^{-1} \text{ yr}^{-1}$ (Fig. 7). Thus, **NO_2^- accumulation** appears to be a reliable proxy for N_2O consumption in the greater ETP **although the mechanisms for why these processes are associated are not entirely clear. It is possible that this co-occurrence is related to nitrifier-denitrification, which can occur in aerobic environments in**

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response to the presence of NO_2 (Beaumont et al., 2004). Another possibility for their relatedness in situ is that both NO_2 and N_2O reductase appear to be inhibited at lower O_2 levels than other relevant enzymes involved in the N cycle (Coyne and Tiedje, 1990; Farias et al., 2007; Körner and Zumft, 1989; Mckenney et al., 1994).’

* p10034, lines 4-11: depth and temperature dependency of N_2O production: In my opinion, it is not meaningful to present the data as is done here. The N_2O production estimated from equation 4 is a flux weighted mean of the production along the entire pathway from the surface to the depth where the parcel was sampled. So you can’t plot it against depth and infer anything about the depth dependency. It works perhaps slightly better for temperature, but also here, it is problematic. The only way out is the estimation of more instantaneous rates, which would require the evaluation of gradients in $\text{N}_2\text{O}_{\text{xs}}$ and age.

A quick clarification - the data presented in Fig. 9 (which are the data the reviewer is referring to) are actually not based on equation 4. We are plotting the $\text{N}_2\text{O}_{\text{xs}}$ /AOU ratio vs. depth and temperature (not N_2OPR). Nonetheless, the referee is correct that both $\text{N}_2\text{O}_{\text{xs}}$ and AOU values are averages over the integrated history of the water mass and that the depth a water mass was at when sampled is not inclusive of all the depths the water mass was at in its past history. Our revised text is as follows:

‘Section 3.4: Depth and temperature dependency of N_2O production

Previously, N_2O production rates from marine nitrification have been suggested to have a temperature dependence (Butler et al., 1989; Elkins et al., 1978). However, this hypothesis has not been strongly supported by laboratory and field studies (Nevison et al., 2003; Punshon and Moore, 2004; Ward, 2008). Based on thermodynamic considerations, pressure has also been suggested to affect N_2O production rates (Butler et al., 1989), but again, we are not aware of any laboratory studies supporting this hypothesis.

To test for in situ evidence for a depth/temperature dependency, multiple previous studies have **used plots of the biotic N_2O /AOU ratio vs. depth** (Butler et al., 1989; Cornejo and Farias, 2012; Elkins et al., 1978; Freing et al., 2009; Suntharalingam and Sarmiento, 2000). **These studies have produced patterns that they considered to be evidence for a depth/temperature effect.** However, the temperature-sensitivity of nitrification rates is non-linear and may be masked or superseded by the dynamics of O_2 consumption (Barnard et al., 2005). **Additionally, the biotic N_2O /AOU ratio reflects the integrated history of depths of the water mass, rather than its current depth, making this ratio an imperfect measure for testing a depth or temperature dependence hypothesis. The MEMENTO data showed a similar pattern to these previous studies at first appearance. However, the depth-dependency pattern was confounded with O_2 levels and the pattern disappeared after correcting for O_2 (Fig. 8). While the focus of this manuscript is not on temperature or depth dependencies, we briefly note that these results call into question what was previously thought to be in situ evidence for the pressure/T dependency hypotheses.'**

Instead of using the $\text{N}_2\text{O}_{\text{xs}}$ /AOU ratio for this section, the referee suggested using gradients in $\text{N}_2\text{O}_{\text{xs}}$ and age to test the depth dependency. Perhaps we are misunderstanding something, but our understanding is that it would be problematic to separate out the evolution of $\text{N}_2\text{O}_{\text{xs}}$ over water mass age from a potential depth dependency because age and depth co-vary.

Figures: I suggest combining figures 7 and 8 into one figure.

We have done this.

Interactive comment on Biogeosciences Discuss., 9, 10019, 2012.

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