

## ***Interactive comment on “Investigating the effect of El Niño on nitrous oxide distribution in the Eastern Tropical South Pacific” by Qixing Ji et al.***

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Anonymous Referee #4 [Referee] p.1 lines 19-24: The deepening of the oxycline and deeper N<sub>2</sub>O peaks is this just due to a deepening of the isopycnal they occur on, or are they shifting to different density surfaces?

[Response] Our data suggest the deepening of the oxycline and deeper N<sub>2</sub>O peaks are more likely due to deepening the isopycnal they occur on. We'll make it clear in the Abstract.

[Referee] p.3, lines 19-25: Additional detail on analysis and calibration of N<sub>2</sub>O isotopologue measurements should be provided.

[Response] We added the following in the revised manuscript: The mass ratio of 45/44

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and 46/44 were used to derive  $\delta^{15}\text{N}_{\text{bulk-N}_2\text{O}}$  and  $\delta^{18}\text{O-N}_2\text{O}$  and, respectively; while the mass ratio 31/30 was used to derive  $\delta^{15}\text{N}_{\alpha\text{-N}_2\text{O}}$ . Then  $\delta^{15}\text{N}_{\beta\text{-N}_2\text{O}}$  was calculated from equation (4) using  $\delta^{15}\text{N}_{\text{bulk-N}_2\text{O}}$  and  $\delta^{15}\text{N}_{\alpha\text{-N}_2\text{O}}$  values. Calibration of  $\delta^{15}\text{N}_{\alpha\text{-N}_2\text{O}}$ ,  $\delta^{15}\text{N}_{\beta\text{-N}_2\text{O}}$  and  $\delta^{18}\text{O-N}_2\text{O}$  was accomplished using 4 certified standard gases (supplied by Joachim Mohn) encompassing the values reported here. The analytical precision of isotope measurements were  $\pm 0.07$ , 0.17, 0.36 and 0.18‰ for  $\delta^{15}\text{N}_{\text{bulk-N}_2\text{O}}$ ,  $\delta^{15}\text{N}_{\alpha\text{-N}_2\text{O}}$ ,  $\delta^{15}\text{N}_{\beta\text{-N}_2\text{O}}$  and  $\delta^{18}\text{O-N}_2\text{O}$ , respectively.

[Referee] p.4, Equation 5: definition of SP should not have the multiple of 1/2.

[Response] Indeed. Corrected.

[Referee] p.6, lines 17-18: how do you interpret the SP values  $< 0$ , especially in the surface which should likely be closer to atmospheric values (18‰)?

[Response] We checked the analysis and we are confident about the measurements. We interpreted as the denitrification dominant  $\text{N}_2\text{O}$  source. Some recent publications showed that  $\text{N}_2\text{O}$  produced by bacterial denitrification has SP values ranging from 0 to minus 10 per mil. Thus we attribute our measurements to denitrification in the water column. We will add these explanation in the revised text. Mothet et al., 2013: <http://dx.doi.org/10.1071/EN13021> Winther et al., 2018: <https://www.biogeosciences.net/15/767/2018/bg-15-767-2018.pdf>

[Referee] p.7, equation 6: I understand that you are using an end member mixing, or 'Keeling Plot' model for estimating the d value of the produced  $\text{N}_2\text{O}$ , but it was less clear how you then attribute the  $\text{N}_2\text{O}$  source based on those values. Please provide additional information, support, justification for the source attributions based on your measurements and calculations.

[Response]  $\text{N}_2\text{O}$  production pathways can be inferred from SP, because SP is independent of isotopic values of  $\text{N}_2\text{O}$  production substrates; generally,  $\text{N}_2\text{O}$  produced via  $\text{NH}_4^+$  oxidation and partial denitrification have distinctive SP values of  $30 \pm 5$  ‰

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and  $0 \pm 5$  ‰ respectively. Simply put, higher produced SP value indicates nitrification whereas lower SP indicates denitrification. It is supposed to be a qualitative, not a quantitative indicator. This is stated immediately followed equation 6 and cited Toyoda et al., 2011. The model and calculation is documented by Fujii et al., 2013 (doi:10.1007/s10872-012-0162-4).

[Referee] p.7, lines 27-28: it seems difficult to explain a SP value of -9‰ under these conditions. I would be concerned here about calibration, and believe that the authors should further discuss their calibration techniques, and possible explanations for such a low SP value in surface waters.

[Response] We double checked the isotopic data; our in-house standard (cold sea-water) and isotopic references showed no sign of inaccuracies. We are confident that the negative SP values are accurately measured. Some recent publications showed that N<sub>2</sub>O produced by bacterial denitrification has SP values ranging from 0 to -10 per mil. Thus we attribute our measurements to denitrification in the water column. We will add these explanation in the revised text. Mothet et al., 2013: <http://dx.doi.org/10.1071/EN13021> Winther et al., 2018: <https://www.biogeosciences.net/15/767/2018/bg-15-767-2018.pdf>

[Referee] p.8, line 1: Is there any other evidence of upwelling/diffusion from suboxic zones influencing the upper water column here?

[Response] Diffusion can occur simply due to a concentration gradient; as the N<sub>2</sub>O concentration gradient near the concentration peak can be 3 – 5 nmol/L/m. We will clarify the sentence here in the revised manuscript.

[Referee] p. 8, lines 19-22: It is not meaningful to apply the model in equation 6 to an environment in which N<sub>2</sub>O is being consumed. Is there any evidence of N<sub>2</sub>O production here, or only consumption?

[Response] This section requires more clarification. In the oxygen deficient zone

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where N<sub>2</sub>O is undersaturated, N<sub>2</sub>O is being produced and consumed at the same time and reaching a dynamic balance. This is demonstrated by tracer incubation studies (Ji et al., 2015 GRL, doi:10.1002/2015GL066853; Babbin et al., 2015, doi:10.1126/science.aaa8380). The net isotope effects during N<sub>2</sub>O production and consumption by denitrification is quite significant that both N and O isotopic compositions increased. Therefore it is valid to apply equation 6 to distinguish N<sub>2</sub>O production.

[Referee] p.8, line 28: Are you excluding nitrifier-denitrification here, or lumping it in with ‘denitrification’?

[Response] Because nitrifier-denitrification and denitrifier-denitrification have similar SP values, we use ‘denitrification’ to represent both possible pathways in this sentence.

[Referee] p.9, lines 1-3: How would you derive N<sub>2</sub>O production rates from nitrate and nitrite isotopes?

[Response] Details can be found in a previous study from Bourbonnais et al., 2017 (doi:10.1002/2016GB005567), in which the authors applied a three-dimensional model to derive N<sub>2</sub>O production rates from isotopic compositions of N<sub>2</sub>O, nitrate and nitrite, and fractionation factors during nitrification and denitrification.

[Referee] p.10: I thought the discussion of El Nino effects on N<sub>2</sub>O was interesting, and wondered to what extent the sampling period represented conditions during the 2015 El Nino event, and how the 2015 El Nino event might reflect other El Nino events in this region. How broadly applicable are the current results?

[Response] The cruise in October 2015 was conducted during a developing strong El Nino since early 2015 (see Figure 1). We realized that our study can be treated as a ‘snapshot’ during El Nino, rather than a continuous record of it. Previous studies (e.g. Stamma et al., 2016, doi:10.5194/os-12-861-2016) have concluded that 2015/16 El Nino can be categorized as “Strong El Nino” based on ONI and other properties. Thus we present comparative study of N<sub>2</sub>O dynamics between El Nino and non-El

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Nino years.

[Referee] Figure 1: Why are these years/data in particular the ones compared in this figure? It seems more relevant to compare the strength of the 2015 to other strong El Nino years to gauge how representative were the conditions sampled here of other El Nino periods.

[Response] Previous studies (e.g. Stamma et al., 2016) have concluded that 2015/16 El Nino can be categorized as “Strong El Nino” based on ONI and other physical properties. Unfortunately, no N2O concentration or isotope data existed in the database for us to compare the N2O dynamics between two strong El Nino events.

[Referee] Figures 3, 4, 5, 7: These section plots are not a particularly effective way to present the data. I understand the desire to present the data in a spatially explicit fashion, but the section plots, with only a few stations, rather large gaps in the data, and considerable smoothing don't help to relay the information to readers. In many of these cases, stacked depth profiles would be a much clearer way of presenting the patterns and comparing to other existing data.

[Response] The authors have tried a number of ways plotting the data, including stacked depth profiles, to present the water column profiles during 2015/16 El Nino. And the current presentation is rather realistic and effective in conveying information. We realized in some cases there's a large gap between stations, so we leave some blank spaces; we realized the smoothing exerted by ODV software and we chose to use “weighted-averaged gridding” instead of the more popular “DIVA gridding”

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