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Interactive comment on "Differences between coastal and open ocean distributions of N_2O in the oxygen minimum zone off Peru" *by* A. Kock et al.

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We would like to thank the reviewers for their useful suggestions to improve our manuscript. We carefully revised our manuscript according to the reviewers' remarks. We included a description of the hydrographic settings and a TS-diagram in the revised manuscript, as suggested by reviewer 1, and re-structured some paragraphs of the manuscript to emphasize the main findings of the manuscript. Please find a detailed reply to the reviews below. Line references refer to the revised manuscript in the original manuscript format.

R2: "I feel that overall, the structural organization of ideas in the introduction and methods are clear, but the results and discussion are not as clear or well organized, and this makes it somewhat difficult to follow. This is likely due to the complexity of the data

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and the many approaches used during interpretation. However, some of the sentences refer to multiple ideas, and could probably be broken up into two or more sentences."

We revised the manuscript according to the reviewer's suggestions to improve the structure of the Results and Discussions.

R2: "Furthermore, some of the ideas put forward in the results/discussion section were not presented in the introduction, and I felt that some of the material in the discussion would be better situated in the introduction (e.g. evidence for increased N2O production following reventilation, and the link between sulfur cycling and N2O cycling)."

We agree with the reviewer that a potential link between sulfur cycling and N2O production and the occurrence of peak N2O production over the shelf should be mentioned in the Introduction. We therefore shifted parts of the Results and Discussion to the Introduction section (lines 59-67).

R2: "One of the most striking ideas is that the data suggest N2O cycling may be coupled to sulfur cycling, though I am surprised that this is not included in the abstract, and would like to see some figures that specifically show the relationship between O2, H2S and N2O. Is it surprising that N2O reduction only takes place in the presence of H2S, given the tendency of conventional O2 measurement techniques to overestimate O2 at low concentrations?"

We did not include any figures showing the relationship between N2O and H2S, because from our data, a direct link between H2S occurrence and peak N2O production cannot be established. Although N2O accumulation has indeed been observed in proximity to H2S plumes in some cases, other stations showed extremely high N2O concentrations without any indication of H2S. We nevertheless included the discussion of this item as we cannot exclude that sulfur cycling influences N2O production, either. The observed differences in N2O and H2S distributions could be due to the different time scales of H2S accumulation and consumption mechanisms, which can be very rapid; and N2O production or consumption mechanisms, which can lead to persistent

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accumulation of N2O under oxic conditions. Moreover, there is evidence that intense sulfur cycling may take place without the accumulation of H2S.

R2: “Another important finding is the inadequacy of a linear N2O/AOU ratio to describe N2O distributions in shelf waters, and this too could be further emphasized. I was under the impression that the N2O/AOU relationship is highly variable, even in the open ocean, and that it is therefore not advisable to estimate N2O concentrations from AOU alone. Nevertheless, the authors’ conclusion that the N2O/AOU relationship is even less reliable in shelf regions underscores this, and I feel this should be emphasized in the abstract and body of the article.”

We agree with the reviewer that the inadequacity of the ΔN2O/AOU relationship to represent the N2O distribution at the Peruvian coast is one of the main findings in our manuscript. We hope that this conclusion is emphasized by the restructuring of the manuscript.

R2:” The authors highlighted the relatively high variability over the shelf, and suggested that advection of N2O from other locations, localized upwelling or re-ventilation may be responsible for some of the deviations from the expected N2O/AOU relationship, but did not include sedimentary processes, riverine/estuarine inputs, or topography as possible explanations. Could these also play a role?”

We found no indication that riverine or sedimentary inputs have a strong direct impact on the N2O distribution. Due to the extremely arid climate in the adjacent Atacama desert riverine inputs are only marginal. Most of the sediments on the shelf and the overlying waters are anoxic and depleted in N2O. A sedimentary source for N2O into the water column off Peru is thus unlikely. An indirect influence of the sediments through the supply of substrates that stimulate N2O production (e.g. NH4+, H2S) cannot be excluded, though. The interaction of the hydrographic settings with topography may indeed influence the N2O distribution. However, we could not find a systematic link between the topography along the Peruvian coast and the N2O distribution, and

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we assume that topography has a rather indirect influence on the N2O distribution.

R2: “I am curious about a few details of the analysis, some only for my own interest, but perhaps others should be included. What volume of gas was injected? Was there a second syringe to accept overflow? What was the final pressure in the vials? Were the vials weighed to confirm the volume of liquid in the vial during equilibration¿‘

The gas sample volume was 10 mL (see line 145). Samples were equipped with a second syringe to collect the overflowing water until the subsample for GC injection was taken. The headspace pressure was therefore equal to the ambient pressure during the measurements. We added this information to the methods section (lines 146-147).

The volume of the sample vials was determined prior to analysis by weighing 10 random sample vials of the same type filled with distilled water and calculating the volume from the density of the samples. The volume of the individual samples was not determined by weighing due to the large number of samples measured and the difficulties of using a balance onboard a ship. We added the standard deviation of the sample volume to the text to account for the uncertainty in the sample volume (line 137).

R2: “Can you list the concentrations of the gas mixtures, and how many were calibrated against the NOAA cylinders?”

The standard gas mixtures used during M77-3& 4 and M90-93 had concentrations of 318.2 ppb (Std 4), 982.2 ppb (Std 5) and 99.9 ppb (Std 3). Std 4 and 5 were calibrated against NOAA standards, while Std 3 was internally calibrated.

R2: “Were any measurements excluded from the analysis due to large difference between replicates? If so, what threshold was used to determine this?”

Measurements with a relative standard deviation above 15% were excluded from the analysis. This applied to less than 1% of all measurements.

R2: “How did you determine that the maximum overestimate would be 17%? What are

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your assumptions (e.g. minimum initial concentration during the year when you expect the water last contacted the surface) Can you list the range of errors that this 17% overestimate could produce for your samples? Or give a general idea of how small the effect is?"

A ∼17% overestimate of [N2O]eq would result from the difference between the 2013 atmospheric mixing ratio of 323 ppb and the preindustrial N2O mixing ratio we assumed to be 275 ppb. The resulting error in [N2O]eq would be largest for cold waters (e.g. resulting in an overestimation of ∼1.2 nM for waters at 2°C). To precisely estimate the effect of this error, the water mass age would be required for all samples. Generally, the oldest waters are also associated with high AOU and delta N2O (except for samples showing signals of N2O consumption, but the determination of the delta N2O / AOU correlation is not applicable for these samples anyway), the error in [N2O]eq would thus marginally change the slope of the delta N2O/AOU regression.

R2: "Is the 'pump-CTD' water collected from the ships flow-through system?"

The pump-CTD is a separate instrument that allows water sampling by directly pumping the water from different sampling depth onboard. It can be used for water profiling of discrete samples in high depth resolution.

R2: "Is it true that N2O depletion coincided with high nitrate to phosphate ratios? I would have thought N2O depletion would coincide with low N:P ratios, consistent with N loss during denitrification?"

N2O depletion at low oxygen concentrations is indeed observed in areas with high N loss and thus low N:P ratios (see e.g. Figure 3). Our data do not indicate the opposite.

Technical corrections:

R2: "I find some of the text in some figures to be too small to read (e.g. Figures 2, 3 and 4)."

The figures were modified to improve their readability.

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R2: “Page 10176 line 2 – consider replacing ‘low N’ and nitrate’, with ‘more negative N’ and low nitrate“

Changed as suggested.

R2: “Page 10178 line 1-2, consider replacing ‘when oxygen reached suboxic’, to ‘when waters reached suboxic”’

Changed as suggested.

R2: “Page 10178 Line 14: do you mean that N2O accumulation took place during and following the ventilation of water? Please clarify.”

Increased N2O production is likely to be triggered by transition from anoxic to oxic conditions and may be restricted to only a short time-period after re-ventilation. We added a few sentences on the oxygen conditions required for increased N2O production to take place to clarify this context.

R2: “Page 10179 line 14: you say ‘at relatively low concentrations’, do you mean low oxygen concentrations or N2O concentrations? Please clarify.”

In this case we meant N2O concentrations to be low. We clarified the sentence as suggested by the reviewer.

Interactive comment on Biogeosciences Discuss., 12, 10167, 2015.