

Review of “Physical and biogeochemical forcing of oxygen changes in the tropical eastern South Pacific along 86 W: 1993 versus 2009” by Llanillo et al., 2012.

Reply to Anonymous Reviewer #2

We are grateful to Reviewer #2 for his/her constructive revision of the manuscript and his many useful comments. Next we reproduce the Reviewer’s comments (italics) followed by our responses.

The manuscript by Llanillo and coauthors describes changes in water mass composition and biogeochemistry along a meridional section crossing the South Eastern Tropical Pacific (SETP) Oxygen Minimum Zone (OMZ) between two opposite phases of ENSO.

OMZs are especially important for ocean biogeochemistry (they are hotspot of N-cycle transformation) and ecosystem (they limit the habitat of many marine species). The distribution and oxygen depletion of OMZs respond to changes in ocean circulation that occur on multiple timescales, from seasons to decades, including possible changes linked to anthropogenic warming. Characterizing the response of OMZs to these climatic forcing is critical, especially in light of the predicted deoxygenation as the oceans warm up.

Thus, the study of Llanillo and Coauthors is timely and welcome, since it investigates the physical and biogeochemical changes of a major OMZ arising from the strongest mode of variability in the equatorial/tropical ocean. The Authors start from observation along two occupations of the meridional section to calculate the contribution of different water-mass end-members, and further quantify the role of water-mass redistribution and biogeochemistry in driving the observed oxygen and nutrients variations. The picture that emerges is qualitatively consistent with the physical changes expected for ENSO-type variability; the study adds a quantitative understanding (with some caveats) to the picture. The manuscript is well structured and written, it presents new data and analyses, and represents a useful contribution to a relevant topic. Overall, I feel that some points could be further discussed and clarified to improve the paper and increase the confidence in the results shown.

Major points:

(1) I wonder if the OMP technique as implemented by the Authors produces an estimate of the error associated with the water mass fraction that could be included in the figures (similarly to the white shadings in Fig. 9). This would help focusing the attention to the parts of the section where the OMP results are most robust/reliable.

Unfortunately this is not possible as the water mass fractions only give an estimate of the mass conservation when added together (mass residual) but do not allow identifying what part of this mass residual corresponds to each water mass fraction. However, after running the extended OMP analysis, we only select for our study those points with a mass residual below 4%. It's worthy to remark that the vast majority of the data points present mass residuals considerably below this 4% limit; therefore, the water mass changes described are reliable. In Figure 1 here (and in the supplementary material of the revised manuscript) we show the residuals associated to mass conservation in those points selected for our analysis, along both latitude and depth.

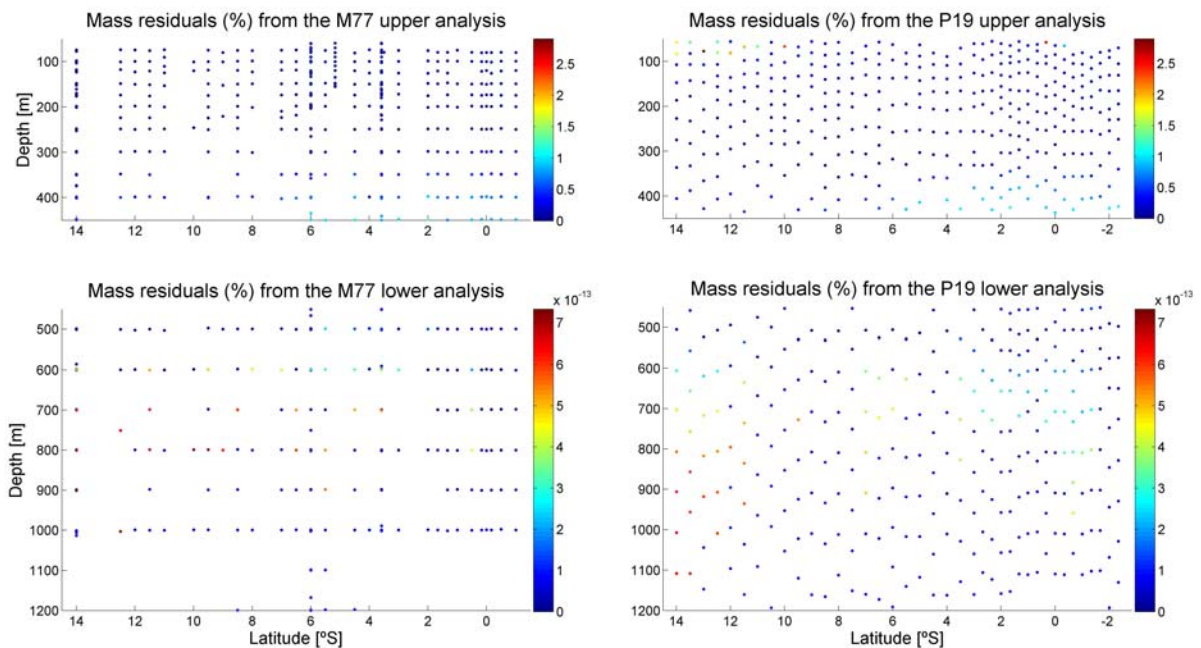


Figure 1. Distribution of the residuals in mass conservation for each extended OMP analysis.

(2) The characterization and quantification of the water mass contribution within the oceanographic section relies heavily on many of the OMP assumptions. The uncertainty stemming from these assumptions could be addressed in more detail. Among these are: (a) choice and number of end members; (b) spatial variations in end member properties (c) temporal variations in end member properties; (d) errors due to the choice of the fixed stoichiometric ratios. I understand that point (a) is limited by observations (4 conservative tracers, once remineralization and denitrification are factored in, allow for ‘unmixing’ of at most 4 water masses). However, I wonder if the results of a Montecarlo-type perturbation (that the Authors mention in page 17591), or some other approach, could be used to assess the robustness of the methods with respect to the uncertainties in (b-c), and possibly be considered for an extended error estimate as discussed in point (1).

Following the reviewer suggestion we have run a more complete series of sensitivity tests by perturbing simultaneously all the water types (end-members) in the source water mass matrix with Gaussian noise in a series of Monte Carlo experiments. We have examined what is the influence on the resulting water mixing fractions obtained after running the extended OMP analysis with the ‘perturbed’ source water mass matrix.

For the first series of sensitivity tests, we consider the influence of natural variability of each parameter in the source regions where the water types were defined. For this purpose we have calculated the standard error associated to each parameter by averaging the standard errors obtained for such parameter in each source region. These standard errors are then multiplied by the Gaussian noise and the result is added to the original water type of the source water mass matrix (for each parameter) and then the OMP is solved.

The influence of temporal changes of seawater properties in the source regions is considered in a second series of sensitivity tests. We have used the (largest) temporal trends in potential temperature ($0.02^{\circ}\text{C}/\text{year}$) and salinity ($-0.0005\text{psu}/\text{year}$) found in the formation region of AAIW in the eastern South Pacific (Schmidtko and Johnson, 2012) to estimate a standard error that would cover the temporal variability for each of these parameters from 1993 to 2009. We could not find in the literature temporal trends in potential temperature or salinity for the source regions of the rest of the water masses so we decided to use the AAIW salinity and potential temperature standard errors for all the remaining water masses. We are aware that the AAIW standard errors will probably

represent overestimates for the remaining water masses (mainly for ESSW and PDW as they are defined below the sea surface). Therefore, all the results from these sensitivity tests (except for AAIW) must be understood as a ‘worst case’ scenario, mainly for ESSW and PDW. For the rest of the parameters (nutrients and oxygen) we have used the same standard errors calculated from the natural variability analysis.

All the above sensitivity tests are run for each subsection for which we have resolved the extended OMP (4 subsections: upper and lower analyses for both the P19 and M77 datasets). The mixing fractions obtained for each data point after each perturbed run were stored and an average standard error was calculated for each mixing fraction from all the data points resolved with the OMP in each subsection.

Finally, a global weighted mean standard error for each water mass mixing fraction is obtained (Table 1). The weighting applied takes into consideration the number of data points in each subsection analysed with the OMP method.

Mean standard error (%)	AAIW	ESSW	STW	SAAW	PDW
Natural variability	2.95	9.11	5.32	4.21	7.89
Temporal variability	2.42	7.64	5.08	5.25	4.45

Table 1. Mean standard errors in the water mass mixing fractions as obtained with the extended OMP analysis after running the sensitivity tests through a series of Monte Carlo simulations.

The global mean standard errors are quite low for AAIW (<3%) under conditions of both natural and temporal variability. This low variability gives us confidence in the results obtained and discussed in this paper. The worst results correspond to ESSW (9%) and PDW (5%). In the case of natural variability, this is probably due to the fact that we are using the averaged standard error (from all source regions) to characterize the natural variability of each parameter and the standard errors in potential temperature and salinity for ESSW and PDW are one or two orders of magnitude smaller than those of the remaining water masses (which were defined at the sea surface). In the case of temporal variability, these relatively large values are related to the fact that we use standard

errors that overestimate the temporal change of potential temperature and salinity for these water masses (as explained above).

(3) I was a little bit surprised to find out that the ESSW end member is a water mass that falls right within the domain of the study. This is somewhat strange, as if possible one would rather include an end member that originates at the boundary of the region considered -if not at the surface. Not surprisingly, the result of the OMP analysis is that the ESSW makes up the bulk of the water-masses inside the section -up to 80-90 % where the properties are closest to the end-member itself. That also brings into question the usefulness of this end member for the biogeochemical estimates, as it imposes 'preformed' properties within a large volume of the section domain, preventing an analysis of their origin (see Fig. 6). Furthermore, I wonder if the choice of this dominant 'internal' end member might bias some of the biogeochemical conclusions.

The reviewer is fully right saying that by defining the water masses with the characteristics they have in their formation region will allow the highest degree on interpretation of the results. Only in such a case one can make statements about the full along-path transformation and biogeochemical cycling. The ESSW is not formed at the surface but is the result of complex water mass transformation of multiple source water masses along the equator and further downstream. It is a “mixed source water” which can be defined as a different water mass because it enters the study region through an exclusive pathway (Tomczak, 1999). This can be a topographic constraint (as in the case of Mediterranean Water entering the Atlantic) or a dynamical constraint (as in our case of the ESSW the Equatorial Undercurrent). Our definition of the ESSW was done using the P19 data between 2°S and 1°N (at the boundary of the region considered) (Figure 1.b of the revised manuscript) and, as can be seen by the high percentage of the ESSW, this is a very good representation.

What is true for water mass fractions is true for the biogeochemical changes – and the bulk biogeochemical processes are derived in reference to the characteristics of the source waters. As the purpose of our study (and accordingly our interpretation) was on the regional remineralization /respiration/ denitrification we do not attempt to over-interpret the data.

...3) I am worried of possibilities similar to the following case: let's say that water mass structure does not change between the two occupations, and only biogeochemistry changes (e.g. export/remineralization). By picking the EESW end member, and assuming its preformed

biogeochemical properties are constant, any biogeochemical change in the bulk of volume dominated by EESW would show up as a change in overall water-mass contributions, even if that was not the case to start with. Obviously this is a limit example that would not apply exactly to this study (water mass do change between different phases of ENSO). Yet it suggests a potential source of error that might be difficult to address.

In case the water mass structure does not change in reference to the conservative parameters (T,S), there will be no change in water mass fractions. All changes will be projected to the biogeochemical part of the linear model. The changes must be either "on-route", that is along all complex trajectories out of the source regions to the point where the sample was taken, or within the source region itself (changes in the source water types for oxygen and nutrients). There is no way to allocate the origin of biogeochemical changes to one specific source water – it will be always a bulk/mixed amount. However, this is not a particular problem as the parameters (T,S) have larger weights and thus more influence on the solution.

(4) I'm not particularly convinced by the assumption of a constant stoichiometry for silicate. As discussed in point (1) adding silicate data to the OMP analysis allows 'unmixing' of an additional water mass. However silicate dissolves with a typical e-folding depth-scale of ~1500-2000 m, compared to ~200 m for organic matter. Therefore silicate would hardly have show a constant ratio with P and N during remineralization/dissolution. This assumption should be at least discussed - if not explicitly addressed in the OMP method.

In order to tackle this issue we have calculated, for each dataset separately and for both datasets together, the best linear fit (silicate = 0 + Ratio*phosphate) for the P19 and 774 datasets by means of a linear regression analysis. Then we have compared the mass residuals produced in the OMP depending of which optimized ratio (silicate : phosphate) is used.

In Table 2 we show the goodness of the fit (R^2) and the quality of the OMP solution (mean mass residual in %) for the 40:1 silicate to phosphate ratio (as suggested by Broecker and Peng (1982) and used in the original manuscript), and for the optimal silicate to phosphate ratios derived from each individual dataset and for both datasets together. We may clearly see that the 40:1 silicate to phosphate ratio produces the worst fit.

Ratio		R ²	Mean mass residual (%)		Std mass residual (%)	
Both	40:1	-	P19	0.4993	P19	0.2977
			M77	0.6273	M77	0.5862
Both	16.61:1	0.4218	P19	0.1397	P19	0.2977
			M77	0.1184	M77	0.1920
M77	14.45:1	0.5741	0.0992		0.1947	
P19	18.37:1	0.5707	0.1233		0.3060	

Table 2. Comparison of the goodness of the fit (R²) of the linear model between silicate and phosphate as obtained for different subsets of data points (P19, M77 or both datasets together). The quality of the OMP solution (mass residuals in %) is also shown.

According to the info summarized in Table 2, we select the ratios (silicate : phosphate) obtained for the P19 and M77 datasets (18.37 and 14.45 respectively) because they produce the smallest mean mass conservation residuals while explaining the largest data variability (R²). Taking into account the potentially different behaviour of silicate with depth (as pointed out by the reviewer) and the difficulty of representing this behaviour with a constant ratio, we have halved the relative weight for silicate (Table 1 in the manuscript) so it is now only a weak constraint in the solution of the OMP. We have used these optimized ratios and the new weight for silicate to obtain the final plots and results to be shown in the revised manuscript.

(5) The Authors should discuss the possible uncertainties/biases arising from the choice of breaking down the OMP analysis at the 450 m depth horizon. I am somewhat concerned that some of the sharp features that are seen in Fig. 9, especially 9a-d, where the changes show a rather abrupt sign change right around 450 m, might be related to this choice. This could be a coincidence, but I wonder if the same features would show up if the break were moved up or down in the water column.

We decided to break the OMP analysis at the 450 m depth horizon because in this way the residuals are minimized in the upper part of the analysis (close to this cutting depth). Additionally, this cutting depth prevents the relatively higher residuals, characteristic of the upper part (0 - 4%), from appearing in the lower part, which is characterized by much lower residuals ($< 0.1\%$). Finally, this partition leads to a smooth transition in the mixing fractions of ESSW and AAIW between the upper and lower part of the analysis.

We have repeated the OMP analysis setting the limit at 350 and 550 m, in order to see how these different choices might affect the results shown in Figures 8 and 9 of the manuscript. When setting the limit at 350 m, the quality of the fit decreases as a band of high residuals appears in the lower portion and close to the separation depth (Figure 2) suggesting the need of a slightly deeper cutting depth.

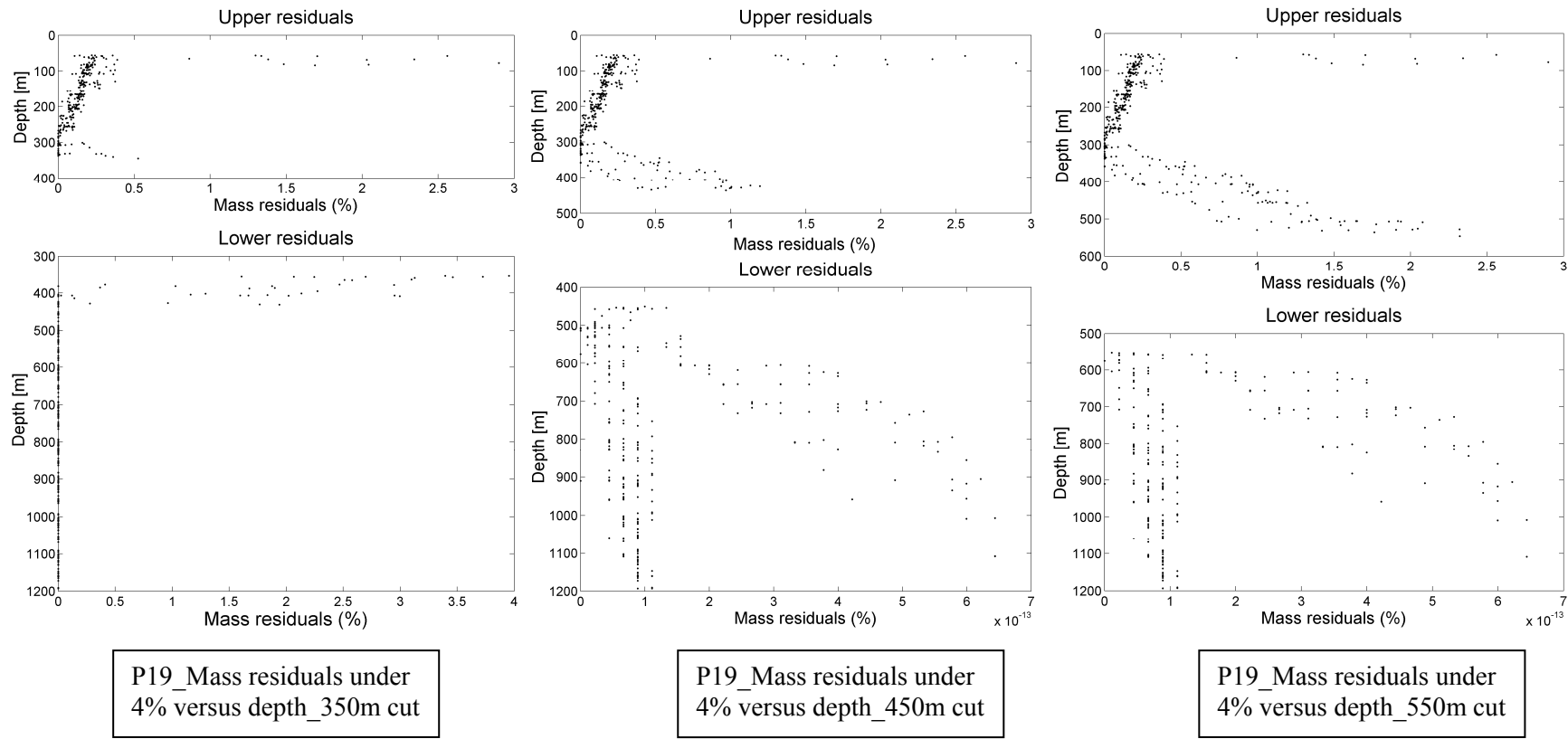


Figure 2. Scattered plot of mass residuals, as resolved with the extended OMP, for three different choices of horizon depth between the upper and lower parts of the water column.

When setting the separation limit at 550 m, we find that the residuals in the upper part of the analysis (close to 550 m depth) are higher than in the case of 450 m depth (Figure 2). Our conclusion is that dividing the analysis at 450 m provides the best results: residuals are smaller close to the separation level and do not propagate into the lower portion of the water column.

Regarding Figure 8 of the original manuscript, the features observed in water mass changes are very much conserved regardless of the selected cutting depth horizon (Figures 3 to 5). Note that the tongue of increasing AAIW between 300 and 600 m is clearly observed for all three cutting depth horizons; however, its shape changes slightly from one case to another. Similar small changes are seen to affect the shape of ESSW change below the cutting depth horizon, as expected because of the reduction from four to three water masses in the OMP analysis. These results grant us confidence on the robustness of the method, in particular on the selection of the 450 m horizon, to estimate the changes in water masses

Regarding Figure 9 of the manuscript, we note that most of the features observed in oxygen respired, nitrate remineralized and nitrate denitrified are well conserved regardless of the selected cutting-depth horizon (Figures 6 to 8). In all three cases we observe a tongue of advective gain of oxygen between 300 and 600 m depths (Fig. 9a in the manuscript); however, the shape of this tongue changes slightly depending on the cutting depth horizon location, which is probably due to the number of water masses used for the OMP analysis in this depth range (three or four depending on where we divide the analysis). The pattern of nitrate advected is also generally conserved; however, we find that the shallower we choose the cutting-depth horizon the shallower we find a sign change in the advection of nitrate. This is probably because AAIW has a greater importance in the mixture when we only use 3 water masses for the analysis (lower analysis); as we move the cutting-depth up in the water column, the influence of AAIW (low content in nitrate) in the water mixture will increase. Finally, the analysis of residuals says that we should trust more the results obtained for the 450 m cutting-depth case, as this case minimizes the OMP residuals. In general, the sign and shape of the observed features in nitrate/oxygen respired and nitrate denitrified are well conserved regardless of the cutting depth horizon.

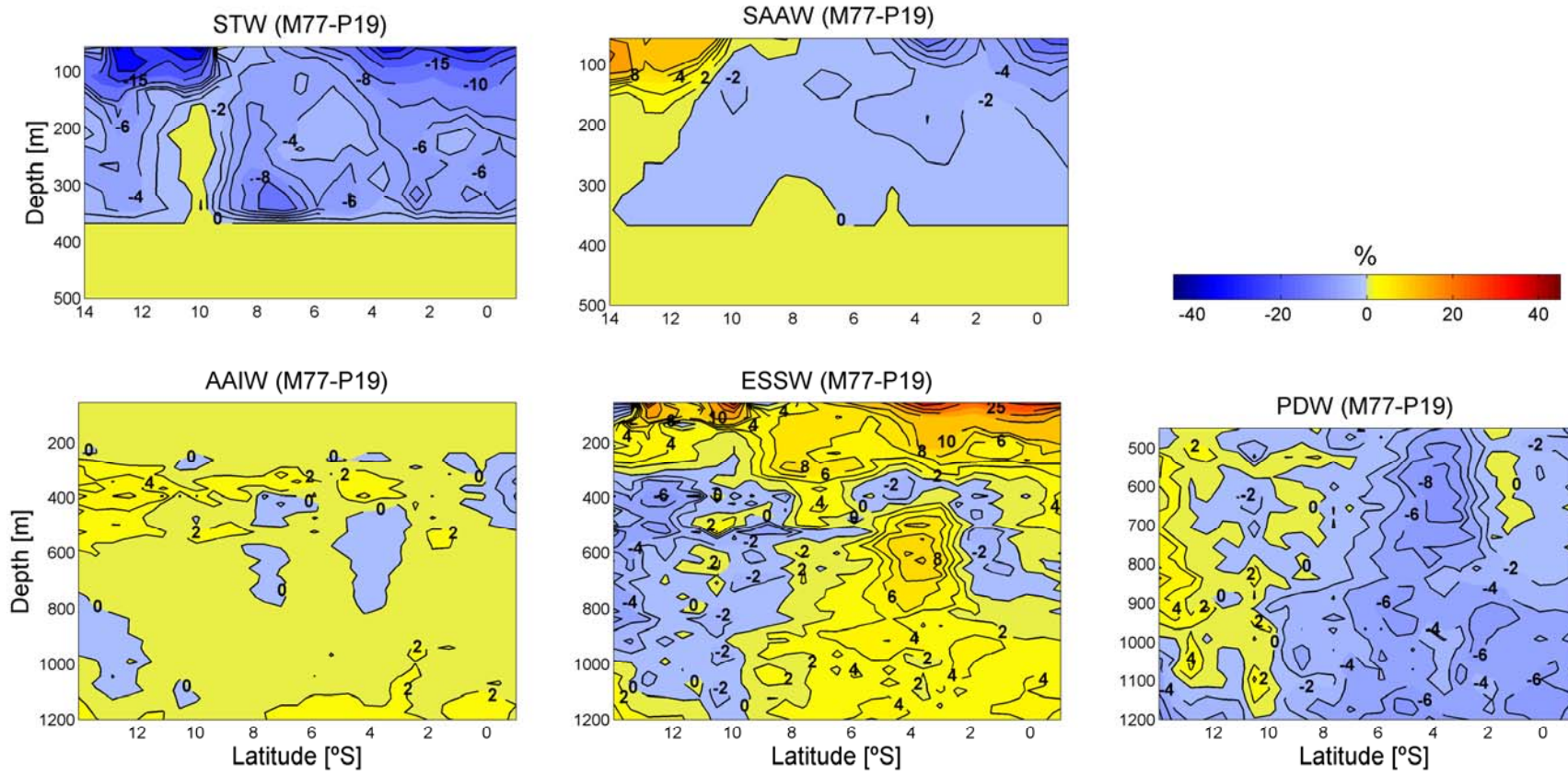


Figure 3. As in Figure 8 of the manuscript, with the dividing horizon at 350 m.

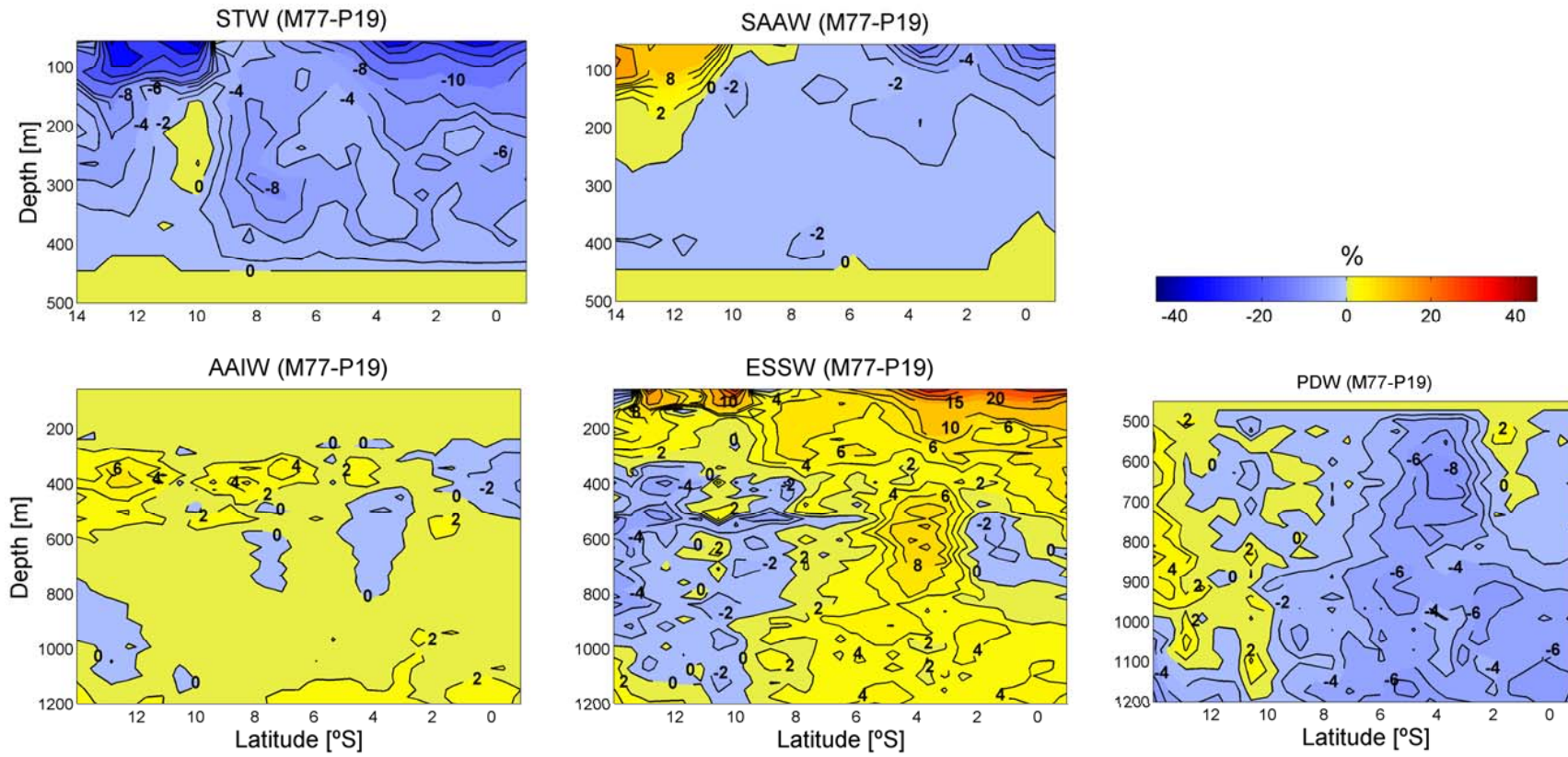


Figure 4. Figure 8 of the manuscript, with the dividing horizon at 450 m.

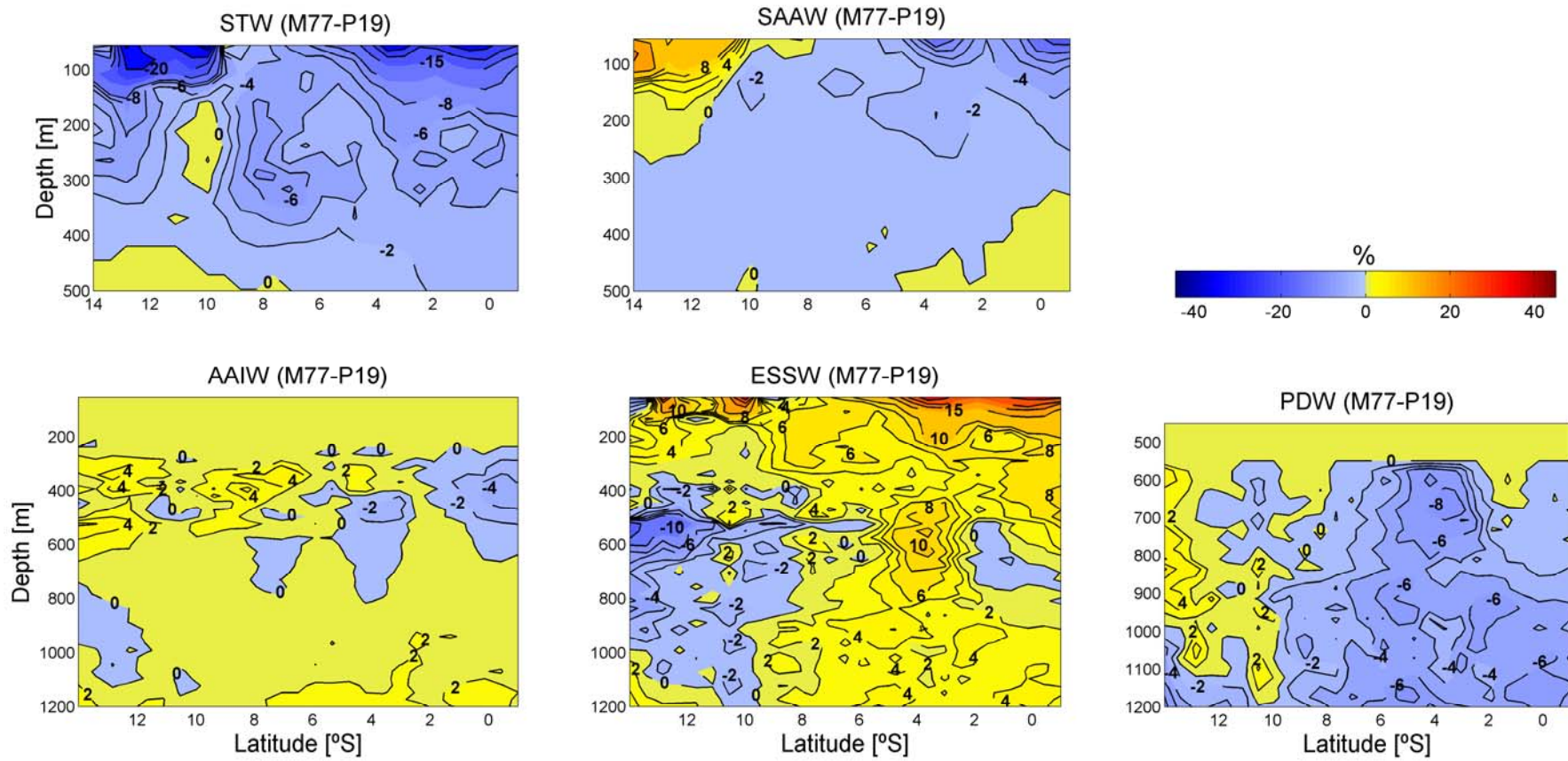


Figure 5. As in Figure 8 of the manuscript, with the dividing horizon at 550 m.

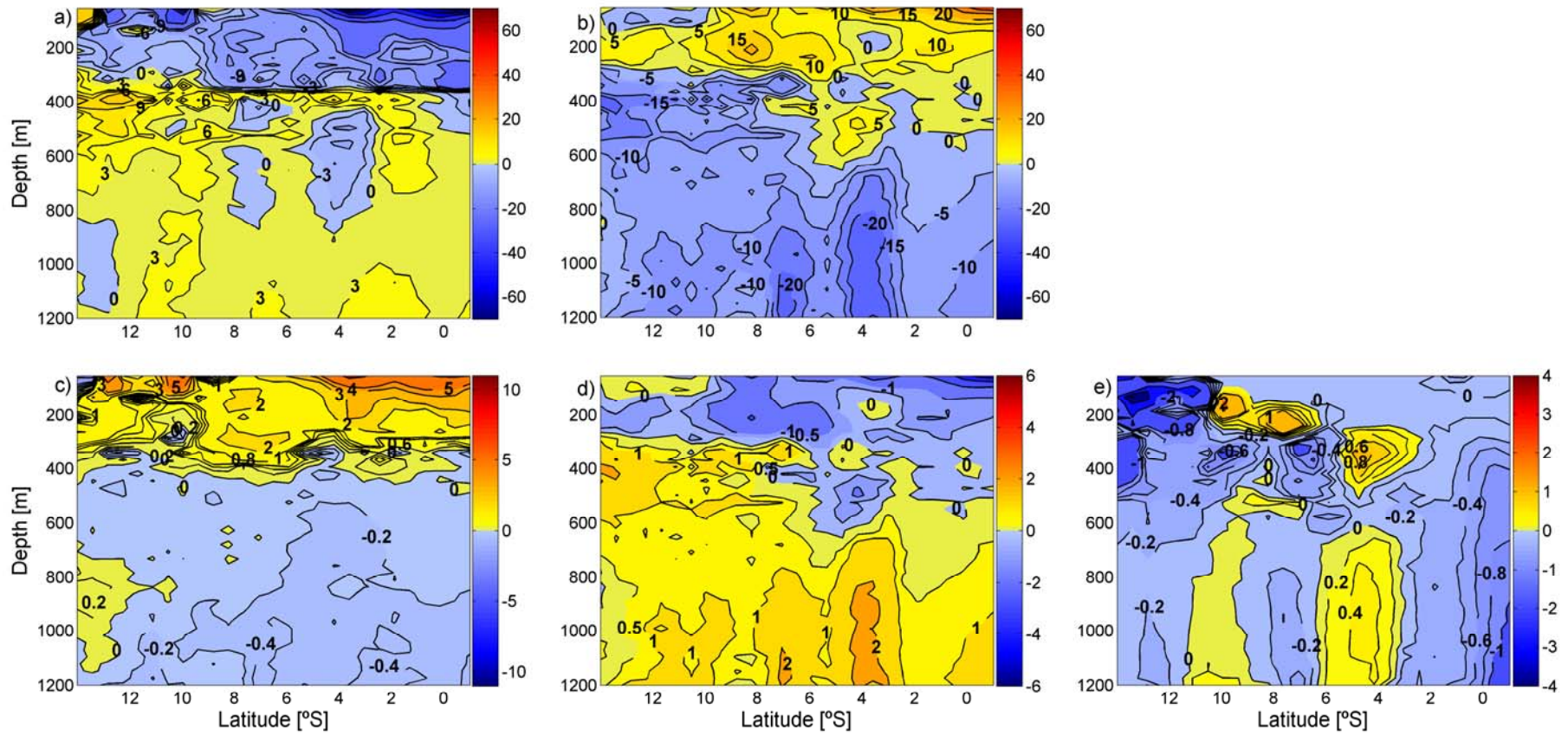


Figure 6. As in Figure 9 of the manuscript, with the dividing horizon at 350 m.

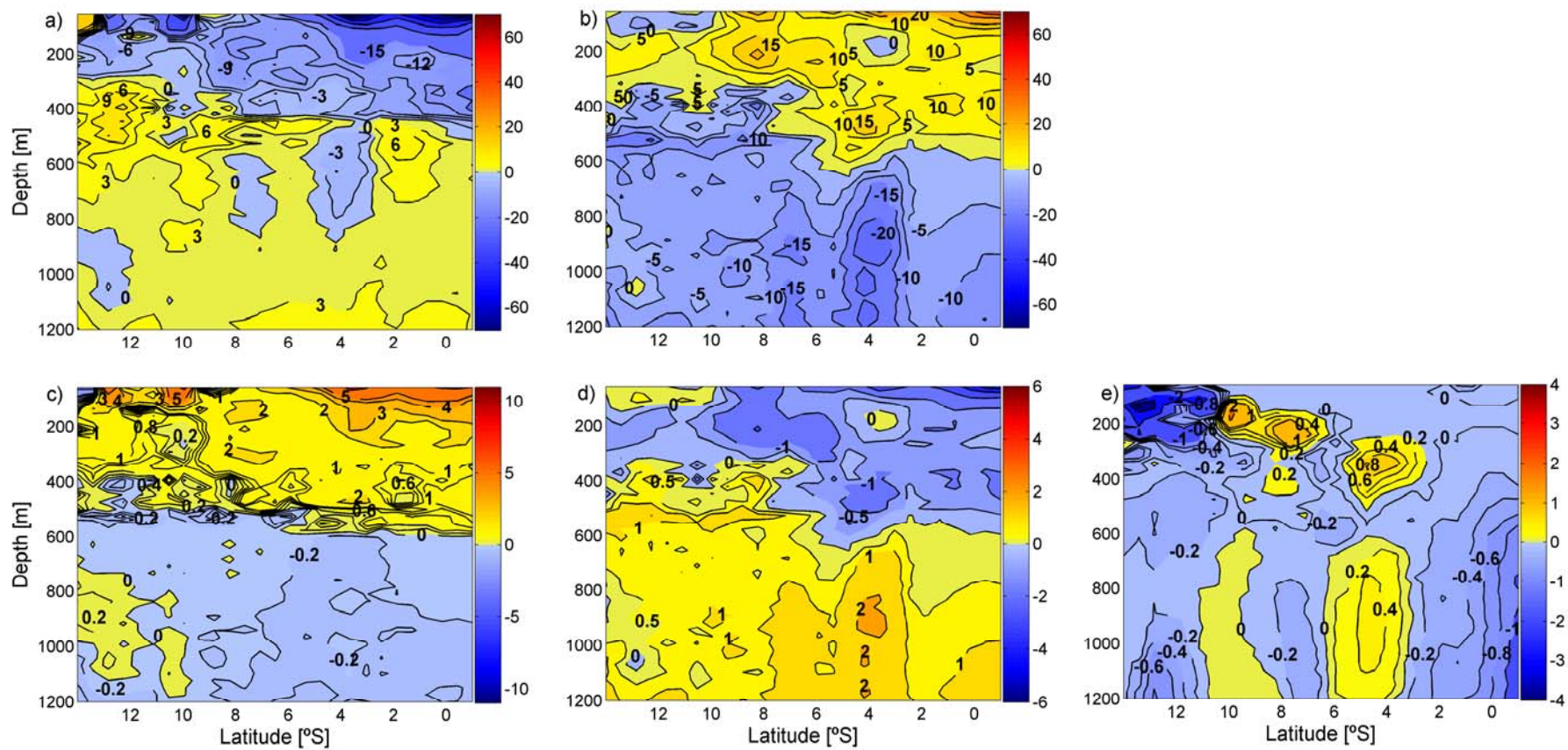


Figure 7. Figure 9 of the manuscript, with the dividing horizon at 450 m.

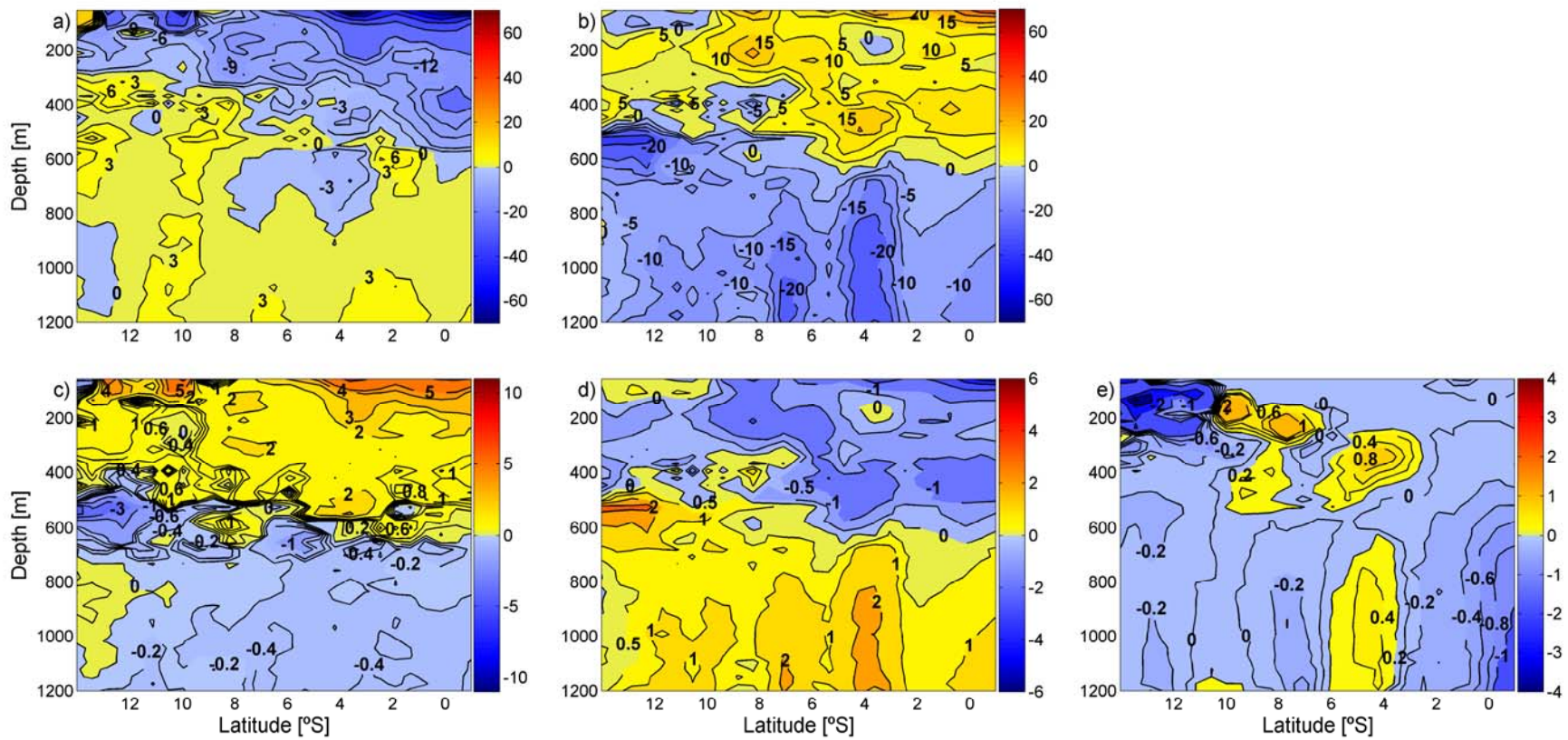


Figure 8. As in Figure 9 of the manuscript, with the dividing horizon at 550 m.

(6) I agree with the importance of showing the results in physical (z) space, especially the biogeochemical changes between occupations (Figs. 7-9). This choice is obviously more intuitive, and more relevant for OMZ volume, nutrient storage, and overall biogeochemical rates. However, the same analysis in density space would shed light on the relative role of isopycnal heaving (possibly the largest source of variability across ENSO phases) versus in situ biogeochemical and remote water mass transport changes. See discussion in pp. 17598, ll. 16-25. This could be shown as supplementary material if space is a concern.

Following the reviewer's suggestion we have done an analysis on density space in order to discern the influence of isopycnal heave on the changes described in the paper. In the density space we still appreciate the tongue of increasing AAIW which flows along shallower isopycnals in 2009, in good agreement with the trend of warming (and density reduction) of the AAIW core in the eastern south Pacific found by Schmidtko and Johnson (2012). This tongue replaces ESSW so relatively more oxygenated waters flow into the OMZ ($26 < \sigma\text{-}\theta < 27$) as proposed in our study (Figures 9 and 10). Figure 9 is included in the revised manuscript as Figure 9B and Figure 10 will be shown in the Appendix to the revised manuscript.

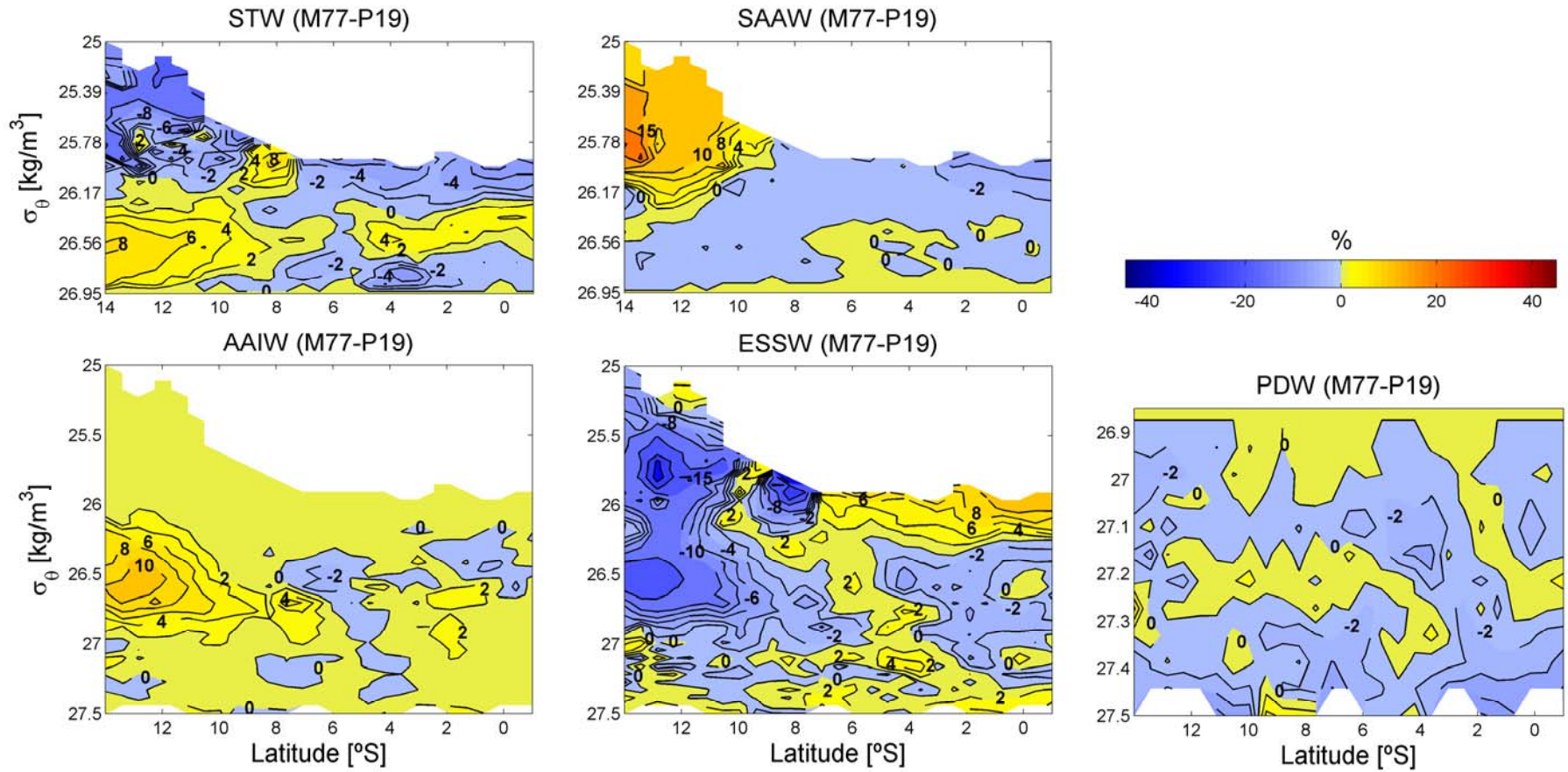


Fig. 9. Water mass changes (%) in density space between March 1993 and February 2009 (M77-P19) for Subtropical Water (STW), Subantarctic Water (SAAW), Antarctic Intermediate Water (AAIW), Equatorial Subsurface Water (ESSW) and Pacific Deep Water (PDW) (Figure included in the revised manuscript).

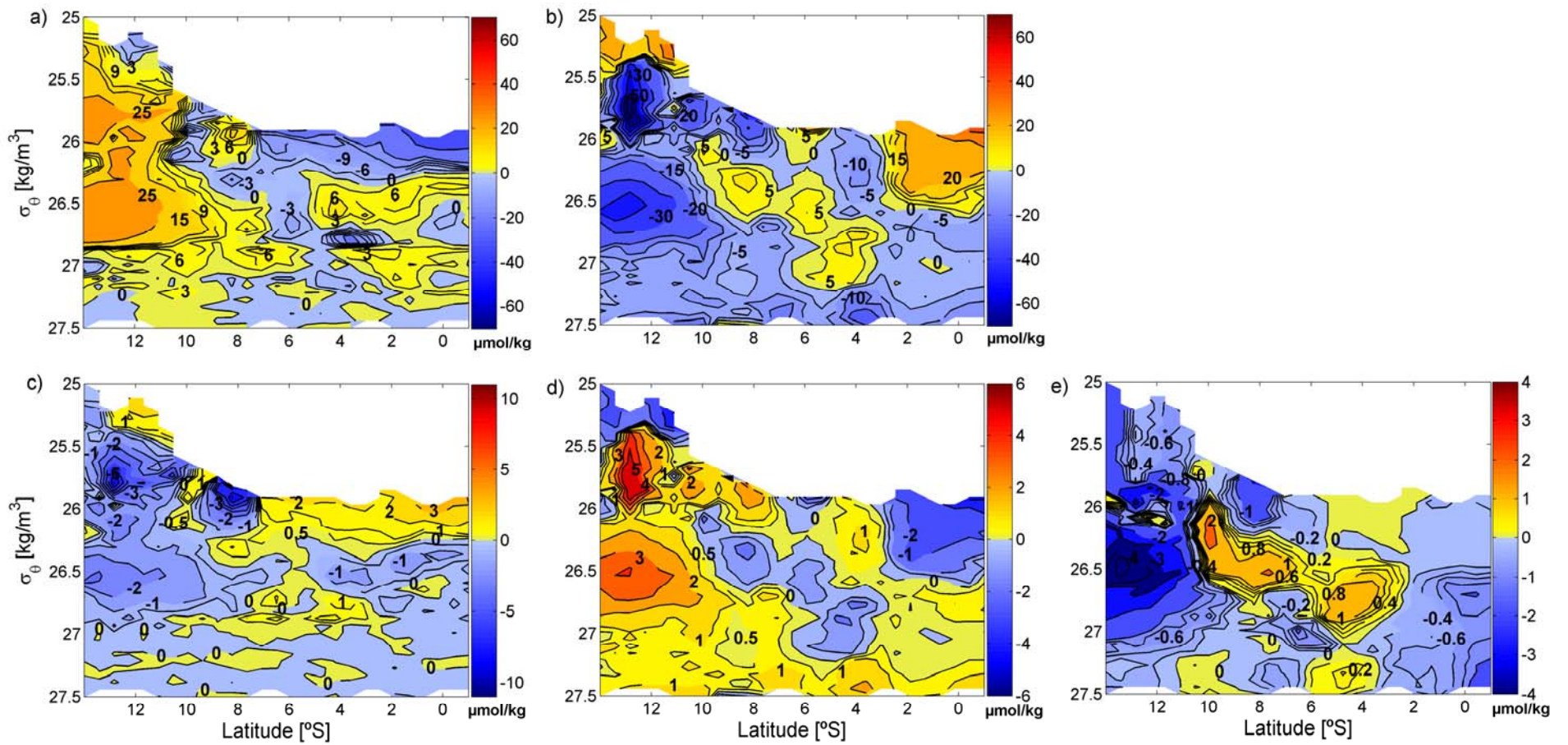


Fig. 10. OMP derived changes in density space between March 1993 and February 2009 (M77-P19): (a) physical transport of oxygen, (b) respired oxygen, (c) physical transport of nitrate, (d) remineralized nitrate, (e) denitrified nitrate shown (Figure included in the Supplementary material).

(7) The change in the contribution of PDW (Fig. 8) is somewhat puzzling. I would intuitively expect the PDW fraction to increase during a La Nina/La Vieja phase, as denser waters move upwards and upwelling strengthens. I wonder about the robustness of this result.

We agree with the reviewer that one might expect to find increasing PDW at slightly shallower depths as the result of the Pacific Decadal Oscillation shift to the cold phase (La Vieja).

Our sensitivity studies, some of them shown above (please also see the response to Reviewer 1), grant us confidence on the robustness of this result. Why PDW mixing fraction changes this way remains an open question, out of the scope of this paper, which is to be mentioned in the revised manuscript.

(8) In the discussion of the biogeochemical changes the Authors often refer to “increase/ decrease” or “strengthening/weakening” of remineralization and denitrification. I am uncomfortable with this terminology as it could lead to interpreting the results in terms of increase or decrease of remineralization/denitrification rates. However the method results can’t be interpreted in terms of biogeochemical rates -but only in terms of biogeochemical signals. For example, the tongue of increasing nitrate deficit observed in the southern side of the section at ~200 m depth (Fig. 9e) does not necessarily mean that denitrification increased across the two occupations. In fact it might just be the signal of increased advection of waters from the peruvian shelf -where I assume that this nitrate deficit originates to propagate offshore -even with no change in overall denitrification rates. Saying something about biogeochemical rates would require at least an estimate of the water mass ages. This should be made clear in the discussion of sections 4.3 and 5 (e.g. pp. 17600-17602) as well as in the Abstract.

We will correct this terminology issue in the revised manuscript. The reviewer is right as an analysis of changes in biogeochemical signals between both occupations in the zonal sections reveals that the tongue of increasing nitrate deficit observed in the southern side of the Meridional section was in fact the signal of increased advection of waters from the Peruvian shelf (Figure 11).

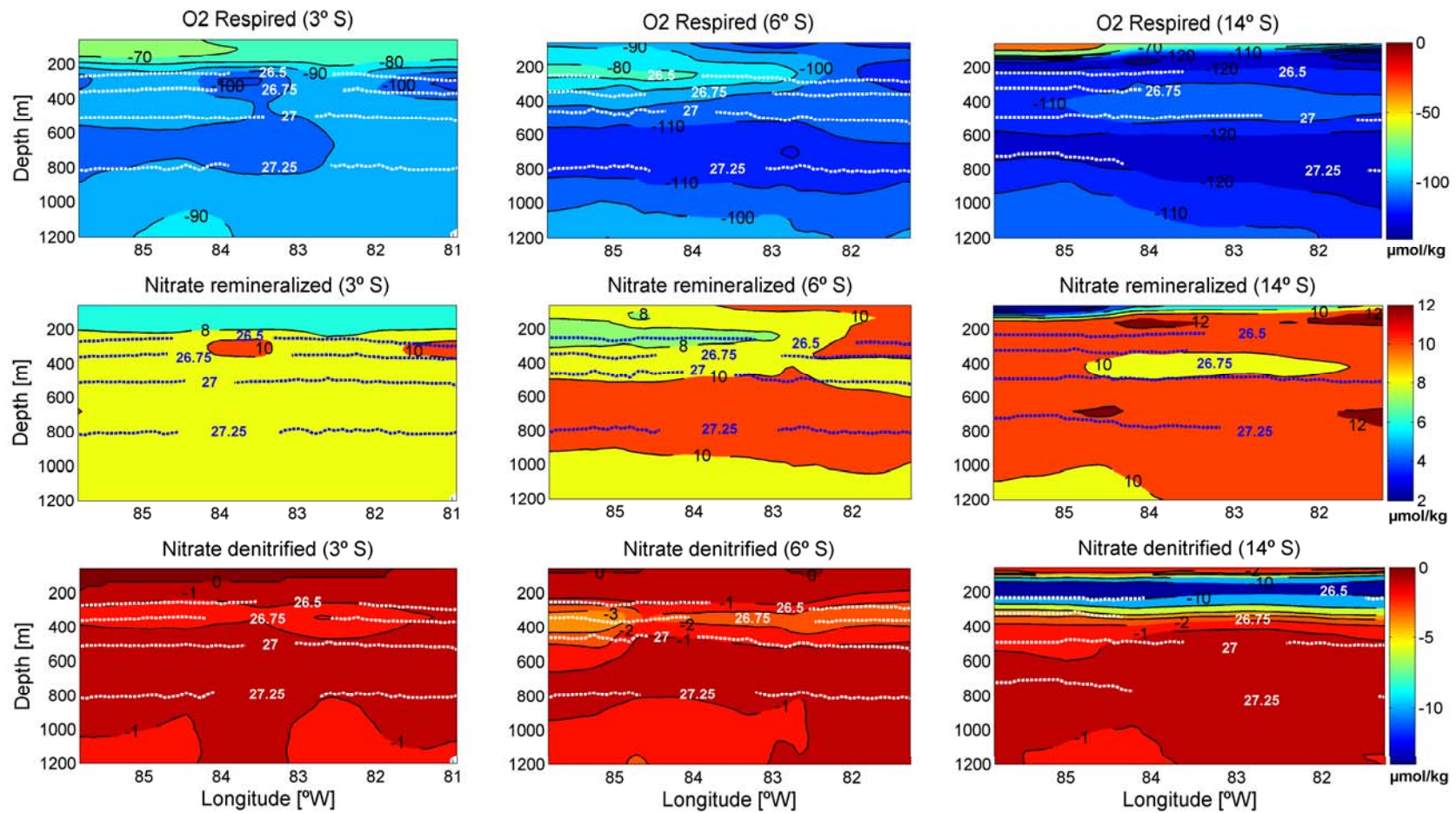


Fig. 11. OMP-derived biogeochemical activity within the water column for the 3 zonal sections (3°S, 6°S and 14°S) completed during the M77 cruise (February 2009). Selected isopycnals are shown, drawn as white/blue dotted lines depending on the background colour.

Minor and technical comments:

(9) I think it is important and useful to show the oxygen (and possibly nitrate) sections especially before discussing the biogeochemical components and the changes in Figs. 6, 7, 9. Perhaps this can be done as supplementary material.

We have prepared this figure (please see Fig. 12) and it will be included in the revised manuscript as Figure 7.

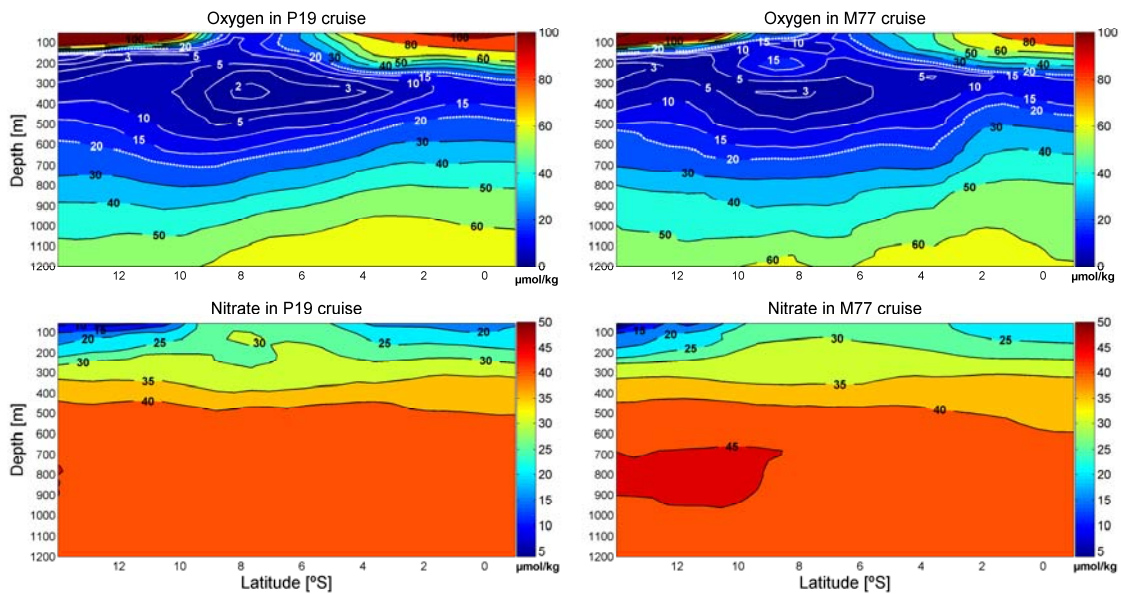


Fig. 12. Meridional section with measured oxygen ($\mu\text{mol kg}^{-1}$) and nitrate ($\mu\text{mol kg}^{-1}$) for March 1993 (P19) and February 2009 (M77).

(10) I would rather refer to the “advective” component directly as “physical” component. As the Authors recognize (p. 17599, ll. 23-24) it includes isopycnal heaving, diffusion, advection, so just referring to it as ‘advection’ - especially in Fig. 9, is somewhat misleading.

This will be corrected in the revised manuscript.

(11) Abstract. It could be useful to add a succinct explanation of the OMP technique for readers not familiar with it.

This will be done in the revised manuscript.

(12) Table 1. Is the “Mass conservation” column necessary?

We will rearrange the Table in order to skip that column, keeping the information about the weight assigned to mass conservation.

(13) Possibly show a figure equivalent to Fig. 6 but for the zonal sections in 2009 (if not in the main paper, as supplementary material). That would shed some light on the origin of some features seen in Fig. 6, for example the shallow (~200 m) denitrification tongue originating at the southern side of the section.

This question was addressed above, please see point 8. The figure shown there (Fig. 8) will be included in the revised manuscript as figure 6B.

(14) p. 17589, l. 18. I don't understand this reference to “calcification” in the context of nutrient and oxygen cycling.

This reference would make sense if we were using dissolved inorganic carbon (DIC) as another parameter in our analysis, as this is not the case we have taken this reference out.

(15) p. 17593 ll. 12-13 it looks from Figs. 4-5 that ESSW (not just STW and SAAW) represents a big contribution even in the shallower layers.

This will be pointed out in the revised manuscript.

(16) pp. 17595, ll. 13. I would question the use of the term “ventilation” in this instance, especially considering that the EESW end member falls inside the section and is already extremely oxygen-depleted. Intuitively ventilation should refer to surface end members.

We understand the point of view of the reviewer but we would prefer to leave the term as it is because ESSW was defined in the equatorial part of the section, where the Equatorial Undercurrent is supposed to carry ‘younger’ and therefore (slightly) more

oxygenated water into the OMZ and, although it presents rather low oxygen concentration, it does (poorly) ventilate the OMZ.

(17) pp. 17595, ll. 21. Please clarify what is meant with “ancient denitrification”.

We meant denitrification occurred previously somewhere else and advected into the section analysed with the OMP. We will properly rephrase this sentence in the manuscript.

(18) pp. 17599, ll. 26-30. The increase of AAIW doesn't seem to univocally result in an advective oxygen gain. For example the match is not that clear in Fig. 9a: around 7°S, ~350 m depth, where the maximum increase of AAIW is observed, advective oxygen is actually seen to decrease. Also see point (5).

This particular issue does not appear any more in the improved plots of the revised version, where the tongue of increasing AAIW fits better the tongue of increased advection of oxygen (Figures 9A and 10 of the revised manuscript). However, one must bear in mind that an increase in AAIW does not always imply an increase in the ‘total’ oxygen advected. This will also depend on how the mixing fractions (of the remaining water masses) have changed in that location. The biogeochemical signals are a ‘bulk’ amount (i.e. total oxygen respired in one specific data point) and therefore cannot be directly associated to one specific water mass.

(19) pp. 17602, ll. 9. I am not sure what the Authors mean with “a natural negative feedback of the ocean circulation against the long term trend of expanding OMZs”. The signals that the Authors describe can be easily accommodated within the framework of interannual/ multidecadal variability, which could also be the driver of the observed OMZ expansion.

We will rephrase it in the revised manuscript.

(20) pp. 17602, ll. 15. Please clarify “differently” (e.g. non-stoichiometrically?)

We meant ‘in a distinct way’. We will rephrase it in the revised manuscript.

References:

Tomczak. (1999) Some historical, theoretical and applied aspects of quantitative water mass analysis. *Journal of Marine Research* Vol.1, 1999).

Broecker, W. S., and Peng, T. H.: *Tracers in the Sea*, edited by: Lamont-Doherty Geological Observatory, C. U., Columbia University, Palisades, N.Y, 1982.