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Interactive comment on "Diapycnal dissolved organic matter supply into the upper Peruvian oxycline" *by* Alexandra N. Loginova et al.

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AC1: First of all, we are very thankful for Anonymous Referee #1 (AR1) for taking time for reading our manuscript and giving his/her comments for our study. In the following, comments of AR1 will be addressed one by one.

RC1: "The basic question posed in the Abstract was "how important is DOM utilization for O2 respiration within the Peruvian OMZ". The answer was not given unambiguously in the Abstract. The answer the authors should give in the Abstract, based on their results, is that "DOM introduced by vertical mixing has no role in contributing to O2 consumption in the core of the OMZ". This answer is given in the Discussion, but it is not in the Abstract. Instead, the authors state that "DOM utilization may play a

significant role for shape of the upper Peruvian oxycline"; but that statement is not the answer to the question posed. The Abstract needs to be written for absolute clarity in terms of question and answer."

AC1: We agree with AR1 that the abstract needs to be revised for clarification of our results: Abstract 9-10 The sentence: "However, the importance of DOM utilization for O2 respiration within the Peruvian OMZ remains unclear so far." will be changed to: "However, the importance of DOM utilization for O2 respiration in the Peruvian upwelling system in general and for shaping the upper oxycline in particular remains unclear so far." Abstract 10-16 The sentence: "Here, we evaluate the diapycnal fluxes of O2, dissolved organic carbon (DOC), dissolved organic nitrogen, dissolved hydrolysable amino acids (DHAA) and dissolved combined carbohydrates (DCCHO) and the composition of DOM in the ETSP off Peru to learn, whether labile DOM is reaching into the core of the OMZ and how important DOM utilization might be for O2 attenuation." will be changed to: "This study reports the first estimates of diapycnal fluxes and supply of O2, dissolved organic carbon (DOC), dissolved organic nitrogen, dissolved hydrolysable amino acids (DHAA) and dissolved combined carbohydrates (DCCHO) to the OMZ for the ETSP off Peru. Diapycnal flux and supply estimates were obtained by combining measured vertical diffusivities and solute concentration gradients. They were analysed together with the molecular composition of DCCHO and DHAA to infer the transport of labile DOM into the upper OMZ and the potential role of DOM utilization for the attenuation of the diapycnal O2 flux that ventilates the OMZ.". Abstract 19 The line: "suggesting that the labile DOM is already utilized" will be changed to: "suggesting that the labile DOM is extensively consumed" Abstract 24-25 The line: "which suggests that DOM utilization may play a significant role for shape of the upper Peruvian oxycline." will be replaced with: "which suggests that DOM utilization plays a significant role for shaping of the upper Peruvian oxycline" We feel that a modification of last sentence in Introduction (3/14) will help also for clarification of our results: The sentence: "Additionally, we analyze the composition of dissolved combined CHO and AA to learn, whether DOM and its labile and semi-labile constituents may be supplied to the core of the OMZ." will be edited to: "Additionally, we analyze the composition of dissolved combined CHO (DCCHO) and dissolved hydrolysable AA (DHAA) to learn, whether DOM and its labile and semi-labile constituents may be supplied to the upper OMZ and the potential contribution of DOM based respiration to O2 flux attenuation."

RC1: I did not find the outcomes of this work to be enlightening. We could see in the data plots that DOC was high at the surface but low at 40, so clearly it was not surviving export by mixing to even 40 m depth. So its small (or non-existent) contribution to export into the OMZ core is pretty obvious just by looking at the distributions; the great effort by the authors to calculate vertical fluxes may have been excessive given the obvious answer to the question. I'm not sure what is the main point of this paper. DOM is essentially not exported to the OMZ, but we did not need to see all the work done by the authors to know that outcome. That it contributes to the "shape of the upper oxycline" is the final finding given in the Abstract, but does that matter? The shape of the oxycline is not discussed elsewhere in the paper.

AC1: We thank AR1 for taking the time to read our work and giving his/her opinion on our outcomes. We take this critical comment that our work is not "enlightening" as a motivation to make the importance of this first quantitative study on oxygen and DOM dynamics clearer for the reviewer and also for the reader. We are convinced that an accurate quantification of O2 and DOM fluxes and even more, the flux divergences (which are more informative for learning about sources and sinks of solutes) is an important contribution to the understanding of biogeochemical and microbial processes in OMZs and that the effort to calculate these fluxes should be valued. In particular, we do not share the statement of AR1 that "looking at the distributions" is sufficient to understand the complex O2 and organic matter dynamics off Peru. The distribution of a component, determined at one time-point does not provide any information on its processing and cannot give any quantitative information on matter fluxes. The ventilation of the OMZ by the physical supply of O2 from the surface ocean is constrained by the biological utilization of oxygen for respiration of OM that happens during trans-

port process. It has been shown that aerobic and microaerobic microbial respiration is the main pathway of organic matter remineralization (Kalvelage et al., 2015) in the oxycline. In order to estimate the attenuation of O2 fluxes by microbial respiration of organic matter and by this the contribution of microbial processes to the formation and maintenance of the OMZ, we need to know the fluxes of O2 and the flux attenuation (supply), i.e. O2 uptake. Here, we give for the first time a quantitative estimate of those parameters and relate them (quantitatively!) to DOM supply (uptake) and to previously estimated oxygen consumption off Peru (Kalvelage et al., 2015). Please, note that the oxycline is considered as being part of the OMZ.

RC1: "DOM introduced by vertical mixing has no role in contributing to O2 consumption in the core of the OMZ . . . DOM contributes to the "shape of the upper oxycline", but does that matter?".

AC1: As there is no oxygen to be consumed within the core of the OMZ, organic matter, if supplied to the core of the OMZ, cannot cause oxygen consumption, unless oxygen is supplied with it. Therefore, looking at O2 and DOM fluxes and their divergences is so important. Turbulent mixing is a major process for ventilating the OMZs, as ventilation by ocean currents is sluggish, and currents are carrying only low-O2 waters to the eastern boundary OMZs. Please see 9/10:" diapycnal supply is often a leading term in the flux divergence balances of O2, nutrients and other solutes in the upper ocean (e.g. Schafstall et al., 2010; Kock et al., 2012; Brandt et al., 2015; Steinfeldt et al., 2015)." Our findings suggest that a substantial part of O2 flux above the OMZ core is attenuated due to respiration of labile DOC. A process we refer to as "shaping of the oxycline" here. We will clarify our description of the O2 concentrations in the OMZ core in the revised manuscript: The sentence (4/6 Methods): "The O2 optode was calibrated by a combination of Winkler titration (Winkler, 1888; Hansen, 1999) and STOX sensor measurements (Revsbech et al., 2009)." will be changed to: "The O2 optode was calibrated by Winkler titration above the oxycline (Winkler, 1888; Hansen, 1999). The STOX sensor measurements, which revealed O2 concentrations of 0.01-0.05 μmol kg-

1 within the OMZ (Revsbech et al., 2009; Thomsen et al., 2016a) were used for O2 optode calibration at low O2 levels."

RC1: "DOM clearly not surviving export by mixing to even 40 m depth".

AC1: Our data represent mean values for the study area at the time of the field campaign and do not resolve episodic processes, which may occur e.g. through submesoscale mixing and supply fresh DOM into the oxycline locally (Ulloa et al., 2012, Thomsen et al., 2016b). Moreover, deepening of the mixed layer and weakening of the stratification, as for instance in Austral winter, may potentially enhance DOM supply to the deeper waters (Thomsen et al., 2016b).

RC1: 1/31 "is one of the largest regions" In what regard? For an OMZ? And, "where the role of O2 concentrations discriminates." Discriminates what? And does an O2 concentration really have "a role"?

AC1: The sentence: "Due to the presence of a pronounced oxygen minimum zone (OMZ) (Karstensen et al., 2008), the eastern tropical South Pacific (ETSP) is one of the largest regions, where the role of O2 concentrations discriminates." will be changed to: "The eastern tropical South Pacific (ETSP) embodies one of the largest oxygen minimum zones (OMZ) in the world ocean (Karstensen et al., 2008; Paulmier and Ruiz-Pino, 2009)."

RC1: 2/7 "anoxia-related processes" not enough information in that phrase.

AC1: The phrase: "anoxia-related processes (Kalvelage et al., 2013)" will be changed to: "anoxia-induced processes, such as denitrification and anammox (Kalvelage et al., 2011, 2013)"

RC1: 2/26: "Accessing" should be "Assessing" AC1: "Accessing" will be replaced with "Assessing"

RC1: 3/18 The acronym "GO" should be spelled out; presumably it is "General Oceanics"

AC1: The line: "Seawater was sampled with a GO rosette" will be replaced with: "Seawater was sampled with a rosette (GO; General Oceanics, USA)"

RC1: 6/2 What exactly is the "diapycnal solute supply"? This term should be explained fully, as it is central to the findings in the manuscript. Telling the reader that it is a 'divergence in flux' is inadequate.

AC1: The diapycnal fluxes and supplies for all the dissolved parameters (solutes) were calculated by similar approach, therefore, the word "solutes" was used in the method for describing calculations used for dissolved oxygen, DOC, DHAA and DCCHO. At the interfaces sediment-water column/air-sea interface it makes sense to speak about fluxes to quantify exchange between reservoirs. Within the water column the change of fluxes over depth (or distance), i.e. the vertical flux attenuation referred to as flux divergences, indicates the rate of consumption or production and is the value that can be compared to sources and sinks. The flux divergence was described and calculated by equation 3. This value is an estimate for the diapycnal solute supply (an equivalent of solute consumption/remineralization), assuming that other sources or sinks (such as mesoscale, submesoscale or upwelling fluxes, or photochemical reactions) were negligible. We discuss, the potential influence of other sources and sinks (page9, line 20), however, these were not quantified in this study nor previously: "Other mixing terms of the O2 transport budget, such as isopycnal O2 supply by meso- (Thomsen et al., 2016a) and submesoscale (Thomsen et al., 2016b) dynamics or O2 fluxes due to upwelling (e.g. Steinfeldt et al., 2015) may provide an additional loss of O2 to the upper ocean, particularly in the region of the continental slope and the shelf. Furthermore, seasonal variations of the diapycnal solute fluxes may occur due to, for instance, deepening the mixed layer during winter season (Echevin et al., 2008). Therefore, our results should be considered as the first estimates of diapycnal fluxes and supply in ETSP off Peru during austral summer. Therefore, more observations shall improve the robustness of the flux estimates." and 9/29 "DOM transport through the water column is also restricted to advective and diffusive mixing processes. However, DOM is affected also by other abiotic or biological processes in the water column. ... Photoreactions could also reduce DON incorporated into large chromophoric molecules through production of volatile N compounds or inorganic N (Zepp et al., 1998). . . . Photochemical degradation to CO, CO2 and other volatile compounds (Zepp et al., 1998) could lower the near surface diapycnal DOC flux, as well." We will improve the description for the diapycnal supply calculation in the revised manuscript. Page 6, lines 2-7 The "Here, we define the diapycnal supply (in mol m-3 s-1) of a solute as its vertical flux divergence, i.e. the change of the diapycnal flux with depth: -(âĹĞΦ_s) ÌĚ=- ∂/∂z (Φ_S) ÌĚ, (3)" will be edited to: "The mean diapycnal supply (-(âĹĞΦ_s) ÌĚ, μmol kg-1 day-1) of a solute was determined as an attenuation of the diapycnal solute flux profile over depth, according to the Eq.3: -(âĹĞΦ_s) ÌĚ=- 1/ ∂/∂z (Φ_S) ÌĚ, (3) where – is the in-situ density of the seawater (kg m-3), z - is depth (m) and (Φ_S) ÌĚ (mmol m-2 day-1) – is the calculated mean diapycnal flux profile of a solute. The mean diapycnal solute supply was interpreted as the amount of a solute that is lost per unit time over a specific depth interval of the water column and was assumed to be an equivalent to microbial utilization rate of the solute. This interpretation assumes that sources other than turbulent mixing or sinks other than microbial consumption are negligible."

RC1: 6/25-26 Surface DOC concentrations >100 umol/L are not found in the ocean unless a river is nearby, which can add terrigenous DOC. The high values seem unrealistic. The values in the surface layer that are closer to 70 uM are more realistic, based on the data reported by Letscher et al. 2015 at nearby locations. The elevated DOC values at greater depth are suspect as well.

AC1: First of all, Letscher et al. (2015) does not include data collected in the nearby locations. The data, that were used in Letscher et al. (2015) for validation of the model are at least 20° off. The eastern tropical South Pacific off Peru represents a highly productive and a very dynamic coastal area with very high spatial gradients. It is influenced by various physical mixing processes, which are often not included in the global circulation models. Global models, in general, do not represent the upwelling regimes

well - for this, specialists use regional models. Furthermore, the near surface DOC concentrations were unlikely used for model validation. It is more likely that a mean value for depths 0-100m was used for the "euphotic zone" run. Even for those data, that have been used by Letscher et al. (2015) the model tends to underestimate or overestimate DOC concentrations, depending on the different model run. Our results, in turn, are well within the previously published range for DOC concentrations in the area off Peru. For instance, Engel and Galgani (2016) (BG) and Zäncker et al. (2017) (Front. Microbiol.) reported concentrations for DOC from 70μmol/L to 130 μmol/L for the sea surface microlayer. Franz et al. (2012) (Deep Sea Res. I) reported DOC concentrations ranging from 50 to 300 μmol/L for the upper 200m. Romankevich and Ljutsarev (1990) (Mar. Chem.) reported DOC concentrations ranging from $\sim$40 μmol L to $\sim$130 μmol L for the upper 100-150 m of the water column. Singular elevated values below surface were also reported by the same authors. Those might be related to the influence of the particle dissolution, DOM production at the deep chl a maximum (Goericke et al., 2000 (Deep Sea Res. I); Lavin et al, 2010 (Environ. Microbiol. Rep.)), etc.

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